DETERMINATION OF THE RELATIVE PHYTO-REMEDIATION ABILITIES OF SELECTED VEGETABLES OBTAINED FROM FARMLANDS OF THREE INDUSTRIAL ESTATE OF KANO METROPOLIS ON SOME HEAVY METALS

BY

MERCY ADENIKE OYENIYI

SPS/11/MCH/00001

A DISSERTATION SUBMITTED TO THE DEPARTMENT OF PURE AND INDUSTRIAL CHEMISTRY, FACULTY OF SCIENCE, BAYERO UNIVERSITY KANO IN PARTIAL FUFILMENT OF THE REQUIREMENTS FOR THE AWARD OF THE DEGREE OF MASTER OF SCIENCE (M. SC) IN ANALYTICAL CHEMISTRY.

DECEMBER, 2016.

DECLARATION

I hereby declare that this work is the product of my research efforts undertaken under the supervision of **Professor A.A Audu** and has not been presented anywhere for the award of a degree or certificate. All sources have been duly acknowledged.

…….....…… …….

MERCY ADENIKE OYENIYI **Date**

SPS/11/MCH/00001

CERTIFICATION

This is to certify that the research work for this dissertation and the subsequent write-up by **Mercy Adenike Oyeniyi** with registration number **SPS/11/MCH/00001** was carried out under my supervision.

……

Prof. A.A Audu
Supervisor

……..

Dr. H. Musa
Head of Department

APPROVAL PAGE

This dissertation has been examined and approved for the award of Master of Science in Analytical Chemistry.

…… **Date ……**
Dr. M.M Ndamitso
External Examiner

…… **Date ……**
Prof. A.A Audu
Supervisor

…….. **Date ……**
Prof. Musa Ibrahim Mohammed
Internal Examiner

…….. **Date …….**
Dr. H. Musa
Chief Examiner (HOD)

…… **Date …….**
Dr. Nafiu Hussaini
Rep. of School of PG Studies

ACKNOWLEDGMENT

Now unto Him that is able to do exceedingly abundantly above all that we ask or think, according to the power that worketh in us, unto Him be glory in the church by Christ Jesus throughout all ages, world without end. Amen.

I express my sincere and profound gratitude to my supervisor, Prof. A. A. Audu for his constructive criticism, guidance, dedication and supervision. May God reward him abundantly (Amen). In addition, my profound regard goes to all the lecturers and staff in the department especially my coordinator Dr Umar Sani, Dr Ibrahim Gaya and Mr. Joshua Kubia for all their support. I am also grateful to the laboratory technicians in Plant Biology Department and soil Department of Agricultural sciences of Bayero University, Kano for their kind assistance.

I am greatly indebted to my dad, Mr. N. A. Oyeniyi for showing me the road to good success and whose words are still alive in me till today even though he is no more. How can I forget my sweet mother who strives to make my education a reality. I appreciate her spiritual, moral and financial supports. May God continue to bless and grant her long life to that she might eat the fruit of her labour. Also, my profound gratitude goes to the entire members of my family for their supports. I specially want to appreciate my husband Mr. Mayowa Danjuma Akintoye for his love and support. I appreciate the contributions of the entire member of Chapel of Victory (B. U. K) especially Prof. Joseph Enamburekhan, Prof. J. A. Falola, Prof. B. A. Adepoju and Elder Kehinde Aliyu, Bar. Gani Sule, and Mr R.C Okoji for their spiritual, financial and moral supports. May God continue to bless and keep them Amen.

DEDICATION

This dissertation is dedicated to the only wise and True God, the father of our lord Jesus Christ the lover of my soul.

Table of Contents

CHAPTER ONE

CHAPTER TWO

CHAPTER THREE

CHAPTER FOUR

CHAPTER FIVE

LIST OF TABLES

LIST OF FIGURES

LIST OF APPENDICES

ABSTRACT

This study was carried out to determine the relative phyto-remediation abilities of selected vegetables (cabbage, garden cress, sesame, lettuce and Sspinach), obtained from farmlands of three industrial estate of kano metropolis on some heavy metals. In this study, the amount of heavy metals (Cd, Cr, Cu, Pb, Zn, Mn, Mo, Ni and Fe) present in the various parts of the vegetables was determined using the atomic Absorption Spectrophotometry technique after wet digestion using a mixture of HNO_3 and H_2O_2. The soil samples were digested using a mixture of HNO_3, HF, and H_2O_2. The results indicated that the average concentration of the selected heavy metals was higher in the soil collected from the industrial farm area than in the soil of the control area. Meanwhile, in various parts of the vegetables (roots stem and leaves) the concentrations of heavy metals were higher in the vegetables collected from the industrial farm area than the control area. The highest concentration of heavy metals in this study was in the roots followed by the stem and the leaves. All the values reported in this study showed Transfer Factor (TF) <1 indicating that the five species of plants are not suitable for clean-up of heavily polluted soil through phyto-remediation. The findings also revealed that all plant species under investigation had Bio-accumulation Factor (BAF) <1. However, spinach sample from the entire site showed Translocation Factor (TrF) >1 of Ni and can be said that spinach is a good accumulator for Ni and can be used for phyto-remediation of soil contaminated with Ni, Sharada samples also showed TrF values >1 for Pb which can be concluded that vegetables grown the area can also be used for phyto-extraction of Pb. However, the metal concentrations in the vegetables and soil were lower than the approved levels specified by the Codex Alimentarius Commission standards and the WHO/FAO guidelines expect for Cd, Pb and Cr which were higher in plant and Cd which was higher in the soil.

CHAPTER ONE

1.0 Introduction

1.1 Heavy Metals

A heavy metal is a member of a loosely-defined subset of elements that exhibit metallic properties. It mainly includes the transition metals, some metalloids, lanthanides, actinides. Many different definitions have been proposed- some based on density, some on atomic number and some on chemical properties or toxicity (John, 2002).

The term heavy metal refers to any metallic chemical element that has a relatively high density (at least $5g/cm^3$) and is toxic or poisonous even at low concentrations. Examples of heavy metals include such metal as: Hg, Cd, As, Cr, Ti, Cu, Sn, Fe and Pb (Michael, 2010). They are natural components of the earth's crust. Heavy metals occur naturally in the ecosystems with large variations in concentration. In modern times, anthropogenic sources of heavy metals, often lead to pollution which destroy the ecosystem (John, 2002). Heavy metals cannot be degraded nor destroyed, but tend to bio-accumulate. To a small extent they are ingested through food, drinking water and air. As trace elements, some heavy metals (like Cu, Fe, Zn, Co, Mn, and Mo) are essential to maintain the metabolism of the human body. However, at higher concentrations they can lead to poisoning (Michael, 2010). Heavy metals are dangerous because they tend to bio-accumulate due to their increase in the concentration in a biological system over time compared to the chemical's concentration in the environment (Michael, 2010). These compounds accumulate in living things any time they are taken up and stored faster than they are broken down, metabolized or excreted (Michael, 2010).

Heavy metals can enter a water supply via industrial and domestic waste, or even from acidic rain or through breaking down of soils and these activities caused the release of heavy metals into streams, lakes, rivers and ground water (Michael, 2010). Heavy metals such as

mercury, platinum, cadmium and lead are toxic metals since they have no known vital or beneficial value on organisms, and their accumulation over time in can cause serious illnesses, even death (Michael, 2010). Certain elements such as vanadium and tungsten that are normally toxic are, for certain organisms but under certain conditions, beneficial (Michael, 2010).

Metals are also derived from natural components or geological sources as well as from human activities or anthropogenic sources. Metals can be dispersed, both naturally and by human activities into air, land and sea. There are numerous sources of metals in soils which include: soil parent materials, volcanic eruption and forest fires; agricultural, sewage, energy mining and smelting, transportation, urban/Industrial complexes and. Recycling operations (Anderson, 2003). Metal contamination issues are becoming increasingly common; the occurrence of metals in soils both natural and polluted has been subject of a number of studies (Muller and Anake, 1994; Sanchez-Camazano *et al.,* 1994; Dudka *et al.,* 1995; Caussy *et al.,* 2003; cui *et al.,* 2004). High concentrations of metals in soil can pose a risk to agricultural production and to human health (Cui *et al.,* 2004).

1.2 Metals of Interest, their Occurrences in Soils and Toxicity

There are about 45 different metals utilized in industrial processes which may lead to their exposure to humans (Nriagu, 1984). Information on metabolism and toxicity in plants animals and humans are well documented for most metals such as Fe, Zn, Cu, Se, Pb, Cd, Hg and As (Nriagu, 1984). Metals can be classified by their known importance to living organisms as essential and non essential elements. The essential elements including Cr, Co, Cu, Fe, Mn, Mo, Ni, Se and Zn as these are required by organisms at micro or trace level and become toxic at higher levels of exposure. Non-essential elements including As, Sb, Cd, Pb, Hg, Ti, Sn, and Ag which are toxic and not required by organisms at any level (Mcgrath, 2001).

This research concentrates on nine metals namely; Cr, Mn, Fe, Ni, Cu, Zn, Mo, Cd and Pb which represent both essential and non-essential elements. The ranges of values above which toxicity is considered to be possible in mg/Kg are 70-400 (Zn), 3-8 (Cd), 60-125 (Cu), 100-400 (Pb), 15000-30000 (Mn), 100 (Ni), (Alloway,1995), and 75-100(Cr) (Rose, 1994).

1.2.1 Chromium (Cr)

Chromium is fairly abundant in the earth crust, with chromites as the only important Cr ore a mineral of the spinel group, with the formula $(Fe,Mg)O(Cr,Al,Fe)_2O_3$ (COBEAP, 1974). The ore contains chromic oxides (Cr_2O_3) and ferrous oxide (FeO). Chromium can exists in various oxidation states, but commonly occurs as trivalent and hexavalent. The important Cr ions are chromates and dichromate, which are easily reduced to trivalent Cr^{3+} in acid solutions and in the presence of organic matter (COBEAP, 1974). The concentration of Cr in soils is usually between 80-200 mg/kg. High Cr content has been associated with infertility of some soils. Chromium is used in the leather tanning industry, the manufacture of catalysts, pigments and paints, fungicides, the ceramic and glass industry, photography, chrome alloy and Cr metal production, chrome plating and corrosion control (WHO, 2003). Chromium is an essential nutrient that helps the body use sugar, protein and fat (Calabrese *et al.,* 1985). Deficiency results in impaired growth and longetivity, and disturbance in glucose lipid, and protein metabolism (Calabrese *et al.,* 1985). Chronic exposure to hexavalent Cr is reported to induce renal failure, anaemia, haemolysis and liver failure (UK FSA, 2003). Also, Low-level exposure of chromium can irritate the skin and cause ulceration. Long-term exposure can cause kidney and liver damage, and damage to circulatory and nerve tissue. Chromium often accumulates in aquatic life, adding to the danger of eating fish that may have been exposed to high levels of chromium. Studies have shown also, that the ingestion of 1 – 5g of “chromate” resulted in severe acute

effects such as gastrointestinal disorders, haemorrhagic diathesis, and convulsions. Death may occur following cardiovascular shock (Janus and Krajnc, 1990).

1.2.2 Manganese (Mn)

Manganese is next to iron in the Periodic Table, and is similar to it in chemical behavior and is often closely associated with it in its natural occurrence (COBEAP, 1974). It is widely distributed in igneous and sedimentary rocks and constitutes about 0.10% of the earth's crust. Manganese can have valencies of 1, 2,3,4,6 and 7 in its compounds. However, it is the divalent state that is the most stable and the pyrolusite dioxide (MnO_2) is the most stable and important mineral ore of Mn. Manganese also occurs as sulphide, silicate and carbonate (COBEAP, 1974). Manganese is used primarily in the production of iron, steel, alloy and a number of other uses such as dry cell batteries, paint driers, pigments, and catalysts (Levy et al., 2004). High concentrations of Mn in soil may be linked to mining and Industrial pollution. Manganese is necessary for the formation of connective tissues and bone, amino acid, carbohydrate and lipid metabolism, embryonic development of the inner ear, and reproductive function (Levy et al., 2004)**.** Manganese is present in food especially green vegetable (2 mg/kg), nuts (814.9 mg/kg), bread (8 mg/kg) (UK FSA, 2003). Manganese is an essential element for many living organisms including humans (Hurley and Keen, 1987). Accordingly, adverse health effects can be caused by inadequate intake. Manganese deficient animals exhibit impaired growth, skeletal abnormalities, reproductive deficits, ataxia of the new born and defects in lipid and carbohydrate metabolism (Hurley and Keen, 1987). Exposure to Mn may occur via food and inhalation. Airborne particles of Mn can be absorbed through inhalation by miners, smelters and workers in the manufacture of dry batteries. Miners who have inhaled Mn contaminated air develop a severe psychiatric disorder resembling schizophrenia, along with progressive central nervous system

deterioration resulting in permanent crippling (Calabrese *et a*l., 1985). This condition is called *laura mangania*

1.2.3 Iron

Iron is common and abundant in the earth crust occurring primarily in oxide ores: hematite and magnetite. The most common Fe containing minerals in soil are the ferric oxy-hydroxides. Iron is combined in crystals structures either as divalent ferrous or trivalent ferric ions. In metallic form, it is chemically unstable and slowly oxidized and converted to ferrous and ferric compounds. In water solutions, it occurs as Fe (II) or Fe (III), or as inorganic or organic ferrous or ferric complexes. Iron is primarily ferric in most soils, although the ferrous state may be predominant in some soils that are flooded and rich in organic matter (COBEAP, 1979; Miller *et al.,* 1981).

Plants require a continuous supply of Fe for growth because it is an essential component of many enzymatic functions and light energy transferring compounds in photosynthesis(COMBEAP, 1975).In the human body, Fe is mainly in the form of hemoglobin within the circulating erythrocytes, which serve to transport oxygen. As a key element in many structural functions, Fe deficiency can cause many abnormalities in growth, and reproduction (COMBEAP, 1975).

The critical toxicity concentrations for total Fe in plants are quite high, measuring 400 to 1000 mg/kg (Mortvedt *et al.,* 1991). In human, acute toxicity of ingested Fe is unlikely to be encountered from any source other than medical Fe (MBEEP, 1979). However, soluble ferric salts may produce irritation of gastrointestinal tract, characterized by abdominal pain and diarrhoea, when given in large dose especially on an empty stomach (Boyd, 1973).

1.2.4 Nickel (Ni).

Nickel is ubiquitous in the earth's crust and mainly occurs in sulphide and oxide ores. It is particularly concentrated in granite (~0.5 mg/kg) (Bennett, 1981). Hence, the Ni content in soil may range widely depending on mineral composition. Nickel is known primarily for its divalent compounds since the most important oxidation state of the element is +2. Nickel also exists as certain compound in which the oxidation state of the metal is between -1 to +4. It is used in stainless steel production, Ni-Cd batteries, alloy and electroplating (Eisler, 1998). Nickel contamination may occur from emissions of metal mining, smelting, and refining operations; nickel plating and alloy manufacturing; land disposal of sludges and disposal as effluent (Eisler, 1998).

Nickel is present in a number of enzymes in plants and micro organisms. In humans, Ni influences Fe absorption and metabolism, and may be an essential component of the hemopoietic process (UK FSA, 2003). Its deficiency has not been observed in humans, but plants containing more than 100 ppm Ni develop symptoms of toxicity (Arun and Mukherjee, 1998). Toxicity in grasses or other monocots closely resembles iron deficiency, exhibiting pale yellow strips running the length of the leaf. In extreme cases, the entire plant may turn white with marginal necrosis of the leaf. In dicots, Ni toxicity causes an intervenial chlorosis (yellowing) that looks very similar to manganese deficiency (David *et al.,* 2008).

Nickel is relatively non-toxic through the oral route due to limited intestinal absorption (Bennett, 1981). Small amounts of nickel are needed by the human body to produce red blood cells, however, in excessive amounts, can become mildly toxic. Short-term exposure to nickel is not known to cause any health problems, but long – term exposure can cause decreased body weight, heart and liver damage, and skin irritation. Nickel can accumulate in aquatic life, but its

presence is not magnified along food chains. Acute nickel intoxications are rare, and most reported cases are the result of industrial exposure to nickel carbonyl (WHO, 2001).

Contact with Ni and with solution of Ni salts may result in dermatitis (COMBEAP, 1975).

Acute Ni exposure is associated with a variety of clinical symptoms and signs including nausea, vomiting, diarrhea, visual disturbance, and headache. Chronic inhalation of Ni and its compounds is associated with an increased risk of lung cancer (UK FSA, 2003).

1.2.5 Copper

Copper occurs naturally in the environment in a wide range of mineral deposits like sulphides, carbonates and silicates. The three most important sources of Cu are chalcocites (Cu_2S), chalcopyrite ($CuFeS_2$), and malachite ($CuCO_3.Cu\ (OH)_2$) (Eisler,1998a). Copper is present in relatively low concentrations in soils at about 50mg/kg. Most Cu is used for the production of electrical equipment, roofing and plumbing pipes. (Irwin, 1997)

In plants copper is essential in seed protection. Excess copper can cause phyto-toxicity in plants and it has been used as an algicide to control algal blooms. It can cause plant damage at very high concentration, example: sewage sludge which is applied to agricultural land (Wase and Forster, 1997). Copper is required in human in trace levels in order to help in the haemoglobin formation and carbohydrate metabolism. It is also incorporated into many Cu proteins such as cytochromeoxidase, tyrosinase, and erythrocyte superoxide dismutase (Irwin, 1997). Cu deficiency and toxicity are rarely observed in humans. Humans can be exposed to Cu via food and drinking water. Single exposure to 30 mg/L of Cu or greater in drinking water can result in gastrointestinal effects (vomiting, diarrhea, and abdominal pain) in healthy humans (Geogopoulos *et al.,* 2001).

1.2.6 Zinc

Zinc constitutes approximately 0.004% of the earth's substances (Browing, 1969). It occurs naturally in ore minerals especially as sphalerites (ZnS) which is often associated with the sulphides of other metallic elements such as Cd, Cu, and Fe. Zinc is also found as zinc carbonates ($ZnCO_3$). Other forms of zinc are usually products of the oxidation of ZnS. In soil solution, it is present as Zn^{2+}, $Zn(OH)_2$, $ZnSO_4$, and $ZnHPO_4$ (Lindsay, 1979).

The main uses of Zn are for galvanization of iron and steel to prevent rust and corrosion. Metallic Zn is mixed with other metals to form alloys such as brass and bronze and also usd to make dry cell batteries. Zinc oxide is used in the manufacture of paints, rubber, ceramic, and many other products. Total zinc in non polluted soil is generally bellow 500 mg/kg, whereas, the concentration in polluted soil could be higher than 3000 mg/kg (Long *et al.,* 2003). The increased level of zinc in soil is mainly caused by disposal of zinc waste from the manufacturing industries. Sludges and fertilizers also contribute to high levels of zinc in the soil. (Long *et al.,* 2003). Many reports have shown that a deficiency of Zn in plants can cause a reduction in photosynthesis by 50% - 70% depending on the plant species and the severity of the deficiency (Alloway, 2004). Excess Zn is toxic to plants and humans. It is generally assumed that Zn levels in excess of 300 – 600 mg/kg dry weight are considered to be toxic to plants (Marschnar, 1995). The information on Zn toxicity in human is scarce.

1.2.7 Molybdenum

Molybdenum naturally occurs in association with other elements e.g. Molybdenite (MoS_2) which is a major mineral ore for Mo. The predominant form of Mo occurring in soil is the molybdate anion, MoO_4^{2-}(Calabrese *et al.,* 1985). Molybdate is quite strongly attached to clay particles or oganic matter in soils. The two major uses of Mo are as an alloy in stainless

steels and in alloy steels. Mo is also an important material for chemical and lubricants industries (Calabrese *et al.,* 1985). As a pure metal, Mo is used because of its high melting temperature (2610^{o}C) as filament support in light bulbs, metal- working die sand furnace parts. In plants, Mo is required in small amount for bacterial nitrogen fixation. In humans, it serve as a component of several enzymes including aldehyde oxidase, sulphite oxidase, and xanthine oxidase, which are important in protein catabolism (Calabrese *et al.,* 1985) High concentrations of Mo in water and food have been associated with gout in humans. (Calabrese *et al.,* 1985)

1.2.8 Cadmium

The natural concentrations of Cadmium in soil are very low and these occurs as the sulphide mineral (CdS). Most Cd is produced as a by-product of zinc smelting, as it is usually found with zinc in the environment. Cd is bound in clay and basic soil but is more mobile in sandy and acidic soils.

Its uses include Ni-Cd batteries, pigments for plastics, Cd coatings, PVC stabilizers and alloys. Cd is present in sewage sludges which are used as fertilizers and can contribute 90% of the total Cd input to soil (Benneth, 1981). It is also release into the environment upon incineration of plastics (Wase and Foster, 1997).

Cadmium is a highly toxic element which in humans can cause damage to the kidney and bones, and is probably best known for its association with itai – itai disease (Wase and Foster, 1997). Humans can be exposed to cadmium by inhalation and ingestion. Various types of foods are the major source of exposure, even though gastrointestinal absorption is limited to 5 % (Nriagu, 1984). It can accumulate in the liver and kidney and at toxic levels; it impairs the function of these organs. However, humans are protected against chronic exposure to low levels Cd by the

sulphur-rich protein called metallothionein (Baird, 1999). This protein can complex almost all ingested Cd^{2+}, and the complex is subsequently eliminated in the urine (Baird, 1999).

1.2.9 Lead

Lead exists in the natural state as the insoluble sulphide ore, galena, PbS (Benneth, 1981). Lead can be found as other compounds including PbO_2, $PbCO_3$, and $PbSO_4$. The Pb contents in soil ranges usually from 10-150 mg/kg (Nriagu, 1984). It is generally high in urban and Industrial areas compared to rural areas. The uses of Pb include; making of batteries, ammunition (lead shot), metal products (solder and pipes), shield x-rays. The uses of Pb can result in sources of transfer to humans, such as from improperly disposed of Industrial waste into agricultural soils and water (Bennett, 1981).

The immobilization of Pb in soil is greatest in soil of high cation exchange capacity (Bennett, 1981). Lead enters plant by root uptake from soil or by direct deposition from air. The natural Pb levels in plants, animals and human are very low.

Lead enters the body mainly by inhalation and ingestion. The most important route of exposure is ingestion of Pd-contaminated food (Nriagu, 1984). The effects of Pb toxicity include hypertension and brain damage (Wase and Foster, 1997). It may cause both acute and chronic effect, mainly in the hematopoietic, nervous, gastrointestinal and renal systems (Bennett, 1981).

1.3 Vegetables

Leafy vegetables are essential components of the daily food intake (Faboya, 1983; Ladeji and Okoye, 1993; Aletor and Adeogun, 1995). They provide the much needed minerals, vitamins and supplementary protein as the populace depend largely on them as starchy staples (Taylor, 1996; Vegetables of Canada, 2006).Vegetables are annuals and biennials, whose succulent parts such as leaves, stems, flowers, shoot, root and tubers are consumed as supplementary foods to

fortify the diet. They are rich sources of essential vitamins and minerals, dietary fibre and provide additional calories and protein (Oyenuga and Fetuga, 1975).

1.3.1. Cabbage (***Brassica oleracea*** or variants).

This is a leafy green or purple biennial plant, porpullarly called kabeji in Hausa language, grown as an annual vegetable for its dense-leaved heads (Oyenuga and Fetuga, 1975). Closely related to other cole crops, such as broccoli, cauliflower, and brussels sprouts, it descends from *B. oleracea var. oleracea*, a wild field cabbage (Gibson, 2012). Under conditions of long sunlight days such as are found at high northern latitudes in summer, cabbages can grow much larger (Ernest 2009; Gibson 2012; USDA, 2012). Vegetables perform best when grown in well-drained soil in a location that receives full sun. Different varieties prefer different soil types, ranging from lighter sand to heavy clay, but cabbage grows or thrives in a well fertile ground with a pH between 6.0 and 6.8 (Bradley *et al.,* 2009). Cabbage is a good source of vitamin K, vitamin C and fiber (USDA, 2007; USFDA, 2008). Cabbage is also an excellent source of manganese, vitamin B6, and foliate; and a good source of thiamin, riboflavin, calcium, potassium, vitamin A, tryptophan, protein, and magnesium. Studies suggest that it, as well as other cruciferous vegetables, may reduce the risk of some cancers, especially those in the colorectal group (Assayed *et al.,* 2009). This is possibly due to the glucosinolates found in cole crops, which stimulate the production of detoxifying enzymes that remove carcinogens created during metabolism (Higdon *et al.,*2007), or due to the sulphoraphane content, also responsible for metabolic anti-carcinogenic activities (Gullet *et al.,* 2010). Purple cabbage also contains anthocyanins, which in other vegetables have been shown to have anti-carcinogenic properties (Katz and Weaver, 2003). Along with other cole crops, cabbage is a source of indole-3-carbinol, a chemical that boosts DNA repair in cells and has been shown—in experiments using cell cultures and animal models—to block the growth of cancer cells (Wu *et*

al., 2010). Research also suggested that boiling these vegetables reduces their anti carcinogenic properties (Wien and Wurr, 1997).

1.3.2. Garden Cress. (*Lepidium sativum)*

Garden Cress popularly refered to lamsir in hausa language and commonly referred to as garden cress is a rather fast-growing, edible herb (Cassidy *et al.,* 2002). Garden cress is genetically related to watercress and mustard, sharing their peppery, tangy flavour and aroma. In some regions, garden cress is known as mustard, cress, garden pepper cress, pepperwort pepper grass, or poor man's pepper (Staub *et al.,* 2008). Garden cress is an annual vegetable that thrives in damp soil. The easiest of the cresses to grow, garden cress can be harvested in as little as two weeks after sowing. Its peppery taste adds zing to salads, but hot weather makes this cool-season crop bitter and inedible. Garden cress requires full sun during winter or early spring. Soil conditions requires well-drained soil or sometimes moist, fertile soil with high organic matter and pH 6.0 to 6.7 Germination temperature ranges from 55°F to 75°F emergence 2 to 7 - In early spring when soils are cold (~45°F), germination may take two weeks(USDA, 2014)

Garden cress seeds, since ancient times, have been used in local traditional medicine of India (NDPID, 1978) Garden cress seeds are bitter, thermogenic, depurative, rubefacient, galactogogue, tonic, aphrodisiac, ophthalmic, antiscorbutic, antihistaminic and diuretic (NDPID, 1978). They are useful in the treatment of asthma, coughs with expectoration, poultices for sprains, leprosy, skin disease, dysentery, diarrhoea, splenomegaly, dyspepsia, lumbago, leucorrhoea, scurvy and seminal weakness (Eddouks *et al.,* 2005). Seeds have been shown to reduce the symptoms of asthma and improve lung function in asthmatics (Archana and Anita 2006). The seeds have been reported as possessing a hypoglycemic property (Eddouks *et al.,* 2005), and the seed mucilage is used as a substitute for gum arabic and tragacanth. (Budgerigars-

Diets, PDSA 2004). The seeds are employed as poultice for removing pains, swells while some people use it in the belief that it can cure asthma, bronchitis bleeding piles, it is also used for the treatment of indigestion and constipation (Najebb *et al.,* 2011; Bhatiya 1996).

1.3.3. Sesame Plant

Ceratotheca sesamoides is a flowering plant in the genus *Ceratotheca*. It is indigenous to Africa and grows both as a wild weed and locally cultivated species. The locally cultivated speies is commonly referred to as false sesame and karkashi in Hausa owing to its marked similarities with common sesame (*Sesamum indicum*) (Falusi *et al.,* 2002). The plant is most commonly cultivated in the African Savannah and other semi-arid areas on the continent (Falusi *et al.,* 2002). False sesame is very flexible with regards to environment and grows best in well drained sandy soils with high exposure to the sun but with less success in rocky areas (Bedigian and Adetula, 2004).

It can be identified by numerous hairs on the stem, its pink flowers often replete with brown and purple dots and a sub-erect growth habit (Falusi *et al.,* 2002). A plant with many practical uses, the leaves and flowers are often consumed as vegetables or used in sauces. The leaves can also have medicinal benefits while the seeds can be employed to produce cooking oil. Despite its many uses and growing domestication at a local level, the plant remains predominantly underused and undervalued. The plant has also been used to treat dysentery and measles (FAO/WHO, 1998). The leaf may be an effective anti-oxidant, anti-inflammatory and anti-hypertensive agent while the mucilage can be used as an emollient and lubricant (Fasakin, 2011). False sesame has been claimed to possess some anti-viral properties and has even been employed as an aphrodisiac (Toyin *et al.,* 2012). The slimy liquid produced by soaking the leaves in water can be used to treat conjunctivitis (Adesiyin and

Uddin, 2011). Warm leaves can be ground up and mixed with ash then applied to inflamed cervical lymph nodes to help expedite delivery in both humans and animals (Bedigian and Adetula, 2004). If the leaves are ground up with the rhizome of *Anchomanes difformis* the ensuing mixture has been used to treat cases of leprosy (Bedigian and Adetula, 2004; Tse and Eslick 2014).

1.3.4. Lettuce (*Lactuca sativa*)

Lettuce popularly called salak in Hausa is an annual plant of the aster or sunflower family Asteraceae. It is most often grown as a leafy vegetable, but sometimes for its stem and seeds. Lettuce grows best in full sun in loose, nitrogen-rich soils with a pH of between 6.0 and 6.8. Heat generally prompts lettuce to bolt, with most varieties growing poorly above 75 °F (24 °C); cool temperatures prompt better performance, with 60 to 65 °F (16 to 18 °C) being preferred and as low as 45 °F (7 °C) being tolerated. Plants in hot areas that are provided partial shade during the hottest part of the day will bolt more slowly. Temperatures above 80 °F (27 °C) will generally result in poor or non-existent germination of lettuce seeds (Bradley *et al.,* 2009). Lettuce is a good source of vitamin A, vitamin K and potassium, with higher concentrations of vitamin A found in darker green lettuces (FAO/WHO, 1998). It also provides some dietary fiber (concentrated in the spine and ribs), carbohydrates, protein and a small amount of fat. With the exception of the iceberg type, lettuce also provides some vitamin C, calcium, iron and copper, with the vitamins and minerals largely found in the leaf (University of Illinois Etention, 2012). Lettuce naturally absorbs and concentrates lithium (Hullin *et al.,* 2003).

1.3.5. Spinach (***Amaranthus hybridus)***

*Amaranthus hybridus(*Spinach*)* originates from North America, as a hybrid between the North and South American (Grubben *et al.,* 2004). Vegetable amaranth (*Amaranthus hybridus*) is

an important vegetable crop in Nigeria and other parts of the world. It is known as *Alayyahu* [Hausa], *Tete* [Yoruba] and *Inine* [lgbo] (Showemimo and Olarenwaju, 2004). It is a member of *Amaranthaceae* and was introduced to Africa from Central and South America (Grubben, 1976). It is planted all year round and harvested for food (Omidiji, 1978; NRC, 1984; Kumar and Owonubi, 1987; Olufolaji and Okelana, 2001).

The a*maranthus* species are traditionally cultivated for consumption of their shoots which are prepared into soups and stews (Oke, 1983). It has been established in various studies that Nigeria leafy vegetables contain substantial amounts of various mineral elements (Faboya, 1983; Bawa and Yadav, 1986; Ladeji and Okoye, 1993; Aletor and Adeogun, 1995). The vegetative parts are rich in essential metabolites, especially vitamins, carotene, protein and crude fibre (Ladeji and Okoye, 1993; Taylor, 1996). *Amaranthus hybridus* is cultivated for its tender stem and succulent leaves. The leaves are alternate, simple and the leaf blades are variable in shape, from lanceolate to triangular (Omidiji, 1978). *Amaranthus* is useful for livestock feed and human consumption. It has high leaf protein concentrates, mineral content (Ca and Fe), vitamins (carotene, riboflavin, niacin) and other essentials needed for feeding young children and people with nutritional deficiencies or malnutrition (Koch et al., 1965; Oyenuga and Fetuga, 1975; Oke, 1980; Taylor, 1996).

Cutting of the leaves start when the plants are 25-30cm tall and fully grown leaves are removed (Choudhry, 1979). The yield of *Amaranthus* leaves may be over 40t/ha of fresh matter or 5t/ha of dry matter and this yield though are less than required for both man and livestock (Makus, 1983). Other uses of *Amaranthus hybridus* are as an ornamental, paste, cake and confections (Ayensu, 1978). Its seeds are used to make an intoxicating drink in south-western Africa (Burkill, 1995).

1.4 Soil

Soil is one of the three major natural resources, alongside air and water. It is one of the marvelous products of nature and without which there would be no life (Nyle and Ray, 1999). Soils are crucial to life on earth. From ozone depletion to rain forest destruction, to water pollution, the global ecosystem is impacted in far-reaching ways by the processes carried out in the soil (US-EPA, 2004). It is the underlying foundation of houses, factories, and motorways as well as a filter for human, Industrial and animal wastes (Fraser, 2004). Still, to most people, soil is the natural medium in which plants grow. Researchers have recognized that soil is more than just a medium; rather, it is an active, ever-changing body and agro-ecosystem which provides the elements essential for plant growth and support (Fraser, 2004).

Soil is also defined as a natural body consisting of layers of mineral constituents of variable thickness, which differ from the parent material in their morphological, physical, chemical and mineralogical characteristics (Birkeland, 1999). It is composed of particles of broken rock that have been altered by chemical and environmental processes that include weathering and erosion. Soil differs from its parent rock due to interactions between the lithosphere, hydrosphere, atmosphere, and the biosphere (Chesworth, 2008). It supports a complex ecosystem, which supports the plants on the surface and creates new soil by breaking down rocks and sand (Voroney, 2006). This microscopic ecosystem has co-evolved with the plants to collect and store water and nutrients in a form usable by plants (Michael, 2010). Soil particles pack loosely, forming a soil structure filled with pore spaces. These pores contain soil solution (liquid) and air (gas) (Taylor and Ashcroft, 1972). Accordingly, soils are often treated as a three state-system (McCarty and Ashcroft, 1972). Soil is also known as earth: it is the substance from which the planet takes its name.

1.4.1. Soil Organic Matter

The smallest component of soil is the soil organic matter, making up only a few percent of the soil volume. It is composed of the partially decayed remains of plants and animals, the organic compounds produced by organisms during decay and the organisms themselves. The organic matter content of a typical well-drained agricultural soil usually does not exceed about 5% by volume (McCarty and Ashcroft, 1972; Milne, 2009).

Soils contain carbon in both organic and inorganic forms. In most soils (with the exception of calcareous soils) the majority of carbon is held as soil organic carbon (SOC). The term soil organic matter (SOM) is used to describe the organic constituents in the soil (Tissues from dead plants and animals products produced as these decompose and the soil microbial biomass). The term "soil organic carbon" refers to the carbon occurring in the soil in soil organic matter (Milne, 2009).

The constituents of soil organic matter can be divided into non-humic substances, which are discrete identifiable compounds such as sugars, amino acids and lipids, and humic substances, which are complex largely unidentifiable organic compounds. As organic compounds, both humic and non-humic substances contain carbon, oxygen and hydrogen and can also contain nitrogen, phosphorus and sulphur (Milne, 2009).

The amount of soil organic carbon depends on soil texture, climate, vegetation and historical and current land use/management. Soil texture affects soil organic carbon because of the stabilizing properties that clay has on organic matter. Organic matter can be trapped in the very small spaces between clay particles making them inaccessible to micro-organism and therefore slowing decomposition. In addition clay offers chemical protection to organic matter through adsorption onto clay surface, which again prevents organic matter from being decomposed by bacteria.

Soils with high clay content therefore tend to have higher soil organic carbon than soils with low clay content under similar land use and climate conductions (Wagai *et al.,* 2008; Milne, 2009).

1.4.2. Soil pH (Acidity and Alkalinity)

Soil pH is a measure of the degree of acid-base equilibrium (the soil reaction that affects all soil chemical, physical and biological properties) (Nyle and Ray, 1999). Soil pH largely controls plant nutrient availability and microbial reaction in soils. It effects will determine which trees, shrubs, or grasses will dominate the landscape under natural conditions and the cultivated crops will grow well or not grow at all in a given field site. Soil reaction also determines the fate of many soil pollutants affecting their breakdown and possible movement from the soil into groundwater and streams. The pH of a soil helps determine the numbers and kinds of soil organisms that change plant residues into valuable soil organic matter. Hence, it influences aggregate stability and, in turn, the movement of air and water in soils.

pH is one of the factors which influence the bioavailability and the transport of heavy metal in the soil and according to Smith (1996), heavy metal mobility decreases with increasing soil pH due to precipitation of hydroxides; carbonates or formation of insoluble organic complexes. Heavy metals are generally more mobile at pH <7 than at pH >7. In other words, metal concentration in soil decreases with increasing acidity but increases with increasing alkalinity of the soil. Also, metal concentration increases with increasing humus content of the soil and vice versa (Dudka and Chlopecha, 1990).

