PHYTOEXTRACTION OF SOME HEAVY METALS FROM SELECTED METAL DUMPSITES IN ZARIA, NIGERIA

BY

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BY

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DECLARATION

I declare that the work in this dissertation entitled "PHYTOEXTRACTION OF SOME HEAVY METALS FROM SELECTED METAL DUMPSITES IN ZARIA, NIGERIA" has been carried out by me in the Department of Chemistry. The information derived from the literature has been duly acknowledged in the text and a list of references provided. No part of this dissertation was previously presented for another degree or diploma at this or any other Institution.

_____ _____

Zakka Israila YASHIM Date

CERTIFICATION

This dissertation entitled "PHYTOEXTRACTION OF SOME HEAVY METALS FROM SELECTED METAL DUMPSITES IN ZARIA, NIGERIA" by Zakka Israila YASHIM meets the regulations governing the award of the degree of PhD Analytical Chemistry of the Ahmadu Bello University, and is approved for its contribution to knowledge and literary presentation.

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ABSTRACT

A field trial to investigate the phyto-extraction of Cd, Co, Cu, Ni, Pb and Zn by *Vetivera zizanioide* (Jema), *Ipomoea asarifolia* (duman kada) *Helianthus annus* (sunflower), *Ricinus communis* L. (Castor oil plant) and *Cymbopogon citratus* (Lemon grass) planted on contaminated soils at Dakace, Gaskiya and Hanwa in Zaria, Nigeria was carried out between July to September, 2013. The effect of application of ethylenediamine-tetraacetic acid (EDTA) on the phyto-extraction of the studied metals by the test plants was also investigated. The harvested plants and the soils collected from the experimental and control sites were analyzed using atomic absorption spectrometry to determine the concentrations of these elements in different parts of each plant species and the soil treated and untreated with EDTA. The physicochemical parameters of the soil such as pH, moisture content, particle size, cation exchange capacity (CEC), organic matter (OM), chloride, phosphates, nitrates and sulphates were determined. The soils was subjected to sequential extraction to ascertain the bioavailability of the metals in the soils. Statistical analysis on the data obtained was carried out using One- way ANOVA. The results indicated that the soils at the experimental and control sites were sandy loam in texture, slightly acidic for the experimental soils and slightly alkaline for the control soil. The %OM and CEC for the experimental soils were higher than the soils of the Nigerian savanna. The concentrations of the studied metals in the soils from experimental sites were higher than the corresponding values from the control site, and higher than the recommended limits given by the Joint Food and Agricultural Organization and the World Health Organization (FAO/WHO). The Nemero Pollution Index showed that soils at the experimental sites were slightly to moderately polluted with Cd, Co, Ni and Zn and very heavily polluted with Pb. The

percentage bioavailability of metals at the experimental sites were: At Dakace Cd - 22.7%, Co - 29.7%, Cu – 80.7%, Ni – 53.2%, Pb – 24.3%, Zn – 64.3%; at Gaskiya, Cd – 22.4%, Co – 30.3%, Cu – 56.7%, Ni – 43.0%, Pb – 22.3%, Zn – 47.6% and at Hanwa, Cd – 21.4%, Co – 34.8%, Cu – 41.2%, Ni -42.5%, Pb – 18.7%, Zn – 63.4%. The Bioaccumulation factor (BF) and Transfer factor (TF) for the metals varied from plant to plant. The percentage removal of the studied metals from the EDTA treated soils and non EDTA treated soils were: At Dakace site, without EDTA application (natural) were: Cd- 52.5%, Co – 0.6%, Cu – 44.3%, Ni – 88.4%, Pb – 13% and Zn – 28%; with EDTA application: Cd – 70.3%, Co – 1.2%, Cu – 70.5%, Ni – 89.9%, Pb – 38.3% and Zn – 36%; At Gaskiya site without EDTA application (natural): Cd – 45.7%, Co – 15.7%, Cu – 24.5%, Ni – 69.7%, Pb – 21.2% and Zn – 17.1%; with EDTA application: Cd -62%, Co – 19.2%, Cu – 60.4%, Ni – 90.5%, Pb – 27.9% and Zn – 29.1%. At Hanwa site without EDTA application (natural): Cd – 36.7%, Co – 1.2%, Cu – 28.4%, Ni – 20.5%, Pb – 17.4% and Zn – 17.2%; with EDTA application: Cd – 59.7%, Co – 2.3%, Cu – 32.1%, Ni – 35.6%, Pb – 42.1% and Zn – 19.9%. The bioaccumulation and transfer factors for the studied metals by the test plant species are indications that these plant species have the potentials for phyto-remediation under field conditions even on soils that were untreated with EDTA. The phyto-extraction potentials of the test plant species were in the order of *Cymbopogon citratus* (Lemon grass) > *Vetivera zizanioide* (Jema) > *Helianthus annus* (sunflower) > *Ricinus communis* L. (Castor oil plant) > *Ipomoea asarifolia* (duman kada).

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ABBREVIATIONS

AAS	Atomic Absorption Spectrometry
ANOVA	Analysis of variance
AR	Analytical Reagent
AREDS	Age-Related Eye Disease Study
ATSDR	Agency for Toxic Substances and Diseases Registry
BF	Bioaccumulation Factor
CA	Citric Acid
DNA	Deoxyribonucleic Acid
DTPA	Diethylenetriamine Pentaacetate
DW	Dry Weight
EAC	European Aminocarboxylates Committee
EDDS	Ethylenediamine disuccinate
EDTA	Ethylenediaminetetraacetic Acid
FAO	Food and Agricultural Organisation
FEPA	Federal Environmental Protection Agency
HEDTA	Hydroxyethyl-ethylenediaminetriacetic Acid
IARC	International Agency for Research on Cancer
ICFRE	Indian Council of Forestry Research and Education
LD_{50}	Lethal Dose
LSD	Linear Standard Deviation
MCL	Maximum Contamination Level
Meq	Mega-equivalent
MESS	Multi-element Standard Solution
NTA	Nitrilotriacetic acid
OM	Organic matter

OSHA	Occupational Safety and Health Administration
SD	Standard Deviation
TCA	Tricarboxylic acid
TF	Transfer Factor
USEPA	United State Environmental Protection Agency
VS	Vetiver System
WHO	World Health ORganisation

CHAPTER ONE

1.0 INTRODUCTION

The global problem concerning contamination of the environment as a consequence of human activities is on the increase. Contamination has resulted from industrial activities, such as mining and smelting of metalliferous ores, electroplating, gas exhaust, energy and fuel production, fertilizer and pesticide application, and generation of municipal wastes (Kabata Pendias and Pendias, 1989). These have resulted in environmental build up of waste products of which heavy metals are of particular concern (Appel and Ma, 2002). Excessive metal concentration in the soil pose significant hazard to human, animal and plant health, and to the ecosystem in general (Nascimento and Xing, 2006).

Heavy metals are conventionally defined as elements with metallic properties (ductility, conductivity, stability as cations, ligand specificity) and with atomic numbers greater than 20 (Lasat, 2002). The most common heavy metal contaminants are: Cd, Cr, Cu, Hg, Pb, and Zn. Metals are natural components in soil. Due to the potential toxicity and high persistence of metals, soils polluted with these elements constitute environmental problem that requires effective and affordable solution. A number of techniques have been developed to remove metals from contaminated soils such as: solidification and stabilization; soil flushing/washing; electrokinetics; chemical reduction/oxidation**;** low temperature thermal desorption; incineration; vitrification; pneumatic fracturing; excavation/retrieval and landfill. These physico-chemical technologies used for soil remediation render the land useless as a medium for plant growth, as they remove all biological activities. These methods of disposal solely shift the contamination problem

elsewhere along with the hazards associated with transportation of contaminated soil and migration of contaminants from landfill into an adjacent environment.

Due to the high cost of these conventional technologies, the use of plants to clean up contaminated environments known as phytoremediation has emerged (Hosh and Ingh, 2005). Phytoremediation takes the advantage of the unique and selective uptake capabilities of plant root systems, together with the translocation, bioaccumulation, and contaminant degradation abilities of the entire plant body. The method is comprised of phytoextraction, phytostabilization, phytovolatilization, phytodegradation and phytofiltration. However, only phytoextraction which can effectively remove contaminants from contaminated soils is the most promising for commercial application (Sun *et al.*, 2011). Successful phytoextraction depends not only on metal concentration in shoots but also on high biomass production. Selection of plant species is based on high tolerance and accumulation rate for several metals, adaptation to local climates, high biomass, depth root structure, growth rate, ease of planting and maintenance, and ability to take up large quantities of water through the roots (*Zhao et al*.,2001). If metal availability in the soil is not adequate for plant uptake, chelates may be used to liberate them into the soil solution (Huang and Cunningham, 1996; Huang *et al*., 1997; Lasat *et al.*, 1998). The dumping of industrial and municipal solid wastes especially scrap-metals into the environment has contributed greatly to the increase in levels of heavy metals in soil and vegetations grown in dumpsites and finally find their way through the food chain into man. The soil and plants on these dumpsites will constitute a serious threat to the health of people living around such areas. Dakace, Gaskiya (both in Zaria L.G.A) and Hanwa (in Sabon Gari L.G.A) are among the locations where such scrap-

metal dumpsites can be found. Farming activities take place and different types of crops are grown on the soil around the dumpsites.

1.1 Statement of the Problem

Toxic metal pollution of soils is a major environmental problem, and most conventional remediation approaches do not provide acceptable solutions.

1.2 Justification

Phytoextraction has been accepted widely both in developed and developing nations for its potential to clean up the polluted and contaminated sites (Sun *et al.,* 2011). This technology is currently gaining considerable importance due to its potential for application to real world ecosystems and, however, it is still in its testing stages. It is cheaper and does not degrade the physical or chemical health of the soil. It seems to be the most promising technique and has received increasing attention from researchers as a technology to clean up metal polluted soils. The majority of phytoextraction studies have focused on pot experiments and laboratory hydroponic studies. Very few studies have attempted to evaluate the potential of natural hyperaccumulators or high biomass crops for phytoextraction under field conditions.

1.3 Aim of the Research

The aim of this research work is to make use of hyper-accumulators and high biomass plants to extract potentially toxic metals from polluted soils under field conditions with a view to either clean up or reduce the level of metal pollution in the soil to tolerable levels.

1.4 Objectives

The aim of the research work will be achieved through the following objectives:

(i) To determine the concentrations of Cd, Co, Cu, Ni, Pb and Zn in the soils before planting and after harvest, and compare with the given standards set by relevant regulatory bodies such as Joint Food and Agricultural Organization and World Health Organisation (FAO/WHO) with a view of assessing levels of pollution.

(ii) To carry out sequential extraction of metals from the soil to determine the bioavailable metals fractions.

(iii) To compare the uptake and distribution of heavy metals within different plant species.

(iv) To determine the actual effectiveness of a plant for cleaning up of metal polluted soils, by calculating the bioaccumulation factor (BF) and the transfer factor (TF).

(v) To investigate the effect of application of chelating agent (EDTA) on the metal levels in different soil fractions and their absorption by the plants.

(vi) To determine the concentrations of the metals in the soils after the application of the EDTA to ascertain the efficiency of the phyto-extraction.

CHAPTER TWO

2.0 LITERATURE REVIEW

The world is facing global challenges which include increasing environmental degradation due to increasing population, industrialization, urbanization as well as agricultural, mining and transport activities in recent times. Heavy metal contamination is frequently mentioned on the heavily polluted urban list.

The disposal of these metals is also a consequence of several activities like chemical manufacturing, painting and coating, mining, extractive metallurgy, nuclear and other industries. The introduction of industrial and municipal solid wastes into the environment has contributed greatly to the increase in levels of heavy metals in soil, and vegetations grown in dumpsites. The soil and plants on these sites constitute a serious threat to the health of people living around such areas (Inuwa *et al*., 2007).

Environment is defined as the totality of circumstances surrounding an organism or group of organisms especially, the combination of external physical conditions that affect and influence the growth, development and survival of organisms (Farlex Incorporated, 2005). A pollutant is any substance in the environment which causes objectionable effects thereby reducing the quality of life and may eventually cause death. Such substance has to be present in the environment beyond a set or tolerance limit. Hence, environmental pollution is the presence of a pollutant in the environment, that is, air, water and soil, which may be poisonous or toxic and will cause harm to living things in the polluted environment (Gore, 1997).

2.1 Municipal Solid Waste Management

According to Federal Environmental Protection Agency (FEPA,1995), solid wastes are useless, unwanted or discarded materials that arise from man's activities and cannot be discarded through sewer pipe. Dumping of solid wastes (especially scrap metals) gives rise to the pollution of some habitable parts of the earth surface. Such places with accumulated solid waste are called refuse dumps but designated places for such sites are known as dumpsites. Although, solid waste is an asset when properly managed, its volume has continued to increase tremendously in recent times in Nigeria as a result of socio-economic development such as wage increase (Olanrewaju and Ilemobade, 2009). In Nigeria, much has been, and is being invested on municipal solid waste management in cities (Onwughara *et al*., 2010). Despite several attempts aimed at managing these wastes, landfill and waste disposal sites are still principal focus for ultimate disposal of residual wastes. The larger the urban area, the lower the quality of the environment due to increase in the number of industries, vehicles. This has been one of the reasons why problems of solid waste disposal and management have reached a critical stage in major towns and cities of Nigeria (Kadafa *et al*., 2013).

In Nigeria, it is generally believed that individuals, government and environmental agencies pay little or no attention to the environmental impact of waste disposal and management, even when it is a statutory responsibility of the parties concerned. Agencies like the Federal Environmental Protection Agency (FEPA), Federal Ministry of Environment, Kaduna State Environmental Protection Agency (KEPA) and even local authorities are responsible for planning a defined line of action for disposal and

management of waste generated on daily basis in our society. Unfortunately, they are not performing as they should (Inuwa *et al*., 2007).

2.2 Heavy Metals

The term ‘‘heavy metals’’ refers to any metallic element that has a relatively high density and is toxic or poisonous even at low concentration (Lenntech Water Treatment and Air Purification, 2004). ‘‘Heavy metals’’ is a general collective term, which applies to the group of metals and metalloids with atomic density greater than 4 g/cm^3, or 5 times or more, greater than the density of water (Hawkes, 1997). However, chemical properties of the heavy metals are the most influencing factors compared to their density. Some heavy metals include Pb, Cd, Ni, Co, Fe, Zn, Cr, As, Ag and Pt.

2.2.1 Heavy Metals Toxicity

Heavy metal contamination in soil is a major concern because of their toxicity and threat to human life and the environment . Toxic metals entering the ecosystem may lead to geo-accumulation, bio-accumulation and bio-magnifications. They get accumulated with time in soils and plants and would have a negative influence on physiological activities of plants such as photosynthesis, gaseous exchange and nutrient absorption, leading to the reductions in plant growth, dry matter accumulation and yield. Heavy metals get into plants via adsorption which refers to binding of materials onto the surface or absorption which implies penetration of metals into the inner matrix. Both mechanisms can occur simultaneously. In small concentrations, the traces of the heavy metals in plants or animals are not toxic except lead, cadmium and mercury which are toxic even at low concentrations. Monitoring of the contamination of soil with heavy metals is of interest due

to their influence on ground water and surface water and also on plants, animals and humans (Fagbote and Olanipekun, 2010). Metal toxicity has high impact and relevance to plants and consequently, it affects the ecosystem, where the plants form an integral component. Contemporary investigations into toxicity and tolerance in metal-stressed plants are prompted by the growing metal pollution in the environment. A few metals, including Cu, Mn, Co, Zn, Fe and Cr are, however, essential to plant metabolism in trace amounts. It is only when metals are present in bioavailable forms and in excessive levels, they have the potential of becoming toxic to plants (Nagajyoti *et al*., 2010).

2.2.2 Heavy Metal Bioavailability

The fate of various metals, including chromium, nickel, copper, manganese, mercury, cadmium, and lead, and metalloids, such as arsenic, antimony, and selenium, in the natural environment is of great concern (David and Joel, 2008; Adriano, 1986). Bioavailability is the proportion of total metals that are available for incorporation into biota (bioaccumulation). Total metal concentrations do not necessarily correspond to metal bioavailability. Metals of major interest in bioavailability studies, as listed by the U.S. Environmental Protection Agency (EPA), are Al, As, Be, Cd, Cr, Cu, Hg, Ni, Pb, Se, and Sb (McKinney and Rogers, 1992). Other metals that are presently of lesser interest to the EPA are Ag, Ba, Co, Mn, Mo, Na, Tl, V, and Zn. These metals were selected because of their potential for human exposure and increased health risk. Different heavy metals behave differently in plants. Pb, Cr and Cu are not very mobile in trees and are retained primarily in roots. In contrast, Cd, Ni and Zn are more easily translocated to the aerial portions of plants (Mohanty *et al*. 2010). Plant uptake of trace elements is generally the first step of their entry into the agricultural food chain and this is dependent on movement of elements

from the soil to the plant root, elements crossing the membrane of epidermal cells of the root, and transport of elements from the epidermal cells to the xylem. The solution of these elements is then transported from roots to shoots, and possible mobilization, from leaves to storage tissues such as seeds, tubers, and fruit used as food, in the phloem transport system. After plant uptake, metals are available to herbivores and humans both directly and through the food chain. The limiting step for elemental entry to the food chain is usually from the soil to the root. This critical step usually depends on element concentrations in soil pore solutions, which are controlled by local soil physical and chemical conditions including water content, pH, redox reaction, and other factors (Adriano, 1992).