Many human activities can influence soil reaction. For example, certain chemical fertilizers and organic wastes react in the soil to form strong inorganic acids, such as HNO_3 and H_2SO_4. These lead to increased soil acidity. Climate also tends to stimulate either acidity or alkalinity in soils. In humid regions, soils tend to be quite acidic because there is sufficient rainfall to leach out

much of the base forming cations ($Ca^{2+,}$ $Mg^{2+,}$ K^+ and Na^+), leaving the exchange complex dominated by Al^{3+} and H^+ ions. In low rainfall areas where leaching is not very intense, the opposite is the case (Nyle and Ray, 1999).

When salts of strong bases and weak acids such as Na_2CO_3, K_2CO_3, and $MgCO_3$, undergo hydrolysis they develop alkalinity.

$2Na^+CO_3^{2-} + 2HOH \rightarrow 2Na^+ + 2OH^- + H_2CO_3$

1.5 Uptake and accumulation of metals in plants

Whereas metal contamination is widespread, the occurrence of heavy metals in agricultural soils is a major concern. Heavy metals taken up by plants may enter the food chain in significant amounts. Hence, people could be at risk of adverse health effects from consuming vegetables grown in soils containing elevated metal concentrations. For instance, it is estimated that approximately half of human Pb intake is through food, with around half originating from plants (Nasreddine and Parent-Massin, 2002). According to the Environmental Protection Agency (EPA), Pb is the most common heavy metal contaminant in the environment (Watanabe, 1997) and may be toxic to organisms even when absorbed in small amounts. Cadmium and Pb are the elements of most concern because of their potential for toxicity or accumulation in plants and animals (Wolnik *et al.,* 1983). Although metals such as Zn, Cu and Mn are essential trace elements for plants and animals, they can also be dangerous at high exposure levels. For example, poisoning incidents with symptoms of gastrointestinal distress, nausea and diarrhea have been reported after a single or short-term exposure to concentrations of Zn in water or beverages concentration of 1000 - 2500 mg/L (WHO, 2001). At high doses of certain metal compounds, of the order of several grams, chronic toxicity or carcinogenicity as well as fatality may occur. Certain crops such as spinach, lettuce, carrot, radish, and zucchini can accumulate

heavy metals e.g. Cd, Cu, Mn, Pb and Zn in their tissues (Cobb *et al.,* 2001; Mattina *et al.,* 2003; Hough *et al.,* 2004; Zhou *et al.,* 2005). Generally, uptake is increased in plants that are grown in areas with increased soil contamination. Among the metals, Cd and Zn are fairly mobile and readily absorbed by plants (Mench *et al.,* 1994). In contrast, Cu and Pb are strongly adsorbed onto soil particles reducing their availability to plants (WHO, 1989; 1998). In addition, they are bound to organic matter, as well as being absorbed by carbonate minerals and hydrous iron and manganese oxides (Sauerbeck, 1991; Muller *et al.,* 1994; Hooda, 1997; Bahemuka and Mubofu, 1999). In recent years, extensive research has been conducted on estimation of the bioavailability and toxicity of metals in soils. However, no methods are currently available to allow accurate prediction of plant uptake or phyto-toxicity, adverse effects on human health, or accu-toxicity resulting from metal pollution of soils (Nolan *et al.,* 2003).

1.6. Significance of the Research

Lands in Challawa, Sharada, and Kwakwache are intensively used for different purposes namely residential, industrial and agricultural among others. Soil pollution is a threat to the environment, to food safety and to sustainable agriculture. Thus, it is necessary to carry out an investigation on the level of heavy metals in these soils. This study is important because vegetable uptake of metals is one of the major pathways which soil-metals enter into food chain and is subsequently bio-accumulated to high concentrations causing serious risk to human health when plant based food stuffs are consumed (Cui, 2004), thus, it is important to determine the level of heavy metals in some of the vegetables (lettuce, cabbage, garden cress, sesame and spinach). This study is also important as one of the vegetable (spinah) studied were recommended for phyto-extraction of nickel in contaminated soil (Duman and Ozturk, 2010).

1.7 Problem Statement

Kano is a large commercial city located in north-west Nigeria, with high industrial and agricultural and domestic activities among others. Also due to its activities there is a great influx of population into the city which has continued to result in a wide variety of environmental problems (Uwah *et al*., 2011). Some of the problems include the current inability of urban authorities to adequately manage large quantities of the generated waste (UNDP, 2006). This has resulted to uncontrolled and unmonitored disposal of waste in open dumps sites and water bodies with the consequence of contamination and subsequent pollution of the environment by heavy metals. This has become a global concern due to their widespread distribution and multiple effects on the ecosystem (Nriagu, 1990; Uwah *et al*., 2011).

Most of these activities which lead to high disposal of untreated wastes to water bodies which are used by farmer for irrigation. These wastes have been known to contain high level of heavy metals which tends to accumulates over time in the soil since they are non bio-degradable. (Nriagu, 1990).

1.8 Justification

Metal contamination issues are becoming increasingly common; the occurrence of metals in soils both natural and polluted has been subject of a number of studies (Caussy *et al.,* 2003; cui *et al.,* 2004). High concentrations of metals in soil can pose a risk to agricultural production and to human health (Cui *et al.,* 2004).Heavy metals taken up by plants may enter the food chain in significant amounts. Hence, people could be at risk of adverse health effects from consuming vegetables grown in soils containing elevated metal concentrations (Caussy *et al.,* 2003). For instance, it is estimated that approximately half of human Pb intake is through food, with around half originating from plants (Nasreddine and Parent-Massin, 2002). vegetable uptake of metals is

one of the major pathways which soil-metals enter into food chain and is subsequently bio-accumulated to high concentrations causing serious risk to human health when plant based food stuffs are consumed (Cui, 2004), These vegetables bio- accumulates heavy metals from the soil and when they are eaten by human beings and animals, the heavy metal accumulate in the body with serious health effects (USEPA, 1989, 2002; UNDP, 2006; Rotich *et al*., 2006). That's why it is important to study the phyto- remediatve abilities of some of these vegetables (lettuce, cabbage, garden cress, sesame and spinach).

1.9. Aims and objectives

This research is aimed at determining the relative pyto-remediation abilities of selected vegetables (lettuce, cabbage, garden cress, sesame and spinach) obtained from farmlands of three industrial estate of kano on some heavy metals (Cd,Cr, Pb, Ni, Fe, Mo, Mn, Cu and Zn). The specific objectives of this study were to

- Evaluate the total concentrations of some heavy metals in the soil
- Determine the uptake level of heavy metals by the selected vegetables.
- Compare the result obtained from the various sampling sites with control, and establish whether or not pollution existed
- Compare the values of the tranfer factor, bio-accumilation factor, and translocation factors in the various vegetable
- Evaluates phyto-remediative properties of the various vegetables of study.

CHAPTER TWO

2.0 Literature Review

\2.1. Phyto-remediation.

Phyto-remediation refers to the technologies that use living plants to clean up soil, air, and water contaminated with hazardous chemicals (Reichenauer and Germida, 2008). It refers to the natural ability of certain plants called hyperaccumulators to bioaccumulate, degrade, or render harmless contaminants in soils, water, or air. Toxic heavy metals and organic pollutants are the major targets for phytoremediation (Reichenauer and Germida, 2008). Knowledge of the physiological and molecular mechanisms of phytoremediation began to emerge in recent years together with biological and engineering strategies designed to optimize and improve phytoremediation (Salt *et al.,* 1998). In addition, several field trials confirmed the feasibility of using plants for environmental cleanup (Salt *et al.,* 1998).

Wojcik *et al.,* (2014) investigated heavy metals (Zn, Pb, Cd, Cu, Ni, Cr) in three Zn-Pb waste deposits in southern Poland for the identification of potential species suitable for phyto-remediation using flame AAS to determine heavy metal concentration in the plant of study. The authors reported that in the upper layers of waste deposit, the total concentration of metals ranged from 7300 to 171790 mg/kg for Zn, 1390 to 22265 mg/kg for Pb, and 66 to 1464 mg/kg for Cd, whereas $CaCl_2$-extracted fractions accounted for 0.034–0.11%, 0.005–0.03%, and 0.28–0.62% of total Zn, Pb and Cd concentrations, respectively. The concentration of metals in the substrate of plant was variable. Low uptake was observed for Cu, Ni, and Cr in the shoots and was similar to background values. Highest mean concentrations of Zn, Pb and Cd were found in

Anthyllis vulneraria L., *Echium vulgare* L., and *Hieracium piloselloides Vill,* were 901.5 mg/kg, 116.92 mg/kg, 26.86 mg kg^{-1} respectively. The study revealed that all the studied species developed a metal exclusion strategy and has the potential for phyto-stabilization of metalliferous wastelands.

Roccotiello *et al.,* (2014) worked on the Mediterranean shrub *Alyssoides utriculata* and investigated its phyto-remediation potential in Ni polluted soils. The technique employed was atomic absorption spectrophometry after wet digestion of plant samples using HNO_3 and H_2O_2 and tri acid digestion for total metal determination in soil samples. The soil available Ni and the total Ni content of this species along with possible interactions with Ca and Mg was calculated. For phyto-extraction or phyto-stabilization, bioaccumulation factor (BF) and the translocation factor (TF) were determined. The leaf concentration of Ni was higher than 1000 μg g^{-1}.The BAF and TF values were greater than 1. These species was classified as hyper-accumulator of Ni. This study revealed for the first time that *A. utriculata* could be suitable for cleaning Ni-contaminated site in phyto-remediation technologies.

Suchkova *et al.,* (2014) studied the natural establishment of plants and the restoration of sewage sludge deposits through phyto-remediation. Different native plant species such as *Amaranthus albus* L. *Amaranthus viridis* L. *Cardaria draba* L. *Chenopodium album* L. *Cynodon dactylon* (L) *Pers*., *Cyperus rotundus* L. *Lolium perenne* L. *Lycopersicon esculentum MilL. Malva parviflora* L. *Portulaca oleracea* L were used or phyto-remediation. The plants were collected for chemical analyses of trace elements (Mn, Cu, Zn, Fe, Cr, Ni, Pb) , macronutrients (Ca, Mg, K, P and Na) using flame AAS to determine trace elements and atomic emission spectroscopy (AES) for the macronutrients determination. The results showed that plants took up macronutrients at relatively high rates and trace elements were removed at a lower rate compared to hyper-accumulators.

This is due to the reduced bioavailability of metals in the substrate because of the sewage sludge. The BCF value for most of the species and trace metal was greater than 1, indicated that the plants have the ability for phytoremediation. The results revealed that selected native plants were not only tolerant to adverse environmental conditions, but also suitable for restoration of sites affected by sewage sludge.

Kumar *et al.,* (2013) investigated the heavy metals phyto-remediation potential of twelve native weed species like *Croton bonplandianum*, *Calotropis procera*, *Solanum nigrum*, *Datura stramonium*, *Cyperus rotundus, Phyllanthus amarus, Sida cordifolia*, *Solanum xanthocarpum*, *Spinacia oleracea, Euphorbia hirta*, *Parthenium hysterophorus* and *Tridax procumbens* growing naturally in the field. The heavy metals (Cr, Cu, Ni, Pb and Cd) concentration in all the plant species was determined using flame AAS and were found to have an enrichment factor >1, which reflected their high metal accumulation potential. The study concluded that land polluted with toxic metals, may be phyto-remediated by these weed species.

Muhammad *et al.,* (2013) investigated the soil and phyto-remediation potential of wild plant species for macro and trace metals (MTM) (K, Ca, Na, Mg, Cu, Mn, Fe, Pb, Cd, Zn, Co, Ni, and Cr) along mafic and ultramafic terrain (chromites mining) in northern Pakistan using flame AAS to determine trace elements and atomic emission spectroscopy (AES) for the macronutrients determination. Soil showed significant ($p<0.001$) contamination levels, while multifold enrichment factor (EF) of Mn, Fe, Cr, Co and Ni were found in plant species such as *Rumex hastatus, Plectranthus rugosus*as and *Selaginella jacquemontii* compared to reference area. The results clearly showed that wild plant species accumulated significant amount of metals concentration and therefore should be used for phyto-remediation and that the high metal (Fe,

Mn, Cr, Ni, Co, and Pb) concentrations in the wild plant species raised toxicological concerns in the study area.

Shah *et al.,* (2013) assessed heavy metals concentration in soils and indigenous plant species along mafic and ultramafic rocks in mélange zone (Chromate mining), Mohmand Agency northern Pakistan using flame AAS to determine heavy metals concentrations in various samples. Plant species grown on these soils were investigated for their bioaccumulation potentials. The serpentine soil showed higher metal concentration as compared to background soil. Correlation matrix was variable between soil sample and plant species metal uptake in the same habitat. The plant species *Chrysopogon zizanioides* and *Lycopersicon esculentum* showed multifold enrichment in Fe, Mn, Ni and Cr and hence proficient to accumulate and transfer these metals to a greater level in their above ground parts. This study suggested that these local indigenous plant species might cause potential health hazards as high concentrations Cr and Ni have toxicological risks.

Ghaderian and Ravandi, (2012) worked on the phyto-remediation abilitiesof selected plants in southeast copper mining area of Iran. Plants and soils were collected from different sites and analyzed for heavy metals using atomic absorption spectrophometry (AAS) after digestion of plant samples using HNO_3 and H_2O_2 and tri-acid digestion for total metal determination in soil samples. The results showed that total concentration among the different sites were different and showed the Zn, Pb, Ni, and Cu concentrations that were up to 1500, 700, 35, and 1300 µg /g and 8, 1.5, 0.5 and 11 µg /g for their exchangeable fractions, respectively. The metal concentrations were also variable, ranging from 2–1074 µg /g for Zn, 1–76 µg /g for Pb, 0.1–22 µg /g for Ni and1 to 4012 µg /g for Cu,. The plant species such as *Onosma stenosiphon* (657 µg /g). *Epilobium hirsutum* (1581 µg /g) *Polypogon fugax* (4012 µg /g), *P. fugax* and *E. hirsutum*

accumulated significant amount of Copper and are considered as provisional hyper-accumulators and should be used for phyto-remediation of copper contamination sites.

Usman *et al.,* (2012) determined the pollution level (PL) of Cr in contaminated soils and native plant species growing in the CCA contaminated site, Gangwon Province, Korea. In this study 19 native plant species along with soil samples were collected along for phyto-remediation potential. The concentrations of Cr in the soil and plant samples were determined and the technique employed was atomic absorption spectrophometry (AAS) after digestion of plant samples using HNO_3 and H_2O_2 and tri-acid digestion for total metal determination in soil samples. His result showed that the metal contamination decreased as the distance between the sampling point and CCA-treated wood structure increased. The plant species of *Iris ensata*, showed highest concentration of Cr (1120 mg kg^{-1}) in its shoot and was identified as a hyper-accumulator. While the 15 plant species showed BAF root values > 1 and TF values < 1 which were consider suitable for phyto-stabilization.

Rashed, (2010) investigated heavy metals and metalloids (Mn, Ni, Zn, Pb, As, Cd, Cr, Cu, Ag, Au, Hg, and Mo) levels in samples of soils, tailings and wild plants (*Acia Raddiena* and *Aerva Javanica*) at a gold mine, in Egypt. The study objective was to find metal concentration and mobility in surrounding soil and plants. The technique employed was atomic absorption spectrophometry (AAS) after wet digestion of plant samples using HNO_3 and H_2O_2 and tri-acid digestion for total metal determination in soil samples. The results showed that as the distance from tailing increased the metal concentrations in soil decreased. Among the plant species *Acia Raddiena* accumulated significant amounts of Pb, Cd and As compared to *Aerva Javanica*. In soil and plants pollution quantifications were intended by using contamination factor (CF), enrichment factors (EF), bioaccumulation factors (BF) and pollution load index (PLI). On the

basis of findings, it was accomplished that the soil and plants showed multifold higher metal concentrations near the gold mine tailing. Therefore, these high concentrations may pose potential threat to the local community thus the plant and soil of the area may not be used for agriculture and grazing purposes.

Shah *et al.,* (2010) studied the mafic and ultramafic terrain northern areas Pakistan with major focus on heavy metals such as (Cr, Cu, Pb, Zn, Cd and Ni) concentration in soils and their bioaccumulation in wild plants. The technique employed in these study was atomic absorption spectrophometry (AAS) after wet digestion of wild plants samples using HNO_3 and H_2O_2 and tri-acid digestion for total metal determination in soil samples.

The result showed greater malleability and manifold higher enrichment in bioaccumulation compared to background samples. Among the 23 wild plants, *Cannabis sativa* showed enrichment for (Zn and Cu); *Indigofera gerardiana* and *Saccharum griffihii* for *(*Ni and Cr) and *Ailanthus altissima* for (Pb) respectively. The results showed that these species can be used for land restoration and mineral aspects.

Ha *et al.,* (2010) worked on the phyto-mining and phyto-remediation of lead–zinc mines in Northern Vietnam. For this purposes, the heavy metals and arsenic total concentrations were determined in the plants, soil and water in both mining and non mining areas. The technique employed was flame atomic absorption spectrophometry (AAS) after ashing and digestion of plant samples using HNO_3 and H_2O_2 and tri-acid digestion for total metal determination in soil samples. The plant species which showed the hyper accumulation levels (1000 mg kg^{-1}dry weight) were *Ageratum houstonianum Mill*, *Potamogeton oxyphyllus Miq*, and *P. vittata* for Pb and *Houttuynia cordata Thunb* and *Pteris vittata* L for As. The result showed that none of the collected plants were suitable for phyto-mining.

Liu *et al.,* (2008) opined that phyto-remediation is an environmentally friendly and cost-effective technology to remove pollutants from polluted sites. In their study 19 plants growing on polluted sites were examined. Soil and plant samples were collected and analyzed for heavy metals concentration using flame atomic absorption spectrophometry (AAS) after ashing and digestion of plant samples using HNO_3 and H_2O_2 and tri-acid digestion for total metal determination in soil samples. The total concentrations of Zn, Pb and Cu in d soil ranges from 36-4,311 mg/kg, while in plant shoots ranged from 6.3-2,029 mg/kg. The results revealed that the two native species (*Tephrosia candida* and *Debregeasia orientalis*) and one cultivated crop (*Ricinus communis* L.) have great potentials for Pb polluted soils and should be used for phyto-remediation

Yoon *et al.,* (2006) evaluated he phyto-remediation potentials of different plant species growing on mine contaminated site in North Florida. Plant and soil samples were analyzed for heavy metal concentrations using flame atomic absorption spectrophometry (AAS) after ashing and digestion of plant samples using HNO_3 and H_2O_2 and tri-acid digestion for total metal determination in soil samples. Among the studied plants, most species were not appropriate for phyto-extraction because no hyper-accumulator was identified. The results showed that the plant species *Phyla nodiflora* was capable in accumulating Zn and Cu in its shoots (TF=6.3 and 12) similarly for phyto-stabilization the *Gentiana pennelliana* was most efficient for Pb, Cu and Zn (BCF=11, 22 and 2.6). Correlation matrix for plant uptake was high, while translocation of Pb was negatively correlated with Cu and Zn though translocation of Cu and Zn were correlated using SPSS. The results revealed that native plant species have the potential for phyto-remediation when growing on contaminated sites.

2.2 Amendment for remediation

Bolan *et al.,* (2014) reviewed the remediation of contaminated soils and bioavailability of heavy metals using different soil amendments. Chelating and desorbing agents when amended in soil increase or mobilize the bioavailability and mobility of metal(loid)s while precipitating agents and sorbent materials when amended decrease or immobilize the bioavailability and mobility of metal(loid)s (Wagai *et al.,* 2008). Mobilizing agents increases the heavy metal(loid)s removal via plant bioaccumulation and soil washing. Immobilizing agents decrease the translocation of metalloids to food chain through plant uptake and groundwater leaching (Milne, 2009). The basic limitations of these mobilizing techniques are the leaching of the mobilized heavy metalloid due to of active plant bioaccumulation. While in immobilization technique the long-term monitoring is needed for the stability of the immobilized heavy metalloid.

Beseeley *et al.,* (2014) studied soils polluted with organic wastes amendment and noted increase in trace element mobility and toxicity. Speciation modeling and toxicity analysis (*Vibrio fischeri* luminescence inhibition and *Loliumperenne germination*) were carried out using a chromatographic system coupled to inductively coupled plasma-mass spectrometry (ICP-MS) to distinguish the mechanisms in controlling the metal distribution and estimating toxicity risk before and after. Biochar decrease free metal concentrations but dissolved organic carbon primarily controlled metal mobility after compost amendment. Individually, both amendments induced considerable solubilization of arsenic to pore water (>2500 mg/dm^3), Thus this study revealed that combining the biochar and compost amendments was most effective at mitigating toxicity risk.

De Lima *et al.,* (2014) reported that due to the large surface area, activated carbon is often used in metal ion adsorption processes. Activated carbon is cost effective and environmentally

friendly material for industrial use. For example, surface area, scanning electronic microscopy, energy dispersive X-ray fluorescence, thermo gravimetric analysis, zeta potential, surface basic and acid groups, iodine number, and ash content were measured. The relationship between these characteristics and the origin of the activated carbons was also examined by using principal component analysis (PCA). The result revealed that some adsorbent was able to remove Cu (II), Cr (VI), and Zn (II) from a metallurgic effluent very efficiently.

Josko *et al.,* (2013) worked on the adsorbents (activated carbon) to reduce the risk associated with the presence of contaminants in sediments. They measured the toxicity of sediment polluted with organic compounds and trace metals with and without the amendment of selected adsorbents. Three carbonaceous materials (CM) activated carbon (AC), biochars (BC1, BC2), and multi-walled carbon nano tubes (CNTs) were used. AC was highly effective with (70%) reduction of seed germination inhibition, (27.5%) reduction of root growth inhibition). the phyto-toxicity reduction of these sediments as a result of amending BC1, BC2 and CNT ranged from 30 to 40% (reduction of seed germination inhibition) and from 17.7 to 28.9% (reduction of root growth inhibition). The biochars diameter decreased with the reduction of sediment toxicity. With the passage of time the CM and sediment had an adverse effect on the reduction of root growth inhibition in the case of all materials tested.

Sabir *et al.,* (2013) studied the effect of activated carbon, poultry manure and press mud on immobilization of Cu, Zn, Ni, Mn, Fe and Pb in the polluted soil, plant growth and metals concentration in shoots of maize. The soil were amended with different adsorption and applied at the rate of 4% which significantly (p<0.001) affected maize shoots biomass and concentrations of selected metals as compared to the control. The treated pots of activated carbon had minimum concentration for AB-DTPA extractable metals except iron and lead. The study revealed that

among the selected amendments activated carbon efficiently immobilized Mn, Ni, Cu and Zn reducing AB-DTPA extractable Ni in the soil, while the application of other amendments increased Fe and Pb.

Fellet *et al.,* (2013) worked on the biochar amendment in mine tailings to minimize the risk of contaminants dispersion. The research was aimed at stabilizing mine tailings on changing the soil condition and plant growth on different types of biochar produced from different feed stocks (pruning residues, fir tree and manure pellets). Different plant species, *Poaalpina* L. *subsp. Alpina, Nyman, Noccaea rotundifolium* L. *Anthyllis vulneraria subsp. Polyphylla* (Dc.) *Moench subsp. Cepaeifolium* was used in pot experiment. The biochars amendment was made at three doses: 0, 1.5 and 3% on dry weight basis. The biochars significantly changed the EC, CEC, pH and bioavailability of the metals. The biochar from pruning residues and manure pellets reduced shoot Cd and Pb uptake and increased biomass production at 1.5% dose. The amendment of biochar for phyto-remediation is of great concern but their effect was dependent on the type of biochar from which it was obtained.

Khan *et al.,* (2013a) studied the effects of sewage sludge biochar (SSBC) upon bioaccumulation of nutrients, biomass yield, metalloids, and green house gas (GHG) emissions. The results revealed that soil total nitrogen, pH, available nutrients and soil organic carbon increased with SSBC amendment while bio-available Ni, Cr, As, Co, and Pb decreased except Cu, Zn and Cd). The grain yield (148.8−175.1%), shoot biomass (71.3−92.2%), and the bioaccumulation of sodium and phosphorus significantly ($p \leq 0.01$) increased in SSBC amended rice plants, though the bioaccumulation of nitrogen (except in grain) and potassium reduced. The SSBC amendment significantly ($p \leq 0.05$) decreased heavy metals (Ni, Cr, As, Co, Cu, Pb) bioaccumulation but

increased Zn and Cd, which were within the range of the permissible limits set by Chinese regulations.

Liu *et al.,* (2012) conducted pot experiment to assess the effects of activated carbon, liquid organic fertilizers and attapulgite clay used as soil amendments to immobilize cadmium (Cd) and lead (Pb) in contaminated soils and growth of tobacco. The results showed that all the three amendments decreased the concentration of DTPA-extractable Cd and Pb in soils as well as in tobacco roots and leaves as compared to the control. The results showed positive correlation between DTPA-extractable Cd and Pb in soil and tobacco leaves and suggested that DTPA-extractable Cd and Pb determination could be a suitable method for investigating Cd and Pb bioavailability.

Modin *et al.,* (2011) studied the absorption and behaviourof granular activated carbon, iron fines and bone meal for their capacity to remove metals from landfill leachate. In the laboratory, the removal of, Co, Cr, Cu, Al, Sr, As, Ca, Cd, Fe, Mn, Mo, Hg, Mg, Zn, Pb, and Ni were studied. Activated carbon removed more than 90% of Cu, Cr, Fe, Mn and Co but less efficiently for Sr, Pb, Zn, Ni and Ca. Iron fines less efficiently removed most metals (Zn, Cu, Cr, Co, Sr, Pb, Mn, Mg, As, Ca, and Fe) to some extent. Bone meal removed over 80% of Fe, Cr, Sr, Hg and Mn and 20–80% of Al, Zn, Cu, Al, Mo, Pb, Ni, Pb and Ca. The study assessed that wide range of metals can be removed by using two or more filter materials combined and that for metal immobilization iron. The oxidation of Fe (0) seems to be important

Achiba *et al.,* (2010) studied the comparison between farmyard manure and municipal solid waste compost on the mobility and bioaccumulation of heavy metals, as well as organic nitrogen and carbon in Tunisian calcareous soil. The study revealed that the soil organic nitrogen and carbon contents significantly increased with the amendment of municipal solid waste and

farmyard manure in comparison with untreated soil. The total metal concentration of Cd, Cu, Pb and Zn significantly increased with municipal solid waste compost in the topsoil as compared to farmyard manure. These heavy metals were mainly present in the macro-organic matter fraction. Pb, Cu and Zn were present in the 150–50 micron and less than 50 macro-organic fractions after municipal solid waste compost application. Cd content also showed significant increase in the 150–50 micron fraction. The result clearly showed that the major fractions for Ni, Zn, Cu and Cr were the residual fraction. In contrast, Cd was present in both the acid-extractable and reducible fraction while Pb was mainly associated with the reducible fraction.

2.3 Mineral Uptake Mechanisms by Plants

Plants obtain the inorganic nutrients they need from soil. However, plants are not perfectly selective so that, in addition to essential nutrients, they may take up minerals that are redundant or even toxic (Marschnar, 1995). Uptake of metals into plant roots is a complex process involving transfer of metals from the soil solution to the root surface and inside the root cells (Reichman, 2002). Ions are absorbed along with water from the solution that surrounds soil particles. The solution enters the root at, the root hairs which are the extensions of epidermal cells.

2.4 Storage Sites and Target Organs for Heavy Metals

Heavy metals accumulate in the body when the detoxifying system is slower than their absorption. They have specific sites and target organs where they accumulate to exert their toxic effects (Lenntech, 2008). Cadmium accumulates in the liver, placenta, kidney, lungs, brain and bones (Maile, 2007). The mechanism of cadmium toxicity is not understood clearly but its effects on cells are known (Patrick, 2003). Cadmium concentration increases 3,000 fold when it binds to cystein-rich protein such as metallothionein (Patrick, 2003). In the liver, the cystein-

metallothionein complex causes hepatotoxicity and then it circulates to the kidney and gets accumulated in the renal tissue causing nephrotoxicity. Cadmium has the capability to bind with cystein, glutamate, histidine and aspartate ligands and can lead to the deficiency of iron (Castagnetto *et al.*, 2002). Cadmium and zinc have the same oxidation states and hence cadmium can replace zinc present in metallothionein, thereby inhibiting it from acting as a free radical scavenger within the cell. When Mn enters the body, it accumulates in the liver, kidney and pancreas but the central nervous system manifests its toxic effects more than these organs (Francis and Forsyth, 1995; Flora, 2008)

Target organs for Pb include bones, brain, blood, kidney and thyroid glands (ATSDR, 2007). Lead metal causes toxicity in living cells by following ionic mechanism and that of oxidative stress (Wadhwa *et al.*, 2012; Flora *et al.*, 2012). Mansy researchers have shown that oxidative stress in living cells is caused by the imbalance between the production of free radicals and the generation of antioxidants to detoxify the reactive intermediates or to repair the resulting damage (Wadhwa *et al.*, 2012; Flora *et al.*, 2012). The ionic mechanism of lead toxicity occurs mainly due to the ability of lead metal ions to replace other bivalent cations like Ca2+, Mg2+, Fe2+ and monovalent cations like Na+, which ultimately disturbs the biological metabolism of the cell. The ionic mechanism of lead toxicity causes significant changes in various biological processes such as cell adhesion, intra- and inter-cellular signaling, protein folding, maturation, apoptosis, ionic transportation, enzyme regulation, and release of neurotransmitters. Lead can substitute calcium even in picomolar concentration affecting protein kinase C, which regulates neural excitation and memory storage (Flora *et al.*, 2012).Lead affect the nervous, blood, kidneys and the cardiovascular systems (ATSDR, 2007), while nickel affects the respiratory, gastrointestinal, blood and the kidney systems mostly, though viral infections that can change the target organs

(ATSDR, 2005). Generally, the negative impacts of heavy metals on humans and animals include; central nervous system depression, organ damage, damage to blood system, respiratory system irritation, skin irritation and potentially carcinogenic (Lawrence, 2008).

CHAPTER THREE

3.0 Experimental

In the preparation of reagents, chemicals of analytical grade purity and distilled water were used. All glass wares and plastics were washed with detergent, rinsed with tap water followed by distilled water and oven drying.

3.1 Sampling

Samples of cabbage, lettuce, spinach, garden cress, sesame plant and soil were randomly collected in Kano metropolis farm areas from February to April and September to October, 2014. The plant samples were authenticated at the Department of Plant Biology Bayero University Kano, Nigeria.

3.2 Sampling Areas

The study was carried out in the city of Kano, located in the North Western Nigeria. The areas involved were Bayero University Kano old Campus, Sharada, Chalawa, and Kwakwachi farm which are located at Gwale, Kano manucipal, Kumbotso and Fagge Local Governments area respectively as shown in (Fig. 3.1).

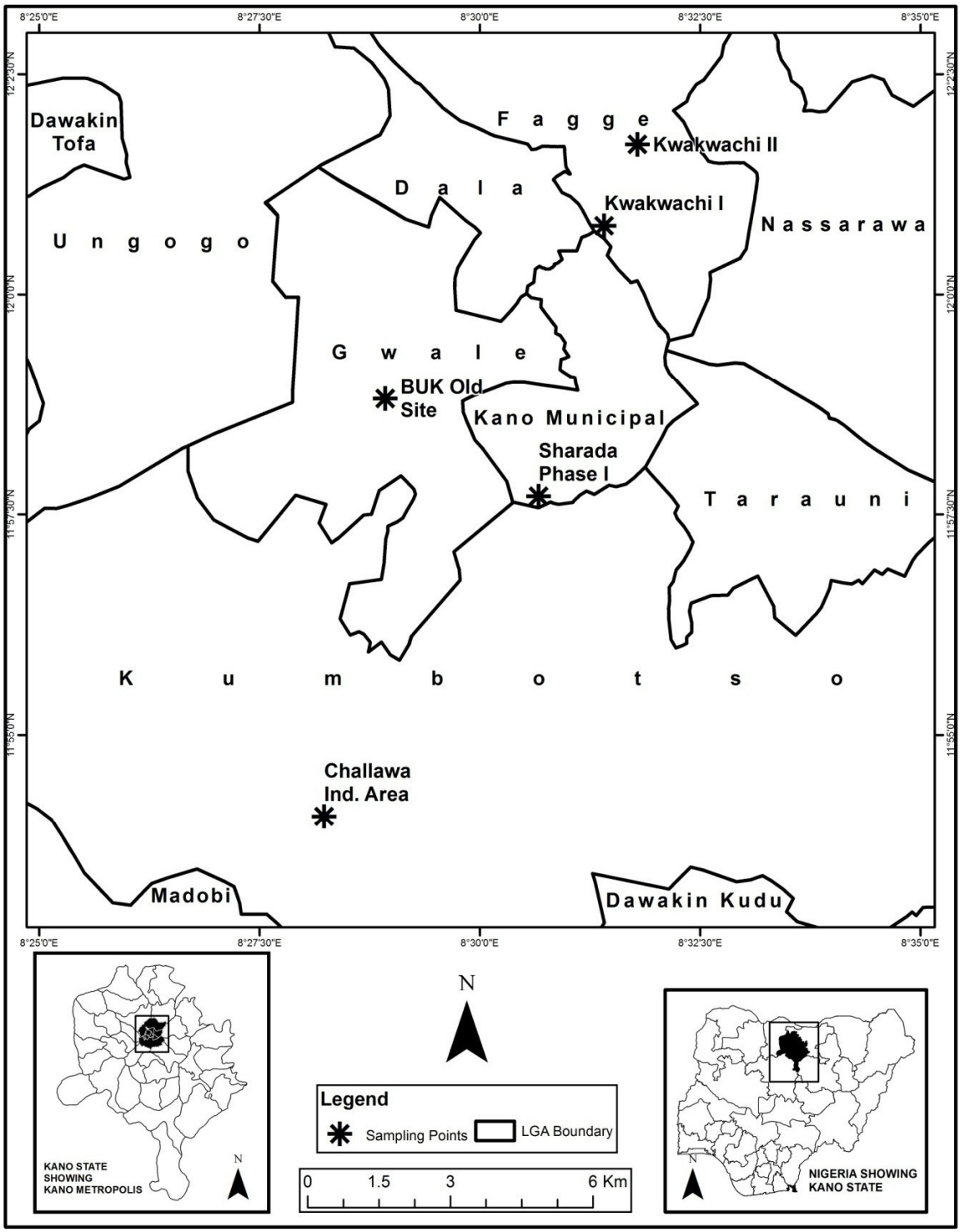


Fig.3.1. Map of metropolitan Kano Showing Sampling Points.

3.3 Sample Pre-Treatment

The collected vegetable samples were washed with distilled water to remove dust and soil particles. The samples were then cut to separate the roots, stems and leaves using a plastic knife. The vegetables were air-dried and then grounded into a fine powder using ceramic pestle and mortar. The powders were sieved and stored in separately labeled polyethylene bags. Soil samples were also collected from the farms air-dried grounded, sieved with 2 mm mesh and stored in separately labeled polyethylene bags.

Preparation of Reagent Solutions

0.1M Nitric Acid

Concentrated nitric acid (S.G. 1.42; 65% W/V) of 6.90 cm^3 was diluted with water in a 100 cm^3 beaker and on cooling was transferred into a 1000 cm^3 volumetric flask and was made up to the mark with distilled water (Marisa, 2007).

0.25M Nitric Acid

Concentrated nitric acid (S.G. 1.42; 65% W/V) of 17.30 cm^3 was diluted with water in a 100 cm^3 beaker and on cooling was transferred into a 1000 cm^3 volumetric flask and was made up to the mark with distilled water (Marisa, 2007).

40% Hydrogen Peroxide

Concentrated Hydrogen Peroxide of 40 cm^3 was measured using a measuring cylinder and added to 20.0 cm^3 water in a 100 cm^3 beaker. The mixture was transferred into a100 cm^3 volumetric flask and was made up to the mark with more distilled water (Marisa, 2007).

60% Hydrogen Peroxide

Concentrated Hydrogen Peroxide of 60 cm^3 was measured using a measuring cylinder and added to 20.0 cm^3 water in a 100 cm^3 beaker. The mixture was transferred into a100cm^3 volumetric flask and was made up to the mark with more distilled water (Marisa, 2007).

1000 mg/dm^3 Ammonium Molybdate Solution

In preparation of 1000 mg/dm^3 ammonium molybdate Solution 1.8402 g of ammonium molybdate tetrahydrate, $(NH_4)_6Mo_7O_{24}.4H_2O$ was dissolved in 10cm^3 of 2M nitric acid in a 1000 cm^3 volumetric flask. 50 mg/dm^3 ammonium molybdate solution was prepared by diluting 50 cm^3 of the stock solution in a 1000 cm^3 volumetric flask and was made up to the mark.

Working-Standard solutions of 0.0, 2.0., 4.0, 6.0, 8.0 and 10.0 mg/dm^3 were prepared by diluting 0, 4, 8, 12, 16 and 20cm^3 respectively of the stock solution of 50 mg/dm^3 concentration in 100 cm^3 volumetric flask (Marisa, 2007).

1000 mg/dm^3 Zinc Solution

In preparation of 1000 mg/dm^3 zinc Solution 4.550 g of zinc nitrate hexahydrate, $Zn(NO_3)_2.6H_2O$ was dissolved in 10 cm^3 of 2M nitric acid in a 1000 cm^3 volumetric flask. 50mg/dm^3 zinc solution was prepared by diluting 50 cm^3 of the stock solution in a 1000 cm^3 volumetric flask and was made up to the mark.

Working-Standard solutions of 0.0, 2.0., 4.0, 6.0, 8.0 and 10.0 mg/dm^3 were prepared by diluting 0, 4, 8, 12, 16 and 20cm^3 respectively of the stock solution of 50 mg/dm^3 concentration in 100 cm^3 volumetric flask (Marisa, 2007).

1000mg/dm^3 Nickel Solution

In preparation of 1000 mg/dm^3 nickel Solution 4.96 g of nickel (ll) nitrate hexahydrate, $Ni(NO_3)_2.6H_2O$ was dissolved in 10 cm^3 of 2M nitric acid in a 1000 cm^3 volumetric flask. 20

mg/dm^3 nickel solution was prepared by diluting 20 cm^3 of the stock solution in a 1000 cm^3 volumetric flask and was made up to the mark. 5 mg/dm^3 nickel solution was further prepared by diluting 250 cm^3 of the 20 mg/dm^3 solution in a 1000 cm^3 volumetric flask and was made up to the mark.

0.0, 2.0., 4.0, 6.0, 8.0 and 10.0 mg/dm^3 Working-Standard solutions were prepared by diluting diluting 0, 4, 8, 12, 16 and 20 cm^{3}respectively of the 5mg/dm^3 solution in 100 cm^3 volumetric flasks (Marisa, 2007).

1000mg/dm^3 Manganese Solution

In preparation of 1000 mg/dm^3 manganese Solution 4.57g of manganese (ll) nitrate tetrahydrate, $Mn(NO_3)_2.4H_2O$ was dissolved in 10cm^3 of 2M nitric acid in a 1000cm^3 volumetric flask. 20mg/dm^3 manganese solution was prepared by diluting 20cm^3 of the stock solution in a 1000cm^3 volumetric flask and was made up to the mark. 5mg/dm^3 solution was further prepared by diluting 250cm^3 of the 20mg/dm^3 solution in a 1000cm^3 volumetric flask.

0.0, 2.0., 4.0, 6.0, 8.0 and 10.0mg/dm^3 Working-Standard solutions were prepared by diluting 0, 4, 8, 12, 16 and 20cm^3 respectively of the 5mg/dm^3 solution in 100cm^3 volumetric flask (Marisa, 2007).

1000mg/dm^3 Lead Solution

In preparation of 1000 mg/dm^3 lead Solution 1.599g of lead nitrate, $Pb(NO_3)_2$ was dissolved in 10cm^3 of 2M nitric acid in a 1000cm^3 volumetric flask. 20mg/dm^3 solution was prepared by diluting 20cm^3 of the stock solution in a 1000cm^3 volumetric flask and was made up to the mark. 5mg/dm^3 lead solution was further prepared by diluting 250cm^3 of the 20mg/dm^3 solution in a 1000cm^3 volumetric flask.

Serial dilution of 0.0, 2.0., 4.0, 6.0, 8.0 and 10.0mg/dm^3 were prepared by diluting 0, 4, 8, 12, 16 and 20cm^3 respectively of the 5mg/dm^3 lead solution in 100cm^3 volumetric flask (Marisa, 2007).

1000mg/dm^3 Chromium Solution

In preparation of 1000 mg/dm^3 chromium Solution 7.696 g of chromium nitrate nonahydrate, $Cr(NO_3)_2 .9H_2O$ was dissolved in 10 cm^3 of 2M nitric acid in a 1000cm^3 volumetric flask. 20 mg/dm^3 solution was prepared by diluting 20 cm^3 of the stock solution in a 1000cm^3 volumetric flask and was made up to the mark. 5 mg/dm^3 chromium solution was prepared by diluting 250 cm^3 of the 20mg/dm^3 solution in a 1000 cm^3 volumetric flask with water.

Working-Standard solutions of 0.0, 2.0., 4.0., 6.0., 8.0.and 10.0 mg/dm^{3}concentrations were prepared by diluting 0, 4, 8, 12, 16 and 20 cm^3 respectively of the 5 mg/dm^3 solution in 100 cm^3 volumetric flask (Marisa, 2007).

1000mg/dm^3 Copper Solution

In preparation of 1000 mg/dm^3 copper Solution 3.80g of copper (ll) nitrate trihydrate, $Cu(NO_3)_2.3H_2O$ was dissolved in 10cm^3 of 2M nitric acid in a 1000 cm^3 volumetric flask. 20 mg/dm^3 solution was prepared by diluting 20 cm^3 of the stock solution in a 1000 cm^3 volumetric flask and was made up to the mark. 5 mg/dm^3 copper solution was prepared by diluting 250 cm^3 of the 20mg/dm^3 in a 1000 cm^3 volumetric flask and was made up to the mark. Working-Standard solutions of 0.0, 2.0., 4.0., 6.0., 8.0.and 10.0 mg/dm^{3}concentration were prepared by diluting 0, 4, 8, 12, 16 and 20 cm^3 respectively of the 5 mg/dm^3 solution in 100 cm^3 volumetric flask (Marisa, 2007).

1000mg/dm^3 Iron Solution

In preparation of 1000 mg/dm^3 iron Solution 7.234 g of iron (ll) nitrate non ahydrate, $Fe(NO_3)_3.9H_2O$ was dissolved in 10 cm^3 of 2M nitric acid in a 1000 cm^3 volumetric flask.

50mg/dm^3 iron solution was prepared by diluting 50 cm^3 of the stock solution in a 1000 cm^3 volumetric flask and was made up to the mark.

Working-Standard solutions of 0.0, 2.0., 4.0., 6.0., 8.0.and 10.0 mg/dm^{3}were prepared by diluting 0, 4, 8, 12, 16 and 20 cm^3 respectively of the stock solution of 50 mg/dm^3 concentration in 100 cm^3 volumetric flasks (Marisa, 2007).

3.4 Measurements of Soil pH and Conductivity

In the measurement of pH and conductivity 20 g of air-dried soil was weighed into 150 cm^3 beaker, and 100 cm^3 of IM KCl solution was added and the suspension stirred several times for 30 minutes. The suspension was allowed to stand for another 30 minutes for the suspended clay to settle. The clear supernatant solution was decanted into a clean 150 cm^3 beaker and the pH and conductivity measured using calibrated Denver PH and Conductivity meter model 20 (IITA, 1979; Eno *et al*., 2009).

3.5 Determination of Organic Carbon

For organic carbon determination 1 g of the air – dried soil sample was weighed into a conical flask. 10cm^3 of 1M $K_2Cr_2O_7$ solution was pipetted into the flask and swirled gently to disperse the soil. 20 cm^3 of conc. H_2SO_4 was added rapidly using an automatic pipette, directing the stream into the suspension. The flask was immediately swirled gently until the soil and reagents were mixed. The flask was swirled more vigorously for one minute and allowed to stand on a sheet of asbestos for thirty minutes. 100 cm^3 of de-ionized water was added into the flask and allowed to stand for another thirty minutes. 5 cm^3 of O-phosphoric acid was added to sharpen the colour change of the end point. 3 drops of indicator (O - phenanthroline monohydrate) was added and titrated with 0.5M Fe $(SO_4).6H_2O$. As the end point approached, the solution changed from orange color to green. The above analysis was repeated two more

times with fresh soil samples. The blank titration in the same manner, but without the soil sample was carried out to standardize the dichromate (IITA, 1979). The organic carbon of the soil sample was calculated according to this formula:

$$\%\ Organi\ Carbon = \frac{\left(MeqK_2Cr_2O_7 - Meq\left(NH_4\right)_2 Fe\left(SO_4\right)_2.6H_2O\right)x\ 0.003\,x100\,x\,F}{Mass\ of\ air\ dry\ soil}$$

Where:

F: Correction Factor = 1.33

Meq: Molarity of solution x volume of solution used. However, % organic matter (OM) or humus was calculated from the relationship:

%: Organic Matter (Humus) = % OC x 1.729

OC Organic Carbon

3.6. Preparation of heavy metal spiked soils

Spiked soil samples at three concentration levels (low, medium and high) and control soil (unadulterated) were used for this study as shown in Table 3.1. A control soil is one to which no spiking of heavy metals had been made. For low concentration level (approximately 5 times unadulterated concentration), a metal solution at the approximate levels (50, 40, 300, 40, 150, 100, 100, 5 and 25 mg/kg for Cr, Mn, Fe, Ni, Cu, Zn, Mo, Cd and Pb respectively) were prepared and used to spike the soil samples. Approximately 300g of the soil was mixed, and placed in a plastic tray. Then, the soil was thoroughly mixed with the metal solution to ensure homogeneity and air dried to allow excessive water to evaporate. The spiked soil was left for two weeks before planting to ensure thorough chemical-soil contact. The medium and high concentration level (approximately 10 and 15 times unadulterated concentration, respectively) were prepared in the same manner as described above (Marisa, 2007)

Table.3.1. Level of metal concentration used to (spike) contaminate the soil (mg/kg)

Element	Control	Low	Medium	High
Cd	0.1	0.5	1	1.5
Cr	1	5	10	15
Cu	30	150	300	450
Fe	100	300	450	600
Mn	8	40	80	120
Mo	2	5	10	15
Pb	0.3	0.5	1	1.5
Ni	20	40	80	120
Zn	60	100	200	300

3.7 Growing of Vegetable Plants and Sample Collection

Seeds of spinach, lettuce, sesame, cabbage and garden cress were obtained directly from the local market. These seeds were germinated in plastic trays containing the contaminated soil and the seedlings transplanted after two weeks into individual plastic pots. These plants were grown in soil contaminated at low, medium and high concentrations respectively. The plants were also grown in control soil. The plants were irrigated daily with tap water and are placed under natural sunlight. The plants were nurtured and monitored until maturity which was between 6-8 weeks (Marisa, 2007).

3.8 Plant Samples Digestion and Analysis

The vegetables were harvested and rinsed with distilled water to remove dust and sand particles. They were cut into smaller sizes separating the leaves, stems and roots and were then air dried for about 2weeks. Thereafter, samples were oven dried at 70^{o}C then grounded sieved and stored in a labeled polyethene bags. 1 g of prepared vegetable samples was weighed into 125

cm3 conical flasks and 10 cm^3 of conc.HNO_3 was added. The mixture was heated for 30 minutes on a water bath at 100 ^oC and the digest was allowed to cool thereafter another 5 cm^3 of Conc.HNO_3 was added and the heating continued for another 1 hour at 100^oC. The volume of the digest was reduced by boiling on the water bath and this was allowed to cool. 5 cm^3 of distilled water was then added. 10 cm^3 of H_2O_2 (60%) was added and heating continued for another 30 mins. The final digest was allowed to cool and filtered. The volume of digest was made up to 50 cm^3 with distilled water and used for the individual into a 50 cm^3 standard flask heavy metal by flame atomic absorption spectrophotometry (Marisa, 2007).

3.9 Digestion of the Soil Samples

0.25 g of the oven dried soil samples were separately weighed into platinum crucibles into which were added 3 cm^3 of HNO_3, 2 cm^3 of. HF and 1 cm^3 of 40% H_2O_2 solution. The mixture was digested on a sand bath at a temperature of 200 – 230 ^0C and until the samples were evaporated to dryness. Thereafter, 20 cm^3 of 0.25 M HNO_3 was added, warmed for 10 minutes on the sand bath and, the digest was then allowed to cool and filtered into 50 cm^3 volumetric plastic container and made to mark with 0.25M HNO_3 solution.(Udoma, 2013)

3.10 AAS Determination of Pb, Cu, Fe, Cr, Cd, Zn, Mn, Mo and Ni.

Metal determinations in the soil and vegetable extracts digests were carried out using BuckUPG 210 atomic absorption spectrometer. Hollow cathode lamps of the various metals were used as light sources and the wave-length characteristics of the metal were then set. The slit width and the amount of currents applied to the hollow cathode lamps were all set according to the manufacturer's instruction. The instrument was then switched on and allowed to warm up for about 30 minutes. The oxidant and the fuel gases (air and acetylene respectively) were then

allowed in at a predetermined steady flow rate and then ignited while the flow rates were adjusted as specified by the manufacturer.

0.25M nitric acid solution was used to set the instrument to zero. Each of the prepared metal standards was individually aspirated into the flame after the Blank and sample digests for any particular metal. After this operation the calibration curve of the metals were plotted by the machine. Concentrations of the analytes in mg/kg of the digested samples were obtained by using the linear regression equation from the calibration curve plotted.

3.11. Transfer Factor (TF):

Metals from soil are absorbed by plant roots and then distributed in various plant tissues. Such transmission of metals from soil to plant tissues is studied using an index called Transfer Factor (TF).It is calculated as a ratio of concentration of a specific metal in plant to the concentration of same metal in soil, both represented in same units (Rangnekar *et al.,* 2013).

$$\mathrm{TF} = \frac{\mathrm{C_{plant}\,(root + stem + leaves)}}{\mathrm{C_{soil}}}$$

Where, the heavy metal concentration in the plant and the soil are represented by C_{plant} and C_{soil}, respectively.

Higher TF values ≥1 indicate higher absorption of metal from soil by the plant and higher suitability of the plant for Phyto-stabilization and Phyto-remediation (Blaylock *et al.,* 1997). On the contrary, lower values indicate poor response of plants towards metal absorption and the plant can be used for consumption.

3.12. Bioaccumulation Factor

Heavy metals are dangerous because they tend to bioaccumulate. Bioaccumulation means an increase in the concentration of a chemical in a biological organism over time, compared to the chemical's concentration in the environment. Compounds accumulate in living

things any time they are taken up and stored faster than they are broken down, metabolized or excreted (Michael, 2010). The food chain (soil– plant–human) route is primarily recognized as being one of the main routes whereby humans are exposed to contaminants in the soil. The transfer of metals from the soil to the plant is one of the key elements of human exposure to metals via the food chain (Zhang *el al.,* 2010). When the BAF is <1 or the BAF=1, it indicates that the plant only absorbs but does not store heavy metals; when the BAF is >1, it is an indication that the plant stores metals.

The bioaccumulation factor (BAF), which is an indicator of the ability of a plant to accumulate a specific metal in contrast to the concentration of the metal in the soil substrate (Ghosh and Singh, 2005) was calculated as follows:

$$\mathrm{BAF} = \frac{\mathrm{C\ (shoot)}}{\mathrm{C\ (soil)}}$$

Where, the heavy metal concentration in the shoot of the plant and the soil are represented by C(shoot) and C(soil), respectively.

3.14. Translocation Factor (TrF):

The gradual movement of solute (metal ions) from soil to plant roots and from roots via stem to plant leaves is referred as translocation of solute materials. It is determined as the ratio of metal concentration in shoot to its concentration in the root tissues (Marchiol et al., 2004). In order to establish the relative translocation of metals from the soil to the other parts of the plant, namely the roots, shoots and leaves, the Translocation Factor (TF) or mobilization ratio was calculated.

$$\mathrm{TrF} = \frac{\text{Contration of metals in the shoot}}{\text{Concentration of metals in the corresponding root}}$$

Note : All calculation were done using Excel SPSS package

CHAPTER FOUR

4.0 Results and Discussion

4.1 Soil pH

The results of some physico-chemical properties of the soil samples are shown in table 4.1. The pH values obtained were found to be in the range of 6.96±0.1 to 6.98±0.1 in comparison with 7.68±0.2 for the Control. The pH values of the farm soils at the various sampling points are essentially consistent with reported values for other farm soils. Loska *et al.,* (2005) (5.0-7.2), Ibrahim *et al.,* (2013) (5.0-6.5) Udoma, (20130) (5.0-7.5). The entire samples were found to fall within the EPA, (2002) permissible limits (6-9). The pH values from the Industrial samples showed lower values compared to the control samples which could be attributed to the waste water or Industrial effluents used for irrigation. Since the pH of the soil samples are about neutral this indicate that there would be less metal uptake by plant from the soils because metals are generally more mobile at pH <7 than at pH >7. In other words, metal concentration in soil decreases with increasing acidity but increases with increasing alkalinity of the soil. This implies that there would be fewer metals available for uptake by the vegetables due to high soil pH . However, interaction with the farmers during the sampling revealed that prior to planting the soil is limed using ash in order to improve the crop productivity of the crop. This practice would increase the level of the metals in the soils for the plant uptake thus resulting in improving yields.

Table.4.1. Soil Physio-chemical Properties

Sampling Site	pH	EC(µS/cm)	OC %	OM %
SHARADA	6.97±0.10	327.30±1.30	0.99±0.00	1.71±0.00
KWAKWACHI	6.96±0.10	421.00±1.40	0.85±0.20	1.46±0.00
CHALAWA	6.98±0.10	236.80±1.00	0.94±0.00	1.62±0.00
CONTROL	7.68±0.20	193.20±1.6	0.67±0.2	1.16±0.0

EC: Electrical conductivity, **OM**: Organic matter, **OC**: Oganic carbon

4.2 Soil Electrical Conductivity

The soil electrical conductivity values obtained were observed to range from 193 to 421 µS/cm as shown in Table 4.1 with highest value in Kwakwachi (421 µS/cm) while the least were observed from control soil samples (193 µS/cm). However, the EC values of the farm soils at the various sampling points are essentially consistent with reported values for other farm soils Abdulmojeed and Audu, 2(012), (185-450 µS/cm); Ibrahim *et al.,* (2013) (397µS/cm) but lower than Udoma, (2013) (495-996 µs/cm). Electrical Conductivity was also found to increase in the present study when compared to the control samples. The possible reason for this may be linked to accumulation of dissolved inorganic (like calcium, magnesium, chloride, sulphate) and organic (like CO_3^{2-}, HCO_3^-) found in the Industrial wastewater used for irrigation (Doerge *et al.,* 1999). Increase in soil conductivity may also be due to elemental input via fertilizers, liming, as well as sewage sludge application or atmospheric deposition (Timo and Philip, 2003).

4.3. Soil Organic Matter and Organic Carbon

The mean soil organic matter in the samples ranged from 1.16-1.71%, while that of organic carbon ranged from (0.67-0.99) as shown in Table.4.1 with the highest value in sharada (OM 1.71%, OC 0.99) and the least was observed in control soil sample (OM 1.16%, OC 0.67).

However, study conducted by Jayashree and Sarma, 2012 (3.93 - 7.34 %) and Udoma, 2013 (0.6-4.6 %.) are consistent with this present study. Also the study showed that all the soil samples had organic matter within the prescribed percentages 1% -100% (US-EPA, 2004). Since these parameters are important because they improves both the physical and the chemical properties of soil. It also decreases soil erosion by stabilizing soil particles. It enhances aeration, increase water-holding capacity and restores and supplies nutrients for the growth of plants and soil micro-organisms (Akoto *et al*., 2008). Metal concentration in the soil increases with increasing organic matter content and vice versa. The organic matter content of the control samples was lower than the Industrial samples. This implies that thee Industrial soil especially Sharada and Challawa would be more suitable for farming due to their higher values of these parameters. The low levels of organic matter are attributable to rapid mineralization under the high temperature and moisture conditions in the soils. Lal (1981) reported a linear decline in soil organic matter content with cumulative soil erosion. Low organic carbon content of the soil can lead to a reduction in soil fertility, land degradation and even desertification.

4.4.0 Concentration of Metals in the Soil

Table.4.2. Concentration of Metals in the Soil (mg/kg)

Metals	Chalawa	Sharada	Kwakwachi	Control	WHO/FAO*
Pb	14.67±0.30	16.25±0.30	19.82±0.20	1.34±0.0	100
Cd	12.53±0.50	11.27±0.50	13.36±0.50	2.36±0.60	3
Cr	19.51±0.40	29.27±0.40	24.02±0.50	7.51±0.50	100
Mn	49.12±1.20	33.78±1.20	40.70±0.80	13.09±1.00	2000
Mo	27.44±0.60	24.27±0.60	25.86±0.60	12.89±0.70	-
Ni	28.22±0.50	20.45±0.50	26.55±0.50	17.13±0.60	50
Fe	194.29±3.40	181.05±3.40	236.19±3.40	95.24±3.40	-
Cu	61.14±1.00	49.78±1.00	61.14±1.20	17.47±1.20	100
Zn	61.67±1.60	82.82±1.60	114.54±2.00	52.86±1.60	300

* WHO/FAO, (2007)

Table.4.3 Showing WHO/FAO Guidelines (WHO/FAO 2007)

Metals	Cd	Cr	Cu	Fe	Mn	Mo	Ni	Pb	Zn
vegetables	0.1	0.5	73	1000	200	-	45	0.3	100

Table. 4.2. Shows the result of the metal concentrations of soil samples obtained from various sampling sites.

The lead contents of the entire farm soil samples ranged from (1.3-19.82) mg/kg as shown in table 4.2 with highest value in kwakwahi (19.82 mg/kg). meanwhile, the metal concentrations in the Control soil samples were found generally to be lower than the Industrial samples as shown in the Table 4.2. Moreover, cadmium concentrations of the soil samples ranged from (2.3-12.6) mg/kg with the highest concentration in kwakwachi (13.36 mg/kg). Cadmium content in the control samples was also observed to be lower than the Industrial soil samples. Analysis of Variance (two ways ANOVA) at ($p < 0.05$) revealed that there are significant differences in cadmium contents of samples obtained from the Industrial area to that of control site. The values obtained were consistent with Abdulmojeed and Audu, (2012), (0.5-14.3 mg/kg) and Udoma, (2013), (0.4-20.5 mg/kg). Similar trend was shown by lead.

High concentration of cadmium and lead in farm soils could be as a result of Industrial activities, use of metal enriched agrochemical materials, including farm manures, sewage sludge as soil amendment material, and waste water irrigation (Freedman and Hutchinson, 1981). In agricultural production systems, soil contamination by heavy metal is mainly related to input and accumulation of these elements through repeated use of metal enriched chemical such as manures and bio-solid (Webber, 1981). In summary, Pb and Cd Concentration for each sampling site follow the order;

Pb: Kwakwachi > Sharada > Challawa > Control

Cd: Kwakwachi > Challawa > Sharada > Control

The chromium contents of the farm samples ranged from (7.51 to 29.27mg/kg) with the highest in sharada (29.27 mg/kg) and the least in control (7.51mg/kg). While, concentration of

Mn, Mo, and Ni, ranged from (12.89 to 49.12 mg/kg), the highest value was observed in chalawa (Mn (49.12 mg/kg), Mo (27.44 mg/kg) Ni (28.22 mg/kg)) while the least was observed in the control samples. ANOVA result at $P < 0.05$ revealed that there are significant differences in concentrations of samples obtained from the industrial area compared to that of control site. The higher level of these metals in the farm soils could be due to the industrial activities, chemical fertilizers, farm manures, sewage sludge and waste water irrigation (Webber, 1981; Freedman and Hutchinson, 1981; He *et al.,* 2001).

The orders of abundance of each element relative to farm sampling locations are as follows;

Mn: Chalawa > Kwakwachi > Sharada > Control

Cr: Sharada > Kwakwachi > Chalawa > Control

Mo: Chalawa > Kwakwachi > Sharda > Control

Ni: Chalawa > Kwackwachi > Sharada > Control

The concentration of Cu, Fe, and Zn in the soil samples ranged from (17.47-236.19 mg/kg) the highest concentration was observed in kwakwachi (Cu (61.14 mg/kg), Fe (236.19 mg/kg), Zn (114.56 mg/kg)). However, the levels in control samples were much lower than the Industrial samples. ANOVA result at $P < 0.05$ revealed that there are significant differences in concentrations of samples obtained from the industrial area compared to that of control site. Similar trend of results was observed by Udoma, (2013) (20 - 304.5) and Batagarwa, (200) (12.6 – 150.54). The higher level of these metals in the farm soils could be ascribed to Industrial activities, addition of chemical fertilizers, farm manures, sewage sludge and waste water irrigation (Webber, 1981; Freedman and Hutchinson, 1981; He *et al.,* 2001; Kabata-Pendias and Pendias, 1999; Kabata-Pendias and Singh, 2001a; 2001b).

The orders of concentration for each metal with respect to each sampling site are as follow:

Fe: Kwakwachi > Challawa > Sharada > Control

Cu: Kwakwachi > Chalawa > Sharada > Control

Zn: Kwakwachi > Sharada > Challawa > Control

Generally it was observed that the metal concentration from the Industrial soil were higher than the control soil. This could be attributed to long time farm on the land with waste water (Swadis *et al.,* 2001) it could also be as a result of contamination from the industry (Yilmaz and Zengin 2004). All metals were also observed to have lower values compared to WHO/FAO standard in Table 4.2 expect for cadmium (Cd) which showed higher value. The highest concentration of Cd was observed in soil obtained from Kwakwachi. The high level of Cd in the farmland could pose a serious health risk since the area is within the Kano urban environment as smallest particles blown can be accumulated in the lungs (Nabulo *et al*., 2006; Joseph *et al*., 2013)

4.5.0 Concentration of Metals in the Vegetable Samples:

Figures 4.1- 4.5 showed the concentrations of lead and Cadmium in the various samples

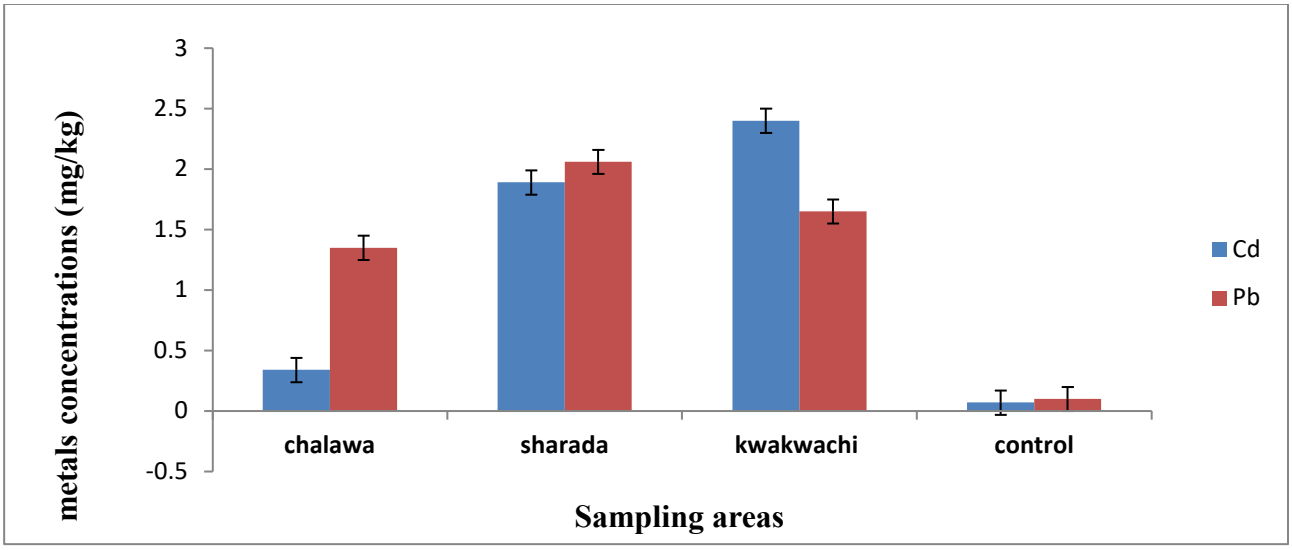


Fig.4.1. Levels of Pb and Cd in the Cabbage Sample Analyzed

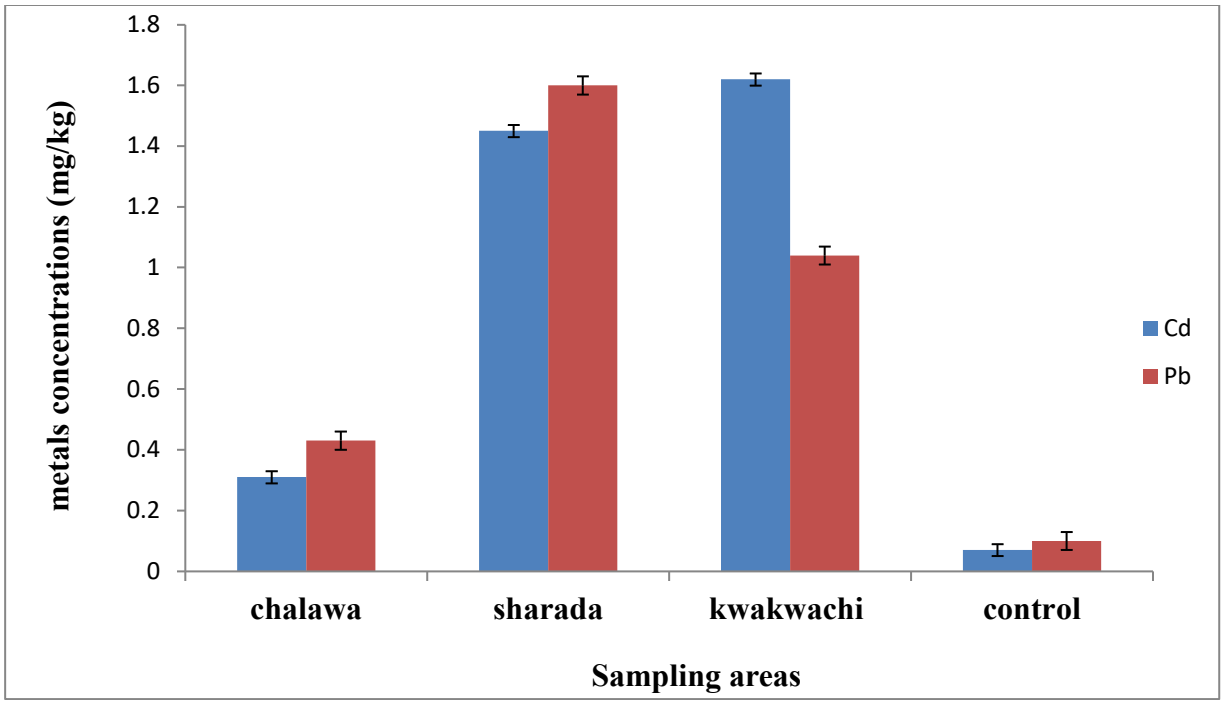


Fig.4.2. Levels of Pb and Cd in Garden cress the Sample analyzed

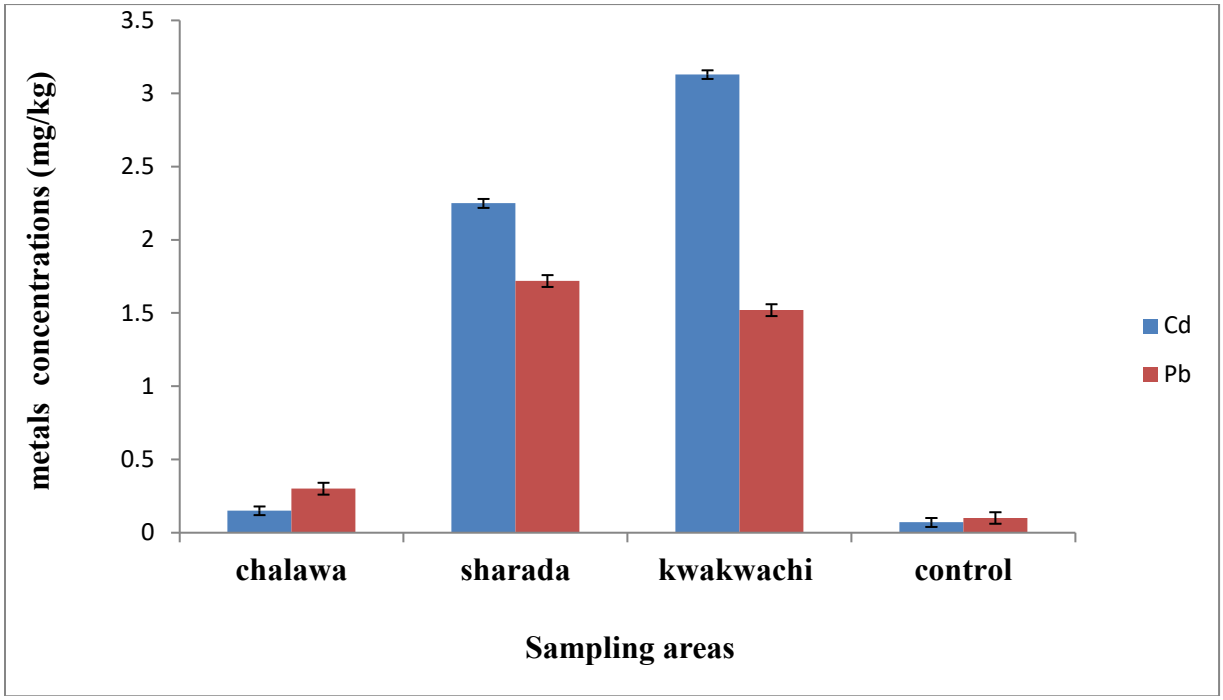


Fig.4.3. Levels of Pb and Cd in the sesame Sample analyzed

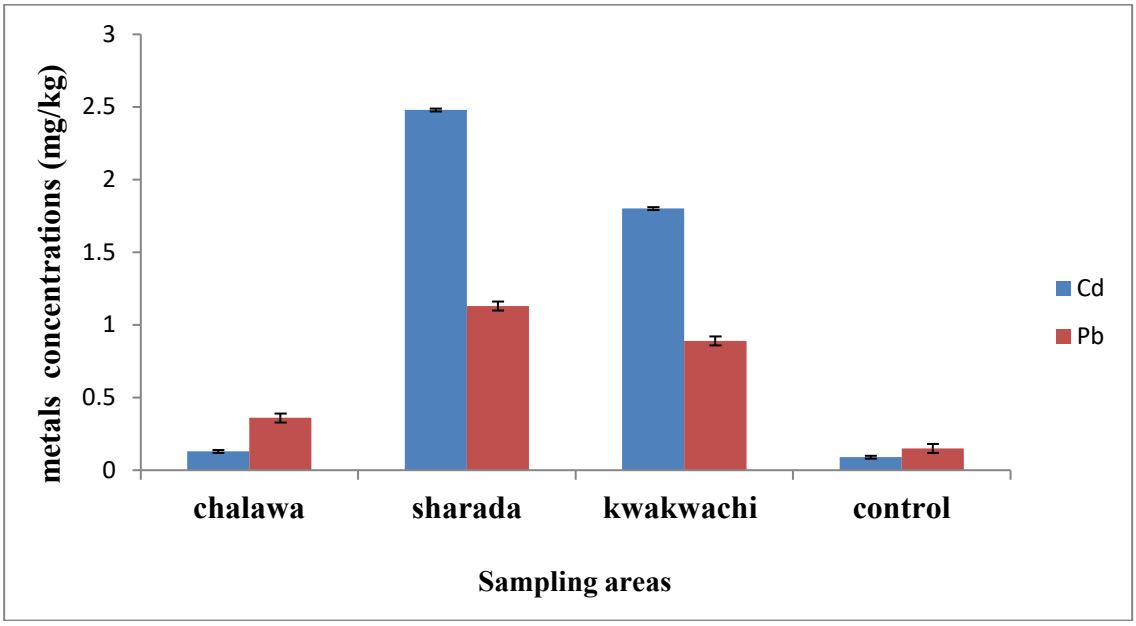


Fig. 4.4. Levels of Pb and Cd in the lettuce Sample analyzed

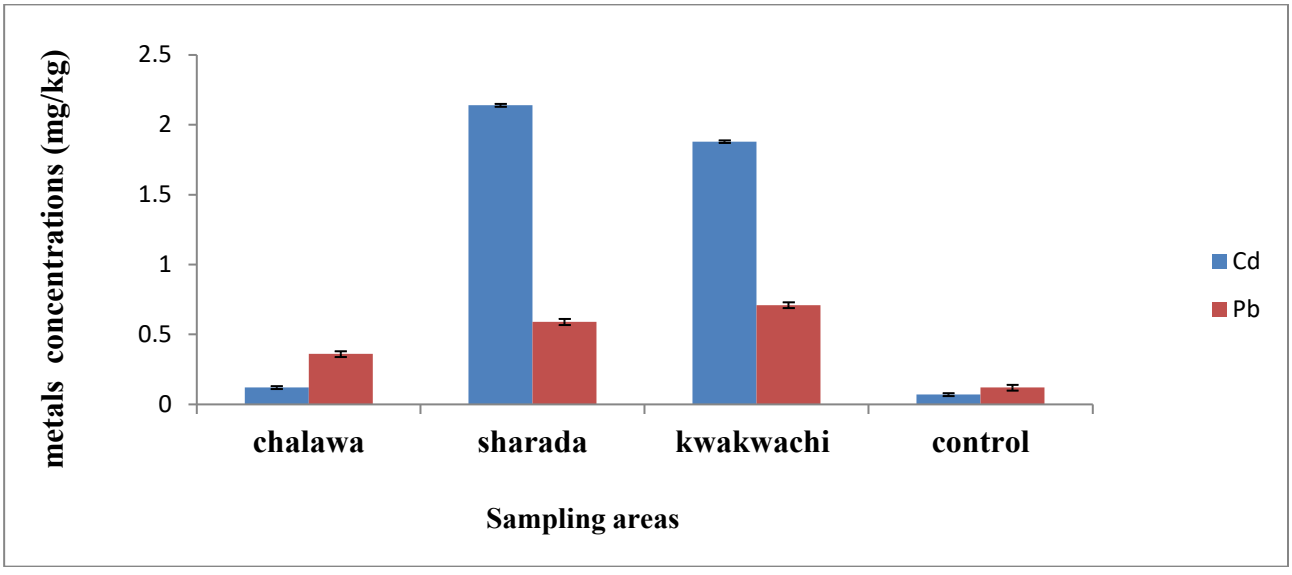


Fig.4.5 Levels of Pb and Cd in the Spinach Sample analyzed

4.5.1 Levels of Pb and Cd in Vegetables Samples

Fig.4.1. - Fig.4.5. Show the concentrations of Cd and Pb in all vegetables studied, Their concentrations ranged from (0.07 to 2.17 mg/kg) for Cd with highest in sharada (2.17 mg/kg)and (0.11-1.16 mg/kg) for Pb with highest in kwakwachi (1.16 mg/kg). Analysis of Variance (ANOVA) results at ($P < 0.05$) revealed that there are significant differences in concentrations of samples obtained from the industrial area and that of control site. ANOVA ($p< 0.05$) results in appendix 2 also revealed that there are significant differences between the uptake levels for Cd and Pb from vegetables cultivated experimentally at different concentrations (low, medium and high). The results indicated the higher the concentrations in the soil, the higher the uptake level. The industrial samples also reflect similar result with the experimental ANOVA. This observation agrees with Sawidis *et al.,* (2001), and Sawidis, (2008); who suggested that uptake of metals by plant is proportional to their concentration in the soil.