Plant species and relative abundance and availability of necessary elements also control metal uptake rates. Abundant bioavailable amounts of essential nutrients, can decrease plant uptake of non-essential elements. More complex interactions are also observed: bioavailability may be related to multi-element amounts or ratios. For example, copper toxicity is related to low abundances of zinc, iron, molybdenum and (or) sulphate (Chaney, 1988). In solid phases, soil, sediment, and surface water particulates, metals may be partitioned into six fractions: (a) dissolved, (b) exchangeable, (c) carbonate, (d) iron-manganese oxide, (e) organic, and (f) crystalline (Elder, 1989; Salomons, 1995). Various metals partition differently among these fractions as shown by sequential partial extraction procedures. Partitioning is affected strongly by variations in pH, redox state, organic content, and other environmental factors (Elder, 1989; Salomons, 1995). The dissolved fraction consists of carbonate complexes, whose abundance increases with pH, and metals in solution, including metal cation and anion complexes and hydrated ions whose solubilities are affected strongly by pH and tend to increase with decreasing pH (Elder,

1989). Exchangeable fractions consist of metals bound to colloidal or particulate material. Metals associated with carbonate minerals in sedimentary rocks and soil constitute the carbonate fraction, which can be newly precipitated in soil. The iron-manganese oxide fraction consists of metals adsorbed to iron-manganese oxide particles or coatings. The organic fraction consists of metals bound to various forms of organic matter. The crystalline fraction consists of metals contained within the crystalline structure of minerals and are not normally available to biota.

2.2.3 Cadmium

Cadmium has atomic number of 48, relative atomic mass 112.4, density 8.7gcm^{-3} , melting point 321°C and boiling point 767°C. The metal is a lustrous, silver-white, ductile, very malleable metal. The element has a bluish tinge and is soft enough to be cut with a knife, but it tarnishes in air. It is soluble in acids but not in alkalis. The element is similar in many respects to zinc but it forms more complex compounds. It is usually found as a mineral combined with other elements such as oxygen as cadmium oxide, chlorine as cadmium chloride, or sulphur as cadmium sulphate and cadmium sulfide (Schult-Schrepping and Piscator, 2000). About three-fourths of cadmium is used in Ni-Cd batteries, most of the remaining one-fourth is used mainly for pigments, coatings and plating, and as stabilizers for plastics (Young, 2005). The metal has been used particularly to electroplate steel where a film of cadmium only 0.05 mm thick will provide complete protection against the sea (Newton, 1995). This metal has the ability to absorb neutrons, so it is used as a barrier to control nuclear fission. The levels of cadmium in the environment vary widely (Zhang *et al*., 2005). The average natural abundance of the element in the earth's crust has most often been reported to be from 0.1 to 0.5 ppm, but much higher and much lower

values have also been cited depending on a large number of factors. Igneous and metamorphic rocks tend to show lower values, from 0.02 to 0.2 ppm whereas sedimentary rocks have much higher values, from 0.1 to 25 ppm. Naturally, zinc, lead and copper ores, which are mainly sulphides and oxides, contain even higher levels, 200 to 14,000 ppm for zinc ores and around 500 ppm for typical lead and copper ores. The raw materials for iron and steel production contain approximately 0.1 to 5.0 ppm, while those for cement production contain about 2 ppm. Fossil fuels contain 0.5 to 1.5 ppm cadmium, but phosphate fertilizers contain from 10 to 200 ppm cadmium (Lenntech, 2013).

Cadmium strongly adsorbs to organic matter in soils. When the element is present in soils it can be extremely dangerous, as the uptake through food will increase. Soils that are acidified enhance the uptake of the metal by plants. Leafy vegetables such as lettuce and spinach and certain staples such as potatoes and cereals exhibit relatively high values from 30 to 150 ppb. Peanuts, soybeans and sunflower seeds also exhibit naturally high values of cadmium with seemingly no adverse health effects. Meat and fish normally contain lower cadmium contents, ranging from 5 to 40 ppb. Animal offal such as kidney and liver can exhibit extraordinarily high cadmium values, up to 1,000 ppb, as these are the organs in animals where cadmium concentrates (WHO, 1992; ATSDR, 2011). The cadmium contents of foodstuffs may vary widely with the agricultural practices utilized in the particular areas such as phosphate fertilizer, sewage sludge and manure application, the types of crops grown, and atmospheric cadmium deposition from natural or anthropogenic sources. Since various studies have shown that man's cadmium intake, at least for non-smokers, comes principally (approximately 95%) from the ingestion of foods rather than from inhalation of cadmium in air, it is the cadmium levels of foods which affect the general population the

most. An exposure to significantly higher cadmium levels occurs when people smoke (Noler *et al*; 2006). Cadmium accumulates in kidneys, where it causes damages. Other health effects that can be caused by cadmium are diarrhea, stomach pains and severe vomiting, bone fracture, reproductive failure and possibly even infertility, damage to the central nervous system, damage to the immune system psychological disorders and possibly DNA damage or cancer development.

2.2.4 Copper

Copper, atomic number 29, relative atomic mass 63.55, density of 8.9gcm^{-3}, melting point of 1083^{o}C and boiling point of 2595^{o}C, is a reddish metal with a face-centered cubic crystalline structure. It is malleable, ductile, and an extremely good conductor of both heat and electricity. It is softer than zinc and can be polished to a bright finish. The metal has low chemical reactivity. In moist air it slowly forms a greenish surface film called patina; this coating protects the metal from further attack. The metal is mostly used for electrical equipment (60%); construction, such as roofing and plumbing (20%); industrial machinery, such as heat exchangers (15%) and alloys (5%) (Emsley, 2003; Seale, 2007). The main long established copper alloys are bronze, brass (a copper-zinc alloy), copper-tin-zinc, which was strong enough to make guns and cannons, and was known as gun metal, copper and nickel, known as cupronickel, which was the preferred metal for low-denomination coins (Lenntech, 2013)

Copper can be released into the environment by both natural sources and human activities. This basically means that more and more copper ends up in the environment. Examples of natural sources are wind-blown dust, decaying vegetation, forest fires and sea

spray. A few examples of human activities that contribute to copper release are mining, metal production, wood production and phosphate fertilizer production. Because copper is released both naturally and through human activity it is very widespread in the environment. The metal is often found near mines, industrial settings, landfills and waste disposals. The copper content of soils ranges from 2 to 100 parts per million (ppm), with an average value of about 30 ppm. Most of this is in unavailable mineral form (Schult and Kelling, 1999). Copper contents of the majority of plant species varies between 20 and 30 mg kg^{-1} dry weight. The critical copper deficiency level in vegetative plant parts is generally 3 to 5 mg kg^{-1} dry weight (Robson and Reuther, 1981); in young grain plants it was reported to be 1.5 mg kg^{-1} dry weight (Robson *et al.*, 1984).

Copper is non-biodegradable and because of that it can accumulate in plants and animals when it is found in soils. The metal gets into the human body through eating acid foods cooked in uncoated copper cookware, or from exposure to excess copper in drinking water or other environmental sources. The U.S. Environmental Protection Agency's Maximum Contaminant Level (MCL) in drinking water is 1.3 milligrams per liter. The Occupational Safety and Health Administration (OSHA) has set a limit of 0.1 mg/m^3 for copper fumes (vapor generated from heating copper) and 1 mg/m^3 for copper dusts (fine metallic copper particles) and mists (aerosol of soluble copper) in workroom air. It is a trace element that is essential for human health. Although humans can handle proportionally large concentrations of copper, but excess of it can still cause eminent health problems (George, 1991). Long-term exposure to the metal can cause irritation of the nose, mouth and eyes and it causes headaches, stomachaches, dizziness, vomiting and diarrhea. Intentionally high uptakes of copper may cause liver and kidney damage and even death

(Davis, 2000). There are scientific articles that indicate a link between long-term exposure to high concentrations of copper and a decline in intelligence with young adolescents. Industrial exposure to copper fumes, dusts, or mists may result in metal fume fever with atrophic changes in nasal mucous membranes. Chronic copper poisoning results in Wilson's Disease, characterized by a hepatic cirrhosis, brain damage, demyelization, renal disease, and copper deposition in the cornea. Acute symptoms of copper poisoning by ingestion include vomiting, hematemesis (vomiting of blood), hypotension (low blood pressure), melena (black "tarry" feces), coma, jaundice (yellowish pigmentation of the skin), and gastrointestinal distress. Some of the effects of aging may be associated with excess copper (Lawrence, 2011).

2.2.5 Nickel

Nickel is silvery-white, hard, malleable, and ductile metal with atomic number 28, relative atomic mass 58.71, density 8.9gcm^{-3}, melting point of 1453°C and boiling point of 2913°C. It is a fairly good conductor of heat and electricity. In its familiar compounds nickel is bivalent, although it assumes other valencies. It also forms a number of complex compounds. Most nickel compounds are blue or green. Nickel dissolves slowly in dilute acids but, like iron, becomes passive when treated with nitric acid. Finely divided nickel adsorbs hydrogen. The major use of nickel is in the preparation of alloys (Kuck, 2012). Nickel alloys are characterized by strength, ductility, and resistance to corrosion and heat. About 65 % of the nickel consumed in the Western World is used to make stainless steel, whose composition can vary but is typically iron with around 18% chromium and 8% nickel. 12 % of all the nickel consumed goes into super alloys. The remaining 23% of consumption is divided between alloy steels, rechargeable batteries, catalysts and other

chemicals, coinage, foundry products, industrial plumbing, spark plugs, machinery parts, and plating (Davis, 2000). Nickel is easy to work and can be drawn into wire. It resists corrosion even at high temperatures and for this reason it is used in gas turbines and rocket engines. Monel is an alloy of nickel and copper (70% nickel, 30% copper with traces of iron, manganese and silicon), which is not only hard but can resist corrosion by sea water, so that it is ideal for propeller shaft in boats and desalination plants (Lenntech, 2013).

Organic matter has a strong ability to absorb the metal which is why coal and oil contain considerable amounts. The nickel content in soil can be as low as 0.2 ppm or as high as 450 ppm in some clay and loamy soils. The average is around 20 ppm. Nickel occurs combined with sulphur in millerite, with arsenic in the mineral niccolite, and with arsenic and sulphur in nickel glance. Nickel occurs naturally in the environment at low levels. Nickel is an essential element in some animal species, and it has been suggested it may be essential for human nutrition. It can also be dangerous when the maximum tolerable amounts are exceeded. Nickel uptake will boost when people eat large quantities of vegetables from polluted soils. Plants are known to accumulate nickel and as a result the nickel uptake from vegetables will be eminent. Smokers have a higher nickel uptake through their lungs. Skin contact with nickel-contaminated soil or water may also result in nickel exposure (Thyssen *et al.*, 2007). Finally, nickel can be found in detergents. An uptake of very large quantities of nickel has the following consequences: higher chances of development of lung cancer, nose cancer, larynx cancer and prostate cancer; sickness and dizziness after exposure to nickel gas; lung embolism; respiratory failure; birth defects; asthma and chronic bronchitis; allergic reactions such as skin rashes, mainly from jewelry and heart disorders. Nickel fumes are respiratory irritants and may cause pneumonitis.

Exposure to nickel and its compounds may result in the development of a dermatitis known as “nickel itch” in sensitized individuals. The first symptom is usually itching, which occurs up to 7 days before skin eruption occurs. The primary skin eruption is erythematous, or follicular, which may be followed by skin ulceration. Nickel sensitivity, once acquired, appears to persist indefinitely (Zhao *et al*., 2009; Das *et al*., 2008).

2.2.6 Cobalt

Cobalt is a naturally occurring element found in rocks, soil, water, plants, and animals. Cobalt is used to produce alloys used in the manufacture of aircraft engines, magnets, grinding and cutting tools, artificial hip and knee joints (Michel *et al*., 1991; Campbell, 2008). Cobalt compounds are also used to color glass, ceramics and paints, and used as a drier for porcelain enamel and paints (Henderson, 2000). Radioactive cobalt is used for commercial and medical purposes. ^{60}Co is used for sterilizing medical equipment and consumer products, radiation therapy for treating cancer patients, manufacturing plastics, and irradiating food (Audi *et al*., 2003). ^{57}Co is used in medical and scientific research (Meyer, 2001; Kalnicky and Singhvi, 2001). Although the average level of cobalt in soils is 8 ppm, there are soils with as little as 0.1 ppm and others with as much as 70 ppm.

Human exposure to low levels of cobalt is by breathing air, eating food, or drinking water. Food and drinking water are the largest sources of exposure to cobalt for the general population and children may absorb more cobalt than adults; working in industries that make or use cutting or grinding tools; mine, smelt, refine, or process cobalt metal or ores; or that produce cobalt alloys or use cobalt. Exposure to radioactive cobalt is rare unless a

person is undergoing radiation therapy. However, workers at nuclear facilities, irradiation facilities, or nuclear waste storage sites may be exposed to radiation from these sources. Cobalt is an essential element for humans because it is part of vitamin B12, but high levels of cobalt can be harmful resulting in lung and heart effects and dermatitis (Basketter *et al*., 2003). Liver and kidney effects have also been observed in animals exposed to high levels of cobalt. Exposure to large amounts of radiation from radioactive cobalt can damage cells in the body. One might also experience acute radiation syndrome that includes nausea, vomiting, diarrhea, bleeding, coma, and even death, which is a rare event. Exposure to high levels of cobalt radiation can cause changes in the genetic materials within cells and may result in the development of some types of cancer. Nonradioactive cobalt has not been found to cause cancer in humans or animals following exposure in food or water. Cancer has been shown, however, in animals that breathed cobalt or when cobalt was placed directly into the muscle or under the skin (Adams and Dafforn, 1997). The International Agency for Research on Cancer (IARC) has determined that cobalt and cobalt compounds are possibly carcinogenic to humans. The LD_{50} values of soluble cobalt salts have been estimated to be between 150 and 500 mg/kg. Thus, for a 100 kg person the LD_{50} would be about 20 grams (ATSDR, 2011).

2.2.7 Lead (Pb)

Lead (Pb), with atomic number 82, relative atomic mass 207.19, and a specific gravity of 11.34, is a bluish or silvery-grey metal with a melting point of 327.5^{o}C and a boiling point at atmospheric pressure of 1740^{o}C. It has four naturally occurring isotopes with relative atomic mass 208, 206, 207 and 204 (in decreasing order of abundance). Despite the fact that lead has four electrons on its valence shell, its typical oxidation state is +2

rather than +4, due to inert pair effect. Apart from nitrate, chlorate, and chloride, most of the inorganic salts of Pb^{2+} have poor solubility in water . Lead (Pb) exists in many forms in the natural sources throughout the world and is now one of the most widely and evenly distributed trace metals. Currently lead is usually found in ore with zinc, silver and copper and it is extracted together with these metals. The main lead mineral is Galena (PbS) and there are also deposits of cerrussite and anglesite which are mined. The element can be found in all parts of our environment – the air, the soil, the water, and even inside our homes (ATSDR, 2011). Alloys include pewter and solder. Tetraethyl lead ($PbEt_4$) is still used in some grades of petrol (gasoline) but is being phased out because it is a source of the metal environmental pollution. Lead is a major constituent of the lead-acid battery used extensively in car batteries. It is used as a coloring element in ceramic glazes, paint, as projectiles and in some candlewick or thread. It is the traditional base metal for organ pipes, and it is used as electrodes in the process of electrolysis. One of its major uses is in the glass of computer and television screens, where it shields the viewer from radiation. Other uses are in sheeting, cables, solders, lead crystal glassware, ammunitions, bearings and as weight in sport equipment, cosmetics, pipes and plumbing materials (Rosen, 2010).