In summary, the average concentrations of Cd and Pb in the entire sample site followed the order,

Cd: Kwakwachi > Sharada > Chalawa > Control.

Pb: Sharada > Kwakwachi > Chalawa > Control**.**

Batagarwa, (2000) reported high level of Pb (10.38 to 154.64mg/kg) in sample of moss plant from Sharada and Bompai Industrial estates in Kano metropolis. Abdulmojeed and Audu, (2014) also reported level of Pb (0.65-103mg/kg) in spinach plant from Bompai, Sharada and Kwakwachi which was consistent with the concentration observed in this study. Akinola and Ekiyoyo, (2006) reported high level of Pb and Cd (2.0 - 5.0mg/kg) in some plant which was also consistent with the values observed in this study. Duka *et al.,* (1999) also reported high level of lead and cadmium (0.95-6.0mg/kg) in plant samples obtained from industrial farm lands. In

general, the concentrations of the industrial samples were observed to exceed the WHO/FAO standard. The high concentrations of Cd and Pb in the analyzed vegetables could have been due to transfer from the soil, as well as activities of the industries and accumulation in soil due to waste water used for irrigation (Sharama *et al.,* 2006; Sawidis *et al.,* 2001).

Heavy metal concentrations varied among different vegetables studied, which may be attributed to differential absorption capacity of the analyzed vegetables for different heavy metals (Zurera *et al.,* 1989). This shows that some other soil factors in addition to the total soil contents of the metals also influenced metal uptake.

4.5.2. Level of Cu, Fe and Zn in vegetable samples.

Figure 4.6 to 4.10 shows concentration of copper, iron, and zinc observed for each vegetable in the entire sample site

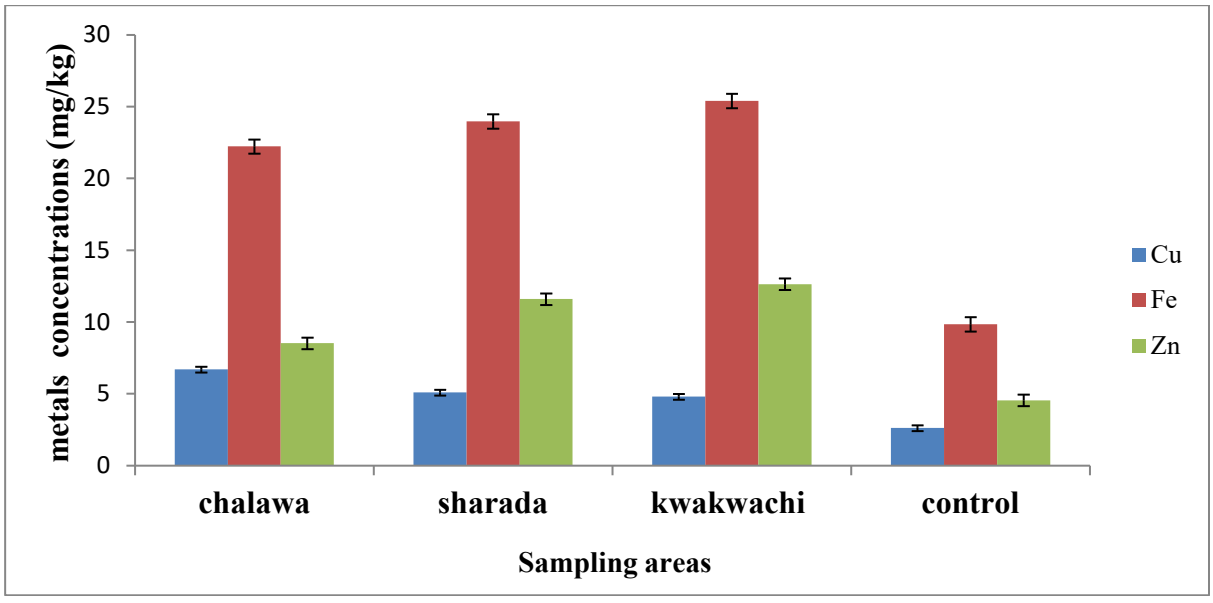


Fig.4.6. Level of Cu, Fe and Zn in the cabbage Sample analyzed

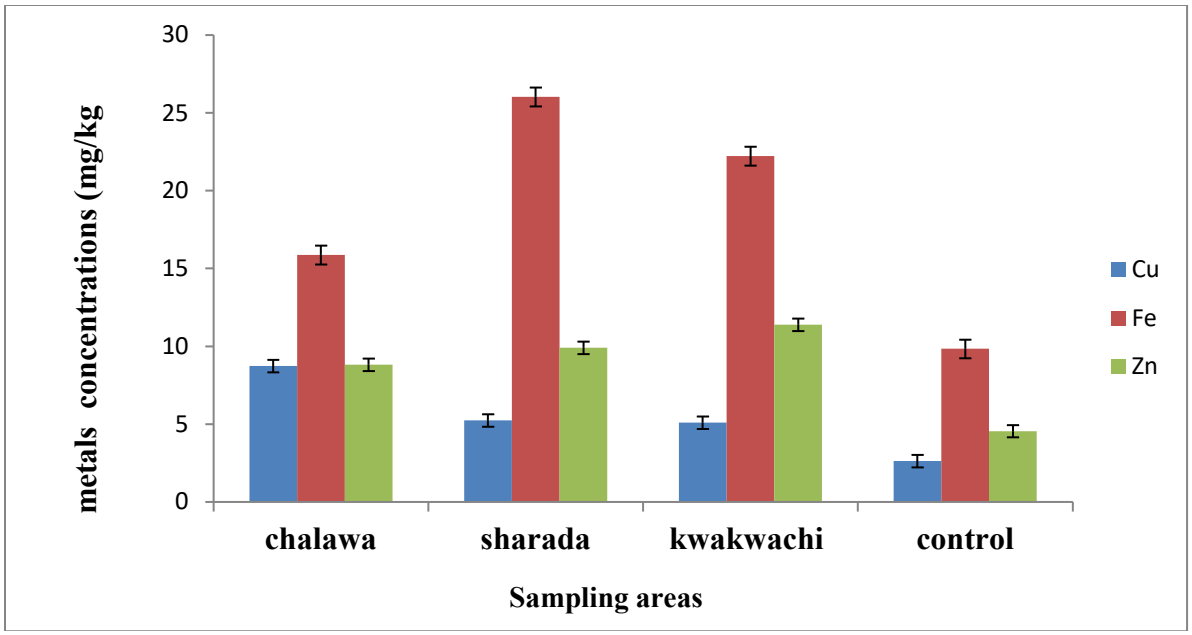


Fig.4.7. Level of Cu, Fe and Zn in the Garden Cress Sample analyzed

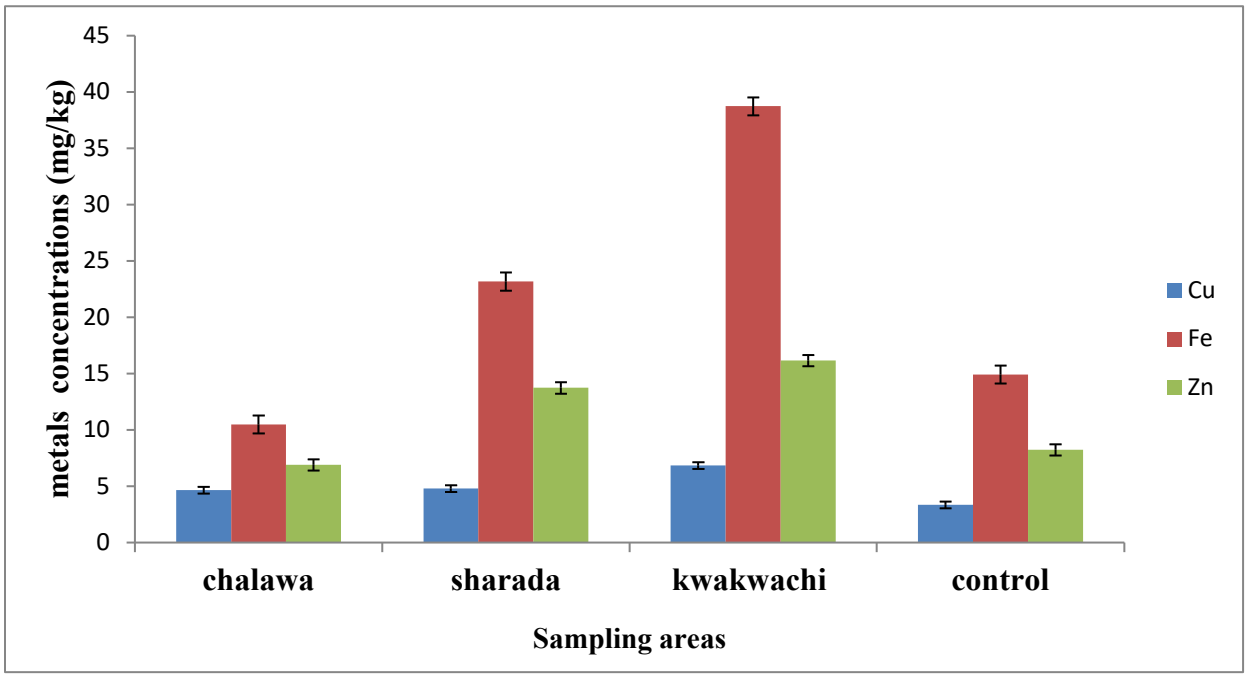


Fig4.8. Level of Cu, Fe and Zn in the Sesame Sample analyzed

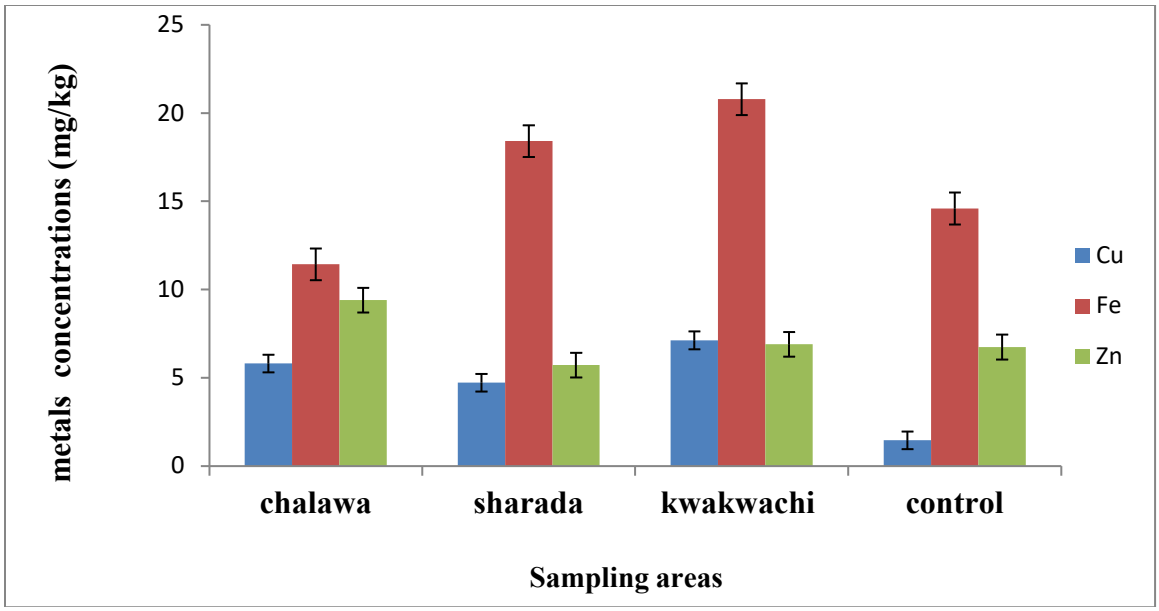


Fig4.9. level of Cu, Fe and Zn in the Lettuce Sample analyzed

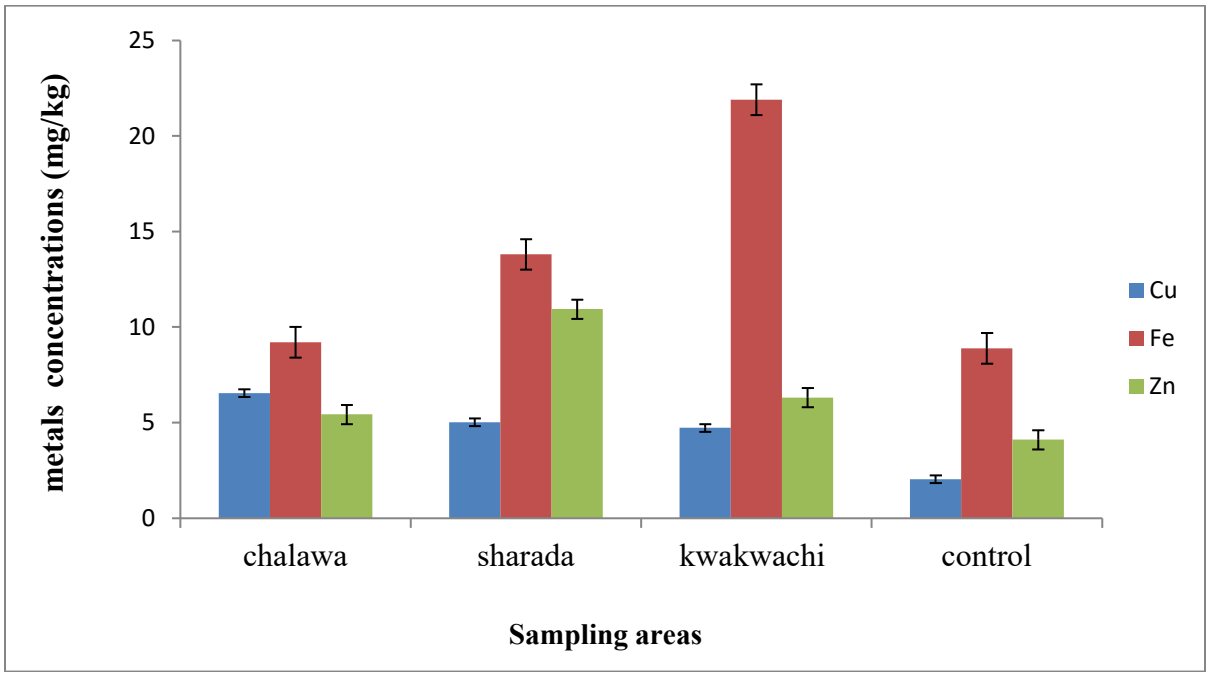


Fig4.10. Level of Cu, Fe and Zn in the spinach Sample analyzed

The mean concentrations of Cu, Fe and Zn in all the vegetable samples ranged from Cu (1.46-8.73mg/kg), Fe (8.89-38.73mg/kg), and Zn (4.11-16.15mg/kg) as shown in Fig.4.6 to 4.10. Garden cress from Sharada had the highest Concentrations of Cu (8.73mg/kg) while the sesame from Kwakwachi had the highest concentration of Fe, (38.73mg/kg). Moreover, the in sesame from Chalawa area had highest concentration of Zn (16.15mg/kg). When compared to the control site the concentrations of these metals from the entire Industrial sites had higher concentration value. ANOVA results ($P>0.05$) for Fe and Zn, revealed that there is no significant difference between the concentrations of samples obtained from the Industrial area and the control samples while, it also revealed that there is significant level ($p<0.05$) of Cu obtained in vegetables from the industries compared to controlled samples. Moreover ANOVA results ($P<0.05$) revealed that there are significant differences in the uptake of Cu, Fe, and Zn by the various vegetable samples cultivated experimentally at different concentrations (low, medium, and high concentrations). This observation agrees with Sawidis *et al.,* 2001 who suggested that uptake of metals by plant is proportional to their concentration in the soil.

In Summary, the order of each metal levels with respect to sampling locations are as follows;

Cu: Chalawa > Kwakwachi > Sharada > Control

Fe: Kwakwachi > Sharada > Chalawa> Control

Zn: Kwakwachi > Sharada > Chalawa > Control

Abdulmojeed and Audu (2011) however, observed lower concentration of Cu for spinach plant (0.30-1.02mg/kg) from Sharada, and Kwakwachi when compare the value to this study. They also observed lower concentration values of Zn from Sharada (6.63mg1kg) but higher value Zn from Kwakwachi when compared to this current study. Al Jaboobi *et al.,* (2001) observed

concentration of Fe in cabbage plant at (378.4mg/kg), Cu (6.1mg/kg) and Zn (16.13mg/kg) which was higher than concentrations in this study. Generally the mean concentration of Cu, Fe and Zn in the Industrial and controlled area showed lower value compared to (NAFDAC values (Cu (40mg/kg) and Zn (150mg/kg) (Abdulmojeed and Audu, 2011) and WHO/FAO food standards. Elevated concentration of Cu,Fe, and Zn in plants sample of Kwakwachi and chalawa could be as a result of activites of the industries and accumulation in soil due to waste water used for irrigation (Sharma *et al.,* 2006). It could also be as a result of high availability of the metals in the soil taken up by the vegetables (Blaylock *et al.,* 1997).

4.5.3. Levels of Cr, Mn, Mo and Ni in vegetables samples

Figure 4.11 to 4.1s shows concentration of Cr, Mn, Mo and Ni observed for each vegetable in the entire sample site

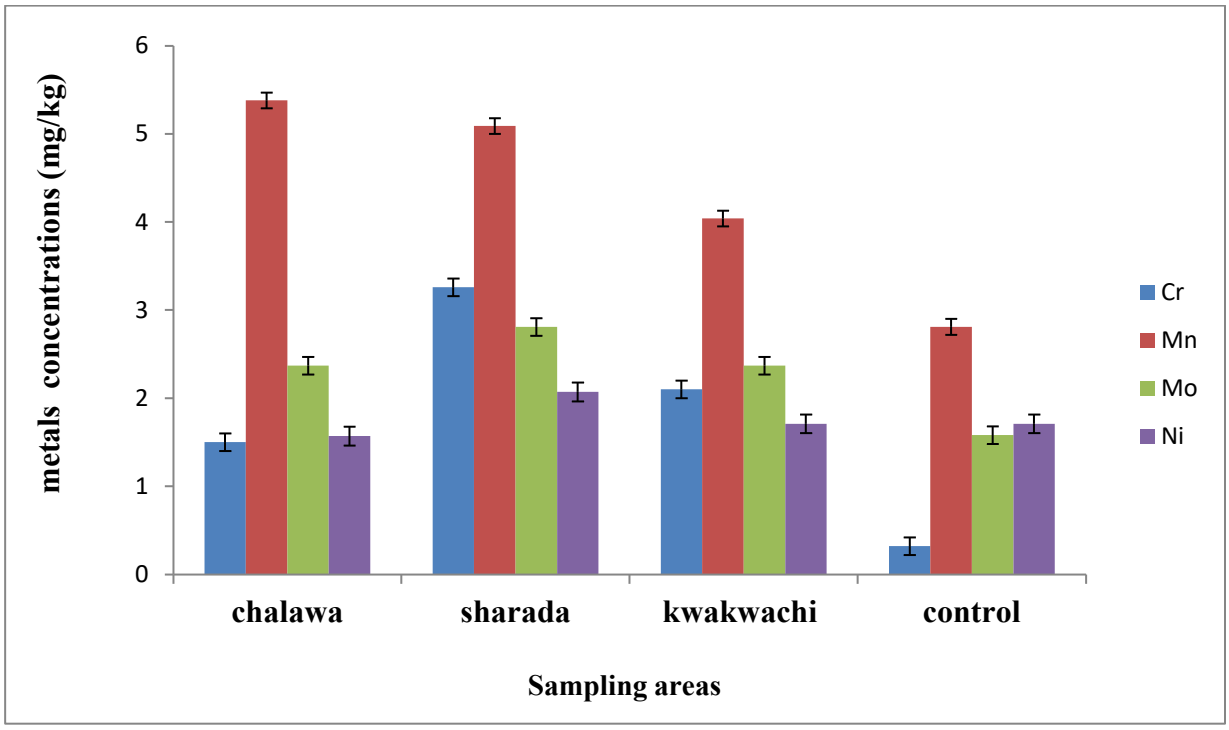


Fig.4.11. Levels of Cr, Mn, Mo and Ni in the Cabbage Sample analyzed

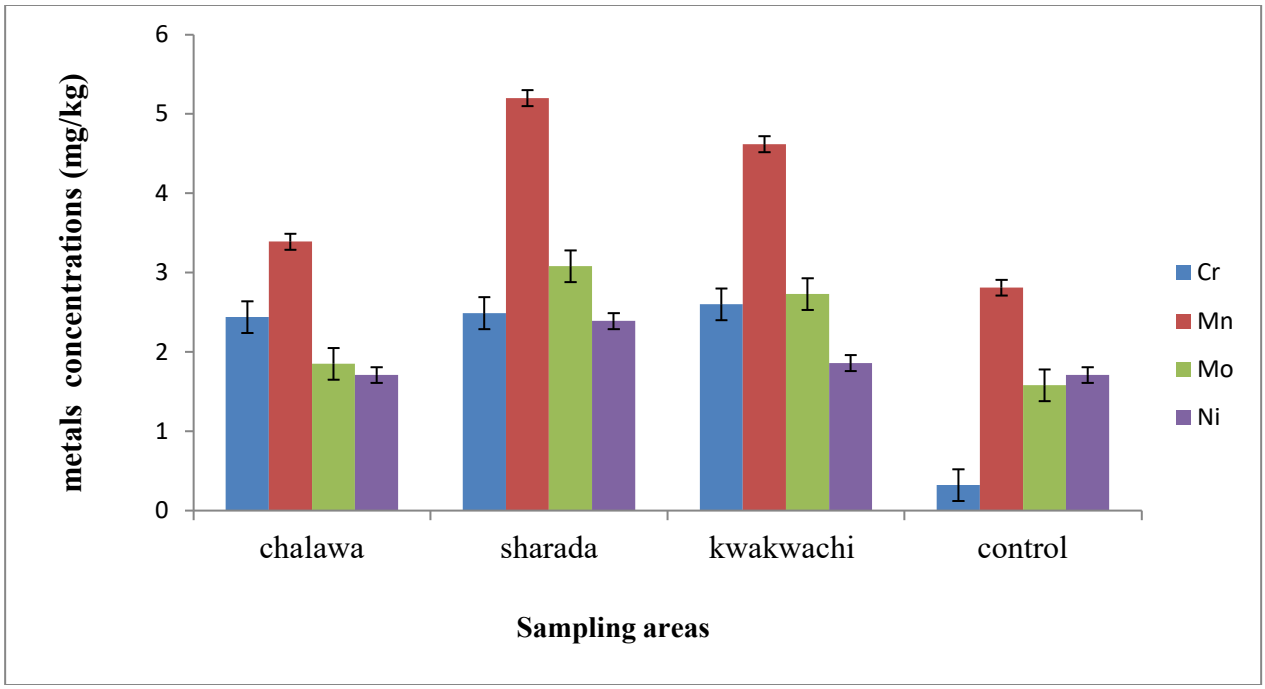


Fig.4.12. Levels of Cr, Mn, Mo and Ni in the Garden cress Sample analyzed

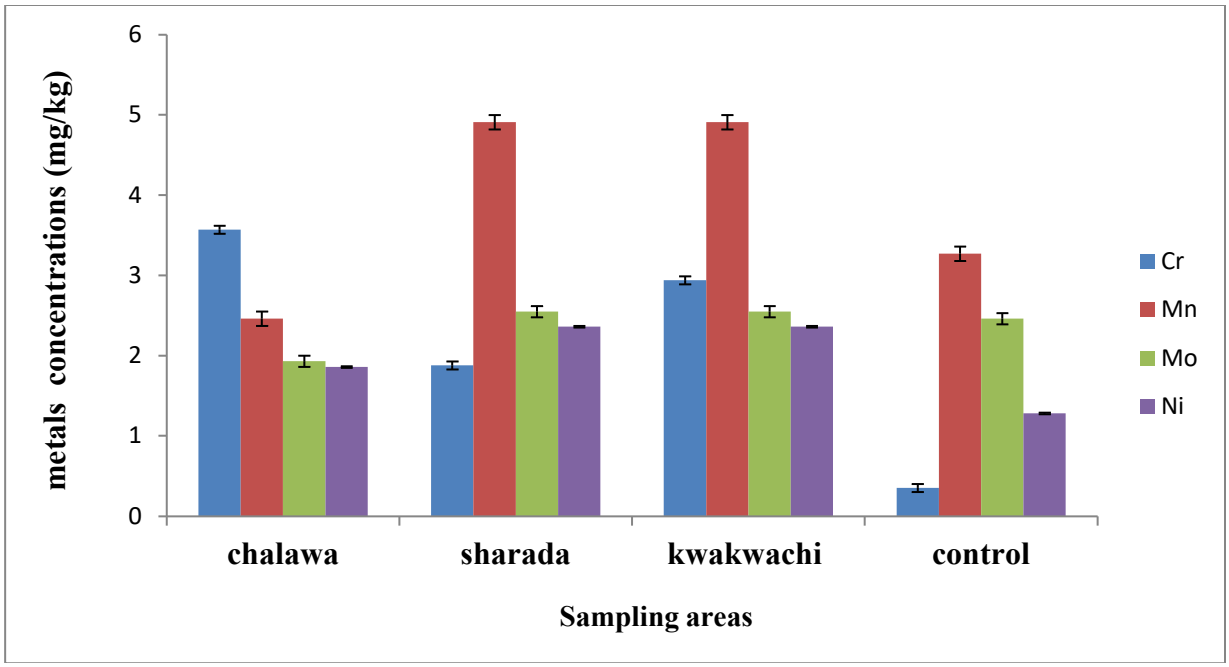


Fig4.13. Levels of Cr, Mn, Mo and Ni in the Sesame Sample analyzed

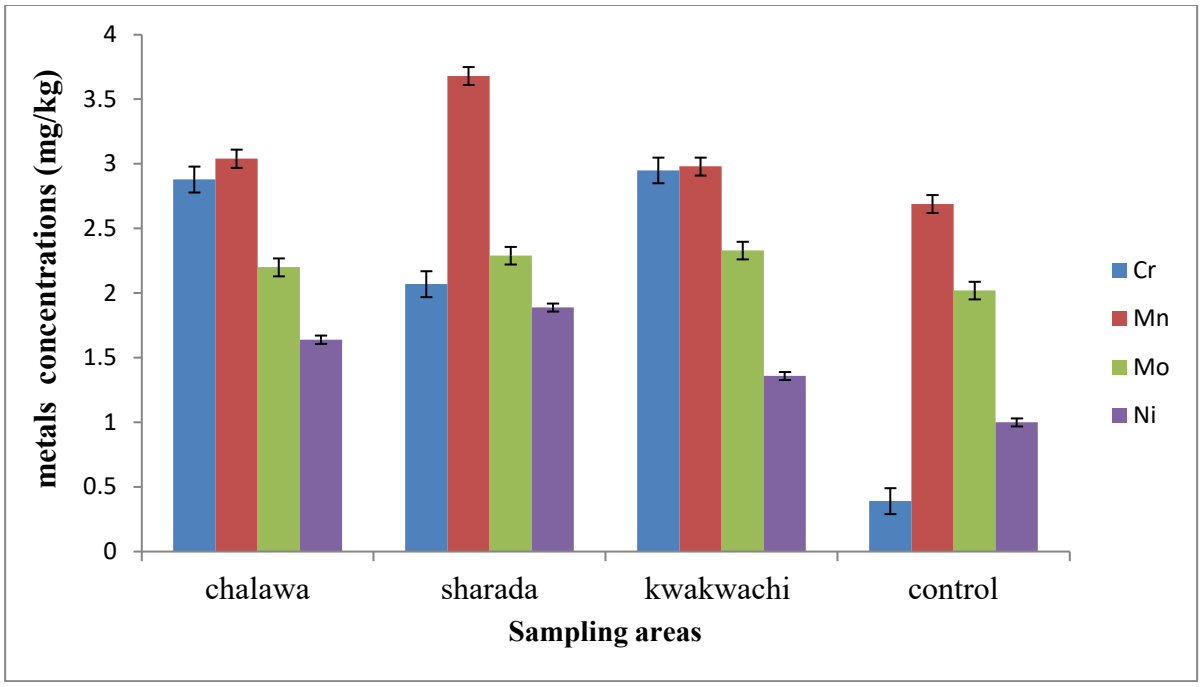


Fig4.14. Levels of Cr, Mn, Mo and Ni in the Lettuce Sample analyzed

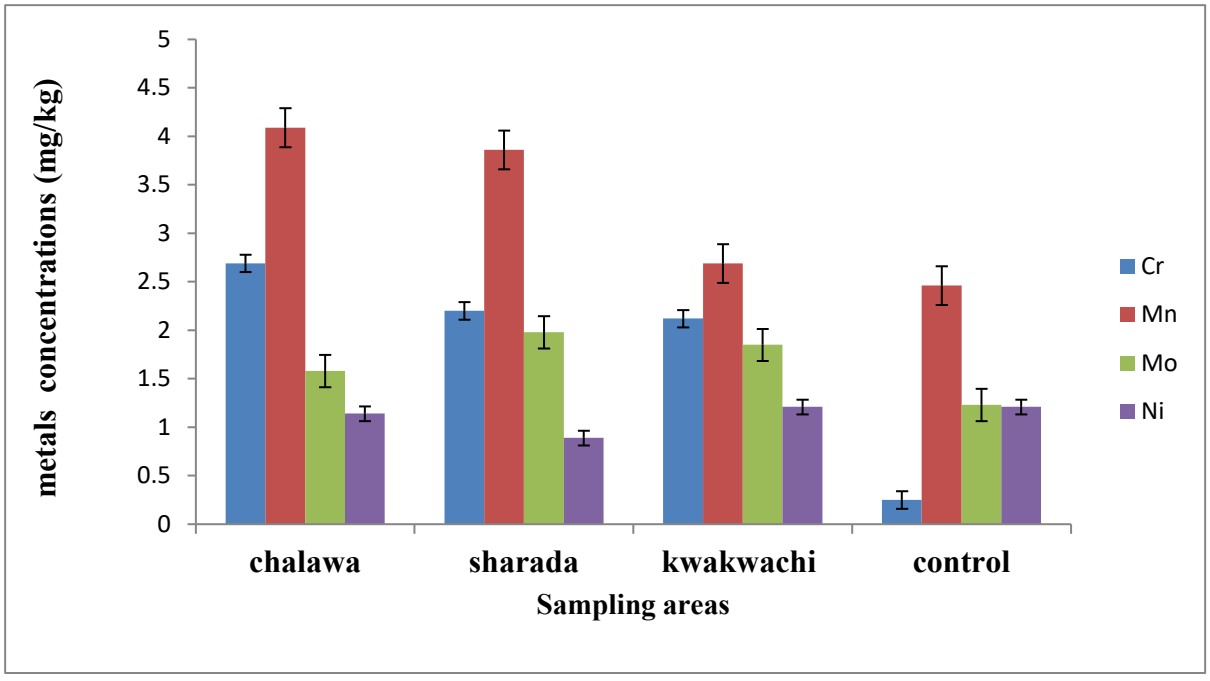


Fig.4.15. Levels of Cr, Mn, Mo and Ni in the Spinach Sample analyzed

Fig.4.11 to 4.15.shows concentrations of Cr, Mn, Mo and Ni in the various investigated vegetable samples which ranged from (0.25-5.38mg/kg). Chalawa had the highest Cr concentration (3.57mg/kg) in sesame plant followed by cabbage sample collected from chalawa with` highest Mn concentration value of (5.38mg/kg). Mo concentration varied for the entire site with the highest concentration from Sharada (3.08mg/kg) in lettuce plant. Meanwhile, Ni was observed to have the highest concentration from Kwakwachi (2.39mg/kg) also in lettuce plant. ANOVA results ($P>0.05$) for Mn, Mo and Ni, revealed that there is no significant difference in concentrations of the vegetables obtained from the Industrial area and the control samples. This could be attributed to the soil phsico-chemical properties which made available these metals in the soil which taken up by these vegetables (Jung *et al.,* 2006). The ANOVA results also revealed that there are significant differences ($p<0.05$) in Cr obtained in vegetables from the industries compared to the control samples. ANOVA results ($P<0.05$) however, revealed that there are significant differences in the uptake of Cr, Mn, Mo and Ni by the various vegetable samples cultivated experimentally at different concentrations. This indicates that the higher the concentration in the soil the higher the uptake. The industrial samples also reflect similar result with the experimental ANOVA result. This observation agrees with Sawidis *et al*., (2001), Sawidis, (2008) who independently suggested that uptake of metals by plant is proportional to their concentration in the soil. (Sharma *et al.,* 2006; Sawidis *et al.,* 2001). Similar trend of results were observed from Dasuki, (2000) and Ghosh and Singh, (2005).

The orders of abundance of each element relative to farm sampling locations are as follows;

Cr: Chalawa>Kwakwachi>Sharada>Control

Mn, Mo and Ni: Sharad>Kwakwachi> Chalawa >Control

Generally it was observed that the concentration of Cr, Mn, Mo and Ni from the Industrial sample was higher compared to the control sample. Comparing the values from the sample sites to the WHO/FAO standards; it was observed that Cr had higher concentrations in the industrial samples. Although, Cr is a trace metal needed by the body but since it had exceeded the limit it may pose danger to health of the people who consume these vegetables from that region.

High concentration of Cr may be attributed to long time irrigation on the farmlands using waste water. It could also be attributed to the careless discharge of tannery and textile effluent from industries located within these areas into the river and tunnels (Akan *et al.,* 2007). Also high concentration of Cr in the plant could be attributed to their high proportion in the soils

4.6. Transfer Factor (TF):

Tables 4.4 to 4.6 show the TF of the selected metals in various vegetables planted experimentally at different concentrations. While Figures 4.16-4.20 shows the TF of the metals in various vegetable samples as obtained from the industrial farmlands.

Table.4.4.The transfer factors of the selected metals in cabbage plant grown experimentally

Metals	control	low Conc.	medium Conc.	High Conc.
Cd	0.09	0.60	0.41	0.48
Cr	0.45	0.26	0.26	0.29
Cu	0.45	0.26	0.26	0.29
Fe	0.31	0.34	0.42	0.32
Mn	0.24	0.33	0.55	0.22
Mo	0.28	0.26	0.26	0.29
Ni	0.30	0.26	0.33	0.25
Pb	0.22	0.40	0.41	0.42
Zn	0.26	0.34	0.40	0.32

Table4.5. The transfer factors of the selected metals in sesame plant grown experimentally

Metals	control	low Conc.	medium Conc.	High Conc.
Cd	0.09	0.60	0.41	0.48
Cr	0.57	0.26	0.39	0.27
Cu	0.57	0.26	0.39	0.27
Fe	0.47	0.45	0.46	0.33
Mn	0.28	0.51	0.50	0.39
Mo	0.44	0.30	0.26	0.17
Ni	0.23	0.38	0.17	0.23
Pb	0.22	0.40	0.41	0.42
Zn	0.47	0.56	0.42	0.48

Table 4.6 The transfer factors of the selected metals in lettuce plant grown experimentally

Metals	control	low Conc.	medium Conc.	High Conc.
Cd	0.11	0.60	0.41	0.48
Cr	0.25	0.23	0.26	0.27
Cu	0.25	0.23	0.26	0.27
Fe	0.46	0.42	0.30	0.32
Mn	0.23	0.38	0.28	0.33
Mo	0.36	0.21	0.17	0.25
Ni	0.17	0.13	0.17	0.25
Pb	0.34	0.40	0.41	0.42
Zn	0.38	0.42	0.26	0.32

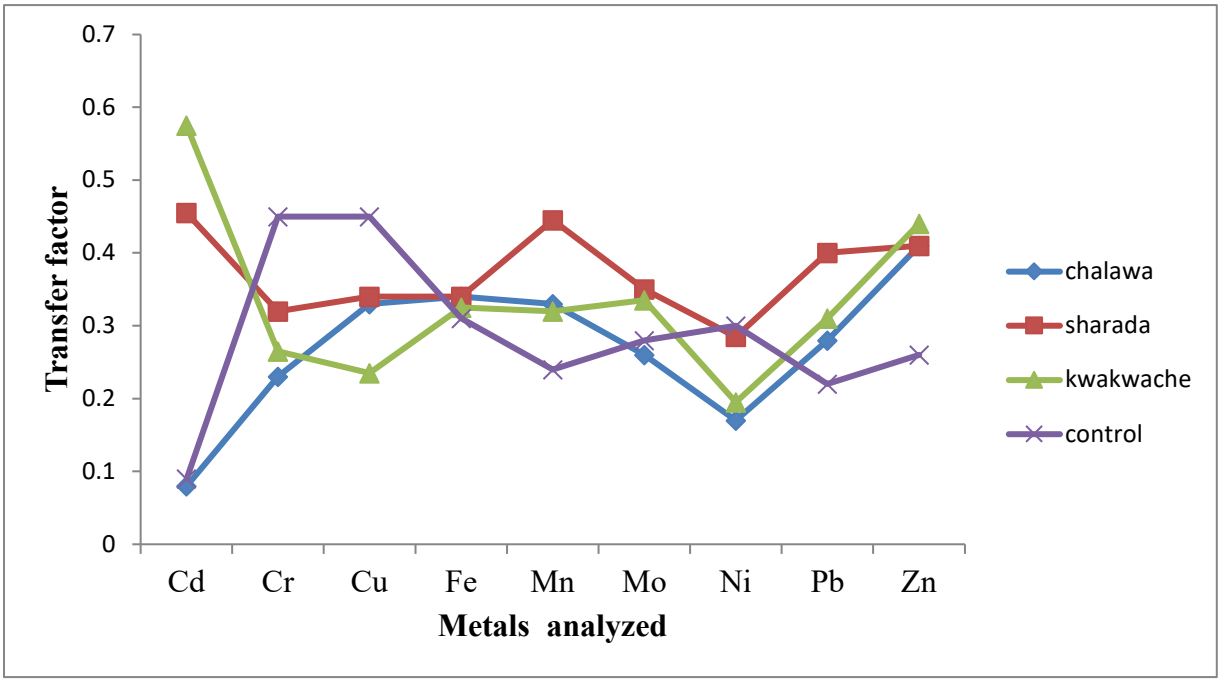


Fig4.16. Transfer Factors of the Selected Metals in Cabbage plant Sample Analyzed

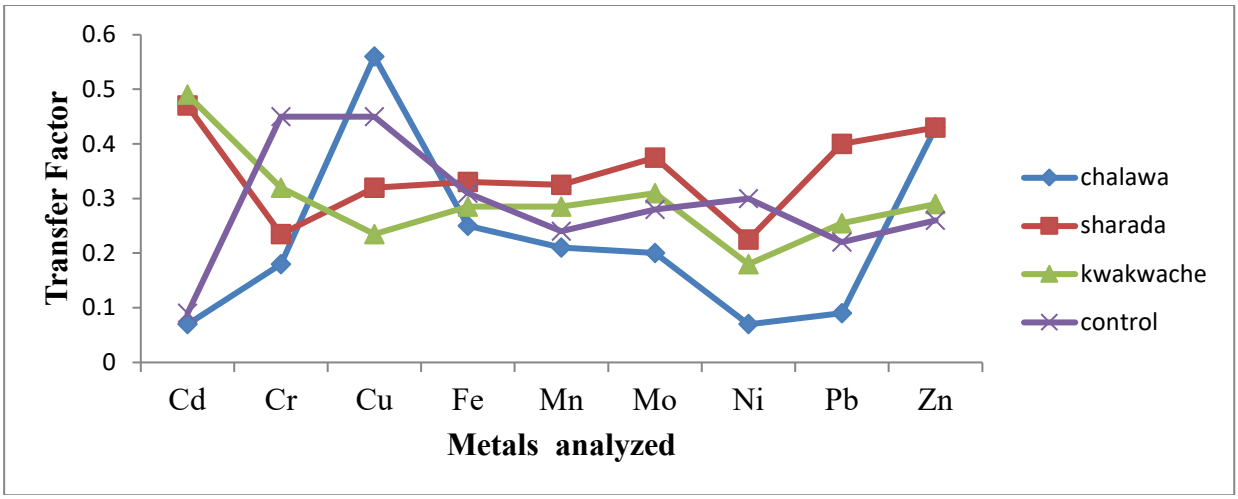


Fig.4.17. Transfer Factors of the Selected Metals in Garden Cress plant Sample Analyzed

Figure.4.16-.4.20 .shows the values of TF for all the nine metals in the various vegetables which varied through the entire sampling sites. In the current study it has been observed that the TF values varied between 0.03 to 0.90 for Cd, 0.18 to 0.56 for Cr, 0.20 to 0.56 for Cu, 0.16 to 0.52 for Fe, 0.15 to 0.75 for Mn, 0.17 to 0.79 for Mo, 0.05 to 0.75 for Ni, 0.06 to 0.52 for Pd and 0.18 to 0.56 for Zn.

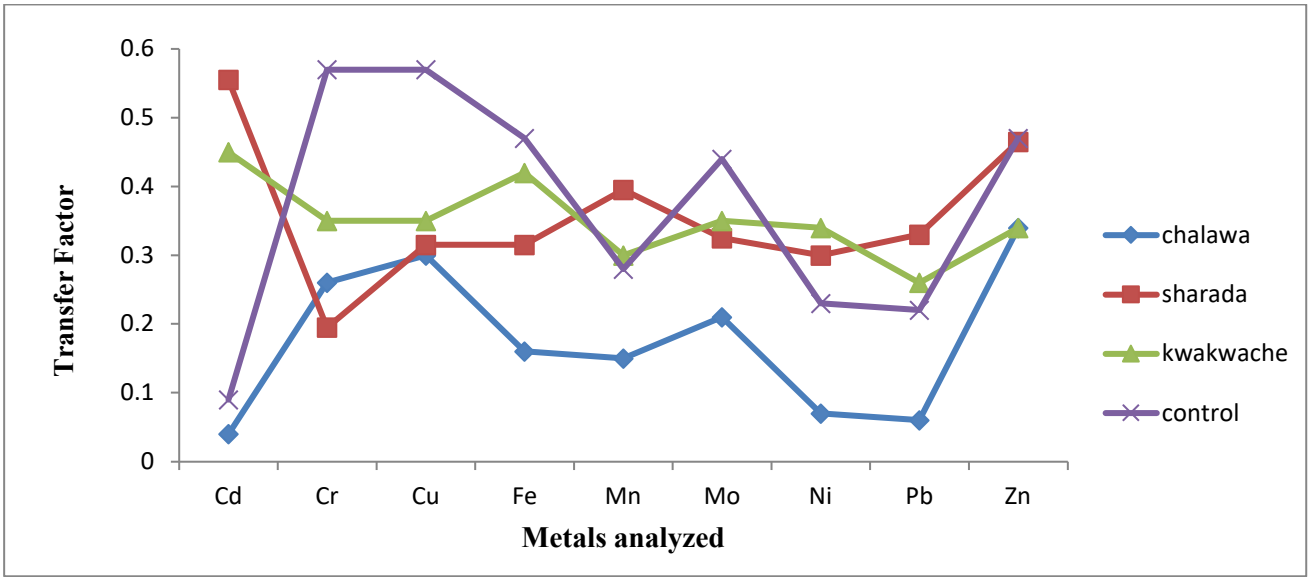


Fig4.18. Transfer Factors of the Selected Metals in sesame plant Sample Analyzed

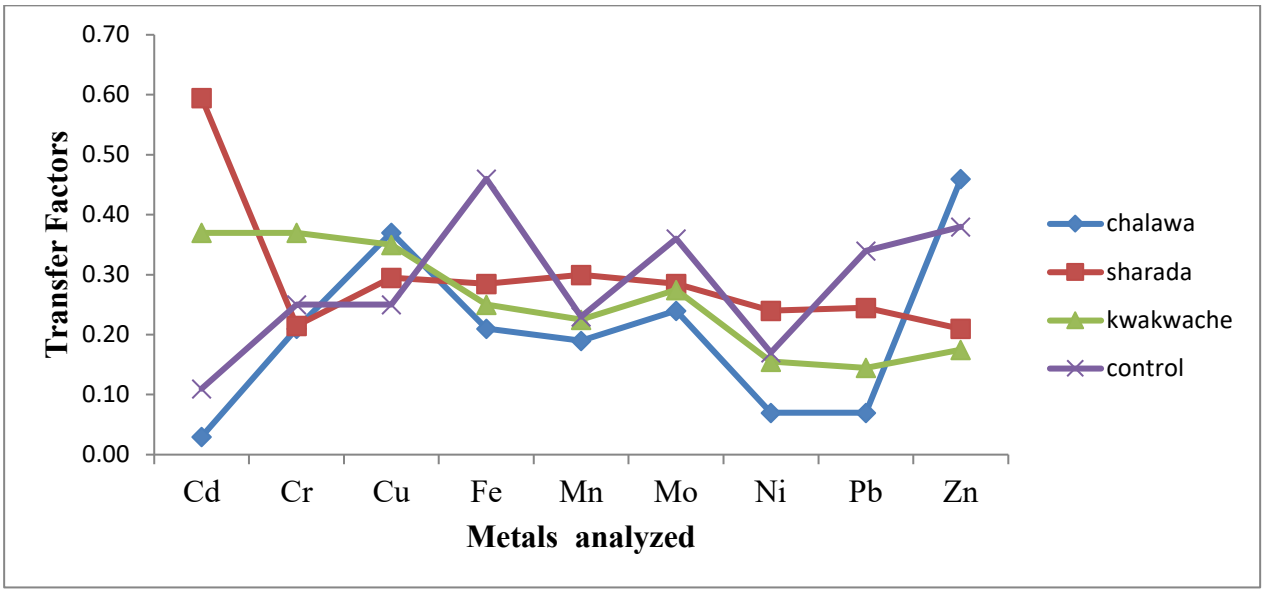


Fig4.19. Transfer Factors of the Selected Metals in lettuce plant Sample Analyzed

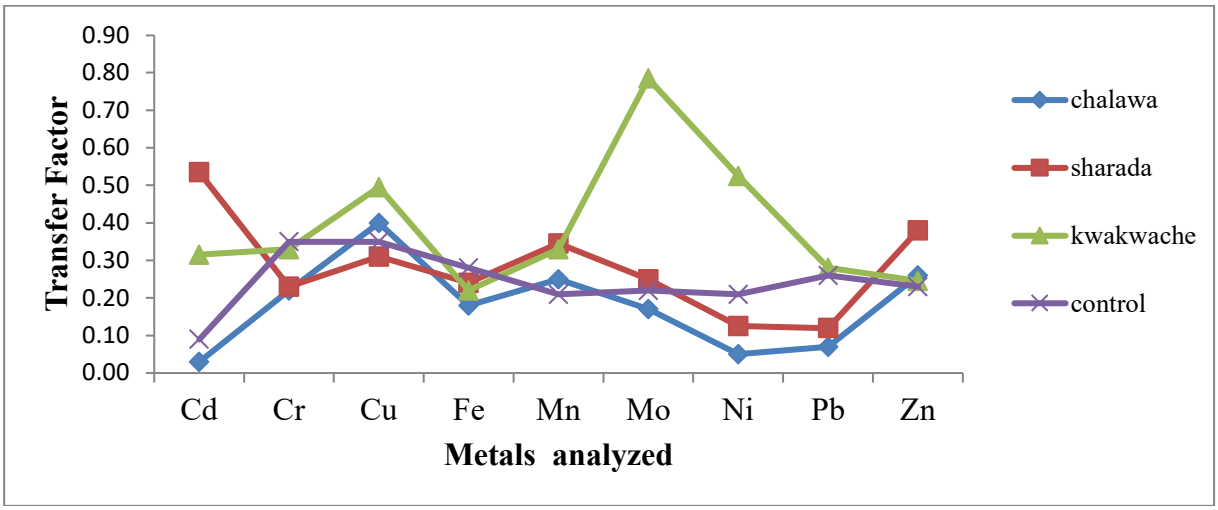


Fig4.20. Transfer Factors of the Selected Metals in spinach plant Sample Analyzed

All the values obtained in this study were found to be less than unit 1 which indicates that the five species of plants are not suitable for clean-up of heavily polluted soil through phyto-

remediation. Tables 4.4-4.6 also showed that some of the experimentally grown plants studied had TF<1 for all the metals inspite of the increase in concentrations of the metals. Analysis of Variance (ANOVA) at $p > 0.05$ revealed that there are no significant differences among the metals in all the sampling sites. Research carried out by Sahu *et al.,* (2012) showed similar result as this study with TF<1 for Ni and Co, By comparison with soil physicochemical parameters, the conclusion can be drawn: if the higher acidity of soil, the migration transformation ability more great, this could be the main reason for TF values below unit 1 in the entire sample area (Jintao *et al.,* 2011). The orders of abundance of each element relative to farm sampling locations are as follows;

Cabbage: Mn > Zn > Cu >Fe ≥ Mo> Cr> Cd ≥ Pb > Ni

Garden cress: Cu > Mn > Zn > Mo > Cr > Fe > Cd > Pb > Ni

Sesame: Mn > Zn > Cu > Mo> Fe ≥ Cr> Cd > Ni > Pb

Lettuce: Mn > Cu ≥ Mo >Zn > Fe > Cd> Cr ≥ Pb > Ni

Spinach: Cu > Mn > Mo > Cr > Zn> Cd > Fe > Ni > Pb

4.7. Bio-accumulation Factor

The bioaccumulation factors (BAFs) that have been calculated for the transfer of heavy metals from soils to the plant are as shown in various Figures bellow

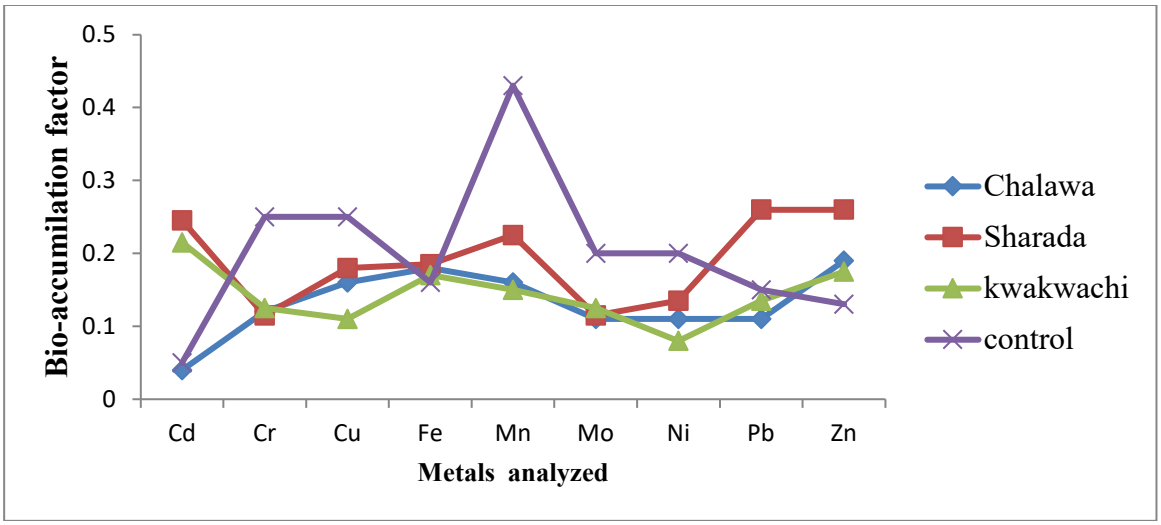


Fig4.21. Bio-accumulation Factors of the Selected Metals in Cabbage plant Sample Analyzed

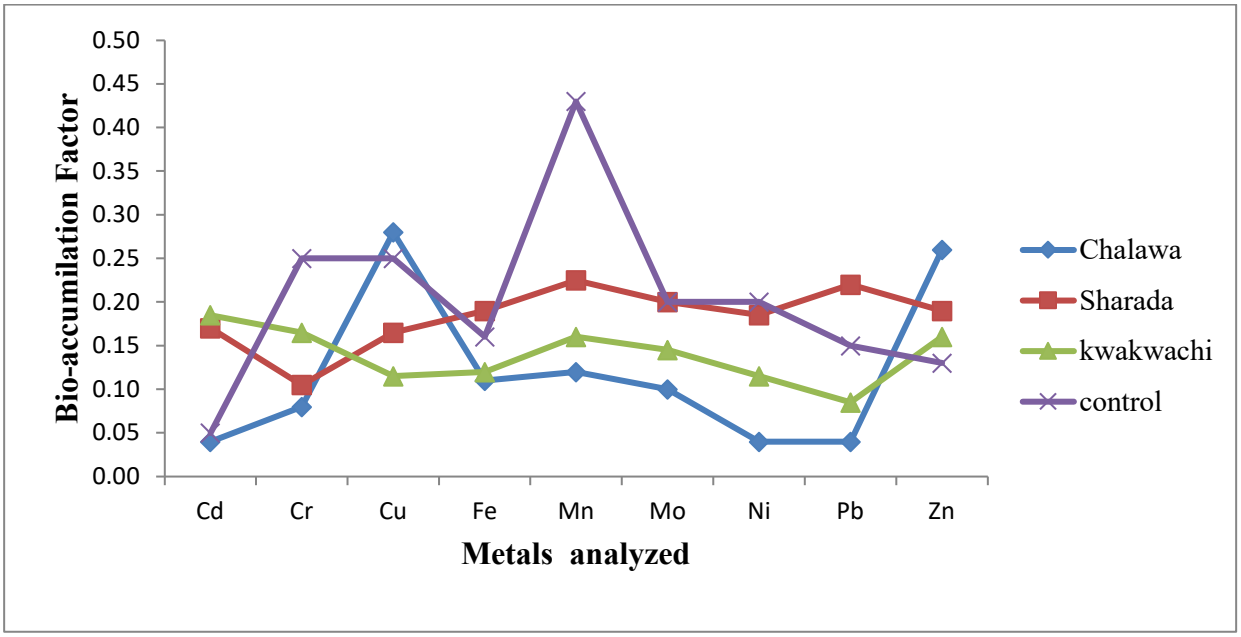


Fig4.22. Bio-accumulation Factors of the Selected Metals in Garden cress plant Sample Analyzed

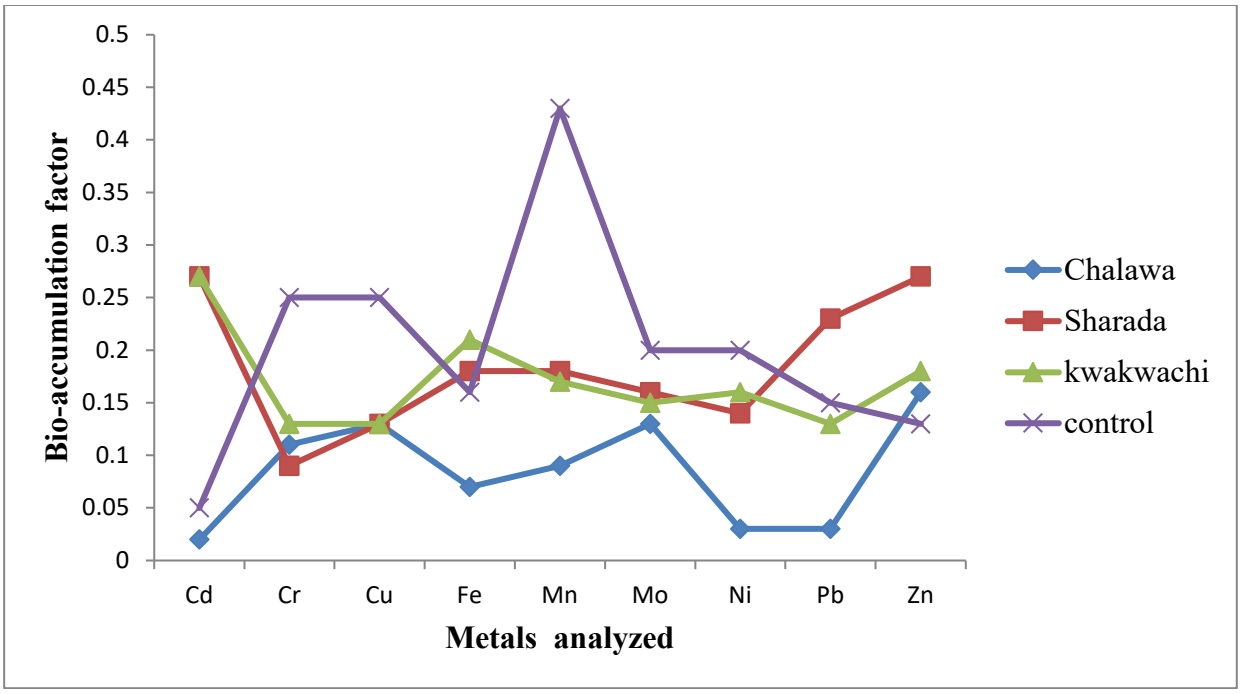


Fig.4.23. Bio-accumulation Factors of the Selected Metals in sesame plant Sample Analyzed

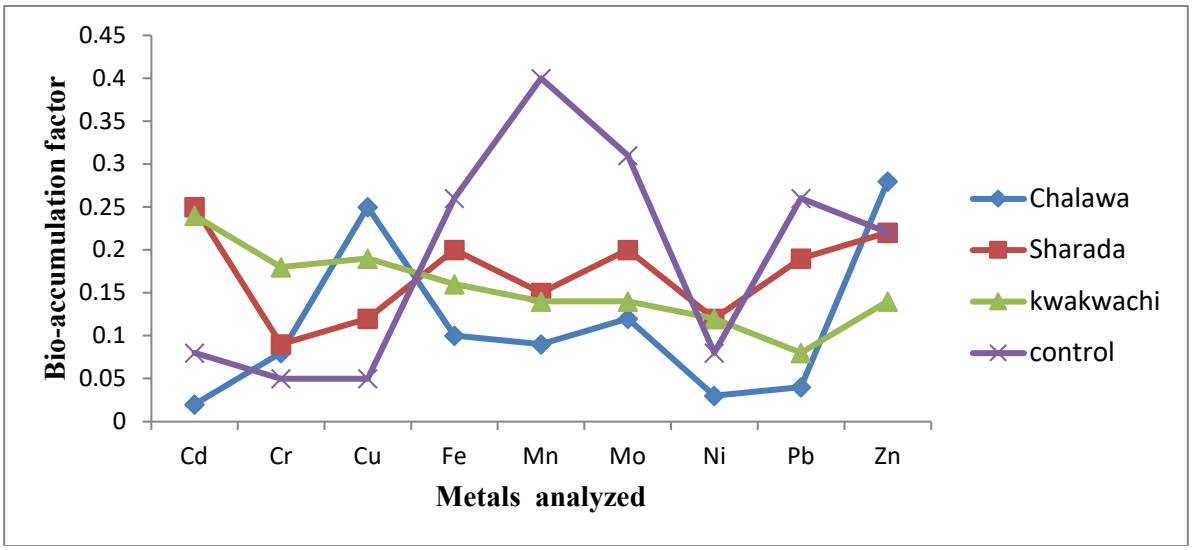


Fig4.24. Bio-accumulation Factors of the Selected Metals in lettuce plant Sample Analyzed

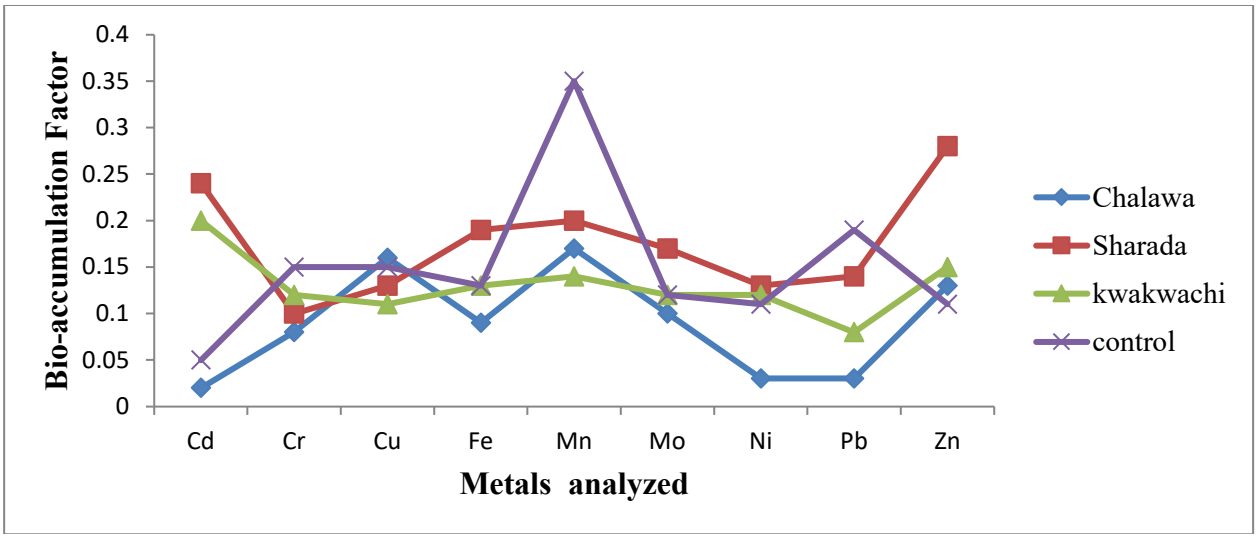


Fig4.25. Bio-accumulation Factors of the Selected Metals in spinach plant Sample Analyzed

.

Fig. 4.21show the BAF of selected metals in cabbage from all the sampling sites and they ranged from (0.04 to 0.43) unit. The Control sample had the highest BAF values for Mn(0.43) unit, Cr and Cu(0.25) unit while the least values was observed in Chalawa for Cd at (0.04). However, Fig. 4.22 shows the BAF of selected metals in garden cress which ranged from (0.04 to 0.43) unit. The highest BAF values was observed in Control sample for Mn at (0.43) unit and the least in Chalawa samples for Cd, Ni and Pb (0.04) unit. Fig. 4.23 also shows the BAF of selected metals in sesame which ranged from (0.02 to 0.43) unit, with highest BAF values in Control sample for Mn at (0.43) unit and the least in Chalawa samples for Pb (0.02) unit. Meanwhile, Fig. 4.24 shows the BAF of selected metals in lettus which ranged from (0.02 to 0.40), with highest BAF values in Control sample for Mn, Mo, Pb and Fe at (0.40, 0.31, and 0.26) unit respectively. The least was observed in Chalawa samples for Cd at (0.02) unit. Fig. 4.25 shows the BAF of selected metals in spinach which ranged from (0.02 to 0.35), with highest BAF values in Control sample for Mn, at (0.35) unit while, the least was observed in Chalawa samples for Cd at (0.02) unit.

High BAF values were observed for Mn,Cr, Cu, Mo and Ni for all the control samples. High BAF values of these metals could be attributed to the availability of these metals in the soil for uptake (Sharma *et al.,* 2007). This implies that these vegetables when monitored could be goog accumulator of these metals especially Mn (Radulescu *et al.,* 2013).

BAF values of unit < 1 were obtained for all the metals analyzed in the vegetable samples The results showed that the bio-accumulation of metals was low in the areas under study. Analysis of Variance (ANOVA) at $p > 0.05$ revealed that there is no significant difference between the metals in entire sample sites. However, Radulescu *et al.,* (2013) observed bioaccumulation factor (BAF) of seven heavy metals in cabbage, which revealed that this vegetable was a poor accumulators of Fe, Ni, Cu, Cd, and Pb (BAF <1), and good accumulator of Mn (BAF >1). Nasser *et al.,* (2014) also observed BAF < 1 unit for Cd, Cr, Cu, Pb, Zn, Mn and Fe in rice plant. Meanwhile, Ibrahim et al., (2013) observed bio-concentration factor (BCF) and bio-accumulation concentration (BAC) of five plants for Zn, Cu, Cd, Ni and Pb less than unit one indicating that these plants can't be used for phyto-stabilization of contaminated soil. Accumulation of selected metals varied greatly among plants species and the uptake of an element by a plant is primarily dependent on the plant species, its inherent controls, and the soil quality (Chunilall *et al.,* 2005). Large number of factors control metal accumulation and bioavailability associated with soil and climatic conditions, plant genotype and agronomic management, including: active/passive transfer processes, sequestration and speciation, redox states, the type of plant root system and the response of plants to elements in relation to seasonal cycles(Kabata and Pendias, 1984). All the vegetables under investigation had shallow root system and when compared to the soil physio-chemical properties also, a conclusion can be drawn that if, a deep root system and lower pH value then BAF values could be greater than unit

1 and would be suitable for phyto-stabilization of contaminated soil (Kabata and Pendias, 2001a; 2001b; 1999, Jintao *et al.,* 2011).

In summary the average BAF values for the selected metals in the entire sample site follow the order;

Cabbage: Mn > Zn > Cu >Fe > Pb> Cr> Cd > Mo > Ni

Garden cress: Mn > Cu > Zn > Mo > Fe ≥Cr > Ni > Pb > Cd

Sesame: Mn > Zn > Cu ≥Fe ≥ Mo > Cr> Cd > Pb > Ni

Lettuce: Zn > Mn > Mo >Fe > Cu ≥ Cd > Pb > Cr > Ni

Spinach: Mn > Zn > Fe ≥ Cu > Mo ≥ Cd > Cr ≥ Pb > Ni

4.9. Translocation Factor (TrF):

The Translocation Factor for all the vegetable from the sampling site varied as shown in Fig 4.26-4.30

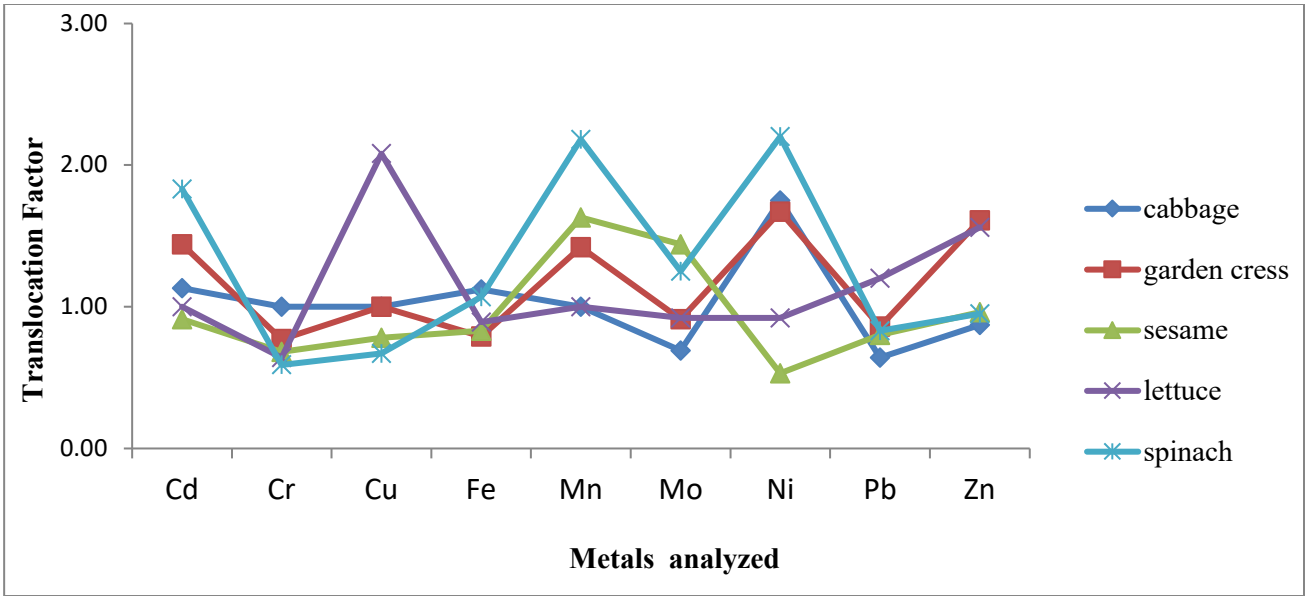


Fig.4.26. Translocation Factors of the Selected Metals for Chalawa samples Analyzed

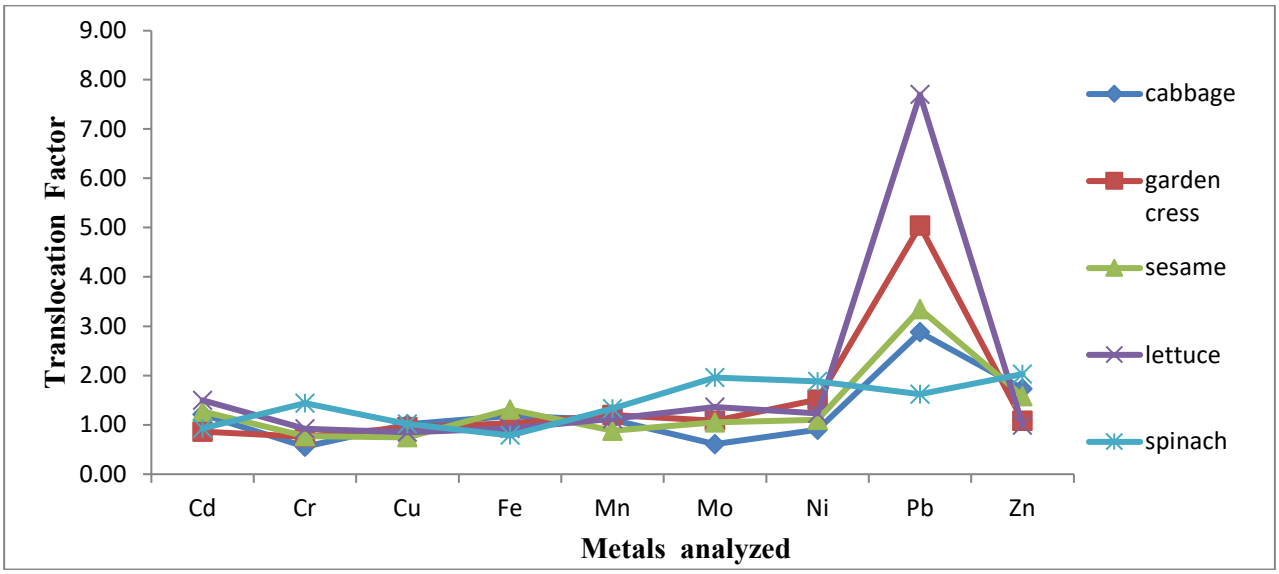


Fig.4.27. Translocation Factors of the Selected Metals for Sharada Samples Analyzed

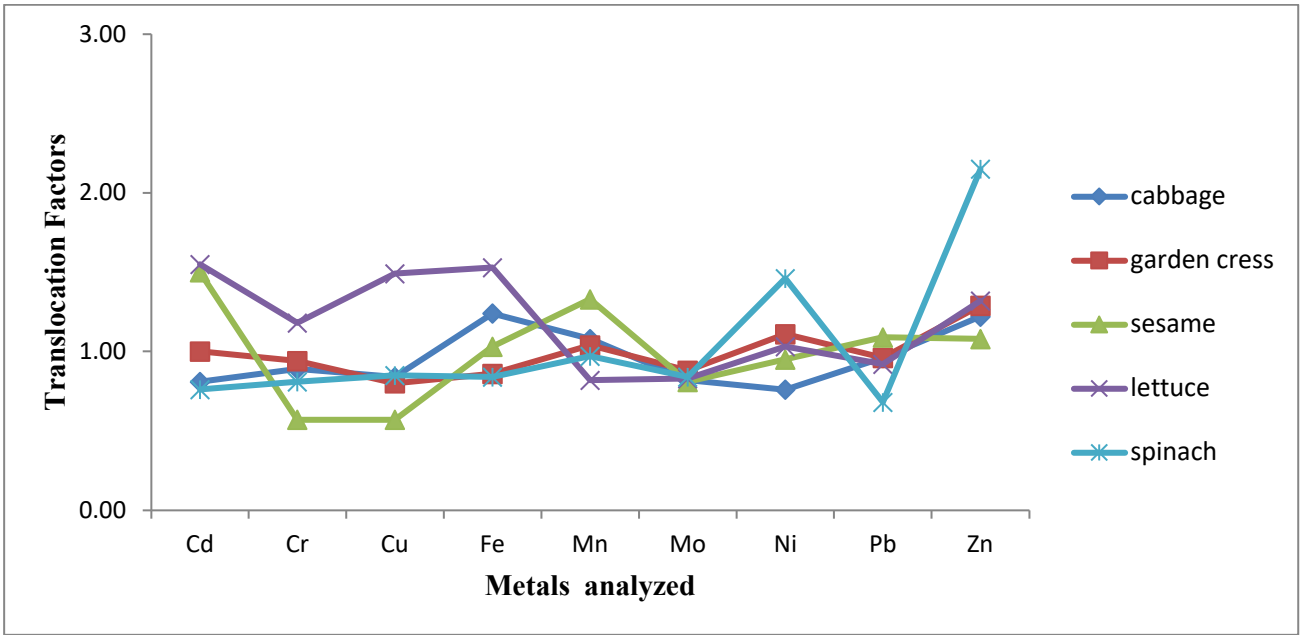


Fig.4.28. Translocation Factor of the Selected Metals for Kwakwachi Samples Analyzed

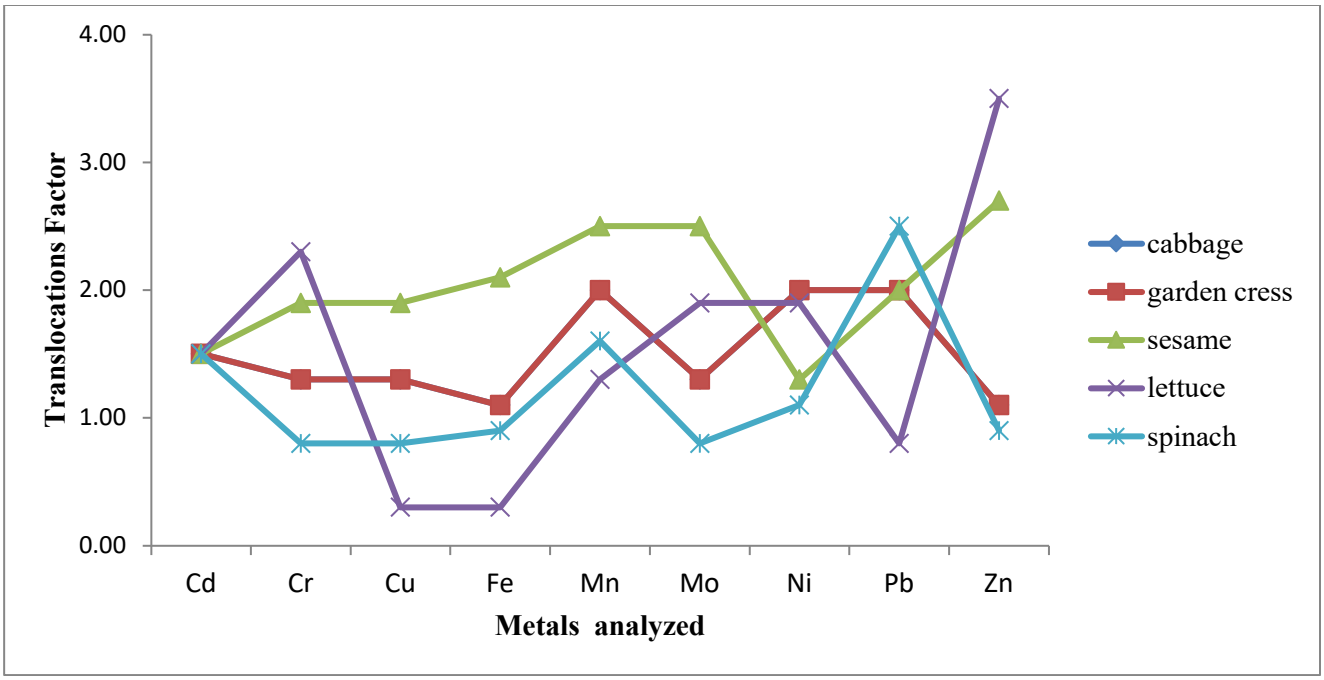


Fig.4.30. Translocation Factor of the Selected Metals for Control Samples Analyzed

Fig.4.26. Revealed that cabbage and garden cress from chalawa showed highest TrF value for Ni (1.75 and 1.67) while, the least TrF was for Pb (0.64) in cabbage and Cr (0.77) in garben cress. Meanwhile, Sesame plant showed the highest TrF values for Mn(1.63) and Mo (1.44) while the least was observed for Ni (0.53). However, Cu (2.08) had the highest value in lettuce and the least from Cr (0.64). Spinach plant showed the highest TrF values for Ni (2.2) and Mn (2.18) while the least was observed for Cr (0.59). ANOVA result ($p>0.05$) showed that there is no significant difference between the vegetables from the sample site.