While natural levels of lead in soil range between 50 and 400 ppm, mining, smelting, and refining activities have resulted in substantial increase in lead concentration in the environment, especially near mining and smelting sites (ATSDR, 2011). Pb^{2+} was found to be very toxic to human beings when present in high amounts. Since Pb^{2+} is not biodegradable, once soil has become contaminated, it remains a long-term source of Pb^{2+} exposure. The metal occurs naturally in the environment. It accumulates in the upper 8 inches of the soil and is highly immobile. Contamination is long-term. Without remedial

action, high soil lead levels will never return to normal . In the environment, lead is known to be toxic to plants, animals, and microorganisms. Effects are generally limited to especially contaminated areas (Rolfe *et al*., 1977). Pb contamination in the environment exists as an insoluble form, and the toxic metals pose serious human health problem (Holmgren, 1993). Lead fulfils no essential function in the human body. It can enter the human body through uptake of food (65%), water (20%) and air (15%). Foods such as fruits, vegetables, meats, grains, seafood, soft drinks and wine may contain significant amounts of lead. Cigarette smoke also contains small amounts of lead. This metal can cause several unwanted effects, such as disruption of the biosynthesis of haemoglobin and anaemia, a rise in blood pressure, kidney damage, miscarriages and subtle abortions, disruption of nervous systems, brain damage, declined fertility of men through sperm damage, diminished learning abilities of children, behavioral disruptions of children, such as aggression, impulsive behavior and hyperactivity. Lead can enter a foetus through the placenta of the mother. Because of this it can cause serious damage to the nervous system and the brains of unborn children (Carrington and Bolger, 1992; Singer and Hanson, 1996).

2.2.8 Zinc

Zinc is a lustrous bluish-white metal. It is found in group IIb of the periodic table. It is brittle and crystalline at ordinary temperatures, but it becomes ductile and malleable when heated between 110°C and 150°C. It has atomic number 30, relative atomic mass 65.37, density 7.11gcm$^{-3,}$ melting point 420°C, boiling point 907°C. It is a fairly reactive metal that combines with oxygen and other non-metals, and reacts with dilute acids to release hydrogen. It is the 23rd most abundant element in the Earth's crust (Emsley, 2003). The dominant ore is zinc blende, also known as sphalerite. Other important zinc ores are

wurzite, smithsonite and hemimorphite. More than 30% of the world's need for zinc is met by recycling. The metal is used principally for galvanizing iron, more than 50% of it goes into galvanizing steel, but is also important in the preparation of certain alloys. It is used for the negative plates in some electric batteries and for roofing and gutters in building construction. The element is the primary metal used in making American pennies, is used in die casting in the automobile industry. Zinc oxide is used as a white pigment in water colors or paints, and as an activator in the rubber industry. As a pigment, zinc is used in plastics, cosmetics, photocopier paper, wallpaper, printing inks etc, while in rubber production its role is to act as a catalyst during manufacture and as a heat disperser in the final product (Emsley, 2003). Zinc metal is included in most single tablet, it is believed to possess anti-oxidant properties, which protect against premature aging of the skin and muscles of the body (ATSDR, 2011; AREDS, 2001).

Zinc occurs naturally in air, water and soil, but zinc concentrations are rising unnaturally, due to addition of zinc through human activities. Most zinc is added during industrial activities, such as mining, coal and waste combustion and steel processing (Broadley *et al*, 2007). Some soils are heavily contaminated with zinc, and these are to be found in areas where zinc has to be mined or refined, or were sewage sludge from industrial areas has been used as fertilizer. When the soils of farmland are polluted with zinc, animals will absorb concentrations that are damaging to their health. Water-soluble zinc that is located in soils can contaminate groundwater. Zinc cannot only be a threat to cattle, but also to plant species. Plants often have a zinc uptake that their systems cannot handle, due to the accumulation of zinc in soils. On zinc-rich soils only a limited number of plants have

a chance of survival. That is why there is not much plant diversity near zinc-disposing factories.

Only dissolved zinc tends to be bioavailable, and bioavailability depends on the physical and chemical characteristics of the environment and biological processes. In anthropogenically contaminated samples, zinc levels of up to 4mg/litre in water, 35g/kg in soil, 15µg/litre in estuarine water, and 8µg/m^3 in air are found. Concentrations in plants and animals are higher. Normal levels of zinc in most crops and pastures are in the range 10–100mg/kg dry weight. Some plants are zinc accumulators, but the extent of the accumulation in plant tissues varies with soil and plant properties.

Zinc is also a trace element that is essential for human health. When people absorb too little zinc they can experience a loss of appetite, decreased sense of taste and smell, slow wound healing and skin sores. Zinc-shortages can even cause birth defects. Although humans can handle proportionally large concentrations of zinc, too much zinc can still cause eminent health problems, such as stomach cramps, skin irritations, vomiting, nausea and anaemia. Very high levels of zinc can damage the pancreas and disturb the protein metabolism, and cause arteriosclerosis. Extensive exposure to zinc chloride can cause respiratory disorders. In the work place environment zinc contagion can lead to a flu-like condition known as metal fever. Zinc can be a danger to unborn and newborn children. When their mothers have absorbed large concentrations of zinc the children may be exposed to it through blood or milk of such mothers (Agbozu and Ekeozor, 2001).

2.3 Phytoremediation

Due to the potential toxicity and high persistence of metals, soils polluted with heavy metals constitute an environmental problem which requires an effective and affordable solution. Remediation of polluted sites is needed to prevent pollutants from leaching into the groundwater or taken up by food crops. The existing conventional remediation technologies are: solidification and stabilization; soil flushing/washing; electrokinetics; chemical reduction/oxidation; low temperature thermal desorption; incineration; vitrification; pneumatic fracturing; excavation/retrieval; and landfill (Mellem, 2008). Some of these conventional remediation techniques are engineering-based and include excavation and disposal of polluted soil into a landfill, excavation and off-site treatments, on-site treatments and containment of polluted soils by plastic, pavement, or a layer of clean soil preventing contact with the polluted soil layer. Remediation by excavation, transportation and treatment are expensive, while containment has negative environmental effects (Wilschut *et al*., 2013). Moreover, these physico-chemical technologies used for soil remediation render the land useless as a medium for plant growth, as they interfere with the soil structure and fertility.

Due to the high cost of these conventional technologies, the use of plants to clean up contaminated environments (phytoremediation) has emerged (Hosh and Ingh, 2005). Phytoremediation is the use of plants, including trees and grasses, and their associated microbes to remove, destroy or sequester toxic contaminants from soil, water and air. The technique is based on naturally occurring processes within the plant itself or in its microbial rhizosphere to extract, degrade and/or stabilize organic and inorganic pollutants (Wilschut *et al*., 2013). The terms phytoremediation and phytoextraction are sometimes incorrectly

used as synonyms, but phytoremediation is a concept while phytoextraction is a specific clean up technology.

2.3.1 Advantages of phytoremediation compared to conventional remediation

Some of the advantages include:

(i) It is more economically viable using the same tools and supplies as agriculture;

(ii) It is less disruptive to the environment and does not involve waiting for new plant communities to re-colonize the site;

(iii) Disposal sites are not needed;

(iv) It is more likely to be accepted by the public as it is more aesthetically pleasing than traditional methods;

(v) It avoids excavation and transport of polluted media thus reducing the risk of spreading the contamination and

(vi) It has the potential to treat sites polluted with more than one type of pollutant (Lasat, 2002).

2.3.2 Disadvantages of phytoremediation compared to conventional remediation

The limitations of the concept are:

(i) It is dependent on the growing conditions required by the plant (i.e., climate, geology, altitude, temperature);

(ii) Large scale operations require access to agricultural equipment and knowledge;

(iii) Success is dependent on the tolerance of the plant to the pollutant;

(iv) Contaminants collected in older tissues (leaves) may be released back into the environment as they fall off;

(v) Contaminants may be collected in woody tissues used as fuel;

(vi) Time taken to remediate sites far exceeds that of other technologies; and,

(vii) Contaminant solubility may be increased leading to greater environmental damage and the possibility of leaching (Lasat, 2002).

Phytoremediation can be accomplished by phyto-extraction, phytodegradation, phytostabilization, phytovolatilization and rhizofiltration (Nascimento and Xing, 2006).

2.3.3 Phytovolatilization

This involves the use of plants to take up contaminants from the soil, transforming them into volatile form and transpiring them into the atmosphere. Some of these contaminants can pass through the plant roots to the leaves and volatilize into the atmosphere at comparatively low concentration (Chaney *et al*., 1997).

2.3.4 Rhizofiltration

It is the use of both terrestrial and aquatic plants to adsorb, concentrate and precipitate contaminants from polluted aqueous sources with low contaminant concentration in their roots. It can partially treat industrial discharge, agricultural run off or acid mine drainage. It has the ability to be used as in-situ or ex-situ application (Chaney *et al*., 1997).

2.3.5 Phytostabilization

It is mostly used for the remediation of soil, sediment and sludge and depends on the ability of roots to limit contaminant mobility and bioavailability in soil. It can occur through the sorption, precipitation, complexation or metal valence reduction. The plants primary purpose is to decrease the amount of water soluble metals percolating through the soil matrix, which may result in the formation of hazardous leachate and prevent soil erosion and distribution of toxic metals to other areas (Chaney *et al*., 1997).

2.3.6 Phytodegradation

It is the breakdown of organic contaminants taken up by the plants (which contain enzymes) to simpler non-toxic molecules that are incorporated into the plant tissues (Chaney *et al*., 1997).

2.3.7 Phytoaccumulation/extraction

Plant roots can remove metals from contaminated soils/sediments and transport them to leaves and stems for harvesting and disposal without destroying the soil structure and fertility (Sun *et al.,* 2011). It is best suited for the remediation of diffusely polluted areas, where pollutants occur only at relatively low concentration and superficially. This can be an effective remediation method at a variety of sites and on numerous contaminants. The success of the phytoextraction process, whereby pollutants are effectively removed from soil, is dependent on an adequate yield of plants and/or the efficient transfer of contaminants from the roots of the plants into their aerial parts (Luo *et a*l., 2005; Evangelou *et al*., 2007). Phytoextraction makes use of natural hyperaccumulators as well as high biomass producing plants (Saifullah *et al*., 2009). Although different approaches have been

employed, the two basic phytoextraction strategies that have been used are (i) chelate-assisted phytoextraction or induced phytoextraction, in which artificial chelates are added to treated soil to increase the mobility and uptake of metal contaminants and (ii) continuous phytoextraction, in which the removal of metal depends on the natural physiological ability of the plant. When phytoextraction is employed, a potentially valuable feature is that the heavy metals taken up by phytoextraction into plant biomass can be captured and recycled (Bhargava *et al*., 2012).

2.3.8 Hyperaccumulators

Hyperaccumulators means plants capable of taking up concentrations of trace metals approximately 100 times greater than normal species (Knight *et al.,* 1997). They are plants that achieve a shoot- to- root metal concentration ratio greater than one. The ability of these plants species to grow in soils polluted with heavy metals, couple with the hyperaccumulation of heavy metals in the shoot material has been recognized as a potential technique to decontaminate polluted soils. This is the most promising technique for commercial application. More than 400 plant species from at least 45 plant families have been reported to hyperaccumulate metals (Lasat, 2002; Prasad, 2003). Selection of plant species is based on high tolerance and accumulation rate for several metals, adaptation to local climates, high biomass, depth root structure, growth rate, ease of planting and maintenance, and ability to take up large quantities of water through the roots (Zhao *et al*.,2001)

2.3.9 Advantages and limitations of phytoremediation

Phytoremediation of heavy metal contaminated soils which is an emerging technology has the following advantages and limitations (Lombi *et al*., 2001):-

Advantages:

(i) the cost of the phytoremediation is lower than that of traditional processes both in situ and ex situ;

(ii) the plants can be easily monitored;

(iii) the possibility of the recovery and re-use of valuable metals (by companies specializing in "phyto mining") and

(iv) it is potentially the least harmful method because it uses naturally occurring organisms and preserves the environment in a more natural state.

Limitations:

(i) Phytoremediation is limited to the surface area and depth occupied by the roots;

(ii) slow growth and low biomass require a long-term commitment;

(iii) with plant-based systems of remediation, it is not possible to completely prevent the leaching of contaminants into the groundwater (without the complete removal of the contaminated ground, which in itself does not resolve the problem of contamination);

(iv) the survival of the plants is affected by the toxicity of the contaminated land and the general condition of the soil and

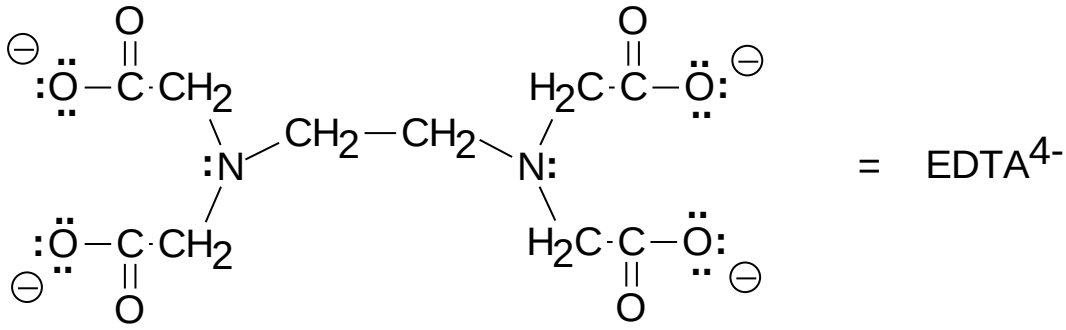
(v) bio-accumulation of contaminants, especially metals, into the plants which then pass into the food chain, from primary level consumers upwards or requires the safe disposal of the affected plant material.

2.3.10 Chelate-assisted phytoextraction

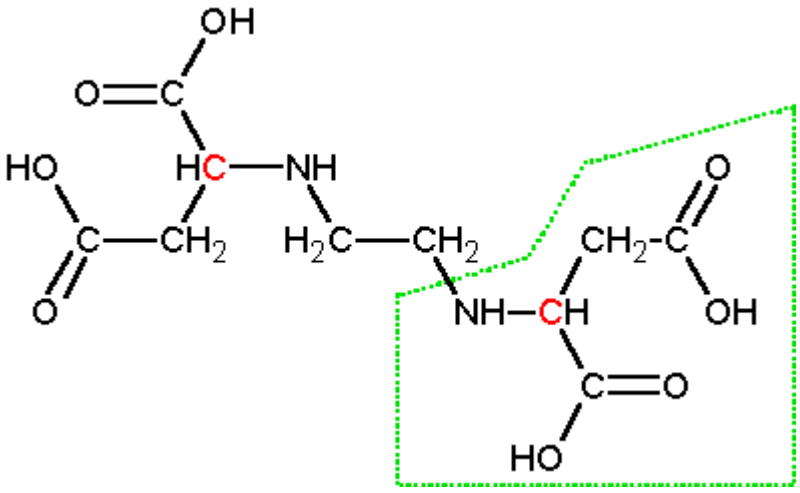
Regarding the phytoremediation process considered as the most effective way of purifying the soil from heavy metals, the induced phytoextraction seems to be the most promising (Salt *et al*. 1998). This process uses commonly cultivated species producing sufficiently large vegetative matter and they are subsequently stimulated to take-up heavy metals by adding particular agents to the soil or directly onto the plants (Jarosz *et al*., 2013). To achieve a sufficiently large weight of the above ground parts of plants used in the process is the basis of induced phytoextraction. For more than four decades, synthetic chelates are being widely used to increase heavy metals bioavailability in both soil and hydroponics, which can enhance phytoextraction. This enhances plant uptake and translocation of heavy metals from roots to green parts of the plants efficiently (Azhar *et al*., 2006). Several studies documented that chelating agents such as ethylenediamine-tetraacetic acid (EDTA), N-(2-hydroxyethyl)-ethylenediaminetriacetic acid (HEDTA), diethylene triamine penta acetate (DTPA), ethylenediamine disuccinate (EDDS), Nitrilotriacetic acid (NTA) and citric acid (CA) can be used to increase metal mobility, thereby enhancing phytoextraction. Chelate ability to facilitate phytoextraction was shown to be directly related to its affinity for metals.

EDTA ($C_{10}H_{16}N_2O_8$), a synthetic chelating agent, is poorly biodegraded in soils although it is effective at complexing metals. EDTA is a non-selective extracting agent that can form a strong complex with a variety of metals in soils including alkaline-earth cations.

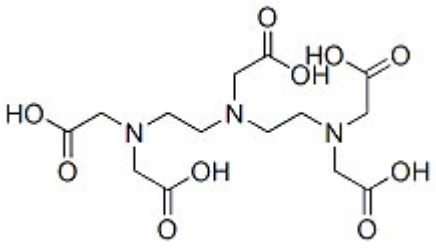
Excess amounts of EDTA may leach to groundwater and cause subsurface water contamination. It was Wallace *et al*. (1974) who first reported that metal–EDTA complexes could increase solubility and phytoavailability of metals in soils. When EDTA is applied to soils, a large fraction of the total metals is dissolved and becomes available for phytoextraction without inducing a strong acidification of the growth medium. Furthermore, as compared to other chemical compounds (such as inorganic acids), EDTA can solubilize metals with fewer undesirable effects on the soil physico-chemical properties. The ability of EDTA to increase concentration of metals in soil solution is influenced by a number of factors, including: concentration of metals and EDTA; presence of competing cations; metal species and their distribution among soil fractions; soil pH; adsorption of free and complexed metals onto charged soil particles and the formation constant of metal–ligand complexes. Due to its high binding affinity for metals, when applied at high concentrations, EDTA has the potential to release metals from solid phases by forming dissolved complexes. The formation of metal–EDTA complexes in soil solution may shift precipitation and sorption equilibria toward increased dissolution of metals (Dushenkov *et al*.,1997). Alternatively, EDTA may interact directly with solid phases by complexing metal ions present in, and/or adsorbed onto primary or secondary minerals (Gonsior *et al*., 1997). Below is the structural formula of EDTA



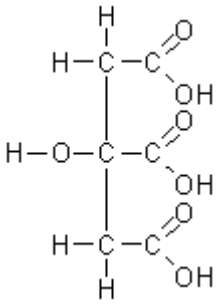
Ethylenediamine disuccinate (EDDS), $C_{10}H_{16}N_2O_8$, is an EDTA isomer, and unlike EDTA, it is a biodegradable chelator. Ethylenediamine disuccinate (EDDS) occurs naturally in soil and is easily decomposed into less detrimental byproducts. The structural formula of EDDS is given as:



Diethylene triamine penta acetate (DTPA), $C_{14}H_{23}N_3O_{10}$, is a synthetic ligand that forms stable complexes with most metals. It has been utilized in water treatment to prevent metal precipitates, and can be borrowed for soil metal extraction in order to enhance metal mobility. The structural formula of DTPA can be written as



Citric acid (CA), $C_6H_8O_7$, is a weak organic acid, and an intermediate in the CA cycle also known as the tricarboxylic acid cycle (TCA cycle), or the Krebs cycle. It occurs in the metabolism of virtually all living things, and can also be used as an environmentally cleaning agent by metal complexing. The structural formula of CA may be written as



Below is a contrast between chemically assisted phytoextraction and natural phytoextraction as reported by Nascimento & Xing (2006):

Chemically assisted phytoextraction	**Natural phytoextraction**
1. Plants are normally metal excluders	Plants naturally hyperaccumulate metals
2. Fast growing, high biomass plants	Slow growing, low biomass production
3. Synthetic chelators and organic acids are used to enhance metal uptake	Natural ability to extract high amount of metals from soils
4. Chemical amendments increase the metal transfer from roots to shoots	Efficient translocation of metals from roots to shoots
5. Low tolerance to metals; the increase in absorption leads to plant death	High tolerance, survival with high concentrations of metals in tissues
6. Risk of leaching of metal chelates to groundwater	No environmental drawback regarding leaching of metal

2.4 Plants for Phytoextraction

2.4.1 *Vetivera zizanioide*

The Vetiver System (VS), which is based on the application of *Vetivera zizanioide* L Nash, now reclassified as *Chrysopogon zizanioide* L Roberty, was first developed by the World Bank for soil and water conservation in India in the mid 1980s (Chomchalow, 2006). Vetiver System is being used as a bioengineering technique for steep slope stabilization, wastewater disposal, photo-remediation of contaminated land and water, and other environmental protection purposes. Vetiver Systems are a very simple, practical, inexpensive, low maintenance and very effective means of soil and water conservation, sediment control, land stabilization and rehabilitation, and phyto-remediation (Percy and Truong, 2005). Being vegetative it is also environmental friendly. When planted in single rows vetiver plants will form a hedge which is very effective in slowing and spreading run off water, reducing soil erosion, conserving soil moisture and trapping sediment and farm chemicals on site (Truong, 2004). Although any hedges can do that, vetiver grass, due to its extraordinary and unique morphological and physiological characteristics mentioned below, can do it better than all other systems tested. In addition, the extremely deep and massively thick root system of vetiver binds the soil and at the same time makes it very difficult for it to be dislodged under high velocity water flows. This very deep and fast growing root system also makes vetiver very drought tolerant and highly suitable for steep slope stabilization.

Vetivera zizanioide does not have stolons or rhizomes. Its massive finely structured root system that can grow very fast, in some applications rooting depth can reach 3- 4m in the first year. The plant is extremely drought tolerant, the stems are stiff and erect, highly

resistant to pests, diseases and fire. A dense hedge is formed when planted close together acting as a very effective sediment filter and water spreader. New shoots develop from the underground crown making vetiver resistant to fire, frosts, traffic and heavy grazing pressure. New roots grow from nodes when buried by trapped sediment. *Vetivera zizanioide* will continue to grow up with the deposited silt eventually forming terraces, if trapped sediment is not removed (Ash and Truong, 2003).

The Physiological characteristics of *Vetivera zizanioide* include**:**

(i) High biomass and high tolerance to extreme climatic variation such as prolonged drought, flood, submergence and extreme temperature from -15ºC to 55ºC (Truong *et al*., 2000);

(ii) Ability to re-grow very quickly after being affected by drought, frosts, salinity and adverse conditions after the weather improves or soil ameliorants added;

(iii) Tolerance to wide range of soil pH from 3.3 to 12.5 without soil amendment;

(iv) High level of tolerance to herbicides and pesticides;

(v) Highly efficient in absorbing dissolved nutrients such as N and P and heavy metals in polluted water;

(vi). Highly tolerant to growing medium high in acidity, alkalinity, salinity, sodicity and magnesium; and,

(vi) Highly tolerant to Al, Mn and heavy metals such as As, Cd, Cr, Ni, Pb, Hg, Se and Zn in the soils (Truong and Baker, 1998; Smeal *et al*., 2003; Truong *et al*., 2000).

2.4.2 *Ipomoea asarifolia* (Convolvulaceae)

It is a species of plant in the Convolvulaceae family, of the genus *Ipomoea*. It is a smooth, hairless succulent perennial plant, trailing on the ground usually several meters long. It reproduces from seeds and stem shoots. It is found throughout West Africa and is a common weed of hydromorphic soils, low lying and inland valleys, streams and river banks. In Nigeria, the traditional names include "Duman kada" in Hausa and "Gboro ayaba" in Yoruba (Jegede *et al*., 2009). The stem is solid near the base but hollow nearer the top on the plant. It has fine longitudinal lines, without hairs or only sparingly hairy. The leaves are alternate, suborbicular, 10-12 cm in diameter, blunt at the apex and heart-shaped at the base. The margins are entire, the blade thick, borne on long petioles about 15 cm long, smooth with nerves radiating from the base. It reproduces from seeds and stem shoots. The water extract from *I. asarifolia* has anti-inflammatory and analgesic properties. In Nigeria, the leaf of *Ipomoea asarifolia* is used as compost material, mulch, as well as constituting weed in farms. Ekenyem (2006) reported that leaf of *Ipomoea asarifolia* could be used as a feed ingredient in pig production. A longer growth period produces biomass that may enhance hyperaccumulation of heavy metals by the plant.

2.4.3 *Cymbopogon citratus* (Lemon grass) plant

Cymbopogon is a genus of about 55 species of grasses, of which the type species is *Cymbopogon citratus*, a natural and soft tea anxiolytic native to warm temperate and tropical regions of the Old World and Oceania. It is a tall perennial grass. Common names include lemon grass, barbed wire grass, silky heads, citronella grass and fever grass. Lemon grass is native to India and tropical Asia. It is widely used as a herb in Asian cuisine. It has a subtle citrus flavor and can be dried and powdered, or used fresh. It is commonly used in

tea (against coughs, colds and fever), soups, and curries. It is also suitable for use with poultry, fish, beef, and sea food. It is often used as a tea in African countries such as Togo and the Democratic Republic of the Congo and Latin American countries such as Mexico. Lemon grass oil is used as a pesticide and a preservative. Research shows that lemon grass oil has antifungal properties (Shadab *et al*., 1992). Despite its ability to repel insects, its oil is commonly used as a "lure" to attract honey bees. "Lemon grass works conveniently just as the pheromone created by the honeybee's nasonov gland, also known as attractant pheromones. Because of this, lemon grass oil can be used as a lure when trapping swarms or attempting to draw the attention of hived bees. *Cymbopogon citratus* is used both as a medical herb and in perfumes. *Cymbopogon citratus* is consumed as a tea for anxiety in Brazilian folk medicine, but a study in humans found no effect. The tea caused a recurrence of contact dermatitis in one case (Annan *et al*., 2013). The lemon grass, available locally in abundance, can be used for stabilization of steep slopes when rows of grasses are planted in the form of slips and root stocks. Clumps of grasses can be collected from adjacent and nearby areas without destroying the grass cover of the adjacent areas. This has been suggested since the grasses are drought tolerant and can colonize fast in low nutrient soil. Due to the presence of fibrous roots grasses can reduce soil erosion as they are the best sand binders (ICFRE, 2010). Lemon grass produced more biomass than vetiver grass therefore could be used for reclamation (phytoremediation) of toxic tailings or polluted areas (Das and Maiti, 2009). Annan *et al*. (2013) reported that some species of medicinal plants, including *Cymbopogon citratus*, accumulate different levels of heavy metals.

2.4.4 *Helianthus annus (*Sunflower)

*Helianthus annus (*Sunflower) is tall, hardy annual or perennial herbs/ plant native to the Americas; it has a rough, hairy stem, broad, coarsely toothed, rough leaves and circular heads of flowers. It is cultivated as ornamentals or garden plants, where the blooms are cherished for their beauty and the seeds can be eaten by both humans and wildlife. Sunflowers commonly grow to heights between 1.5 and 3.5 m (5–12 ft.). Most cultivars are variants of *H. annus*, but four other species (all perennials) are also domesticated. An example is *H. tuberosus*, the Jerusalem artichoke, which produces edible tubers that are important agricultural commodities. Every part of the sunflower has a use for something, and no part goes to waste. Sunflower is a higher biomass producing crop and has been considered as a hyperaccumulating plant (Zhi *et al*., 2011). Sunflowers can be used in phytoremediation to extract toxic ingredients from soil, such as lead, arsenic and uranium, and used in rhizofiltration to neutralize radionuclides and other toxic ingredients and harmful bacteria from water. They were used to remove caesium-137 and strontium-90 from a nearby pond after the Chernobyl disaster, and a similar campaign was mounted in response to the Fukushima Daiichi nuclear disaster (Cooney, 1996). Phytotech, Inc., a Princeton, NJ-based company, reported that it had developed transgenic strains of sunflowers, Helianthus sp., that could remove as much as 95% of toxic contaminants in as little as 24 hours. Subsequently, Helianthus was planted on a Styrofoam raft at one end of a contaminated pond near Chernobyl, and in twelve days the cesium concentrations within its roots were reportedly 8,000 times that of the water, while the strontium concentrations were 2,000 times that of the water. It removes radiation, fluoride, salt, pesticides, bacteria, dirt and other contaminants from any water (Gary, 2012). U. S., Russian, and Ukrainian defense ministers planted sunflowers on the site of a former Soviet missile silo; the sunflowers were

also decontaminating the soil, removing heavy metals and toxins accumulated in the area. Tangahu *et al.* (2011) reported that for sunflower, the 1.0g/kg rate of chelate addition resulted in maximal removal of the three non essential heavy metals (Cd, Ni, and Pb). Uptake of the essential heavy metals by sunflower was little affected by the EDTA. The leaves of sunflower grown with 1.0g $Na_4EDTA{\cdot}2H_2O$/kg soil accumulated more Cd, Ni, and Pb than leaves of sunflower grown without the EDTA salt. Removal of the non-essential heavy metals by sunflower was greater at the higher plant density compared to the lower one.

2.4.5 *Ricinus communis* (Castor oil) plant

The *Ricinus communis (*castor oil plant) is a species of flowering plant in the spurge family, Euphorbiaceae. It belongs to a monotypic genus, *Ricinus,* and subtribe, *Ricininae*. The castor oil plant can vary greatly in its growth habit and appearance. It is a fast-growing, suckering perennial shrub that can reach the size of a small tree (around 12 metres or 39 feet), but it is not cold hardy. The glossy leaves are 15–45 centimetres (5.9–18 in) long, long-stalked, alternate and palmate with 5–12 deep lobes with coarsely toothed segments, the roots are thick and fibrous. Although castor is indigenous to the southeastern Mediterranean Basin, Eastern Africa, and India, probably native to Africa, this species has become naturalized throughout the tropical world. In areas with a suitable climate, castor establishes itself easily where it can become an invasive plant and can often be found on wasteland. It is also used extensively as a decorative plant in parks and other public areas, particularly as a "dot plant" in traditional bedding schemes. Castor oil plant spreads over sandy soil areas, creek banks and gullies. It is often abundant along watercourses and flood plains, disturbed or waste land and roadsides with high tolerance for growth under harsh

environmental conditions, such as low rainfall and heat". It may be common locally after heavy rains or floods. This can lead to a significant loss of prime grazing land. The seeds of castor oil contain ricin, a poison that is extremely toxic to livestock and humans. Leaves have a lesser amount of toxin. Poisoning in livestock is rarely reported though, as castor oil plant is seldom grazed by stock when other pasture plants are available. Castor seed is the source of castor oil, which has a wide variety of uses in medicine and other applications.

Castor bean is an appropriate plant to be used as indicator plant for Cd and tolerant for Pb in contaminated solution and it can be potentially used for phytoremediation of contaminated areas. *R. communis* was found more tolerant to salinity and drought in presence of Cd. *R. communis* produced 23 and 12 fold higher biomass in terms of fresh weight and dry weight (Souza *et al*., 2012). Castor bean (*Ricinus communis* L.), which was investigated by Olivares *et al*. (2013). The potential of castor bean to remediate sites polluted with mine tailings containing high concentrations of Cu, Zn, Mn, Pb and Cd and as an energy crop was investigated. The plant species has attracted considerable attention because of its ability to grow in heavily polluted soil together with its capacity for metal ion accumulation. The possibilities of easily growing *R. cummunis* in different climate and using its biomas in biofuel industries can make heavy metals contaminated soils productive, and although slowly, restore them at the same time (Rajkumar and Freitas, 2008).

2.5 Soil Parameters

2.5.1 Cation exchange capacity (CEC)

The cation exchange capacity of a soil is simply a measure of the quantity of sites on soil surfaces that can retain positively charged ions by electrostatic forces. Cations retained electrostatically are easily exchangeable with other cations in the soil solution and

are thus readily available for plant uptake(Bodar *et al*., 2006). Thus, CEC is important for maintaining adequate quantities of plant available calcium (Ca^{2+}), magnesium (Mg^{2+}) and potassium (K^{+}) in soils. Under acid conditions (pH <5.5), aluminum (Al^{3+}) may also be present as an exchangeable cation (Mordi *et al*., 2002). Soil CEC is normally expressed in units of charge per weight of soil. Commonly two sets of units are used: meq/100g (milliequivalents of charge per 100g of dry soil) or cmolc/kg (centimoles of charge per kilogram of dry soil). While a soil with a higher CEC may not necessarily be more fertile, when combined with other measures of soil fertility, CEC is a good indicator of soil quality and productivity. Cation exchange sites are found primarily on clay and organic matter surfaces (Krzystof *et al*., 2012). Normal CEC ranges in soils would be from < 3 cmol/kg, for sandy soils low in OM, to >25 cmol/kg for soils high in certain types of clay or OM. Soil OM will develop a greater CEC at near-neutral pH than under acidic conditions. Additions of an organic material will likely increase a soil's CEC. Soil CEC may also decrease with time through acidification and OM decomposition (Donald, 2000) .

2.5.2 Soil pH

Soil pH is an indication of the acidity or alkalinity of soil. pH is defined as the negative logarithm (base 10) of the activity of hydronium ions (H^{+} or, more precisely, $H_3O^{+}aq$) in a solution.As the amount of hydrogen ions in the soil increases the soil pH decreases thus becoming more acidic. Soil pH controls many chemical processes that take place. It specifically affects plant nutrient availability by controlling the chemical forms of the nutrient. The optimum pH range for most plants is between 5.5 and 7.0 (Perry, 2012), however many plants have adapted to thrive at pH values outside this range. Acidity in soils comes from H^{+} and Al^{3+} ions in the soil solution and sorbed to soil surfaces. While pH is

the measure of H^+ in solution, Al^{3+} is important in acid soils because between pH 4 and 6, Al^{3+} reacts with water (H_2O) forming $AlOH^{2+}$, and $Al(OH)^{2+}$, releasing extra H^+ ions. Every Al^{3+} ion can create $3H^+$ ions. Many other processes contribute to the formation of acid soils including rainfall, fertilizer use, plant root activity and the weathering of primary and secondary soil minerals. Acid soils can also be caused by pollutants such as acid rain and mine spoiling (Sparks, 2003).