Figure .4.27. indicates that the whole plants from Sharada showed highest TrF value for Pb which ranged from (1.6- 7.7) while low TrF values were observed in four of the plants for Cr which ranged from (0.56-0.92) but spinach had its least value for Fe(0.79). ANOVA result ($p< 0.05$) showed that there were significant differences these values for the vegetables from the entire sampling sites.

Figure.4.28. indicate that cabbage and garden cress from Kwakwachi showed highest TrF value for Fe (1.24) and Zn (1.29) respectively while the least TrF was for Ni (0.74) in cabbage and Cu (0.80) in garden cress. Meanwhile, sesame plant showed the highest TrF values for Cd (1.5) and Mn(1.3) while the least was observed for Cr and Cu (0.57). However, Cd (1.55), Fe (1.53) and Cu (2.08) had the highest TrF value in lettuce and the least was observed for Mn (0.82). Spinach plant showed the highest TrF values for Ni(1.46) and Zn(2.15) while the least was observed for Pb (0.68). ANOVA result ($p>0.05$) showed that there were no significant difference among the vegetables from the sampling sites.

Figure.4.29. Showed that the whole plants from control site showed TrF>1 value for all the metals expect for Cu(0.30),Fe(0.30),Pb(0.80) in lettuce plant and Cr(0.80), Cu(0.80), Fe(0.90),Mo(0.80), and Zn(0.90) in spinach plant. TrF values **≤1**, indicate increased retention of metals in plant roots with very less movement to above soil plant parts (Mellem *et al.,* 2012)**.** ANOVA result ($p>0.05$) showed that there were no significant difference between the vegetables from the sample site. In summary the TrF for all the Metals in the vegetables from the entire sample sites follow the order

Challawa: Mn > Ni > Cd >Zn > Cu> Mo> Fe > Pb > Cr
Sharada: Pb > Zn > Ni > Mo > Cd >Mn > Fe > Cu > Cr
Kwakwache: Zn > Cd > Fe >Ni >Mn > Pb> Cu > Cr > Mo

Control: Mn > Zn > Pb >Ni > Mo >Cr > Cd > Cu > Fe

Generally, spinach sample from the entire site showed TrF>1 for Ni and can be concluded that spinach is a good accumulator for Ni and can be used for Phyto-extraction of soil contaminated with Ni. Rangnekar *et al.,* (2013) support this argument. Similar results were also found by (Duman and Ozturk (2010) while studying on Ni contaminated soil. Sharada samples for Pb also showed TrF values >1. Elavated TrF values in these sites could be attributed to the ability of the

root to transfer more metals to the aerial part of the plants, which implies that plant from that area pose danger for consumption. In addition, it may be useful to determine the translocation pattern of metals from the roots to other parts of a plant in order to biologically monitor contamination by heavy metals and to differentiate between those plant species that accumulate metals and those that are tolerant to metal contamination. The translocation of metals in plants is a key element in ascertaining the distribution of the metals in the various plant tissues (Xian, 1989). High root to shoot translocation of these metals indicated that these plants have vital characteristics to be used in phyto-extraction of these metals as indicated by Ghosh and Singh (2005) and La´zaro *et al.,* (2006). According to Ghosh and Singh (2005) phyto-extraction is a process to remove the contamination from soil without destroying soil structure and fertility.

Plant species with slow plant growth, shallow root system and small biomass production are not generally preferred for phyto-remediation (Baker *et al.,* 2000). These five species had high biomass and based on high TrF values could have enormous potential to be used for phyto-extraction of Pb in Sharada Industrial estate. Yoon *et al.,* (2006) , Garbisu and Alkorta, (2001) observed that plant species with high TrF values were considered suitable for phyto-extraction generally requires translocation of heavy metals in easily harvestable plant parts i.e., shoots.

CHAPTER FIVE

5.0 Conclusion and Recommendations

5.1. Summary

This study was carried out to determine the relative pyto-remediation abilities of selected vegetables (lettuce, cabbage, garden cress, sesame and spinach) obtained from farmlands of three industrial estate of Kano on some heavy metals (Cd,Cr, Pb, Ni, Fe, Mo, Mn, Cu and Zn). The findings revealed that the metal concentrations in the industrial soils and the control were within the approved limits except for Cd. Meanwhile, the metal concentrations in the vegetables were also less than the recommended limit as specified by the WHO/FAO guidelines expect for Cd, Pb and Cr which were higher.

All the values reported in this study showed TF <1 which indicate that the five plant species are not suitable for clean-up of heavily pollutedsoil through phytoremediation. The findings also revealed that all plant species under investigation had BAF <1. However, spinach sample from the entire site showed TrF>1 for Ni and can be said that spinach is a good accumulator for Ni and can be used for phyto-remediation of soil contaminated with Ni, Sharada plant samples also showed Pb has TrF values >1 which can be concluded that vegetables grown in the area can also be used for the phytoextraction of Pb.

5.2. Conclusions

The findings revealed that the metal concentrations in the Industrial and controlled soils were within the approved limits except for Cd in industrial soil sample which was approximately five times higher than the recommended limit as specified by the WHO/FAO, (2007) guidelines. Meanwhile, the metal concentrations in the plant samples were less than the approved levels specified by the WHO/FAO, (2007) guidelines expect for Cd, Pb and Cr. Cr is approximately 4 times higher, while Pb is 5 times higher and Cd is approximately 22 times higher than

WHO/FAO, (2007) guidelines. All the values reported in this study showed TF <1 and they follow the order; Mn > Cu > Zn > Mo > Fe > Cr > Cd > Pb > Ni. BAF <1 unit was obtained for all the vegetable samples follow the order; Mn > Zn > Cu > Fe > Mo > Cd > Cr > Pb > Ni. This indicated that the five species of plants are not suitable for clean-up of heavily polluted soil through phyto-stabilization. However, spinach sample from the entire site showed TrF>1 for Ni and can be concluded that spinach is a good accumulator for Ni and could pose danger to people that consume spinach from these farm locations. Sharada samples for Pb also showed TrF values >1 which can be concluded that vegetables grown in the area can also be used for phyto-extraction of Pb. Also the consumption vegetables of study from Sharada sites could pose danger to the health of many especially children. The TrF values also follow the partern; Pb > Zn > Mn > Ni Cd > Mo > Fe > Cu > Cr. Conclusively vegetables from kwakwachi and chalawa are recommended for consumption because of it high content essential metals (Fe, Zn, Cu and Mn) and less contaminants of toxic metals (Cd and Pb).

5.3 Recommendation

The vegetables should be planted experimentally but on lower pH values to check their uptake and see if they could be hyper-accumulators of these metals. Also more research should be done on plants that could be used for phyto-stabilization so as to help remedy the contaminated soils for healthy consumptions of vegetables grown in these farm lands. Industries within these vicinities should find means of disposing their Industrial effluents appropriately as to reduce the cadmium and lead levels in the soils of the areas.

References

.

Abdulmojeed O. Lawal and Abdulrahman A. Audu, (2011). Analysis of heavy metals found in vegetables from some Cultivated irrigated gardens in kano metropolis. *Journal of Enviroental Chemistry and Ecotoxicology* vol. 3(6), pp.142-148

Achiba,W. B., Lakhdar, A., Gabteni, N., Laing, G. D., Verloo, M., Boeckx, P., Cleemput, O.V., Jedidi, N. and Gallali, T., (2010). Accumulation and fractionation of trace metals in a Tunisian calcareous soil amended with farmyard manure and municipal solid waste compost. *Journal of Hazard Mater*, 176, 99-108

.

Adefemi S.O, O. A Ibigbami and E. E. Awokunmi (2012): Level of heavy metals in some edible plants collected from selected dumpsites in ekiti state, Nigeria. Global Advance *Research Journal of Environmental Sciences and Toxicology* pp.132-136

Adesiyin, A.A, and Uddin, R.O. (2011). Insects Associated with Bungu, Ceratotheca sesamoides Endl (Pedaliaceae) in Ilorin, Nigeria. *Agriculture and Biology Journal of North America*, Vol.2 (6), pp. 974–980.

Agency for Toxic Substance and Disease Registry (ATSDR, 2005). Toxicological Profile for Nickel. http:www.atsdr.cdc.gov/toxprofiles/tp15.html (Retrieved; 8 March, 2012).

Agency for Toxic Substance and Disease Registry (ATSDR, 2007). CERCLA Priority List of Hazardous Substance. http://www.atsdr.cdc.gov/cercla/05list.html(Retrieved: 8 March, 2012)

Akan,J. C. Ogugbuaja V.O. Abdulrahaman F. I. and J.T Ayodele, (2007). The determination of pollutant levels in water of river challawa and in tap water from Kano Industrial Area, Kano State, Nigeria. *Research Journal of Environmental Sciences* 1 (5): 211-219, ISSN 1819-3412.

Akinola MO, Ekiyoyo TA (2006). Accumulation of lead, cadmium and chromium in some plants cultivated along the bank of river Ribila at Odo-nla area of Ikorodu, Lagos State, Nigeria. *Journal of Environmental Biology*., 27(3): 597-599.

Akoto, O., Ephraim, J.H., and Darko, G. (2008). Heavy Metals Pollution in Surface Soils in the Vicinity of Abundant Railway Servicing Workshop in Kumasi, Ghana, *International Journal Environs Research*. 2(4): 359 – 364.

Aletor, M.V.A. and Adeogun, O.A. (1995). Nutrient and Antinutrient Components of some Tropic Leafy Vegetables. *Food Chemistry* 53 : 375 – 379.

Alloway, B. J. (1995). Soil Processes and the Behaviour of Heavy Metals. in Alloway, B. J. (Ed.)*Heavy Metals in Soils.* Glasgow: Blackie Academic and Professional.

Alloway, B. J. (2004). 'Zinc in Soils and Crop Nutrition', International Zinc Association',Available at: http://www.zinc-crops.org/Crops/Alloway-Pdf/ Alloway_Print .pdf (Accessed: 8 March 2007).

Anderson, D. (2003). 'Introduction to Heavy Metal Monitoring', Centre for Ecology and Hydrology', Available at: http://www.heavymetals.ceh.ac.uk/resources/ CEH_hm_intro.PDF (Accessed: 2 March 2007).

Archana N.P and Anita A.M. (2006). "A study on clinical efficacy of Lepidium sativum seeds in treatment of bronchial asthma". *Iran Journal Pharmacol Ther* 5: 55–59.

Arun, B. and Mukherjee, A. (1998). Nickel: A Review of Occurrence, Uses, Emissions and Concentration in the Environment in Finland. *International Journal Environs Research*. 2(5): 59 –64.

Asscyed, M. E., Abd El-Aty, A. M., Abd El-Aty, B. Y., (2009). "Cruciferous plants: Phytochemical toxicity versus cancer chemo protection". *Mini-Reviews in Medicinal Chemistry* **9** (13): 1470–1478.

Ayensu, E.S. (1978). Medicinal Plants of West Africa. Reference Publications Algonac, Michigan. Pg 330

Bahemuka, T. E., and Mubofu, E. B. (1999). 'Heavy Metals in Edible Green Vegetables Grown Along the Sites of the Sinza and Msimbazi Rivers in Dar Es Salaam, Tanzania', *Food Chemistry,* 66, 63

Baird, C. (1999). Environmental Chemistry. 2nd Ed. New York: W.H. Freeman and Company

Baker, A.J.M., Grath Mc, Reeves R.D. and Smith J.A.C. (2000). Metal hyperaccumulator plants: a review of the ecology and physiology of a biological resource for phytoremediation of metal-polluted soils. In: Phytoremediation of contaminated soil and water. (Eds.): N. Terry and G. Ban˜uelos.Lewis Publishers, Boca Raton, FL, pp. 85-107.

Batagarawa S.M (2000). *Funaria hygrometrica* as bio-indicator of heavy metals in Kano metropolis. Bayero University, Kano-Nigeria, M. Sc. Thesis.

Bawa, S.F. and Yadav, S.P. (1986). Protein and Mineral Contents of Green Leafy Vegetables consumed by Sokoto Population. *Journal of Science, Food and Agriculture*. 37: 504 – 506.

Bedigian, D. and Adetula, O.A., (2004). Ceratotheca sesamoides Endl. In: Grubben, G.J.H. and Denton,O.A. (Editors). PROTA 2: Vegetables/Légumes. [CD-Rom]. PROTA,Wageningen, Netherlands. pp44

Beesley, L., Inneh, O.S., Norton, G.J., Moreno-Jimenez, E., Pardo, T., Clemente, R. and Dawson, J.J.(2014). Assessing the influence of compost and biochar amendments on the mobility and toxicity of metals and arsenic in a naturally contaminated mine soil. *Journal of Environ Pollution.,* 186,195-202.

Bennett, B. G. (1981). 'Exposure Commitment Assessments of Environmental Pollutants Vol. 1. NQ.1'. London: University of London. (MARC Report Number 34) p. 50-57

Bhatiya, KN (1996). *Modern Approach to Botany*. India: Surya publications. p. 516.

Birkeland, P.W., (1999). *Soils and Geomorphology* [brd.Ed.] Oxford University Press, New York.pp 55-63

Blaylock M.J., Dushenkov D., Gussman C., Kapulkin Y., Ensley B., Raskin I., (1997), Enhanced accumulation of Pb in Indian Mustard by soil-applied chelant agents, *Environ. Science and Technology.* 31, 860- 865.

Bolan, N., Kunhikrishnan, A., Thangarajan, R., Kumpiene, J., Park, J., Makino, T., Kirkham, M.B. and Scheckel, K., (2014). Remediation of heavy metal (loid) s contaminated soils to mobilize or to immobilize? *Journal of Hazard Matter*., 266, 141-166.

Boyd, E. M. (1973). *Toxicity of Pure Foods.* Ohio: The CRC Press Inc. pp 50

Bradley, Fern Marshall; Ellis, Barbara W.; Martin U, Deborah L., (2009). The organic Gardener's Handbook of Natural Pest and Disease Control. Rodale, Inc. ISBN 978-1-60529-6777.

Browing, E. (1969). Toxicity of Industrial Metals. 2nd Ed, London: Butterworths. Pp60-69

Budgergars-diets,PDSAhttp://www.organicindia.com/PR_OH_chandrashoor.php.Retrieved 2012

Burkill, H.M. (1995). *Useful Plants of West Tropical Africa*. Royal Botanic Gardens Press, Kenton UK. Pp45-48

Calabrese: E. J., Canada, A. T., and Sacco, C; (1985). 'Trace Elements and Public Health', *Annual Review of Public Health,* 6,131-146.

Cassidy D, Frederic G. and Hall, J H. (2002)*Dictionary of American regional English* Harvard University Press,. Page 97. ISBN 0-674-00884-7, ISBN 978-0-674-00884-7

Castagnetto JM, Hennessy SW, Roberts VA, Getzoff ED, Tainer JA, Pique ME.(2002). MDB: the metalloprotein database and browser at the Scripps Research Institute. *Nucleic Acids Res* **30**(1): 379–382.

Caussy, D., Gochfeld, M., Gurzau, E., Neagu, C., and Ruedel, H. (2003). 'Lessons from Case Studies of Metals: Investigating Exposure, Bioavailability, and Risk', *Ecotoxicology and Environmental Safety,* 56, 45-51.

Chesworth, E.[2008]. *Encyclopedia of Soil Science*, Dordrectcht, Netherlands. Pp. 93 – 98

Choudhry, B. (1979). Vegetables. 6th Edition, *National Book Trust*, New Delhi, India.pp 48

Chunilall, V, A. Kindness and S.B. Jonnalagadda. (2005).Heavy metal uptake by two edible Amaranthus herbs grown on soils contaminated with Lead, Mercury,Cadmium and Nickel. J.Environ. Sci. Health, 40: 375-384

Cobb, G. P., Sands, K., Waters, M., Wixson, B. G., and Dorward-king, E. (2001). Accumulation of Heavy Metals by Vegetables Grown in Mine Wastes', Environmental toxicology and chemistry, 19, 600-607

Committee on Biologic Effects of Atmospheric Pollutants (1973'). *Manganese.* Washinton D.C.:National Academy of Sciences. Pp34-45

Committee on Biologic Effects of Atmospheric Pollutants (1974). *Chromium.* Washinton D.C.: National Academy of Sciences.

Committee on Medical and Biologic Effects of Environmental Pollutants (1975). *Nickel.* Washington D.C.: National Academy of Sciences.45-76

Committee on Medical and Biologic Effects of Environmental Pollutants (1979). *Iron.* Baltimore: University Park Press.79-85

Cui,Y .J., Zhu, Y.-G., Zhai, R.-H., Chen, D.-Y., Huang, Y.-Z., Qiu, Y., and Liang; J.-Z. (2004). 'Transfer of Metals from Soil to Vegetables in an Area near a Smelter in Nanning, China', *Environment International,* 30, 785-791.

Dasuki IA (2000). Analysis of trace metals and some selected chemical pollutants in effluents from Challawa, Bompai and Sharada Industrial areas of Kano. (Unpublished master's dissertation) Bayero University Kano, Nigeria.

David, H.H, Jean, M, Catherine, S, (2008). Heavy Metal North Caroline Soil, Occurrence and Significance. Retrieved on 10th March, 2011, from http://www.ncagr.gov/agronmic 67-76

De Lima, L.S., Quináia, S.P., Melquiades, F.L., de Biasi, G.E. and Garcia, J.R., (2014). Characterization of activated carbons from different sources and the simultaneous adsorption of Cu, Cr, and Zn from metallurgic effluent. *Seperational. Purification. Technology*., 122, 421-430.

Dudka S and Chlopecka, A. (1990). Effect of Solid Phase Speciation on Metal Mobility and Photovailability in Shudge – *Amended Soil. Water, Air and Soil Pollution* 51: 153– 160.

Dudka, S.M., Piotrowaska, A, Chlopecka and lopatek, J. (1995). Trace Element Contamination of Soil and Crop Plants by Mining and Melting Industry in South – West Poland. Geochem. Explore 52: 237 – 250.

Dudka, S.M., Piotrowaska, A, Chlopecka and lopatek, J. (1996). Trace Element Contamination of Soil and Crop Plants by Mining and Melting Industry in South – West Poland. Geochem. Explore 52: 237 – 250.

Duman F. and Ozturk F., (2010) Nickel accumulation and its effect on biomass, protein content and antioxidative enzymes in roots and leaves of watercress (Nasturtium ocinale R. Br.), *Journal of Environmental Sciences*, 22(4), 526–532

Eddouks, M; Maghrani M; Zeggwagh NA; Michel JB (2005). "Study of the hypoglycaemic activity of Lepidium sativum L. aqueous extract in normal and diabetic rats". *Journal of Ethno pharmacology* 97: 391–395.

Eisler, R. (1998). *'Nickel Hazards to Fish, Wildlife, and Invertebrates: A Synoptic Review'*. MD: U.S. Geological Survey. (Contaminant Hazard Reviews Report No.34). 28-39

Eisler, R. (1998a). *'Copper Hazards to Fish, Wildlife, and Invertebrates: A Synoptic Review'*. MD: U.S. Geological Survey, Biological Resources Division. (Biological Science Report USGS/BRD/BSR--1998--0002). 76-85

Eno, J.U, Tren Chard, O.I Jospeh A.O, Anthony, O.A., Ivargy E.E (2009). *Manual of Soil Plant and Water Analysis* Sibon Books Ltd, Lagos Pp8 – 15.

Faboya, O.P. (1983). The Mineral Content of Some Green Leafy Vegetables Commonly found in the Western Nigeria. *Food Chemistry* 12: 213 – 216.

Falusi, O.A, Funmi, F.M, Salako, E.A. (2002). Inheritance of Hairiness of Stem and Petiole in a Selection from Local (Nigeria) Germoplasm of Sesame. *Tropicultura*. 20, 3, 156-158.

Fasakin, K. (2004). Proximate* composition of bungu (Ceratotheca sesamoides). Leaves and seeds. *Journal of Biochemistry*. 16(2), 88-92.

Federal Development Authority (1979). Methods for Routine Soil Analysis in Nigeria. FDA, Lagos Pp 69 – 80.

Fellet, G., Marmiroli, M. and Marchiol, L., 2014. Elements uptake by metal accumulator species grown on mine tailings amended with three types of biochar. *Science of Total Environ*., *468*, 98-608.

Flora SJS, Mittal M, Mehta A. (2008). Heavy metal induced oxidative stress & its possible reversal by chelation therapy. *Indian Journal of Medical Research* **128**: 501–523.

Food Authority Organization and World Health Organization (FAO/WHO), (1998). Requirement of Vitamin A, Iron Folate and Vitamin B_{12} Reports of a Joints FAO/WHO Export Consultation. FAO Food and Nutritional Series, No. 23.

Francis A. A and Forsyth, C. (1995). Toxicity Summary for Manganese. Risk Assessment Information System. Oaths Ridge Reservation Environmental Program. http://raise.oral.govt/tax/profile/mn.shtml

Fraser,P.M.(2004) what is Soil? Retrieved from http://www.compostingvermont.org/artilcles/whatissoil.htm, 24th July, 2010.

Freedman B. and Hut Chinson, T.C (1981). Sources of Metal and Elemental Contamination of Terrestrial Environment. App Sci Pub. Pp 35 – 94

Garbisu C, Alkorta I (2001). Phytoextraction: a cost-effective plant-based technology for the removal of metals from the environment. Bioresour. Technol. 77: 229-236.

Geogopoulous, P. G., Roy, A., Yonone-Loiy,M. J., Opiekun, R. E., and Lioy, P. J. (2001) 'Copper: Environmental Dynamics and Human Exposure Issues', The International Copper Association. Environmental and Occupational health Sciences Institutes (EOHSI) available at: http://ccl.rutgers.edu/reports/ica2002_copper1.pdf (Accessed: 10 January 2007) pp56-67

Ghaderian, S.M. and Ravandi A.G., (2012). Accumulation of copper and other heavy metals by plants growing on Sarcheshmeh copper mining area, Iran. *Journal of Geochemisty. Exploraton*., 123, 25- 32.

Ghosh, M. and Singh, S.P. 2005. A review on phytoremediation of heavy metals and utilization of its by products. *Applied Ecology of Enviromental. Research*., 3: 1-18.

Gibson, A C. (2012) "Colewart and the Cole Crops". University of California – Los Angeles. Retrieved 10th August,2012

Grubben, G.J.H. (1976). The Cultivation of *Amaranthus* as a Tropical Leaf Vegetable with Special Reference to Southern Dahomey. Royal Tropical Institute, Netherlands. No 67.

Gullett, N.P.; Ruhul Amin, A.R.; Bayraktar, S.; Pezzuto, J.M.; Shin, D.M.; Khuri, F.R.; Aggarwal, B.B.; Surh, Y.J.; Kucuk, O. (2010). "Cancer prevention with natural compounds". *Seminars in Oncology* **37** (3): 258–281. Doi: 10.1053/j.seminoncol.2010.06.014. PMID 20709209

Ha, N.T.H., Sakakibara, M., Sano, S. and Nhuan, M.T., 2011. Uptake of metals and metalloids by plants growing in a lead–zinc mine area, Northern Vietnam. *Journal of Hazardous Matter.*, 186, 1384-1391.

He, X.T, Trainer, S.J. Logan, T.J. (1992). Chemical Properties of Municipal Solid Waste Compost Environment Quality 21:318-329.

He, Z,L. Xiaoe, E.Y, Stoffella P.J. and Calvert, D.V. (2001). Plant Nutrition Benefits of Phosphorous, Potassium, Calcium, Magnesium and Micro Nutrient from Compost Utilization. In Compost Utilization in Horticultural Cropping.

Higdon, J. V.; Delage, B.; Williams, D. E.; Dashwood, R. H. (2007). "Cruciferous vegetables and human cancer risk: Epidemiologic evidence and mechanistic basis". *Pharmacological Research* 55 (3): 224–236. doi:10.1016/j.phrs.2007.01.009. PMC 2737735. PMID 17317210.

Hirsch, David P. (2005) The Moosewood Restaurant kitchen garden: creative gardening for the adventurous cook. Ten Speed Press, 2005. ISBN 1-58008-666-7, ISBN 978-1-58008-666-0

Hooda, P. S. {1997). 'Plant Availability of Heavy Metals in Soils Previously. Amended with Heavy Applications of Sewage Sludge', *Journal of the Science of Food and Agriculture,*73,446-454.

Hough, R. L., Breward, N., Young, S. D., Crout, N. M.J., Tye, A. M., Moir, A. M., and Thornton, I. (2004). 'Assessing Potential Risk of Heavy Metal Exposure from Consumption of Home-Produced Vegetables by Urban Populations', *Environmental Health Perspectives,* 112, 215-221.

Hullin, R. P.; Kapel M., Jennifer A. Dl (2007). "The lithium contents of some consumable items". *International Journal of Food Science and Technology* 4 (3): 235240. doi:10.1111/j.1365-2621.1969.tb01519.x. ISSN 0950-5423.

Hurley, L.S, Keen C.L. (1987). Trace Elements in Human and Animal Nutrition. New York, NY, Academic Press. Vol. 1: 185-223.

Ibrahim M.M., A.A. alsahli and G. El-gaaly, (2013). Evaluation of phytoremediation potential of six wild plants for metal in a site polluted by Industrial wastes: a field study in riyadh, saudi arabia *Pakistan Journal of Botany*. 42(2): 571-576

International Institute for Tropical Agriculture (IITA, 1979). Selected Method for Soil and Plant Analysis. IITA, Oyo Road, Ibadan. Pp 6-20.

Irwin, R. J. (1997). 'Environmental contaminant encyclopedia copper entry', water Resources Division, Water Operations Branch Available at http://www.nature.nps.gov/hazardssafety/toxic/ copper .pdf. (Accessed: 15 March 2007). Pp45

Janick, Jules (2011). Plant Breeding Reviews 35, p. 51. John Wiley and Sons. ISBN 978-1-118-10049-3.

Janus, J.A. Krajnc, E.I (1990). Integrated Criteria Document Chromium: Effects. Beethoven, Netherlands National Institute of Public Health and Environmental Protection. Appendix.65-80

Jayasherree Deka and H. P. Sarma, (2012). Heavy metal contamination in soil obtained from industrial zone and its relation with some soil properties. Archives of Applied science Research, 4(2): 831-836.

Jintao Liang , Cuicui Chen, Xiuli Song, Yulan Han, Zhenhai Liang (2011)**.** Assessment of Heavy Metal Pollution in Soil and Plants from Dunhua Sewage Irrigation Area *International. Journal of Electrochemistry and Sciences*., 6 5314 – 5324

John, H.D. (2002). Heavy Metals (IUPAC Technical Report), Pure and Applied Chemistry, Vol. 74 pp 793-807.

Joseph C. A, Stephen I. A, Zakari M, Victor O. O, (2013). Assessment of heavy metals, pH, organic matter and organic carbon in roadside soils in makurdi metropolis, benue state, nigeria *journal of environmental protection*, 4, 618-628

Jośko, I., Oleszczuk, P., Pranagal, J., Lehmann, J., Xing, B. and Cornelissen, G., 2013. Effect of biochars, activated carbon and multiwalled carbon nanotubes on phytotoxicity of sediment contaminated by inorganic and organic pollutants. *Ecological journal. England.,* 60, 50-59.

Jung C. H., Matsuto T. and Tanaka N. (2006), Flow analysis of metals in a municipal solid waste management system. *Journal of Waste Management*. 26: 1337-1348.

Kabata- Pendias, A. and Pendias, H. (2001a) *Trace Element in Soil and Plant.* 3rd ed. CRC Press Boca Taron pp 412-418.

Kabata, C, and Singh, B.R. (2001b). Fraction and Mobility of Copper, Lead and Zinc in Soil Profile in the Vicinity of a Copper Smelter. *Journal of Quals*, 30:485-492

.

Kabata, Pendias, A and Pendias, H (1999). *Biochemistry of trace element*. New owe press, Warsaw,Poland, pp 99-105.

Kabata-Pendias, A, and H. Pendias, 1984. Trace Elements in Soils and Plants. CRC Press, BocaRaton, FL.

Katz, S H and Weaver, W W (2003). *Encyclopedia of Food and Culture*. Volume 2.Scribner.Pg 375-376. ISBN 978-0-684-80565-8.

Khan, S., Chao, C., Waqas, M., Arp, H.P.H. and Zhu, Y.G., (2013a). Sewage sludge biochar influence upon rice (*Oryza sativa L*) yield, metal bioaccumulation and greenhouse gas emissions from acidic paddy soil. *Journal of Enviromental. Science and Technology.,* 47, 8624-8632.

Khan, S., Naz, A., Asim, M., Ahmad, S.A., Yousaf, S. and Muhammad, S., (2013). Toxicity an bioaccumulation of heavy metals in spinach seedlings grown on freshly contaminated soil. *Pak. J. Bot.,* 45, 501-508.

Kimberly, M.F.H. and Willian, H. (1999). Trace Metal in Montreal Urban Soil and the leaves of Teraxacum Officinal Can. J. Soil Sci. 79:385-387.

Koch, B.; Kota, M.; and Horvath, M.I. (1965). Fodder Crops as Leafy Protein. *Agrobotanica* 1: 19 – 28.

Kumar, N., Bauddh, K., Kumar, S., Dwivedi, N., Singh, D.P. and Barman, S.C. (2013). Accumulation of metals in weed species grown on the soil contaminated with Industrial waste and their phytoremediation potential. *Ecology journal of England., 61*, 491-495

.

Kumar, U. and Owonubi, J.J. (1987). Crop Climate Implications on the Irrigated Cropping Pattern in Northern Nigeria. 10th National Irrigation and Drainage Seminar held at the National Water Resource Institute, Kaduna, 23 – 26.

La´zaro, D.J., Kiddb P.S. and Martý´neza C.M., (2006). A phytogeochemical study of the Tra´s-os-Montes region (NE Portugal): Possible species for plant-based soil remediation technologies. *Science of the Total Environment*, 354: 265- 277.

Ladeji, O and Okoye, Z.S. (1993). Chemical Evaluation of the Nutritive Value of leaf of fluted pumpkin (*Telfera occidentalis). Food Chemistry* 53: 353 – 355.

Lal, R. (1981). Analysis of Different Process Governing Soil Erosion by Water in the Tropics Proc. Florence Symp. June, 1981, JAHS, 133:351-364.

Lawrence, W. (2008). Toxic Metals in Human Health and Disease Retrieved from http://www.toxic-metals.html. Retrieved 14th December, 2014.

Lenntech,(2008). Heavy Metals. Retrieved from http://www.lentech.html Retrieved 14th December, 2014

Levy, L. S., Aitken, R. J., Holmes, P., Hughes, J., Hurley, F., Rumsby, P. C., Searl, A., Shuker., L. K., Spurgeon, A., and Warren,F. (2004). *'Occupational Exposure Limits: Criteria Document for Manganese and Inorganic Manganese Compounds'.*

Leicester: the Institute for Environment and Health and the Institute of Occupational Medicine. (IEH Web Report WI7).

Lindsay, W. L. (1979). *Chemical Equilibria in Soils.* New York: John Wiley and Sons.

Liu, J., Wang, J., Qi, J., Li, X., Chen, Y., Wang, C., Wu, Y., (2012). Heavy Metal Contamination in Arable Soils and Vegetables around a Sulfuric Acid Factory, *China.Clean-Soil Air Wate*r, 40, 766-772.

Liu, X., Gao, Y., Khan, S., Duan, G., Chen, A., Ling, Li., Zhao, L., Liu, Z. and Wu, X., (2008). Accumulation of Pb, Cu, and Zn in native plants growing on contaminated sites and potential accumulation capacity in Heqing, Yunnan. *Journal of Enviromental. Science-China*, *20*, 1469-1474.

Long, X. X., Yang, X. E., Ni W. Z., Ye, Z. Q., He, Z. I., calvert, D. V., and Stoffella, J. P. (2003) 'Accessing Zinc thresholds for phytotoxicity and potential dietry toxicity in selected vegetables crops', communication in soil science and plant analysis, 34, 1421-1434.