Alkaline soils have a high saturation of base cations (K^+, Ca^{2+}, Mg^{2+} and Na^+). This is due to an accumulation of soluble salts which are classified as either saline soil, sodic soil, saline-sodic soil or alkaline soil. All saline and sodic soils have high salt concentrations, with saline soils being dominated by calcium and magnesium salts and sodic soils being dominated by sodium. Alkaline soils are characterized by the presence of carbonates. Soil in areas with limestone near the surface are alkaline from the calcium carbonate in limestone constantly mixing with the soil (Brandy and Weil, 2002).

Both macronutrient and micronutrient availability are affected by soil pH. In slightly to moderately alkaline soils, molybdenum and macronutrient (except for phosphorus) availability is increased, but P, Fe, Mn, Zn Cu, and Co levels are reduced and may adversely affect plant growth. In acidic soils, micronutrient availability (except for Mo and Bo) is increased (Hansson, 2011).

2.5.3 Particulate size

Particulate size and resulting total surface area available for adsorption are both important factors in adsorption processes and can affect metal bioavailability (Luoma, 1989). Small particles with large surface-area-to mass ratios allow more adsorption than an

equivalent mass of large particles with small surface-area-to-mass ratios. Reduced adsorption can increase metal bioavailability by increasing concentrations of dissolved metals in associated water (De Gregori *et al*., 1996). The size of particles released during mining depends on mining and beneficiation methods. Finely milled ore may release much smaller particles that can both be more widely dispersed by water and wind, and which can also serve as sites of enhanced adsorption. Consequently, mine tailings released into fine-grained sediment such as silty clays found in many places can have much lower environmental impact than those released into sand or coarse-grained sediment with lower surface area and adsorption (David and Joel, 2008).

2.5.4 Organic matter

Of all the components of soil, organic matter is probably the most important. Organic matter serves as a reservoir of nutrients and water in the soil, aids in reducing compaction and surface crusting, and increases water infiltration into the soil. Soil organic matter is the fraction of the soil that consists of plant or animal tissue in various stages of breakdown (decomposition). Most of the productive agricultural soils have between 3 and 6% organic matter. It increases the soil's CEC or its ability to hold onto and supply over time essential nutrients such as calcium, magnesium and potassium; Improves the ability of a soil to resist pH change (this is also known as buffering capacity) and accelerates decomposition of soil minerals over time, making the nutrients in the minerals available for plant uptake. Within the soil profile, the organic matter content is always highest in the surface horizon (Mega *et al*., 2008).

2.5.5 Soil moisture content

The amount of water associated with a given volume or mass of soil ("soil water" or "soil moisture") is a highly variable property. It can change on time scales of minutes to years. However, most soil properties are more stable, and should be referenced to dry soil weight. Soil moisture content is very dependent on soil type. A saturated coarse, sandy soil can hold far less water than a saturated heavy silty clay. Sand has large particles which take up a lot of physical space. Also, as sand particles do not bind water, a lot of water will drain out of the sand due to gravity before field capacity is reached. For these two reasons, sand has a much lower maximum and minimum water content than a clay soil does. Sand readily releases its moisture and the most sand can hold is around 30%. Clay soils often have a maximum moisture reading of 50% or more, so 20% is very dry. The clay particles also bind water to themselves and at low moisture contents like 20%, the clay will not give the water up for the roots to use (Ripoche, 2014).

Drying a soil to constant weight at 105°C (sometimes 50-80°C for plant tissue) is the traditional method of arriving at a “dry” sample weight. This temperature is somewhat arbitrary, and clay minerals in particular may contain 10-15% water (dry basis) at 400°C (Gardner, 1986). As temperature increases, first water in soil pores evaporates, then water adsorbed to mineral surfaces, followed by water between lattice layers and that which forms part of the mineral lattice itself. The exact quantities and patterns of release in a hetergeneous mixture like soil depends on the particular mix of minerals making up a sample. Water adsorbed to organic components (as well as other volatile organic substances) will also evaporate over a range of temperatures. The key point is to specify the temperature used when reporting moisture data.

2.5.6 Nitrates

Nitrates exist as NO_3^- and are highly soluble. As such they move readily to the roots and are highly available to the plants. They are also subject to leaching and if they move out of the root zone they can eventually cause contamination of the ground water. This is highly dependent on soil texture. Nitrate (NO_3^-) is a naturally occurring form of nitrogen in soil. This form of nitrogen is created when nitrification, the conversion of ammonium into nitrate, occurs. Nitrate is used as food by plants for growth and production. The level of nitrate in soil varies widely, depending upon the type of soil, climate conditions, rainfall and fertilizing practices. The normal background level of nitrates in soil not fertilized or used for commercial crops ranges from 5 to 10 parts per 1 million (ppm). Optimum nitrate level for soil used for corn (*Zea mays*) production is more than 25 ppm. Nitrate levels between or higher than 25 ppm to 30 ppm are sufficient to grow plants in a vegetable garden. Nitrate levels are highest in soils that have finer textures, such as clay and silt, rather than those with rough textures, such as sand. Because nitrates are moved through soil by water, sandy soil often loses nitrates due to leaching, and heavy, coarsely textured soil loses nitrates due to denitrification, a process in which anaerobic bacteria in the soil converts nitrates to gaseous forms of nitrogen. Leaching and denitrification can cause nitrate pollution of water supplies and should be considered when deciding whether or not to apply additional nitrogen to soil (Nesic *et al*., 2008).

Climate conditions can directly affect the amount of nitrate in soil. Excessive rainfall or standing water on soil can lead to leaching and denitrification, particularly in warm weather. Heavy rains after nitrogen applications can create considerable loss of soil nitrates,and create a source of pollution. Soil nitrate levels are increased through rapid

nitrification in well-aerated soils with a pH of 6 to 8 and temperatures greater than 50^{o}C. Wet, cold or acidic soils do not contain high levels of nitrate (Tori, 2014).

2.5.7 Chloride

Most soil Cl^- is highly soluble and is found predominantly dissolved in the soil water. Chloride is found in the soil as the chloride anion. Being an anion it is fully mobile except where held by soil anion exchange sites (Kaolinite clays, Iron and Aluminum Oxides). In areas where rainfall is relatively high and internal soil drainage is good, it may be leached from the soil profile. Chloride, nitrate, sulphate are all anions in their available forms, and in that form they are antagonistic to each other. Therefore, an excess of one can decrease the availability of another. Contaminated soil has higher concentration of chloride than non-contaminated soil. This is due to disposal of waste product which include wastewater, human and animals sewage and so on. The excess of chloride has negative effect on metallic pipes and structures as well as agricultural plants.

2.5.8 Phosphorus

In the tropics, phosphorus is often the most limiting plant nutrient. This is primarily due to the challenges in the management of phosphorus. In plants, the concentration of phosphorus ranges from 0.1-0.5%. The orthophosphates, $H_2PO_4^-$ and HPO_4^{2-}, are the primary forms of phosphorus taken up by plants. When the soil pH is less than 7.0, $H_2PO_4^-$ is the predominant form in the soil. Although less common, certain organic phosphorus forms can also be directly taken up by plants. Plant roots absorb phosphorus from the soil solution. In comparison to other macronutrients, the phosphorus concentration in the soil solution is much lower and ranges from 0.001 mg/L to 1 mg/L (Brady and Weil, 2002). Abundant bioavailable amounts of essential nutrients, including phosphorous and calcium,

can decrease plant uptake of non-essential but chemically similar elements, including arsenic and cadmium, respectively. Phosphate ions reduce the uptake of Cd and Zn in plants, and diminish the toxic effects of As, as observed on soils treated with arsenic pesticides (Smilde *et al*., 1992).

2.6 Temperature and Climate

Temperature exerts an important effect on metal speciation, because most chemical reaction rates are highly sensitive to temperature changes (Elder, 1989). An increase of 10^{o} C can double biochemical reaction rates, which are often the driving force in earth surface conditions for reactions that are kinetically slow, and enhance the tendency of a system to reach equilibrium. Temperature may also affect quantities of metal uptake by an organism, because biological process rates (as noted above) typically double with every 10^{o} C temperature increment (Luoma, 1983; Prosi, 1989). Because increased temperature may affect both influx and efflux rates of metals, net bioaccumulation may or may not increase (Luoma, 1983). Climate strongly influences soil types which largely control element (metals and metalloids) mobility and availability. In tropical climate conditions, accumulation of oxide minerals of iron, manganese, and aluminum in soil profiles may limit the mobility and bioavailability of both metals and metalloids.

The climate conditions in the northern part of Nigeria exhibit only two different seasons, a short wet season and a prolonged dry season. Temperature during the day remains constantly high while humidity is relatively low throughout the year, with little or no cloud cover. There are wide diurnal ranges in temperature (between nights and days) particukarly in the very hot months. The mean monthly temperatures during the day exceed

36^{o}C while the mean monthly temperatures at night fall, mostly to below 22^{o}C. In the north, a single wet/raining season is between June and September.

CHAPTER THREE

3.0 MATERIALS AND METHODS

All the chemicals and Reagents used were of analytical grade (AR).

De-ionized water was used throughout the research work.

3.1 Study Areas

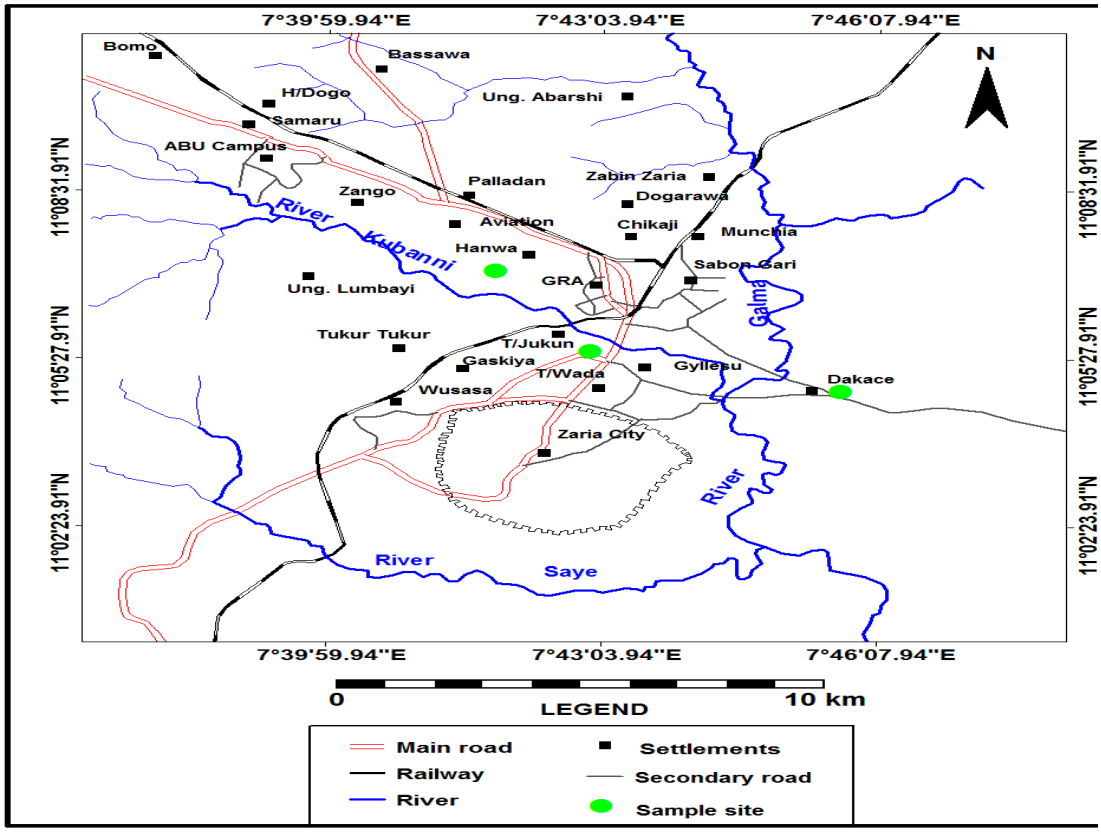
Three areas (Figure 3.1) in Zaria, Nigeria (11^o 07' 51" N; 7^o 43' 43" E) were selected for the research work because of the activities that involve disposal of metal containing materials into the biosphere, which may lead to increase in the amount of toxic metals entering the environment: Gaskiya (metal scrap dump site) and Dakace (old metal dump site) are in Zaria L.G.A, and each dumpsite occupies an estimated area of 20m x 6m. While the dumpsite at Hanwa (Yankarfe or New Pantaka) is in Sabon Gari L.G.A of Kaduna state, Nigeria with an estimated area of 70m x 100m.

3.2 Experimental Design

The field experiment was carried out from July to September of 2013 in Zaria,Nigeria. The climate is typically of the climatic conditions in the northern part of Nigeria that exhibit only two different seasons, a short wet season and a prolonged dry season. Temperature during the day remains constantly high while humidity is relatively low throughout the year, with little or no cloud cover. There are wide diurnal ranges in temperature (between nights and days) particularly in the very hot months. The mean monthly temperatures during the day exceed 36^oC while the mean monthly temperatures at night fall, mostly to below 22^oC. In the north, a single wet/raining season is between June and September. The study was performed on three contaminated sites (Dakace, Gaskiya and Hanwa) and one non-contaminated site (control site) which is about 5km away, where

there are no activities involving disposal of metal containing materials . An test area of 6m x 4m was selected at each site and divided into two parts (3m x 2m) where the studied plants were grown. The seedlings of *Vetivera zizanioide* (Jema), *Helianthus annus* (sunflower), *Ricinus communis* L. (Castor oil plant), *Ipomoea asarifolia* (duman kada) and *Cymbopogon citratus* (Lemon grass) were obtained from farmlands not contaminated, taken to the Department of Biological Sciences, Ahmadu Bello University, Zaria, where they were identified by Mr U. S. Gallah with voucher numbers, 4217,1890, 2679, 1919 and 1772 respectively and transplanted to the field. The various plant species were planted in the designated field plots with spacing of 20cm x 20cm for all the tested plants as described by Zhuang *et al*. (2007). The plants were allowed to grow naturally under natural climatic conditions and exposed to natural day and night temperatures, with neither mineral fertilisation nor optimum irrigation so as to assess the feasibility of the remediation process. Weeds were controlled by mechanical method. After 10 weeks when the plants might had achieved maximum biomass production, a single dose of 5mmol/kg EDTA (Na_2-EDTA) was applied to the soil of one part of the plots at each study site. Seven days after the application of the EDTA solution, the plants were harvested and the associated soil samples were collected.

The choice of these plants was based on their widespread availability and demonstration of tolerance to conditions not favourable for the growth of other plants in Nigeria. Also, these plant species have the ability to co-exist on the same field (Okoronkwo *et al*., 2014). This feature prompted their simultaneous study under the similar test conditions.



Source: Modified from Topographic Map of Zaria

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Figure 3.1: Map of Zaria Showing the Study Areas



Plate 3.1: Picture Showing Hanwa Metal Dumpsite



Plate 3.2: Picture Showing Gaskiya Metal Dumpsite



Plate 3.3: Picture Showing Dakace Metal Dumpsite



Plate 3.4: Picture Showing Plants Grown at Dakace Study Site



Plate 3.5: Picture Showing the Plants Grown at Hanwa Study Site



Plate 3.6: Picture Showing Some Plants Grown at Gaskiya Study Site

3.3 Sample Collection and Treatment

Whole plant samples of *Vetivera zizanioide* (Jema), *Ipomoea asarifolia* (duman kada) *Helianthus annus* (sunflower), *Ricinus communis* L. (Castor oil plant) and *Cymbopogon citratus* (Lemon grass) were harvested from each of the study areas; Soil samples (150g) were collected from the surface to a depth of 15cm around each plant root zone, using hand trowel and then mixed together (n = 20).

Background soil (150g) and plant samples were also obtained as control from a farmland that is 5km distance away from the dumpsite (n = 20). The collection was done by dividing the test and control sites each into four quadrants, five plant samples or soil samples were collected from each quadrant in a diagonal basis by following the methods of Nuonom *et al*., 2000.

The soil samples were taken to the laboratory, air-dried, ground and sieved through a 2mm mesh,then kept in polythene bags for further analyses. Plant samples were washed with running tap water and then rinsed with distilled water. The roots, stems and leaves of each plant (*Vetivera zizanioide* and *Cymbopogon citratus* have only leaves and roots) were separated, air-dried and again dried in an oven at 60 ± 1^{o}C for 16hrs. The dry plant materials were ground, placed in polythene bags and kept dry in a dessicator for further analyses.

3.4 Preparation of 5mmol/kg EDTA Solution

Reagents

Disodiumethylenediamine-tetraacetic acid (Na_2-EDTA), $Na_2H_2C_{10}H_{12}O_8N_2.2H_2O$ (AR)

Procedure

Accurately, 1.861g of Na_2-EDTA dihydrate (dried at 80^oC) was weighed onto a watch glass and carefully transferred to the volumetric flask (1L) through a clean, dry, glass funnel. A clean, dry, spatula was used to transfer some of the EDTA from the watch glass to the funnel. The spatula, watch glass and the funnel were rinsed several times with the de-ionized water to wash the remaining EDTA into the flask. The volumetric flask was filled to the mark with water.

3.5 Modified Tessier's Sequential Extraction (Masa *et al*., 2013)

Preparation of Reagents

Magnesium nitrate (1M) solution: 64.10g of $Mg(NO_3)_2.6H_2O$ was dissolved and made up to $250cm^3$ with water.

Ammonium acetate (1M) solution: 77.08g of CH_3COONH_4 was dissolved and made up to $1dm^3$ with water.

Hydroxylammonium Chloride (0.1M) solution: 69.49g of $HONH_3Cl$ was dissolved and made up to $1dm^3$ with water.

Nitric acid (0.02M) solution: $1.26cm^3$ of conc. HNO_3 (69% v/v, sp Gr. 1.42) was pipetted into $1dm^3$ volumetric flask containing small amount of water, shaken and made up to the mark.

Hydrogen peroxide (30%v/v)

Aqua regia: conc. HCl was mixed with conc. HNO_3 in the ratio 3:1 (HCl : HNO_3).

Procedure

The water soluble fraction (F1): 1g of air dried soil sample was weighed into a 60 cm^3 capacity polythene container; 10 cm^3 of water was added and shaken for 1hr. The soil colloids was then centrifuged with a Baird & TatLock autobench centrifuging machine at

4000 rpm for 20 min. The supernatant was decanted and filtered through Whatman No.42 filter paper into a 50cm^3 volumetric flask, then made up to the mark with water.

The exchangeable fraction (F2): To the residual soil sample from F1, 10cm^3 of 1M $MgNO_3$ solution was added and shaken for 2 hrs, then treated as in F1.

The fraction bound to carbonates (F3): The residual soil sample from F2, 10cm^3 of 1M NH_4OAc solution was added to it; the pH was adjusted to 5 and shaken for 5 hrs. This was again treated as above.

The fraction bound to Fe and Mn oxides (F4): 20cm^3 of 0.1M $NH_2OH.HCl$ solution was added to the residual soil sample from F3; the pH was adjusted to 2 and shaken for 12hrs. This was again treated as above.

The fraction bound to organic matter(F5): To the residual soil sample from F4, 3cm^3 of 0.02M HNO_3 solution and 5 cm^3 of 30% v/v H_2O_2 were added and heated for 3 hrs at 85^o C, followed by adding 15cm^3 of 1M NH_4OAc solution and shaken for 30 min. This was again treated as above.

The final residual fraction (F6): The residual soil sample from F5 was digested with 10cm^3 of aqua regia. The clear solution was filtered through a Whatman No.42 filter paper into 50cm^3 volumetric flask, then made to the mark with water.

The concentration of the heavy metals was determined by Atomic absorption spectrometry (AAS), model D100XB4J, for each fractionation sequence. The final fractional recovery of the metals was calculated by comparing the sum of their

concentration in all six fractions with their pseudototal concentration (assessed by aqua regia digestion) in the corresponding soil.

3.6 Determination of Soil pH (Bodeck *et al.*, 1988)

Procedure

Twenty grams of sieved soil sample of each soil was placed in a 50 cm^3 beaker, 20cm^3 of water was added, stirred with glass rod and allowed to stand for 10 minutes. Then, stirred again and the pH meter (Grison MicropH 2000) immersed into the water/soil suspension and the reading noted. The pH meter was rinsed with water for each soil sample in order to obtain the accurate result that is required.

3.7 Determination of Soil Moisture Content (Waggler and Bodeck, 1989)

Procedure

The empty crucible was weighed (W_1) and crucible plus soil sample was weighed (W_2) then placed in a the dry oven of temperature 105^oC and dried to a constant weight. The sample was removed and placed in dessicator to cool. The crucible with the contents was weighed again (W_3).

Calculation

$$\% \text{ Moisture Content} = \frac{W_2 - W_3}{W_2 - W_1} \times 100 \qquad 3.1$$

where W_1 = Weight of empty crucible (g), W_2 = Weight of crucible + soil sample (g) and W_3 = Weight of crucible + dried soil sample (g).

3.8 Particle Size/ Soil Texture (Agbenin, 1995)

Procedure

Fifty gram (50 g) of the soil was pulverized and placed in a tall, slender jar (35cm height and 6cm diameter) to about a one-quarter full of soil. De-ionized water was added until the jar was three-quarters full. A teaspoon of powdered, non-forming dishwasher detergent was added. The jar was shaken for 15minutes to break apart the soil aggregates and separates the soil into individual mineral particles. The jar was kept undisturbed for 3 days. The soil particles that settled after 1 minute according to its size were marked on the jar depth of the sand. After 2 hours the level of the silt was marked on the jar, and after 3 days the level of clay was marked on the jar.

Calculation

$$\% \text{ sand} = \frac{\text{Thickness of sand} \times 100}{\text{Total thickness}} \quad 3.2$$

$$\% \text{ clay} = \frac{\text{Thickness of clay} \times 100}{\text{Total thickness}} \quad 3.3$$

$$\% \text{ silt} = \frac{\text{Thickness of silt} \times 100}{\text{Total thickness}} \quad 3.4$$

The soil texture was determined from the texture triangle (Appendix LXX).

3.9 Cation Exchange Capacity Determination by $BaCl_2$ Compulsive Exchange Method (Gillman and Sumpter, 1986).

Preparation of Reagents

Barium chloride (0.1M $BaCl_2.2H_2O$) solution: 24.428g of $BaCl_2.2H_2O$ was dissolved in a 1L standard volumetric flask containing 800cm^3 of water then diluted to the mark.

Barium chloride (2mM $BaCl_2.2H_2O$) equilibrating solution: Dilute 20 cm^3 of the 0.1 M $BaCl_2$ solution to 1 L with water.

Magnesium sulphate (0.1M $MgSO_4.7H_2O$) solution: 24.648g of $MgSO_4.7H_2O$ was dissolved in a 1L standard volumetric flask that contains about 800cm^3 of water and diluted to the mark.

Magnesium sulphate (1.5mM and 5mM $MgSO_4.7H_2O$) solution: 15 cm^3 and 50 cm^3 of the 0.1M $MgSO_4$ solution were diluted separately with water and made up to 1L in a standard volumetric flask respectively.

Sulphuric acid (0.05M H_2SO_4) solution: 2.8 cm^3 of concentrated H_2SO_4 (98% v/v, sp.gr. 1.84) was poured into a 1L standard volumetric flask almost filled with water, shaken thoroughly and allowed to cool before it was made to the mark.

Procedure

Two gram (2.00g) of soil was weighed into a 30cm^3 centrifuge tube and 20cm^3 of 0.1M $BaCl_2.2H_2O$ solution was added, shaken for 2 hours, centrifuged at about 4,000 rpm and decanted. Then 20cm^3 of 2mM $BaCl_2.2H_2O$ solution was added and shaken for 1 hour vigorously at first to disperse soil pellet; It was then centrifuged and the supernatant discarded. The pH of the slurry was determined. To the slurry, 10.00cm^3 of 5mM $MgSO_4$ solution was added and shaken gently for one hour. The conductivity of the 1.5 mM $MgSO_4$ solution was determined (this should be ~300 umhos). The conductivity and the pH of the sample solution were adjusted (as necessary) using 0.1 M $MgSO_4$ and 0.05 M H_2SO_4 solutions respectively until the solution conductivity and pH were that of the 1.5 mM $MgSO_4$ solution.

Calculation

CEC (meq/100g) = [Total Mg added(meq) - Mg in final solution (meq)] x 50 3.5

where Total Mg added (meq) = 0.1 meq [meq in 10 cm^3 of 5mM $MgSO_4$ solution] + meq added in 0.1 M $MgSO_4$[cm^3 of 0.1 M $MgSO_4$ x 0.2 meq/cm^3 (0.1 M $MgSO_4$ solution has 0.2 meq/cm^3)] and Mg in final solution (meq) = total solution (cm^3) x 0.003 (meq/cm^3) [1.5mM $MgSO_4$ solution has 0.003 meq/cm^3]. 50 was to convert from 2 g of soil to 100 g].

3.10 Determination of Chloride in Soil (Henson, 1973)

Preparation of Reagents:

Silver nitrate (0.01 moldm^{-3} $AgNO_3$) solution: 1.6987g of $AgNO_3$ was dissolved in water in 1litre standard volumetric flask and made up to the mark.

Potassium chromate (0.1moldm^{-3} K_2CrO_4) solution: 19.40 g of K_2CrO_4 was dissolved in water in a 1L standard volumetric flask and made up to the mark.

Soil Extract

Soil sample (5g) was weighed into a 100 cm^3 flask and 50 cm^3 of water was added and shaken for 1 hour. The suspension was filtered into a 250 cm^3 beaker and the residue was washed with deioniesd water and added to the filtrate.

Procedure

The burette was filled with a standard 0.01 moldm^{-3}$AgNO_3$ solution. Using a pipette, 10 cm^3 of the filtrate was transferred into a 250 cm^3 conical flask and made up to

50 cm^3, 2cm^3 of 0.1$moldm^{-3}$ K_2CrO_4 solution was added as indicator, mixed thoroughly and titrated with 0.01 $moldm^{-3}$ $AgNO_3$ solution to a muddy yellow colour.

Calculation

$$Cl^-(mg/kg) = \frac{\text{Titre value x 35.5 x 1000 x conc. of } AgNO_3}{\text{Weight of sample (g)}} \quad 3.6$$

3.11 Determination of Phosphate Concentration in Soil (Pierzynski *et al*., 2011)

Reagents:

Concentrated sulphuric acid (AR), 98% v/v

Ammonium molybdate, $(NH_4)_6$ $M_{O7}O_{24}.4H_2O$ (0.01M): 40g of the solid salt was dissolved in 800cm3 of water in a 1L volumetric flask and made up to the mark with the water

Ascorbic acid solid (vitamin C)

Ammonium sulphate solid, $(NH_4)_2$ SO_4, BDH (AR)

Potassium dihydrogen Phosphate, KH_2PO_4 (AR)

Soil-extract

Procedure

Accurately, 0.75g of dried ammonium sulphate was weighed and dissolved in 50 cm^3 of water, 5 cm^3 of concentrated sulphuric acid was added slowly. The solution was allowed to cool, then diluted to 250 cm^3 with water. To 10g of dry soil sample 200 cm^3 of sulphuric acid/ammonium sulphate mixture was added and shaken occasionally for 30 minutes then filtered through a Whatman No. 42 filter paper.

Preparation of standard phosphate stock Solution (100ppm)

Standard phosphate solution (100ppm) was prepared by dissolving 0.220g of solid KH_2PO_4 in 160 cm^3 of water in a 500 cm^3 volumetric flask, and diluted to the mark.

Working standard phosphate solution (5ppm)

Using a pipette, 5 cm^3 of the standard phosphate stock solution was transferred into a 100 cm^3 volumetric flasks and diluted to the mark. A set of standard phosphate solutions 0 cm^3, 0.5 cm^3, 1.0 cm^3, 2.0 cm^3, 3.0 cm^3, 4.0 cm^3 and 5.0 cm^3 were pipetted into separate 50 cm^3 volumetric flasks and made up to the mark with water in each case. These solutions with concentrations of 0, 0.1,0.2, 0.4, 0.6, 0.8 and 1.0ppm respectively were taken in separate test-tubes, 4.0 cm^3 of 0.01moldm^{-}3 molybdate reagent and a spatula ascorbic (Vitamin C) crystals were added to each. The solutions were heated slowly to boiling, until a deep blue or green color developed and then it was allowed to cool.

The wavelength region of maximum absorbance (λmax) of the coloured substance was determined. Absorbances of the various solutions of standard phosphate were measured at λmax and corrected with a blank. This data was used to construct a calibration curve.

Preparation of sample solution

A volume of 5cm^3 of the soil extract was pipette into a 25 cm^3 volumetric flask and 10 cm^3 of water was added, followed by 4 cm^3 of molybdate solution and one spatula of ascorbic acid (Vitamins C) crystals. The mixture was shaken and made up to the mark. The solution was transferred into a 150 cm^3 conical flask and heated slowly to boiling, until a

deep blue or green color developed and allowed to cool. The absorbance was measured at λmax and the phosphate concentration was calculated from the calibration curve.

Calculation

$$PO_4\text{-P (mg/kg)} = \frac{\text{conc.of } PO_4^{2-} \times 1000}{\text{Weight of sample (g)}} \qquad 3.7$$

3.12 Determination of Sulphate in Soil (Agbenin, 1995)

Soil – Extraction: (KH_2PO_4 Extraction method)

KH_2PO_4 solution (0.016mol/dm^3): 2.14g of KH_2PO_4 was dissolved in water and then made up to 1L in a standard volumetric flask. This solution was used as the extracting solution to extract both soluble and adsorbed sulphate.

Air – dried soil sample (5.0g) was weighed into an Erlenmeyer flask, 25cm^3 of the extracting solution was added and the flask was shaken on a mechanical shaker for 30 minutes. The suspension was filtered through a Whatman No. 42 filter paper.

Preparation of Reagent

Barium chloride solution (5% w/v): 5g of $BaCl_2$ was dissolved in water and then made up to 100cm^3.

Hydrochloric Acid (2.0mol/dm^3): 168cm^3 of concentrated HCl (37% v/v, sp gr. 1.18) was measured into 1dm^3 volumetric flask containing some little amount of water. After a thorough shaking, the solution was made up to mark.

Sulphate stock solution (100mg/l): 0.181g of K_2SO_4 was dissolved in water in a 1L volumetric flask and made up to the mark.

Procedure

Separate volumes of 0cm^3, 2.0cm^3, 4.0cm^3 6.0cm^3, and 8cm^3 of the stock solution were pipetted into separate 50cm^3 volumetric flasks and made up to the mark with water in each case. These solutions had the concentrations of 1.0, 2.0, 3.0, 4.0 and 5.0mg/L respectively. A portion of each of these solutions was taken in a separate test-tube, then 1cm^3 of the 5% m/v $BaCl_2$ solution followed by 1cm^3 of the 2mol/dm^3 of HCl solution were added into each test-tube. The solution was allowed to stand for 30minutes.

The concentration of the unknown was determined by construction of calibration curve of absorbance against concentration of standard solution.

Calculation

$$SO_4^{2-}(mg/kg) = \frac{R \times VE \times DF}{W} \qquad 3.8$$

where R = sample concentration from calibration curve ,VE = volume of Extraction solution (25cm^3), DF = dilution factor and W = weight of sample.

3.13 Determination of Nitrate (Devarda alloy method by Agbenin, 1995)

Preparation of Reagent

Boric acid solution (0.328M H_2BO_3): 20g of boric acid was dissolved in about 850 cm^3 of water.

Indicator stock solution: 0.198g of bromocresol green and 0.132g of methyl red were dissolved in 200 cm^3 of ethanol.

Boric acid-indicator solution: 15 cm^3 of the Indicator stock solution was added to the boric acid solution and 0.1M NaOH solution was added slowly until the solution had a reddish purple tint. The solution was thoroughly mixed and made up to 1L with water.

Potassium chloride (2M KCl) solution: 150g of the salt was dissolved in water and made up to 1L mark in a standard volumetric flask.

Sulphamic acid solution (0.021M NH_2SO_3H): 2g of the salt was dissolved in water and made up to 1L.

Sulphuric acid solution (0.01M H_2SO_4): 0.56 cm^3 of the concentrated acid was pippetted into a 1L standard volumetric flask containing some water and made up to the mark.

Devarda alloy (45% Al, 50% Cu, 5% Fe).