Loska, K. Wauchula, D. and Pelezar, J. (2005). Application of Enrichment Factor to Assessment of Zinc Enrichment /Depletion in Farming Soil. *Communication in Soil Science and Plant Analysis* 36 (9-10): 1117-1128.

Maile, P. (2007). Health Effects of Exposure to Heavy Metals. Retrieved from http://www.be.weller.com (article) Health-effects of Exposure –to –heavy-Metals.

Makus, D.J. (1983). *Amaranthus tricolour L*. Performances and Potential in the Midsouth. *Amaranth Newsletter* 3: 3 – 4.

Marchiol L., Assolari S., Sacco P. and Zerbi G., (2004). Phytoextraction of heavy metals by canola and radish grown on multi-contaminated soil, *Environ.Pollution*. 132, 21-27

Marisa Intawongse, (2007). Uptake of heavy metals by vegetable plants grown on contaminated soils, their bioavailabity and speciation. (Doctorial thesis) Northumbria University Namibia

Marschnar, H. (1995). *Mineral Nutrition of Higher Plants.* 2nd Ed. London: Academic Press.

Mattina, M. I., .Iannucci-Berger, W., Musante, C., and White, J. C. (2003). 'Concurrent Plant Uptake of Heavy Metals and Persistent Organic Pollutants from Soil', *Environmental Pollution,* 124,375-378**.**

McCarty, S.A. and Ashcroft, G.L. (1972). Essentials of Soil Mechanics and Foundations. Pp 42,-49.

McGrath S. P. (2001). 'How Organisms Live with Heavy Metals in the Environment', The International Council on Metals and the Environment: Available at: www.icme.com (Accessed: 1 March 2007).

Mellem J.J., Baijnath H. and Odhav B., (2012). Bioaccumulation of Cr, Hg, As, Pb, Cu and Ni with the ability for hyperaccumulation by *Amaranthusdubius*, *African Journal of Agricultural Research*, 7(4**)**, 591-596

Mench, M., Vangronsveld, J., Dider, V., and clijsters, H. (1994). Evaluation of metal mobility, plant availability and immobilization by chemical agents in a limed-silty soil', environmental pollution, 86, 279-286

Michach, M, (2003). Soil ecology and the Food Web. Retrieved from http://www.soilsecrets.com, on 24th July, 2010.

Michael, C.H. (2010). Heavy Metal Encyclopedia of Earth. *National Council for Science and the Environment*. Washington D.C.123-134

Miller, D. D., Schricker, B. R., Rasmussen, R. R., and Campen, D. V. (1981). 'An *in Vitro* Method for Estimation of Iron Availability from Meals', *The American Journal of Clinical Nutrition,* 34,2248-2256.

Milne, E. (2009). Soil Organic Carbon Retrieved from http://www.org/article/soilorganiccarbon, on 27th December, 2010.

Modin, H., Persson, K.M., Andersson, A. and van Praagh, M., 2011. Removal of metals from landfill leachate by sorption to activated carbon, bone meal and iron fines. *Journal of Hazardous Matter*., *189*, 749-754.

Mortvedt, J. J., Cox, F. R., Shunman, L. M., and Welch, R. M. (1991). *Micro-nutrients in Agriculture*. 2nd Ed. Soil science of Americal, Inc. 77-86

Muamar AL-Jaboobi, Abdelmajid Zouahri, M'hamed Tijane, Abdellah El Housni, Zakaria Mennane, Hasna Yachou and Mohammed Bouksaim (2014). Evaluation of heavy metals pollution in groundwater, soil and some vegetables irrigated with wastewater in the Skhirat region "Morocco" *J. Mater. Environ. Sci. 5 (3) 961-966 ISSN : 2028-2508 CODEN: JMESCN* 961

Muhammad, S., Shah, M.T., Khan, S., Saddique, U., Gul, N., Khan, M.U., Malik, R.N., Farooq, M. and Naz, A., (2013). Wild Plant Assessment for Heavy Metal Phytoremediation Potential along the Mafic and Ultramafic Terrain in Northern, Pakistan. *BioMed. Research International.*35:45-55

Muller,M., and Anke, M. (1994). 'Distribution of Cadmium in the Food Chain (Soil- Plant-Human) of a Cadmium Exposed Area and the Health Risks of the General Population', *The Science of the Total Environment,* 156, 151-158.

Nabulo G, Oryem-Origa H, Diamond M (2006). Assessment of lead, cadmium and zinc contamination of roadside soils, surface films, and vegetables in Kampala City, Uganda. ISSN:0013-9351. *Enviromental Resources*. 101: 42-52.

Najeeb-Ur-Rehman, Mehmood MH, Alkharfy KM, Gilani AU, (2011) "Prokinetic and laxative activities of Lepidium sativum seed extract with species and tissue selective gut stimulatory actions. *Journal of Ethnopharmacology*.

Nasreddine, L., and Parent-Massin, D. (2002). 'Food Contamination by Metals and Pesticides in the European Union. Should We Worry?' *Toxicology Letters,* 127, 29- 41.

Nasser A, Khairiah, J.,Talib M.L, Ismail, B.S, Anizan I (2014).Accumulation And Translocation of Heavy Metals in Soil & Paddy Plant Samples Collected from Rice Fields Irrigated with Recycled And Non-Recycled Water In MADA Kedah, Malaysia. International Journal of ChemTech Research CODEN (USA): IJCRGG ISSN : 0974-4290 Vol.6, No.4, pp 2347-2356.

National Research Council (1984). *Modern Prospect for an Ancient Crop*. National Academy Press, Washington DC. Pg 81

New Delhi: Publication and information Directorate. The Wealth of Indian Raw Materials*,* 1979. pp. CSIR Vol 9, Page 71–72.

Nolan, A. L., Lombi, E., and McLaughlin, M. J. (2003). 'Metal Bioaccumulation and Toxicity in Soils - Why Bother with Speciation?' *Australian Journal of Chemistry,* 56, 77-91.

Nriagu J. O. (1984). Changing Metal Cycles and Human Health*.* Berlin: Springer-Verlag67-75

Nriagu, J.O. (1990) Global metal pollution. Poisoning the biosphere? Environment, 32, 7-33

Nyle, C.B. and Ray, R.W. (1999). The Nature and Properties of Soil Prentice Hall, Inc. U.S.A. Pp 4-70.

Oke, O.L. (1983). "*Handbook of Tropical Foods*" Edited by H.T. Chann Jr. Marcel-Dekker Inc., New York. Pg 1 – 7

Olufolaji, A.O. and Okelana, O.A. (2001). Grain Amaranth Response to Plant Density and Phosphorus Nutrition under the Humid Condition of South Western *Nigeria. Journal Hortiticultural Science,* 5: 58 – 66.

Omidiji, M.O. (1978). Tropical Leafy and Fruit Vegetables in Nigeria. *Vegetables for the Hot Humid Tropics* 3: 6 -8.

Oyenuga, V.A. and Fetuga, B.L. (1975). Dietary Importance of Fruits and Vegetables. First National Seminar on Fruits and Vegetables held at University of Ibadan. Pg 122 - 131.

Patrick L. (2003). Toxic metals and antioxidants: Part II. The role of antioxidants in arsenic and cadmium toxicity. *Altern Med Rev* **8**(2): 106–128.

Radulescu, C. Stihi, I.V. Popescu, I. D. Dulama, E.D. Chelarescu, A. Chilian, (2013). Heavy metal accumulation and translocation in *brassica oleracea L Environ. Science and Technology.* 32, 860- 865.

Radulescu, J.V; Archana N.P; Anita A.M (2013). "A study on clinical efficacy of Lepidium sativum seeds in treatment of bronchial asthma". *Iran Journal of Pharmacology Ther* 5: 55–59.

Rangnekar S.S., Sahu S.K., Pandit G.G. and Gaikwad V.B. (2013) Accumulation and Translocation of Nickel and Cobalt in Nutritionallyimportant Indian vegetables grown in artificially contaminated soil ofMumbai, India *Research Journal of Agriculture and Forestry Sciences* Vol. 1(10), 15-21.

Rashed, M.N., (2010). Monitoring of contaminated toxic and heavy metals, from mine tailings through age accumulation, in soil and some wild plants at Southeast Egypt. *Journal of Hazardous Matter*., 178, 739-746.

Reichman, S. M. (2002). *'The Responses of Plants to Metal Toxicity: A Review Focusing on Copper, Manganese and Zinc',* Melbourne: Australian Minerals and Energy Environment Foundation.70-86

Roccotiello, E., Serrano, H. C., Mariotti, M. G., and Branquinho, C. (2014). Nickel phytoremediation potential of the Mediterranean *Alyssoides utriculata* (L) medik *Chemosphere*, http://dx.doi.org/10.1016/j.chemosphere. retrieved 31st February, 2014.

Ross S. M. (1994). 'Retention, Transformation and Mobility of Toxic Metals in Soils', in Ross, S. M. (Ed.) *Toxic Metals in Soil-Plant Systems.*Chichester:John Wiley and Sons.

Rotich, K.H., Zhao, Y. & Dong, J. (2006). Municipal solid waste management challenges in the developing countries- Kenyan case study. *Waste Management,* 26, 92-100.

Sabir, M., Musa Hanafi, M., Aziz, T., Raza Ahmad, H., Zia-Ur-Rehman, M., Murtaza, G. andRehman, H,K., (2013). Comparative Effect of Activated Carbon, Pressmud and Poultry manure on Immobilization and Concentration of Metals in Maize (*Zea mays*) Grown on Contaminated Soil. *International Journal of Agriculture and Biology*, *15*.

Sahu, G.K., S. Upadhyay and B.B. Saho. (2012). Mercury induced phytotoxicity and oxidative stress in wheat (*Triticum aestivum* L.) plants. *Physiol. Mol. Biol. Plant.,* 18(1): 21-31.

Sanchez-Camazano, M., Sanchez-Martin, M. J., and Lorenzo, L. F, (1994). 'Lead and Cadmium in Soils and Vegetables from Urban Gardens of Salamanca (Spain)'. *The Science of the Total Environment,* 146/147, 163-168.

Sauerbeck, D. R. (1991). 'Plant, Element and Soil Properties Governing Uptake and Availability of Heavy Metals Derived from Sewage Sludge', *Water, Air and Soil Pollution,* 57-58, 227-237.

Sawidis T, Chettri MK, Papaionnou A, Zachariadis G, Stratis J (2001). A study of metal distribution from lignite fuels using trees as biological monitors. *Ecotoxicology of Enviromental, Safety*, 48: 27-35.

Sawidis, T. (2008). Effect of cadmium on pollen germination and tube growth in *Lilium longiflorum* and *Nicotiana tabacum*. *Protoplasma*, 233: 95-106.

Shah, M.T., Ara, J., Muhammad, S., Khan, S., Asad, S.A., Ali, L., (2013). Potential heavy metal accumulation of indigenous plant species along the mafic and ultramafic terrain in the Mohmand agency, Pakistan. *Clean-Soil, Air, Water*, 42, 339-346.

Shah, M.T., Begum, S. and Khan, S., (2010). Pedo and biogeochemical studies of mafic and ultramfic rocks in the Mingora and Kabal areas, Swat, Pakistan. *Environ. Earth Sci*., 60,1091-1102.

Sharma RK, Agrawal M, Marshall F (2006). Heavy Metals Contamination in Vegetables grown in wastewater irrigated areas of Varanasi, India Ecotoxicology and environmental safety, 77: 312-318.

Sharma RK, Agrawal M, Marshall FM (2007). Heavy Metals Contamination in Vegetables grown in Surban area of Varanasi, India. Ecotoxicology and environmental safety, 66: 258-266.

Showemimo, F.A. and Olarenwaju, J.D. (2004). Growth Analysis, Protein and Yield of Vegetable Amaranth under Varying Nitrogen Fertilizer Levels. *Journal of Horticultural. Science* 9: 29 – 34.

Small, Ernst (2009). Top 100 Food Plants. NRC Research Press. p. 127. ISBN 978-0-660-19858-3.

Smith, S.R. (1996) Agriculture Recycling of Sewage Sludge and the Environment. CAB Intentional, Walling fork, U K. pp 382 – 390.

Staub, Jack E, Buchert, Ellen. *75 Exceptional Herbs for Your Garden* Published by Gibbs Smith, 2008. ISBN 1-4236-0251-X, 9781423602514

Subhashini V., A. V. V. S, Swamy, R. Hema Krihna., (2013). Pot experiment. To study the uptake of Zinc by different plant species in artificially conterminated soil. World Journal of Environmental Engineering, vol 1; 27-33.

Suchkova, N., Tsiripidis, I., Alifragkis, D., Ganoulis, J., Darakas, E. and Sawidis, T., 2014. Assessment of phytoremediation potential of native plants during the reclamation of an area affected by sewage sludge. *Ecol. Eng.*, 69, 160-169.

Taylor, O.A. (1996). Potentials of Grain Amaranth Utilization as Food. Proceedings of National *Training Workshop on Grain Amaranth Production and Utilization*. NIHORT, Ibadan, Nigeria Pg 17 – 28.

Taylor, S.A. and Ashcroft, G.L. (1972). Physical Edaphology. PP56-58.

Timo, T, and Philipp, S, T. (2003). Heavy Metal Enrichment Factors for Different Analytical Methods. Geological Survey of Finland, Special Paper 36: 61-65.

Toyin, Y.M, Khadijat, O.F, Saoban, S.S, Olakunle, A.T, Abraham, B.F, Luqman, Q.A (2012).Antidiarrheal activity of aqueous leaf extract of *Ceratothecea sesamoides* in rats. *Bangladesh Journal of Pharmacology*. Vol. 7 Issue 1, 14-20.

Tse, G; Eslick, G.D. (2014). "Cruciferous vegetables and risk of colorectal neoplasm systematic review and meta-analysis". Nutrition and Cancer **66** (1):128–139. Doi:10. 1080/01635581. 2014.852686. PMID 24341734.

U.S. Environmental Protection Agency USEPA (1989). Guidance manual for assessing human health risks from chemically contaminated, fish and shellfish. *In:* AGENCY, U.S. E.P. (ed.) *Office of Water Regulations and Standard.* Washington, D.C: Retrived Oct; 2014

U.S. Environmental Protection Agency. USEPA (2002). Solid Waste and Emergency Response. *In:* AGENCY, U.S.E P. Retrived Dec; 2014

Uduma A U (2013), Assessment of heavy metal enrichment/depletion in selected farming soils in the vicinity of mining and dumping sites in Nigeria (unpublished Doctorial thesis) Bayero University, Kano. Nigeria

UK Food Standards Agency. (2003). 'Safe Upper Levels for Vitamins and Minerals', Expert Group on Vitamins and Minerals. Available at: http://www.food.gov.uk/multimedia/pdfs/vitmin2003.pdf (Accessed: 15 January 2007).

United Nation Development Programme, UNDP 2006. Practical Action. Technology Challenging Poverty. United Nation Development Programme Report. Retrived Dec; 2012

United States Department of Agriculture "Brassica oleracea L.". Retrieved 2012-08-12.
United States Department of Agriculture 2007. "Classification for species *Brassica oleracea* L.". *PLANTS database*. Retrieved 2012-08-10.

University of Illinois Extension. Lettuce Retrieved from http://www.lentech.html 25th march,2012.

US Food and Drug Administration, (2012). Chapter IV. Outbreaks Associated with Fresh and Fresh-Cut Produce. Incidence, Growth, and Survival of Pathogens in Fresh and Fresh Cut Produce". Analysis and Evaluation of Preventive Control Measures for the Control and Reduction/Elimination of Microbial Hazards on Fresh and Fresh-Cut Produce.

US Department of Agriculture, National Nutrient Database for Standard Reference, "USDA database table for raw cabbage ". version SR-27. 2014. Retrieved 4th December 2014.

US-Enviromental Planning Agency, (2004) (US-EPA). Risk Assessment Guidance for Super Fun Human Health Evaluation Manual, Office of Emergency and Remedial Response. Washington DC. 20450.

Usman, A.R., Lee, S.S., Awad, Y.M., Lim, K.J., Yang, J.E. and Ok, Y.S., 2012. Soil pollution assessment and identification of hyperaccumulating plants in chromated copper arsenate (CCA) contaminated sites, Korea. *Chemosphere*, *87*, 872-878.

Vegetables of Canada (2006). Uses of Vegetables Published by NRC Research Press. ISBN 0-660-19503-8, ISBN 978-0-660- 19503-2

Voroney, R.P. (2006). *The Soil Habitat in Soil Microbiology, Ecology and Biochemistry*. Eldor, Netherland. PP 50-56.

Wadhwa N, Mathew BB, Jatawa S, Tiwari A. (2012). Lipid peroxidation: mechanism, models and signifi cance. *International Journal of Curr Sci* 3: 29–38.

Wagai, R, Mayer, L.M. Kitayama K. and Knickers, H. (2008). Climate and Parent Material Controls on Organic Matter Storage in Surface Soils. *Geoderm*a 147: 23-33.

Wase, J., and Forster, C. (1997). *Biosorbents for Metallons.* London: Taylor and Francis Ltd.

Watanabe, M. A. (1997). 'Phytoremediation on the Brink of Commercialization " *Environmental Science and Technology,* 31, l82A-186A.

Webber, J. (1981). Trace Metals in Agriculture: Effect of Heavy Metal Pollution on Plant, London and New Jersey. Appl. Sci. Pub. 11:59-184.

Wei, S, Zhou, Q, Xin, W. (2005). Identification of Weed Plant Excluding the Uptake of Heavy Metals. Enut. Int. 31:829-834.

WHO/FAO, (2007). Joint FAO/WHO Food Standard Programme Codex AlimentariusCommission 13th Session. Report of the Thirty eight Session of the Codex Committee on Food Hygiene, Houston, United States of America, ALINORM 07/30/13.

Wien, H. C. and Wurr, D. C. E. (1997). "Cauliflower, broccoli, cabbage and brussel sprouts" In Wien, H. C. (ed.). The Physiology of Vegetable Crops.P. 512-515, p. 533CAB International.ISBN 978-0-85199-146-7.

Wójcik, M., Sugier, P. and Siebielec, G., (2014). Metal accumulation strategies in plants spontaneously inhabiting Zn-Pb waste deposits. *Scicence of Total Environ.,* 487, 313-322.

Wolnik, K. A., Fricke, F. L., Capar,-8. G., Braude, G. L., Meyer, M. W., Satzger, R. D., and Bonnin, E. (1983). 'Elements in Major Raw Agricultural Crops in the Unit~ States. 1. Cadmium and Lead in Lettuce, Peanuts, Potatoes, Soybeans, Sweet Corn, and Wheat', *Journal of Agriculture and Food Chemistry,* 31, 1240-1244.

World Health Organization (WHO). (1989). 'Environmental Health Criteria for Lead', Available at: http://www.inchem.org/documents/ehc/ehc/ehc85.htm (Accessed: I February 2007).

World Health Organization (WHO). (1998). 'Environmental Health Criteria for Copper',Available at: http://www.inchem.org/documents/ehc/ehc/ehc221.htm (Accessed: 1 February 2007).

World Health Organization (WHO). (2001). 'Environmental Health Criteria for Zinc', Available at: http://www.inchem.org/documents/ehc/ehc/ehc221.htm (Accessed: 1 February 2007).

World Health Organization (WHO). (2003). 'Chromium in Drinking-Water: Background Document for Development of WHO Guidelines for Drinking-Water Quality'. Available:http://www.who.int/water_sanitation_health/dwq/chemicals/chromium. pdf (Accessed: 12 January 2007).

Wu, Y.; Feng, X.; Jin, Y.; Wu, Z.; Hankey, W.; Paisie, C.; Li, L.; Liu, F.; Barsky, S. H.; Zhang, W.;Ganju, R.; Zou, X. (2010). "A novel mechanism of indole-3-carbinol effects on breast carcinogenesis involves induction of Cdc25A degradation".*Cancer Prevention Research* 3 (7) 818–828.Doi:10.1158/1940-6207.CAPR-09-0213. PMID 20587702.

Xian X 1989. Effect of chemical forms of cadmium, zinc, and lead in polluted soils on their uptake by cabbage plants. *Plant and Soil.*;113(2):257-264.

Yilmaz S, Zengin M (2004). Monitoring environmental pollution in Erzurum by chemical analysis of Scot pine (*Pinus sylvestris* L.) needles. Environ. Int., 29(8): 1041-1047.

Yoon, J., Cao, X., Zhou, Q. and Ma, L.Q., 2006. Accumulation of Pb, Cu, and Zn in native plants growing on a contaminated Florida site. *Science. Total of Enviroment.,* 368, 456-464.

Zhang BY, Zheng JS, Sharp RG (2010). Phytoremediation in engineered wetlands: Mechanisms and Applications. ISSN:1878-0296 *Procedia Enviromental. Science*`. 2: 1315-1325.

Zhou, D.-M., Hao, X.-Z., Wang,Y.-J., Dong, Y.-H., and Cang, L. (2005). 'Copper and Zinc Uptake by Radish and Pakchoi as Affected by Application of Livestock and Poultry Manures', *Chemosphere,* 59,167-175.

Zurera G., Moreno R., Salmeron J., Pozo R., (1989). Heavy Metal Uptake from Greenhouse Boarder Soils for Edible Vegetables. *Journal of the science of food and Agriculture* 49:307-314.

Appendix 1: Industrial and Control Samples ANOVAs Result

ANOVAs result for Cd

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	15.50675	3	5.168917	30.36	6.93E-06	3.490295
Within Groups	2.04305	12	0.170254			
Total	17.5498	15				

ANOVAs result for Pb

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	3.52925	3	1.176417	12.11812	0.000608	3.490295
Within Groups	1.16495	12	0.097079			
Total	4.6942	15				

ANOVAs result for Cr

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	16.19733	3	5.399108	47.29664	6.37E-07	3.490295
Within Groups	1.36985	12	0.114154			
Total	17.56718	15				

ANOVAs result for Mn

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	5.798725	3	1.932908	3.19478	0.062528	3.490295
Within Groups	7.26025	12	0.605021			
Total	13.05898	15				

Anova result for Fe

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	566.1415	3	188.7138	6.259812	0.008398	3.490295
Within Groups	361.7627	12	30.14689			
Total	927.9042	15				

ANOVAs result for Mo

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	1.304569	3	0.434856	2.443613	0.114437	3.490295
Within Groups	2.135475	12	0.177956			
Total	3.440044	15				

ANOVAs result for Ni

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.713319	3	0.237773	1.002407	0.42523	3.490295
Within Groups	2.846425	12	0.237202			
Total	3.559744	15				

ANOVAs result for Cu

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	39.52817	3	13.17606	10.30639	0.001221	3.490295
Within Groups	15.34123	12	1.278435			
Total	54.86939	15				

ANOVAs result for Zn

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	51.15003	3	17.05001	1.75083	0.209929	3.490295
Within Groups	116.859	12	9.738246			
Total	168.009	15				

Appendix 2: Experimentally planted Samples ANOVAs results

ANOVA
Cadmium

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	62.89068	3	20.96356	838542.3	3.46E-32	3.49
Within Groups	0.0003	12	0.000025			
Total	62.89098	15				

ANOVA
Chromium

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	16.39823	3	5.466075	18.73253	8.02E-05	3.49
Within Groups	3.50155	12	0.291796			
Total	19.89978	15				

ANOVA Copper

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	117.4286	3	39.14287	19.13599	7.23E-05	3.49
Within Groups	24.54613	12	2.04551			
Total	141.9747	15				

ANOVA Iron

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	1244.36	3	414.7866	19.43463	6.7E-05	3.49
Within Groups	256.1119	12	21.34265			
Total	1500.472	15				

ANOVA Zinc

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	370.5418	3	123.5139	13.28623	0.000403	3.49
Within Groups	111.5567	12	9.29639			
Total	482.0985	15				

ANOVA
Manganese

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	168.1583	3	56.05278	29.25198	8.42E-06	3.490295
Within Groups	22.99445	12	1.916204			
Total	191.1528	15				

ANOVA
Molybdenum

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	16.25293	3	5.417642	8.934044	0.002199	3.490295
Within Groups	7.27685	12	0.606404			
Total	23.52978	15				

ANOVA Nickel

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	24.75353	3	8.251175	6.373266	0.007884	3.490295
Within Groups	15.53585	12	1.294654			
Total	40.2893	15				

ANOVA Lead

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	14.99507	3	4.998356	43.336	1.03E-06	3.490295
Within Groups	1.384075	12	0.11534			
Total	16.37914	15				

Appendix 3. ANOVA results for Transfer Factor factor of heavy metals in vegetable samples

ANOVA reults for Transfer factor in Cabbage plant

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.095589	8	0.011949	0.870235	0.552929	2.305313
Within Groups	0.370719	27	0.01373			
Total	0.466308	35				

ANOVA results for Transfer factor in Garden Cress plant

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.12291	8	0.015364	0.830949	0.583362	2.305313
Within Groups	0.499213	27	0.018489			
Total	0.622122	35				

ANOVA results for Transfer factor in sesame plant

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.154268	8	0.019284	0.696709	0.691322	2.305313
Within Groups	0.747306	27	0.027678			
Total	0.901574	35				

ANOVA results for Transfer factor in lettuce plant

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.109518	8	0.01369	0.710259	0.68028	2.305313
Within Groups	0.520406	27	0.019274			
Total	0.629924	35				

ANOVA results for Transfer factor in spinach plant

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.179906	8	0.022488	0.916016	0.518474	2.305313
Within Groups	0.66285	27	0.02455			
Total	0.842756	35				

Appendix 4 ANOVA results for Bio- accumulation factor of heavy metals in vegetable samples

ANOVA results for Bio- accumulation factor of heavy metals in cabbage plant

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.037339	8	0.004667	0.876538	0.548117	2.305313
Within Groups	0.143769	27	0.005325			
Total	0.181108	35				

ANOVA results for Bio- accumulation factor of heavy metals in garden cress plant

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.050025	8	0.006253	1.028224	0.439515	2.305313
Within Groups	0.1642	27	0.006081			
Total	0.214225	35				

ANOVAresults for Bio- accumulation factor of heavy metals in sesame plant

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.022472	8	0.002809	0.365292	0.92977	2.305313
Within Groups	0.207625	27	0.00769			
Total	0.230097	35				

ANOVA results for Bio- accumulation factor of heavy metals in lettuce plant

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.059989	8	0.007499	0.958743	0.487435	2.305313
Within Groups	0.211175	27	0.007821			
Total	0.271164	35				

ANOVA results for Bio- accumulation factor of heavy metals in spinach plant plant

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.04035	8	0.005044	1.215361	0.327538	2.305313
Within Groups	0.11205	27	0.00415			
Total	0.1524	35				

Appendix 5 ANOVA results for Translocation factor of heavy metals in vegetable samples

ANOVA results for Translocation factor from challawa samples

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	2.33876	8	0.292345	1.79354	0.110727	2.208518
Within Groups	5.86796	36	0.162999			
Total	8.20672	44				

ANOVA results for Translocation factor from Sharada samples

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	40.69671	8	5.087089	7.200749	1.16E-05	2.208518
Within Groups	25.4328	36	0.706467			
Total	66.12951	44				

ANOVA results for Translocation factor from Kwakwache samples

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	1.238791	8	0.154849	2.003047	0.074224	2.208518
Within Groups	2.78304	36	0.077307			
Total	4.021831	44				

ANOVA results for Translocation factor from Control samples

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	3.513778	8	0.439222	1.066073	0.407839	2.208518
Within Groups	14.832	36	0.412			
Total	18.34578	44				

Apendix 6 Anova results for Metal Concentrations in soil Samples

Anova: Two-Factor Without Replication

SUMMARY	*Count*	*Sum*	*Average*	*Variance*
chalawa	8	440.37	55.04625	3566.822
Sharada	8	428.49	53.56125	3163.396
Kwakwachi	8	535.63	66.95375	5750.615
control	8	232.731	29.09138	1002.014
Cd	4	38.5	9.625	31.2455
Pb	4	57.083	14.27075	32.57341
Cu	4	189.527	47.38175	426.4076
Fe	4	706.768	176.692	3501.149
Zn	4	311.893	77.97325	752.3129
Cr	4	80.305	20.07625	86.14506
Mo	4	94.457	23.61425	21.78855
Mn	4	158.688	39.672	48.6834

ANOVA for metal concentrations in the soil

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	6058.685	3	2019.562	4.907389	0.009726	3.072467
Columns	85737.69	7	12248.24	29.76234	1.59E-09	2.487578
Error	8642.232	21	411.5349			
Total	100438.6	31				

Apendix 7: Metals Level in Cabbage Planted Experimental at different concentrations

low	Cd	Cr	Cu	Fe	Mn	Mo	Ni	Pb	Zn
soil	**12.56**	**22.514**	**52.402**	**171.429**	**42.105**	**31.662**	**25.696**	**6.7**	**79.295**
root	**3.34**	**3.002**	**6.987**	**28.571**	**7.018**	**4.222**	**3.426**	**1.586**	**13.216**
stem	**2.088**	**1.876**	**4.367**	**15.238**	**3.509**	**2.639**	**2.141**	**0.991**	**7.048**
leaves	**2.088**	**0.938**	**2.183**	**15.238**	**3.509**	**1.319**	**1.071**	**0.099**	**7.048**
mean	**2.51**	**1.94**	**4.51**	**19.68**	**4.68**	**2.73**	**2.21**	**0.89**	**9.10**
Medium									
soil	**23.6**	**33.771**	**78.603**	**243.81**	**63.158**	**47.493**	**38.544**	**13.4**	**112.775**
root	**4.175**	**4.69**	**10.917**	**50.476**	**18.596**	**5.277**	**5.353**	**2.973**	**23.348**
stem	**3.34**	**3.002**	**6.987**	**33.333**	**10.526**	**4.222**	**5.353**	**1.586**	**13.216**
leaves	**2.088**	**0.938**	**2.183**	**19.048**	**5.614**	**2.639**	**2.141**	**0.991**	**8.811**
mean	**3.20**	**2.88**	**6.70**	**34.29**	**11.58**	**4.05**	**4.28**	**1.85**	**15.13**
High									
soil	**35.4**	**45.028**	**104.803**	**323.81**	**89.825**	**63.325**	**51.392**	**20.10**	**149.78**
root	**8.351**	**6.567**	**15.284**	**50.476**	**10.526**	**9.235**	**7.495**	**4.46**	**23.348**
stem	**5.219**	**4.69**	**10.917**	**28.571**	**5.614**	**6.596**	**3.426**	**2.973**	**13.216**
leaves	**3.34**	**1.876**	**4.367**	**23.81**	**3.509**	**2.639**	**2.141**	**0.991**	**11.013**
mean	**5.64**	**4.38**	**10.19**	**34.29**	**6.55**	**6.16**	**4.35**	**2.81**	**15.86**
control									
soil	**2.36**	**7.51**	**17.467**	**95.238**	**35.088**	**16.887**	**17.131**	**1.34**	**52.863**
root	**0.08**	**1.5**	**3.49**	**14.29**	**2.81**	**2.11**	**1.71**	**0.1**	**6.61**
stem	**0.02**	**0.94**	**2.18**	**7.62**	**2.81**	**1.32**	**1.71**	**0.15**	**3.52**
leaves	**0.1**	**0.94**	**2.18**	**7.62**	**2.81**	**1.32**	**1.71**	**0.05**	**3.52**
mean	**0.08**	**0.45**	**0.45**	**0.31**	**0.24**	**0.28**	**0.30**	**0.22**	**0.26**

Apendix 8: Metals Level in Garden cress Planted Experimental at different concentrations

low	Cd	Cr	Cu	Fe	Mn	Mo	Ni	Pb	Zn
soil	**12.56**	**22.514**	**52.402**	**171.429**	**42.105**	**31.662**	**25.696**	**6.7**	**79.295**
root	**3.34**	**3.002**	**6.987**	**33.333**	**10.526**	**4.222**	**3.426**	**1.586**	**15.419**
stem	**2.088**	**1.876**	**4.367**	**23.81**	**8.772**	**4.222**	**4.283**	**0.991**	**13.216**
leaves	**2.088**	**1.876**	**4.367**	**23.81**	**5.614**	**4.222**	**2.141**	**0.099**	**8.811**
Mean	**2.51**	**2.25**	**5.24**	**26.98**	**8.30**	**4.22**	**3.28**	**0.89**	**12.48**
Medium									
soil	**23.6**	**33.771**	**78.603**	**243.81**	**63.158**	**47.493**	**38.544**	**13.4**	**112.775**
root	**4.175**	**3.752**	**8.734**	**42.857**	**15.789**	**5.277**	**6.424**	**2.973**	**23.348**
stem	**3.34**	**3.002**	**6.987**	**38.095**	**8.772**	**4.222**	**5.353**	**1.586**	**13.216**
leaves	**2.088**	**3.002**	**6.987**	**23.81**	**5.614**	**2.639**	**3.426**	**0.991**	**8.811**
Mean	**3.20**	**3.25**	**7.57**	**34.92**	**10.06**	**4.05**	**5.07**	**1.85**	**15.13**
High									
soil	**35.4**	**45.028**	**104.83**	**323.81**	**89.825**	**63.325**	**51.392**	**20.10**	**149.78**
root	**8.351**	**5.629**	**13.1**	**42.857**	**14.035**	**7.916**	**7.495**	**4.46**	**23.348**
stem	**5.219**	**3.002**	**6.987**	**23.81**	**10.526**	**4.222**	**6.424**	**2.973**	**17.621**
leaves	**3.34**	**1.876**	**4.367**	**28.571**	**7.018**	**4.222**	**3.426**	**0.991**	**13.216**
Mean	**5.64**	**3.50**	**8.15**	**31.75**	**10.53**	**5.45**	**5.78**	**2.81**	**18.06**
control									
soil	**2.36**	**7.51**	**17.467**	**95.238**	**35.088**	**16.887**	**17.131**	**1.34**	**52.863**
root	**0.08**	**1.5**	**3.49**	**14.29**	**2.81**	**2.11**	**1.71**	**0.1**	**6.61**
stem	**0.02**	**0.94**	**2.18**	**7.62**	**2.81**	**1.32**	**1.71**	**0.15**	**3.52**
leaves	**0.1**	**0.94**	**2.18**	**7.62**	**2.81**	**1.32**	**1.71**	**0.05**	**3.52**
Mean	**0.08**	**0.45**	**0.45**	**0.31**	**0.24**	**0.28**	**0.30**	**0.22**	**0.26**

Appendix 9: Metals Level in Sesame Planted Experimentally at Different Concentreations

low	Cd	Cr	Cu	Fe	Mn	Mo	Ni	Pb	Zn
soil	**12.56**	**22.514**	**52.402**	**171.429**	**42.105**	**31.662**	**25.696**	**6.7**	**79.295**
root	**3.34**	**3.002**	**6.987**	**38.095**	**12.281**	**4.222**	**5.353**	**1.586**	**17.621**
stem	**2.088**	**1.876**	**4.367**	**23.81**	**5.614**	**2.639**	**3.426**	**0.991**	**15.419**
leaves	**2.088**	**0.938**	**2.183**	**15.238**	**3.509**	**2.639**	**1.071**	**0.099**	**11.013**
Mean	**2.51**	**1.94**	**4.51**	**25.71**	**7.13**	**3.17**	**3.28**	**0.89**	**14.68**
Medium									
soil	**23.6**	**33.771**	**78.603**	**243.81**	**63.158**	**47.493**	**38.544**	**13.4**	**112.775**
root	**4.175**	**6.567**	**15.284**	**50.476**	**12.281**	**6.596**	**3.426**	**2.973**	**23.348**
stem	**3.34**	**4.69**	**10.917**	**38.095**	**12.281**	**4.222**	**2.141**	**1.586**	**15.419**
leaves	**2.088**	**1.876**	**4.367**	**23.81**	**7.018**	**1.319**	**1.071**	**0.991**	**8.811**
Mean	**3.20**	**4.38**	**10.19**	**37.46**	**10.53**	**4.05**	**2.21**	**1.85**	**15.86**
High									
soil	**35.4**	**45.028**	**104.803**	**323.81**	**89.825**	**63.325**	**51.392**	**20.10**	**149.78**
root	**8.351**	**6.567**	**15.284**	**50.476**	**15.789**	**5.277**	**6.424**	**4.46**	**35.242**
stem	**5.219**	**3.752**	**8.734**	**33.333**	**12.281**	**4.222**	**4.283**	**2.973**	**23.348**
leaves	**3.34**	**1.876**	**4.367**	**23.81**	**7.018**	**1.319**	**1.071**	**0.991**	**13.216**
Mean	**5.64**	**4.07**	**9.46**	**35.87**	**11.70**	**3.61**	**3.93**	**2.81**	**23.94**
control									
soil	**2.36**	**7.51**	**17.467**	**95.238**	**35.088**	**16.887**	**17.131**	**1.34**	**52.863**
root	**0.08**	**1.501**	**3.493**	**14.286**	**2.807**	**2.111**	**1.713**	**0.1**	**6.608**
stem	**0.02**	**0.938**	**2.183**	**15.238**	**3.509**	**2.639**	**1.071**	**0.15**	**11.013**
leaves	**0.1**	**1.876**	**4.367**	**15.238**	**3.509**	**2.639**	**1.071**	**0.05**	**7.048**
Mean	**0.08**	**0.57**	**0.57**	**0.47**	**0.28**	**0.44**	**0.23**	**0.22**	**0.47**