Procedure

Soil extract

Ten grams (10g) of the soil was weighed into 250 cm^3 extracting bottle and 100 cm^3 of 2M KCl solution was added, followed by 1cm^3 of 0.021M sulphamic acid to destroy NO_2-N. The bottle was shaken on a mechanical shaker for 1hr, the suspension filtered through a filter paper (whatman No. 42) and then stored in a refrigerator.

The soil extract (filtrate) was taken into a Kjeldahl distillation flask and 0.2g of Devarda alloy was added through a long-stem funnel (to reduce NO_3- N to NH_4-N). The

flask was attached to the distillation apparatus and the distillate collected in a 50 cm^3 erlenmeyer flask containing 5 cm^3 aliquot of boric acid-indicator solution. When 30 cm^3 of the distillate had been collected, the distillation was stopped and the distillate titrated with 0.01M H_2SO_4 solution. The end-point was when a colour change occurred from green to a permanent faint pink.

Calculation

1 cm^3 of 0.01M $H_2SO_4 \equiv$ 70mg of NH_4-N

$$NO_3^-(mg/g) = (V \times M \times 14 \times 10^3)/W \qquad 3.9$$

where V = titre value and M = concentration of H_2SO_4

3.14 Determination of Organic Matter (dichromate oxidation method by Walkley-Black, 1937)

Preparation of Reagents

Potassium dichromate solution (0.2M): 49.04g K_2CrO_7 was dissolved in water and made up to 1L in a standard volumetric flask.

Ferrous ammonium sulphate solution (0.4M): 156.90g of the sulphate salt was dissolved in water, 20cm^3 conc. H_2SO_4 added and shaken, the solution was made up to 1L.

Sulphuric acid reagent: 15g $AgSO_4$ was added to 1L conc. H_2SO_4 (ratio 15g : 1L).

Concentrated phosphoric acid (85% v/v).

Ferroin indicator.

Procedure

One gram of the soil sample was weighed into 250cm^3 conical flask and 10cm^3 of 0.2M K_2CrO_7 solution was added, the flask swirled gently to disperse the soil in solution. Then 20cm^3 of conc. H_2SO_4 was added quickly and then thoroughly mixed. The mixture was allowed to cool for 30 minutes after which 200cm^3 of water was added, followed by 10cm^3 of concentrated phosphoric acid and 2-3 drops of ferroin indicator. The solution was titrated against 0.4M ferrous ammonium sulphate solution. A colour change from bluish green to brilliant green indicated the end point.

A blank titration was carried out using deionized water without the soil sample.

Calculation

$$\% \text{ OM} = \frac{10(B - S)}{ZB} \times \frac{12}{4000} \times \frac{1.72}{0.77} \times 100 \qquad 3.10$$

where B = titre value for blank, S = titre value for sample, Z = weight of soil sample used, 1.72 = factor for organic matter from carbon, 0.77 = Walkley's recovery factor, 12/4000 = meq weight of carbon, 10 = conversion factor for units.

Therefore,

$$\% \text{ OM} = \frac{(B-S)x\ 6.7}{ZB} \qquad 3.11$$

3.15 Determination of Cd, Co, Cu, Ni, Pb and Zn by Atomic Absorption Spectrophotometry (AAS)

Reagents

Nitric acid AR (69% v/v, sp. Gr. 1.42)

Hydrochloric acid AR (37% v/v, sp. Gr. 1.18)

Procedure

One gram of each of the soil and plant samples was digested separately with 10 cm^3 of aqua regia (a mixture of 3 parts concentrated HCl to 1 part concentrated HNO_3) on a hot plate in a fume cupboard, until a clear solution was obtained. Water was added periodically to avoid drying up of the digest. To the hot solution, 30 cm^3 of water was then added and filtered through a Whatman No. 42 filter paper into a 50 cm^3 standard volumetric flask and then made up to the mark (Kisku *et al*, 2000).

Cadmium, cobalt, copper, nickel, lead and zinc were analysed in the plant and soil samples using a D100XB4J model atomic absorption spectrometer (Kisku et al, 2000), with the analyses being done in triplicate.

3.16 Preparation of Calibration Curve

Stock solutions

Cadmium solution (1000ppm): 2.7435g of $Cd(NO_3)_2.4H_2O$ was dissolved in 5 cm^3 of 2M HNO_3 solution and diluted with water to 1L in a standard volumetric flask.

Cobalt solution (1000ppm): 4.9407g of $Co(NO_3)_2.6H_2O$ was dissolved in 5 cm^3 of 2M HNO_3 solution and diluted with water to 1L in a standard volumetric flask.

Copper solution (1000ppm): 3.8052g of $Cu(NO_3)_2.3H_2O$ was dissolved in 5 cm^3 of 2M HNO_3 solution and diluted with water to 1L in a standard volumetric flask.

Nickel solution (1000ppm): 4.9529g of $Ni(NO_3)_2.6H_2O$ was dissolved in 5 cm^3 of 2M HNO_3 solution and diluted with water to 1L in a standard volumetric flask.

Lead solution (1000ppm): 1.5985g of $Pb(NO_3)_2$ was dissolved in 5 cm^3 of 2M HNO_3 solution and diluted with water to 1L in a standard volumetric flask.

Zinc solution (1000ppm): 1.2447g of ZnO was dissolved in 5 cm^3 of 2M HNO_3 solution and diluted with water to 1L in a standard volumetric flask.

Procedure

Appropriate working standards were prepared for each metal by serial dilution of the stock solutions and then aspirated into the flame and their absorbances recorded. A calibration curve was prepared by plotting absorbance against concentrations.

The digested sample solutions were aspirated into the flame and the absorbance values recorded. The metal concentration was calculated from the calibration curve in each case.

3.17 Pollution Index (Hong-gui *et al*., 2012)

Single Contamination index (CI)

Single contamination index (CI) is employed to evaluate the real quantitative information of key pollution multiples which is one of the current methods used in evaluation of the degree of heavy metal pollution in soil.

The single contamination index may be obtained from the expression:

$$CI = \frac{\text{concentration of metal}}{\text{background value}} \qquad 3.12$$

where CI = contamination index

Nemero Pollution Index

The single contamination index method cannot express accurately the comprehensive impact caused by each kind of heavy metals. The Nemero Index method takes not only the extreme value but also the environmental quality index based on weighted multi-factors. The method can reflect the degree of soil pollution caused by various heavy metal pollutants.

The Nemero Pollution Index was obtained from the expression:

$$P_i = \sqrt{[(P_{jmax})^2 + (P_{jave.})^2]}/2 \qquad 3.13$$

where P_i = Nemero Pollution Index , P_{jmax} = corresponding maximum value in the single contamination pollution index and $P_{jave.}$ = the corresponding average value in the single contamination pollution index.

3.18 Quality Assurance Validation

Validation of the technique for the metal determination was conducted on digested plant and soil samples. This was done by spiking the pre-digested samples with multi-element standard solution (0.5mg/l of Cd, Co, Cu, Ni, Pb and Zn) as reported by Awofolu (2005).

3.18.1 Preparation of multi-element standard solution (MESS)

1mg/l $Cd(NO_3)_2.4H_2O$ solution: 0.0027g of the salt was dissolved in 2 cm^3 of 2M HNO_3 solution in a beaker and then transferred quantitatively into a 1 dm^3 standard volumetric flask. The beaker was rinsed thoroughly with deionized water into the flask. Similarly, 0.0049g of $Co(NO_3)_2.6H_2O$, 0.0038g of $Cu(NO_3)_2.3H_2O$, 0.0050g of $Ni(NO_3)_2.6H_2O$,

0.0016g of $Pb(NO_3)_2$, and 0.0012g of ZnO were separately dissolved in 2 cm^3 of 2M HNO_3 solution in a beaker and then transferred into the same flask above. The solution in the flask was made up to the mark with the deionized water to give 1mg/L of the multi-element standard solution which was used in the spiking experiment.

3.18.2 Spiking experiment

Multi-element standard solution (20cm^3) was pippetted to spike three different samples. These were digested as in section 3.15 and their metal concentrations determined by AAS. The concentration of metals in the spiked and their corresponding unspiked samples were used to calculate the percentage recovery in order to validate the method.

Calculation:

$$\text{Amount of metal used in spiking} = \frac{\text{vol.of MESS used x conc.of metal in MESS}}{1000} \quad (3.14)$$

$$= X \text{ mg}$$

$$\text{Amount of metal in spiked sample} = \frac{\text{vol.of digest of spiked x conc.(mg/L)}}{1000} \quad (3.15)$$

$$= Y \text{ mg}$$

$$\text{Amount of metal in unspiked sample} = \frac{\text{vol.of digest of unspiked x conc.(mg/L)}}{1000} \quad (3.16)$$

$$= Z \text{ mg}$$

Recovered amount of metal used in a spiked sample = $Y - Z$

$$\% \text{ recovery} = \frac{Y - Z}{X} \times 100 \quad (3.17)$$

3.19 Statistical Analysis

All treatments in the experiment were done in triplicates. The mean and standard deviations (SD) were calculated using the Microsoft Office Excel 2003. One-way analysis of variance (ANOVA) was carried out with statistical package for the social sciences (SPSS) version 20.0.

CHAPTER FOUR

4.0 RESULTS

4.1 Physicochemical Parameters of Soils

The result of the analysis for physicochemical parameters of soils is shown in Table 4.1 which shows that all study area soils were more of sandy and predominantly sandy loamy in texture. The pH values ranged from 6.78 to 7.50, that is slightly acidic(for the test soils) to slightly alkaline (for control soil). The soil at Dakace had higher moisture (4.80±0.05) and phosphate (3.23±0.11) contents than the other soils under study. The soil at Gaskiya showed higher percentage organic matter (5.10±0.05), cation exchange capacity (12.80±0.07 meg/100), chloride content, nitrate content (250.46±30.11 mg/kg) and sulphate content (277.34±3.00 mg/kg) when compared to other test soils.

4.2 Quality Assurance Validation

The results for the validation of the technique for the metal determination conducted on digested plant and soil samples are presented in Table 4.2. The percentage recovery of the studied metals for the three sample were as follows:

Sample 1: Cd – 89.5%, Co – 113%, Cu – 91.5%, Ni – 80.5%, Pb – 94.1% and Zn – 111%.
Sample 2: Cd – 80%, Co – 116%, Cu – 94.5%, Ni – 84%, Pb – 117% and Zn 77%
Sample 3: Cd – 79%, Co – 115%, Cu – 89.5%, Ni – 80.5%, Pb – 112% and Zn – 109%.

4.3 Metal Levels in Soils

The mean concentration of the studied metals in the soils at the three study areas and the control are represented in Figure 4.1 and Appendix I. All the values for the studied metals were higher than the control. Soil at Dakace had the lowest values in Co (8.30±0.04

mg/kg) and Pb (69.30±0.04 mg/kg), but highest in Cd (8.00±0.03 mg/kg), Cu (6.50±0.03 mg/kg) and Zn (55.93±0.11 mg/kg) as compared to their corresponding values at Gaskiya and Hanwa soils. The soil at Gaskiya showed lowest value of Cu (5.30±0.03 mg/kg) only, but highest in Co (9.90±0.05 mg/kg) and Ni (84.93±0.07 mg/kg). The soil at Hanwa showed lowest values of Cd (6.00±0.02 mg/kg), Ni (47.90±0.06 mg/kg) and Zn (25.58±0.06 mg/kg), but highest in Pb (76.90±0.05 mg/kg) when compared with those of Dakace and Gaskiya

Figure 4.3 and appendix II show the single contamination index calculated for the triplicate results obtained for the soils at the test and control sites. The mean results indicated that the contamination index for Pb was highest for all the soils, and followed the order Hanwa > Gaskiya > Dakace; for Cd, Dakace > Gaskiya > Hanwa; for Co, Gaskiya > Hanwa > Dakace; for Cu, Dakace > Gaskiya > Hanwa; for Ni, Gaskiya > Dakace > Hanwa; for Zn, Dakace > Gaskiya > Hanwa. The Nemero pollution index (Figure 4.3 and Appendix III) showed that at Dakace study site, Pb > Cd > Ni >Co > Zn > Cu; at Gaskiya site, Pb > Ni > Cd > Co > Zn > Cu; at Hanwa site, Pb > Cd > Co > Ni > Zn > Cu. The grade standard of the Nemero Pollution Index presented in Table 4.3, shows that all the studied soils are clean in respect to Zn and Cu (also Cd and Ni for the control), slightly polluted with Cd, Co, Ni (but in control) and Pb in in control, and very heavily polluted with Pb (and Ni at Gaskiya) but not at the control site.

4.4 Concentration of Metals in Different Fractions of the Soils

Figure 4.4 and Appendix IV show the results of the sequential extraction of metals in different fractions of the soils at Dakace. The bioavailable fractions (F1+ F2+F3) constitute

Table 4.1: Physicochemical Parameters of Soils at the Three Study Areas and the Control

Physicochemical parameters	Dakace	Gaskiya	Hanwa	Control
Particlesize(%): Clay	12	10	15	11
Silt	18	17	7	18
Sand	70	73	78	71
Soil texture	Sandy loamy	Sandy loamy	Sandy loamy	Sandy loamy
Soil pH	6.80±0.02	6.86±0.01	6.78±0.02	7.50±0.03
Moisture content (%)	4.80±0.05	3.90±0.03	4.50±0.03	4.00±0.02
Organic matter (%)	4.53±0.07	5.10±0.05	4.02±0.06	4.87±0.05
Catio exchange cap., CEC, (cmol/kg^{-1})	9.80±0.10	12.80±0.07	10.20±0.15	15.60±0.17
Chloride content (mg/kg)	235.06±35.01	250.46±30.11	240.17±24.05	265.91±32.21
Phosphates content (mg/kg)	3.23±0.11	2.23±0.08	1.73±0.05	1.67±0.03
Nitrates content (mg/kg)	142.43±0.17	156.23±0.10	152.44±0.09	112.56±0.11
Sulphates content (mg/kg)	261.20±1.50	277.34±3.00	268.00±2.50	260.00±2.50

Table 4.2: Percentage Recovery of Metals in Spiked Samples

	Conc. of spiked sample (mg/kg)			Conc. of unspiked sample (mg/kg)			% Recovery		
	1	2	3	1	2	3	1	2	3
Cd	1.92±0.02	1.72±0.02	173±0.03	0.13±0.02	0.12±0.01	0.14±0.03	89.5	80	79
Co	6.49±0.06	2.76±0.07	5.65±0.10	4.23±0.04	1.65±0.06	3.36±0.02	113	116	115
Cu	3.26±0.03	3.56±0.03	3.70±0.02	1.43±0.02	1.67±0.04	1.91±0.03	91.5	94.5	89.5
Ni	1.69±0.05	2.36±0.06	4.09±0.05	0.18±0.05	1.08±0.02	2.48±0.05	80.5	84	80.5
Pb	22.15±0.06	10.63±0.04	10.61±0.01	3.33±0.03	8.29±0.03	8.39±0.05	94.1	117	112
Zn	7.96±0.05	97.82±0.04	6.89±0.03	5.74±0.02	82.42±0.02	4.41±0.11	111	77	109