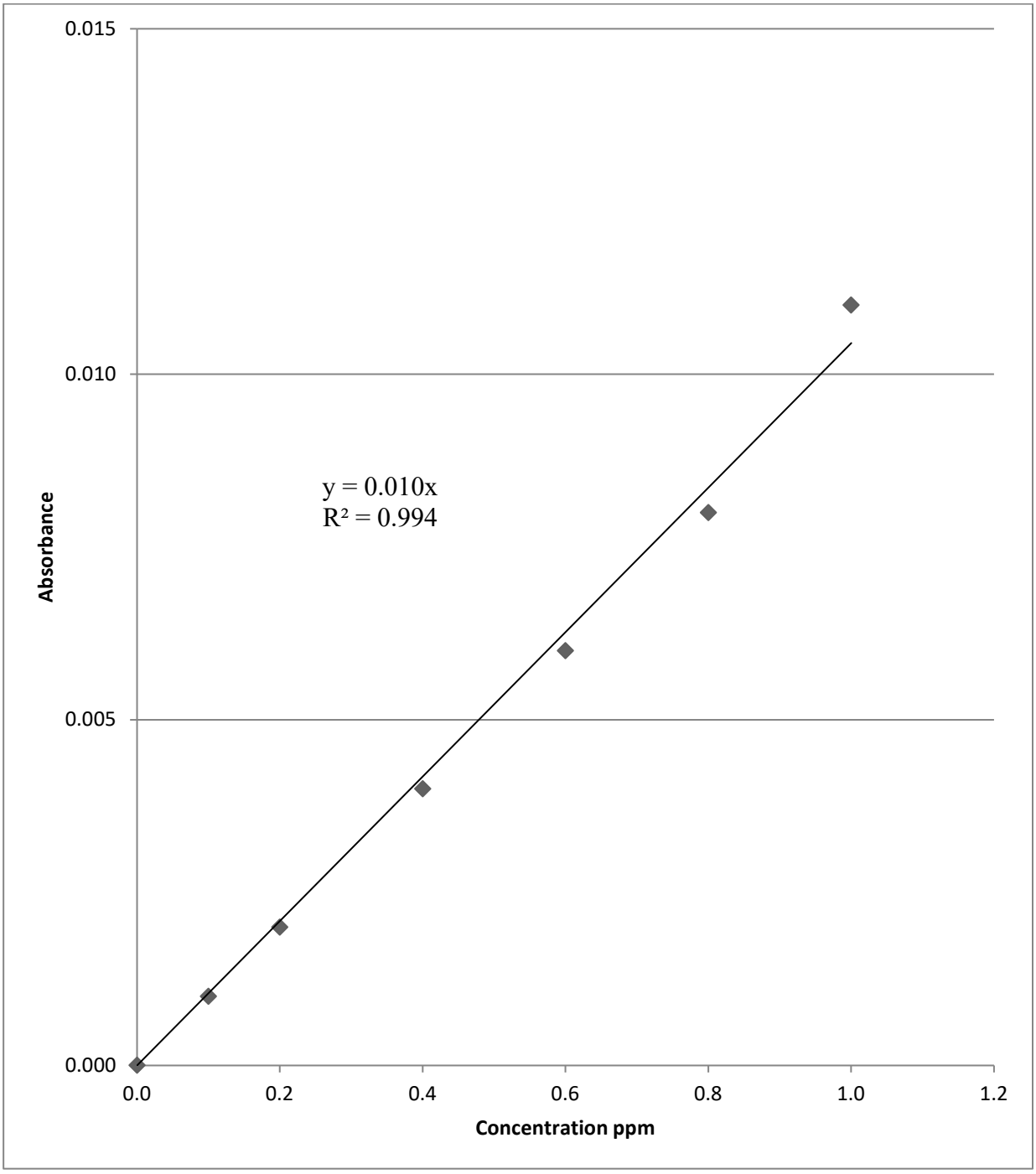
Appendix 10: Metals Level in Lettuce Planted Experimentally at Different Concentreations.

low	Cd	Cr	Cu	Fe	Mn	Mo	Ni	Pb	Zn
soil	**12.56**	**22.514**	**52.402**	**171.429**	**42.105**	**31.662**	**25.696**	**6.7**	**79.295**
root	**3.34**	**3.002**	**6.987**	**33.333**	**8.772**	**2.639**	**2.141**	**1.586**	**15.419**
stem	**2.088**	**1.876**	**4.367**	**23.81**	**5.614**	**1.319**	**1.071**	**0.991**	**11.013**
leaves	**2.088**	**0.188**	**0.437**	**15.238**	**1.754**	**2.639**	**0.214**	**0.099**	**7.048**
Mean	**2.51**	**1.69**	**3.93**	**24.13**	**5.38**	**2.20**	**1.14**	**0.89**	**11.16**
Medium									
soil	**23.6**	**33.771**	**78.603**	**243.81**	**63.158**	**47.493**	**38.544**	**13.4**	**112.775**
root	**4.175**	**4.69**	**10.917**	**33.333**	**8.772**	**4.222**	**3.426**	**2.973**	**13.216**
stem	**3.34**	**3.002**	**6.987**	**23.81**	**5.614**	**2.639**	**2.141**	**1.586**	**8.811**
leaves	**2.088**	**0.938**	**2.183**	**15.238**	**3.509**	**1.319**	**1.071**	**0.991**	**7.048**
Mean	**3.20**	**2.88**	**6.70**	**24.13**	**5.97**	**2.73**	**2.21**	**1.85**	**9.69**
High									
soil	**35.4**	**45.028**	**104.803**	**323.81**	**89.825**	**63.325**	**51.392**	**20.10**	**149.78**
root	**8.351**	**5.629**	**13.1**	**50.476**	**18.596**	**7.916**	**6.424**	**4.46**	**23.348**
stem	**5.219**	**4.69**	**10.917**	**33.333**	**5.614**	**5.277**	**4.283**	**2.973**	**15.419**
leaves	**3.34**	**1.876**	**4.367**	**19.048**	**5.614**	**2.639**	**2.141**	**0.991**	**8.811**
Mean	**5.64**	**4.07**	**9.46**	**34.29**	**9.94**	**5.28**	**4.28**	**2.81**	**15.86**
control									
soil	**2.36**	**7.51**	**17.467**	**95.238**	**35.088**	**16.887**	**17.131**	**1.34**	**52.863**
root	**0.08**	**1.5**	**3.49**	**19.05**	**2.81**	**2.11**	**1.71**	**0.1**	**8.81**
stem	**0.09**	**0.19**	**0.44**	**15.24**	**1.75**	**2.64**	**0.21**	**0.2**	**7.05**
leaves	**0.09**	**0.19**	**0.44**	**9.52**	**3.51**	**1.32**	**1.07**	**0.15**	**4.41**
Mean	**0.11**	**0.25**	**0.25**	**0.46**	**0.23**	**0.36**	**0.17**	**0.34**	**0.38**

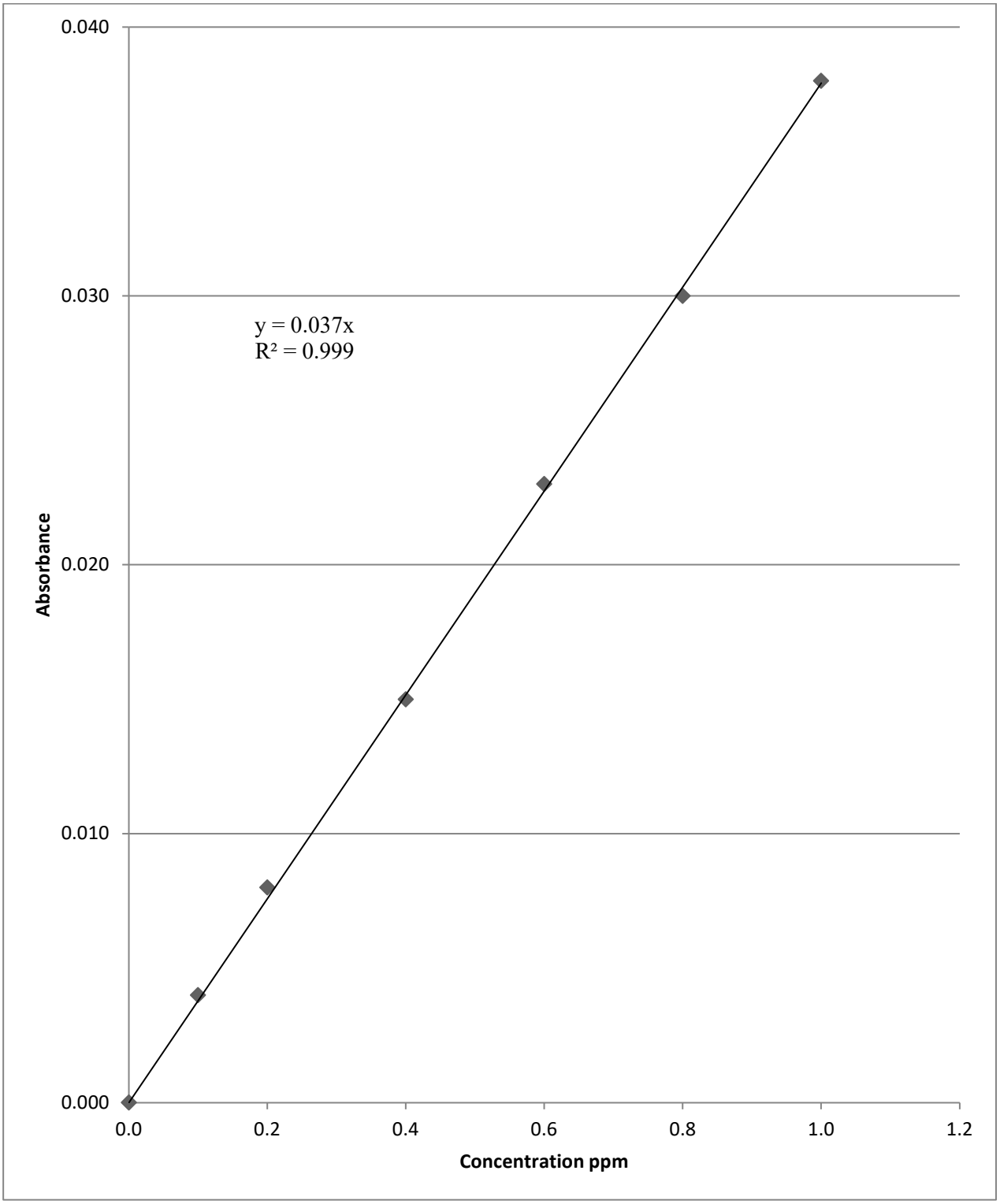
Appendix 11: Metals Level in Spinach Planted Experimentally at Different Concentreations.

Low	Cd	Cr	Cu	Fe	Mn	Mo	Ni	Pb	Zn
soil	**12.56**	**22.514**	**52.402**	**171.429**	**42.105**	**31.662**	**25.696**	**6.7**	**79.295**
root	**3.34**	**3.002**	**6.987**	**23.81**	**8.772**	**4.222**	**2.141**	**1.586**	**13.216**
stem	**2.088**	**1.876**	**4.367**	**15.238**	**5.614**	**2.639**	**1.071**	**0.991**	**7.048**
leaves	**2.088**	**0.188**	**0.437**	**9.524**	**1.754**	**1.319**	**1.071**	**0.099**	**4.405**
Mean	**2.51**	**1.69**	**3.93**	**16.19**	**5.38**	**2.73**	**1.43**	**0.89**	**8.22**
Medium									
soil	**23.6**	**33.771**	**78.603**	**243.81**	**63.158**	**47.493**	**38.544**	**13.4**	**112.775**
root	**4.175**	**3.752**	**8.734**	**33.333**	**10.526**	**5.277**	**4.283**	**2.973**	**13.216**
stem	**3.34**	**1.876**	**4.367**	**19.048**	**7.018**	**2.639**	**2.141**	**1.586**	**8.811**
leaves	**2.088**	**0.938**	**2.183**	**15.238**	**3.509**	**1.319**	**1.071**	**0.991**	**7.048**
Mean	**3.20**	**2.19**	**5.09**	**22.54**	**7.02**	**3.08**	**2.50**	**1.85**	**9.69**
High									
soil	**35.4**	**45.028**	**104.803**	**323.81**	**89.825**	**63.325**	**51.392**	**20.10**	**149.78**
root	**8.351**	**4.69**	**10.917**	**50.476**	**18.596**	**6.596**	**5.353**	**4.46**	**28.194**
stem	**5.219**	**3.002**	**6.987**	**42.857**	**15.789**	**4.222**	**3.426**	**2.973**	**19.824**
leaves	**3.34**	**1.876**	**4.367**	**19.048**	**7.018**	**2.639**	**2.141**	**0.991**	**11.013**
Mean	**5.64**	**3.19**	**7.42**	**37.46**	**13.80**	**4.49**	**3.64**	**2.81**	**19.68**
control									
soil	**2.36**	**7.51**	**17.467**	**95.238**	**35.088**	**16.887**	**17.131**	**1.34**	**52.863**
root	**0.08**	**1.501**	**3.493**	**14.286**	**2.807**	**2.111**	**1.713**	**0.1**	**6.608**
stem	**0.02**	**0.938**	**2.183**	**7.619**	**2.807**	**1.319**	**1.713**	**0.2**	**3.524**
leaves	**0.1**	**0.188**	**0.437**	**4.762**	**1.754**	**0.264**	**0.214**	**0.05**	**2.203**
Mean	**0.08**	**0.35**	**0.35**	**0.28**	**0.21**	**0.22**	**0.21**	**0.26**	**0.23**

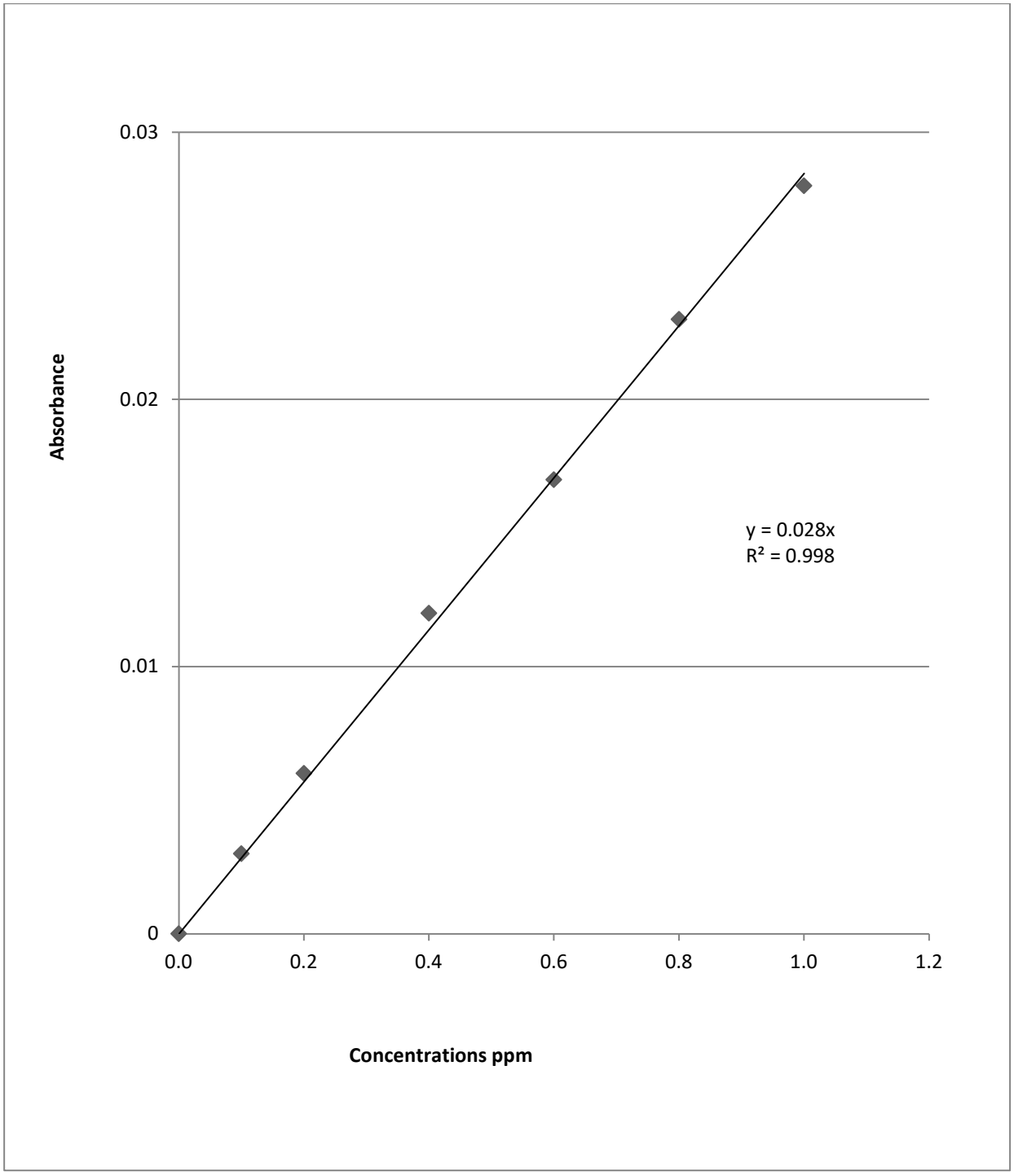
Appendix 12 Calibration Curve for Iron Standard.



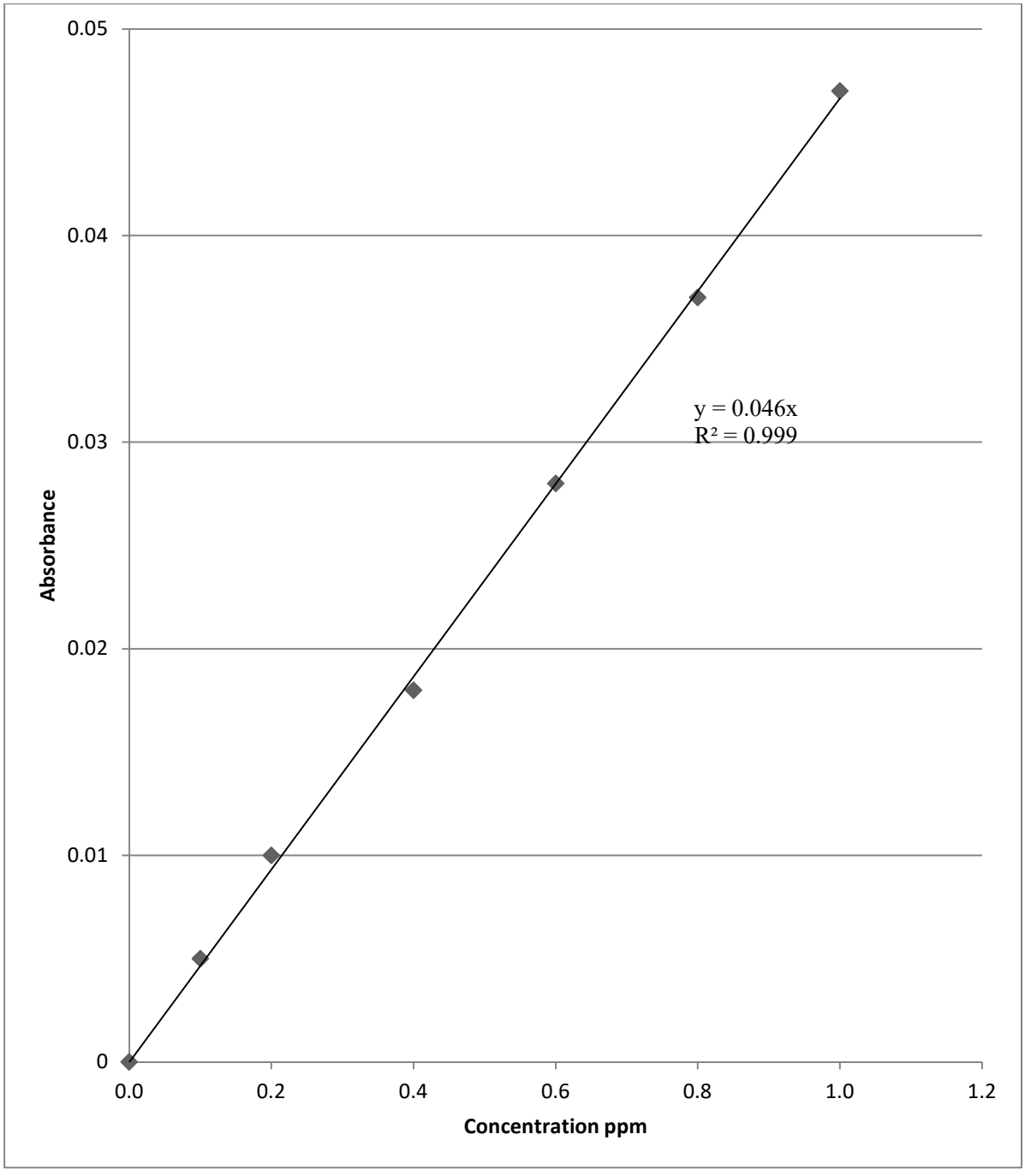
Appendix 13 Calibration Curve for Molybdenum Standard.



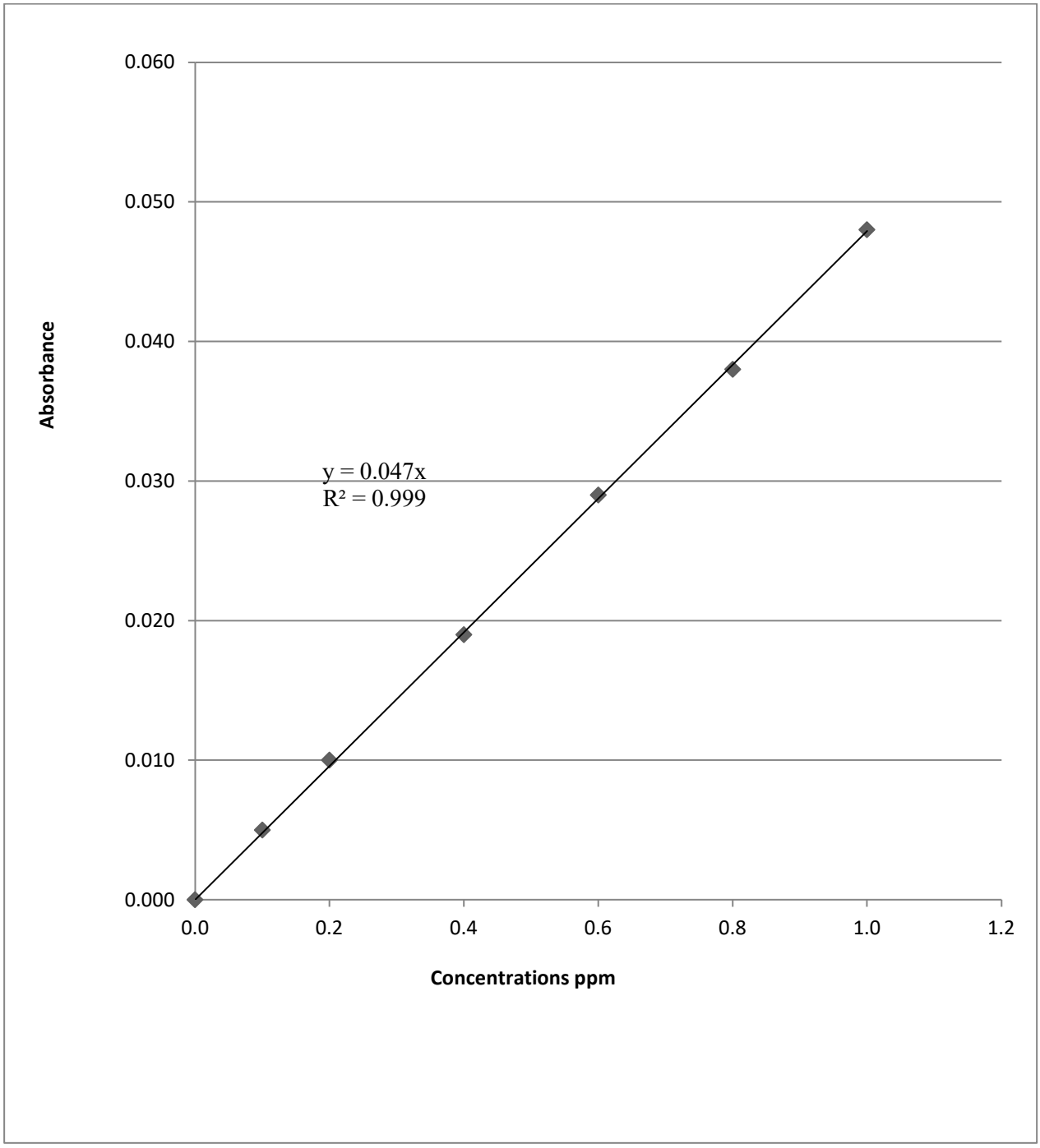
Appendix 14 Calibration Curve for Manganese Standard.



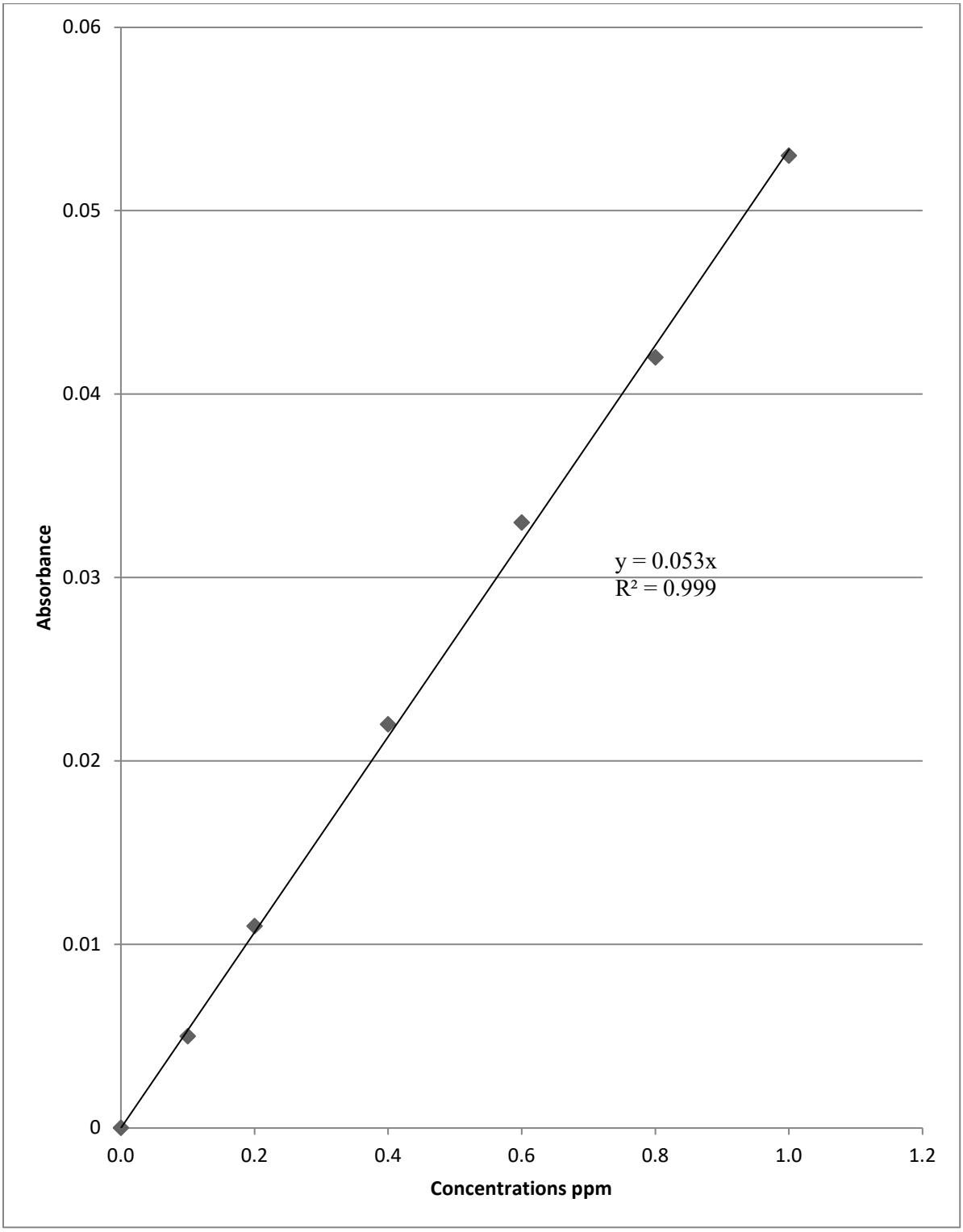
Appendix 15 Calibration Curve for Nickel Standard.



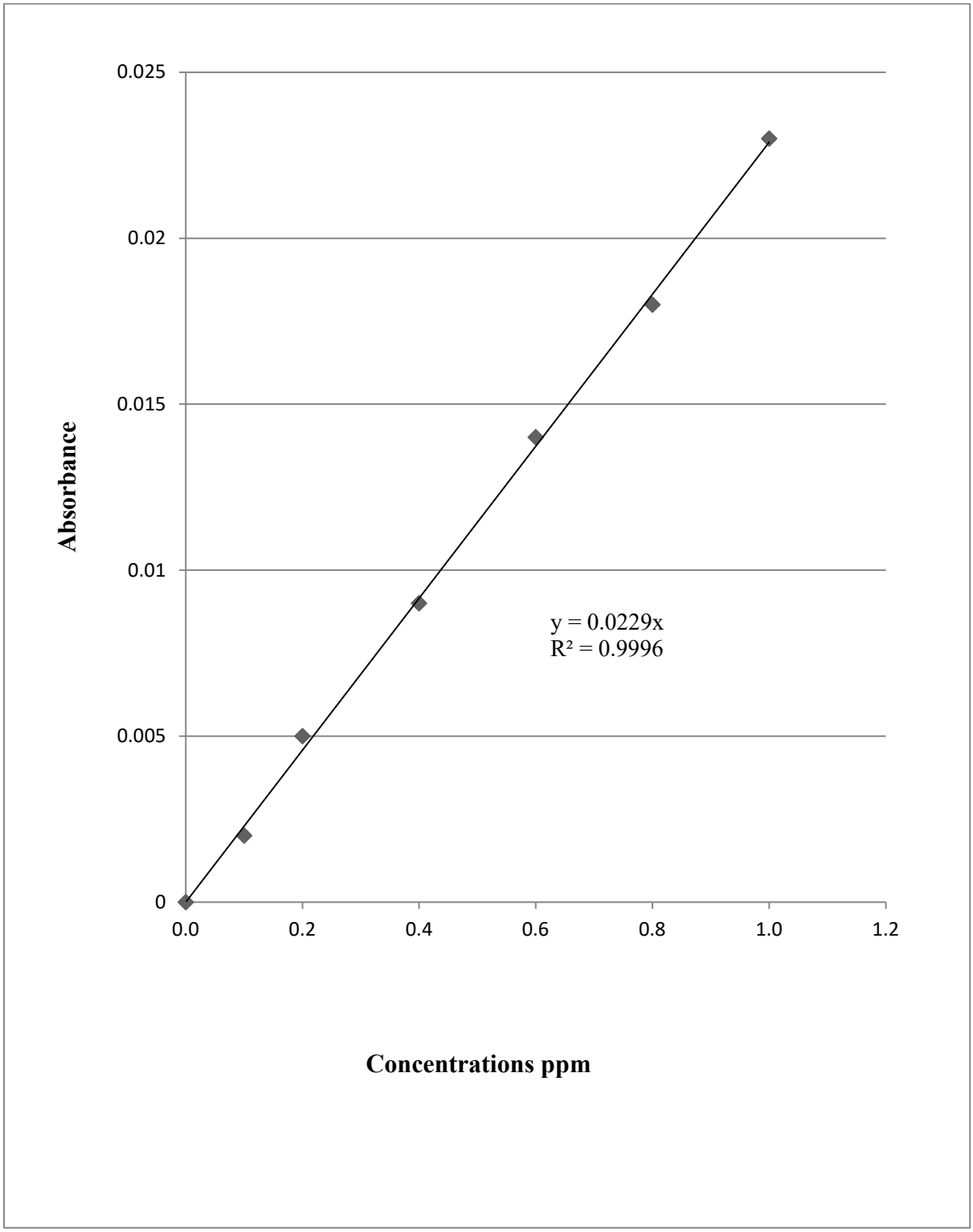
Appendix 16 Calibration Curve for Cadmium Standard.



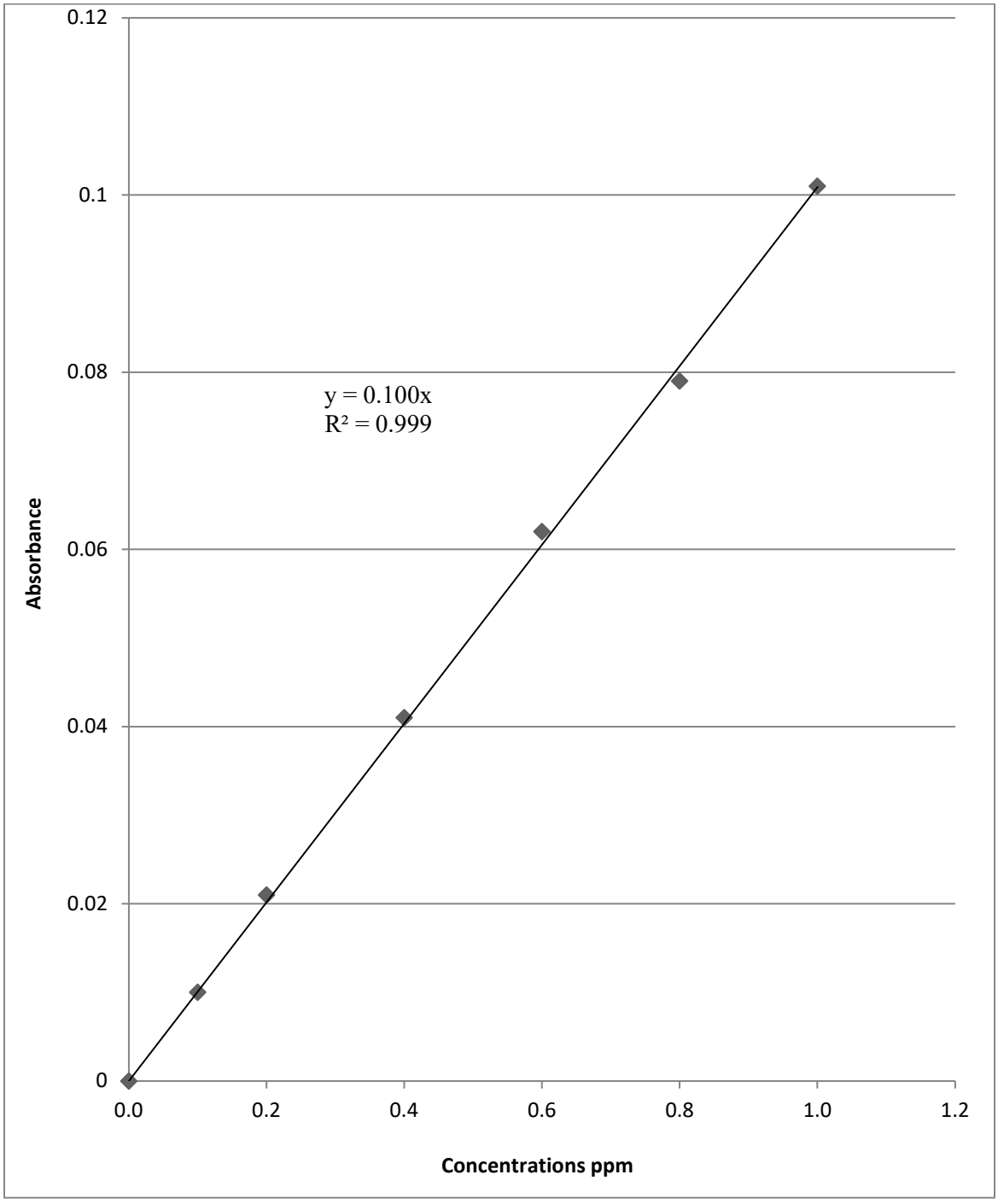
Appendix 17 Calibration Curve for Chromium Standard.



Appendix 18 Calibration Curve for Copper Standard.



Appendix 19 Calibration Curve for Lead Standard.



Appendix 20 Calibration Curve for Zinc Standard.