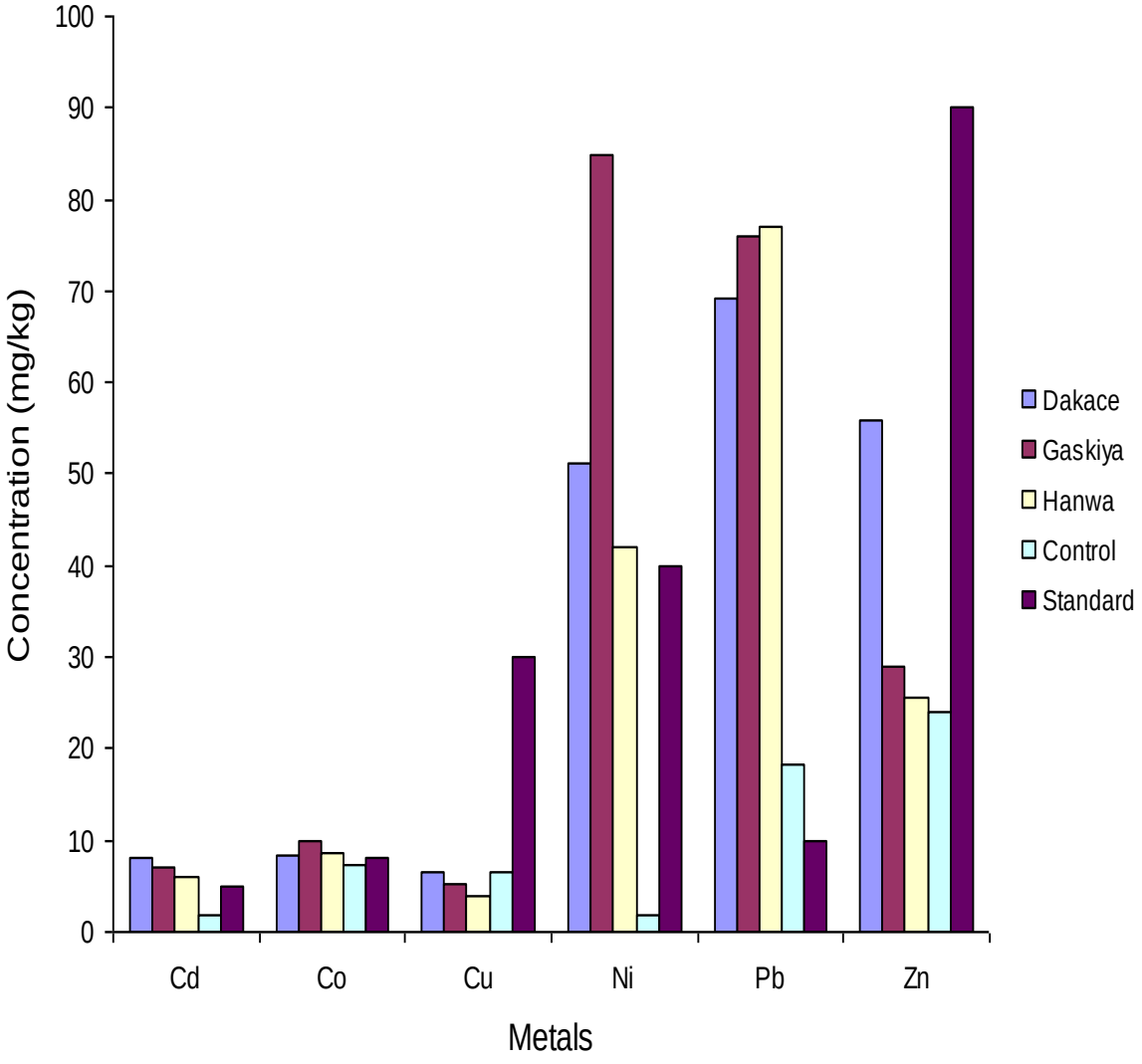


Figure 4.1: Concentrations of Metals at the Study Areas Before Planting

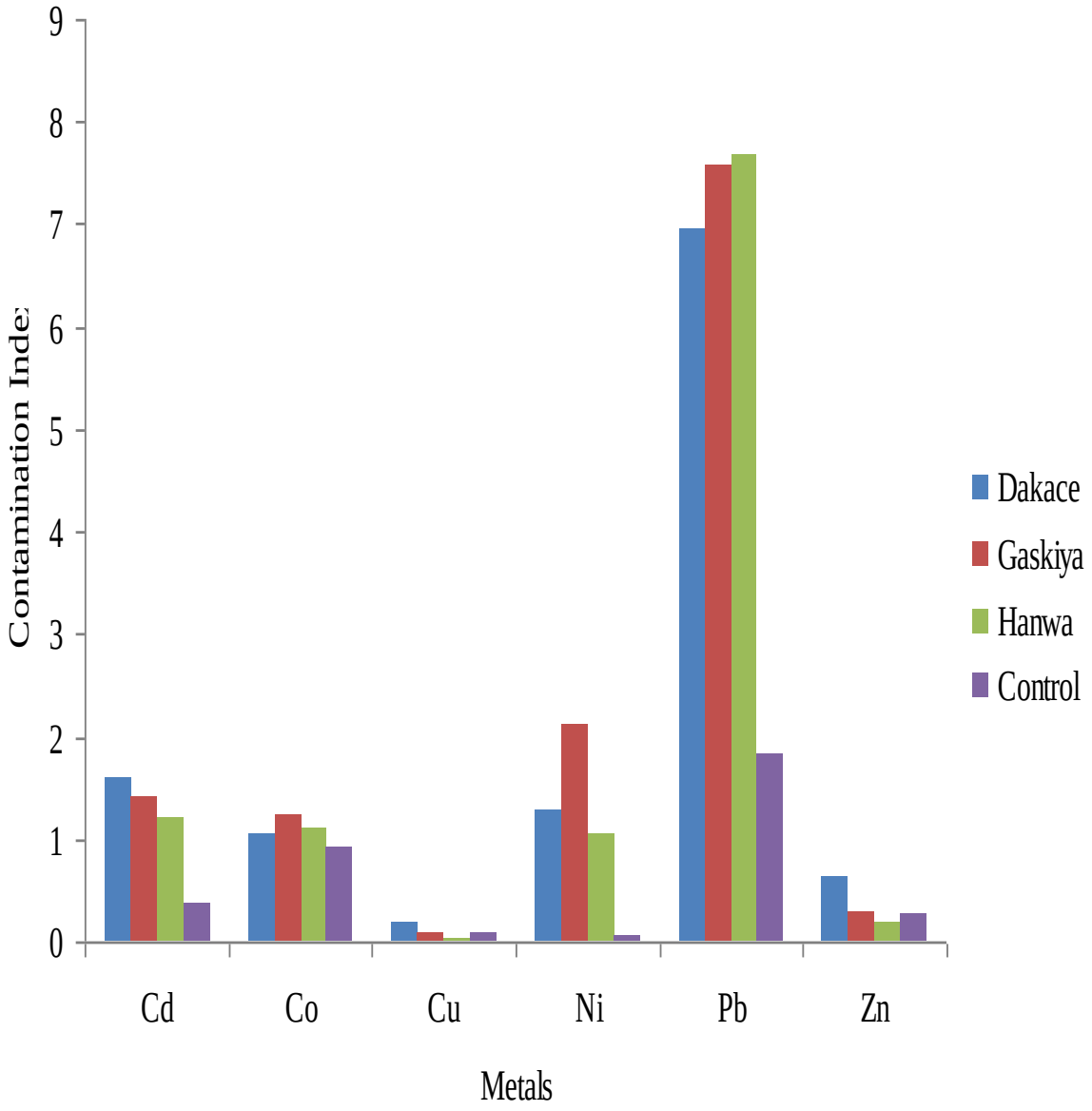


Figure 4.2: Single Contamination Index for Soils at the Study Areas

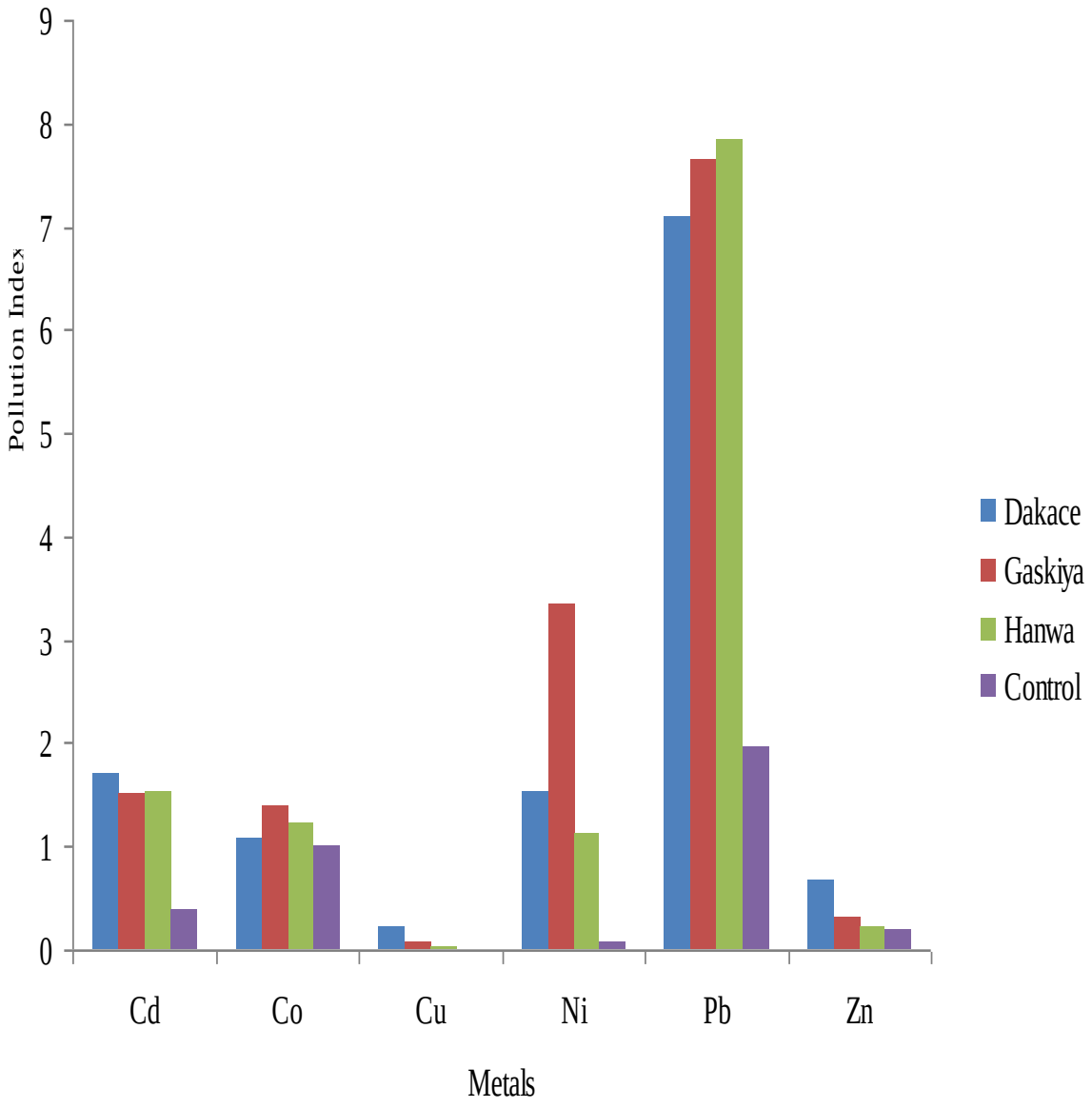


Figure 4.3: Nemero Pollution Index for Soils at the Study Areas

Table 4.3: The Grade Standard of the Nemero Pollution Index Method for Soils Before Planting

	I P≤ 0.7 Clean	II 0.7□ P ≤ 1 warning	III 1 □ P ≤ 2 slight	IV 2 □ P ≤ 3 heavy	V P > 3 very heavy
Dakace	Zn, Cu	-	Cd, Co, Ni	-	Pb
Gaskiya	Zn, Cu	-	Cd, Co	-	Ni, Pb
Hanwa	Zn, Cu	-	Cd, Co, Ni		Pb
Control	Cd, Cu, Ni, Zn	-	Co, Pb	-	-

about 40% Cd, 39% Co, 91% Cu, 66% Ni, 42% Pb and 73% Zn. The residual fraction (F6) has the highest level of Cd (31%) and Co (29%), while the Pb (21%) was highest in organic fraction (F5).

At Gaskiya study area (Figure 4.5 and Appendix V), the bioavailable fractions (F1+F2+F3) for Cd, Co, Cu, Ni, Pb and Zn were 39%, 48%, 74%, 59%, 41% and 60% respectively. The highest percentage of Cd (36%) was found in the residual fraction (F6), Co was 18%, 20% and 19% in F3, F5 and F6 respectively. The percentage of Cu found in F5 was 16%. For Pb, 18% - 21% were found in other fractions (F4 – F6). The organic fraction (F5) contains about 22% Zn, while the Fe – Mn oxides had 16% Zn.

Hanwa study area (Figure 4.6 and Appendix VI) showed that Co, Cu, Ni and Zn were highest in the exchangeable fraction (F2), while Cd (32%) and Pb (20%) were highest in residual (F6) and organic fraction (F5) respectively. The predominant form of Cd (32%) available in the entire fractions is the residual fraction. Up to 79% of Zn is bioavailable (F1+F2+F3), while other fractions are weak. A good proportion of Cu (27%) was found in the organic fraction (F5).

At the Control site, the different fractions contain various metal levels as shown in Figure 4.7 and Appendix VII. The percentage bioavailability (F1+ F2+F3) of the studied metals were: Cd - 38%, Co – 36%, Cu – 59%, Ni – 50%, Pb – 39% and Zn – 44%. The highest percentage of Cd (32%) was found in the residual fraction (F6), Co was 19% and 14% in F5 and F6 respectively. The percentage of Cu found in F4 and F5 were 18% and 43% respectively. For Pb, 14% - 23% were found in other fractions (F4 – F6). The organic fraction

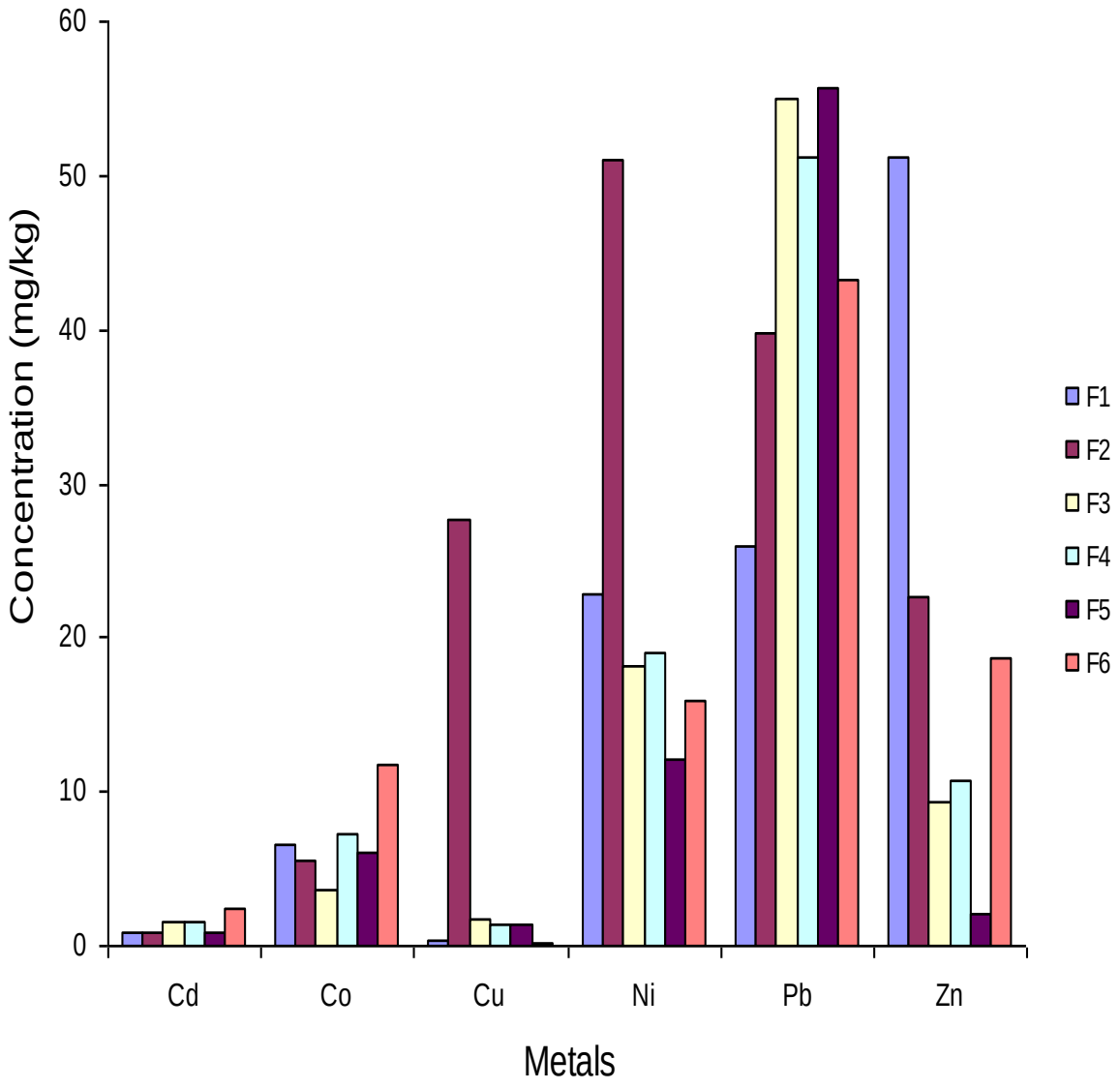


Figure 4.4: Concentrations (mg/kg) of Metals in Different Fractions of the Soil at Dakace

F1= water soluble Fraction, F2 = Exchangeable Fraction, F3 = Carbonate bound Fraction, F4 = Fe and Mn oxides bound Fraction, F5 = Organic matter bound Fraction, F6 = Residual Fraction.

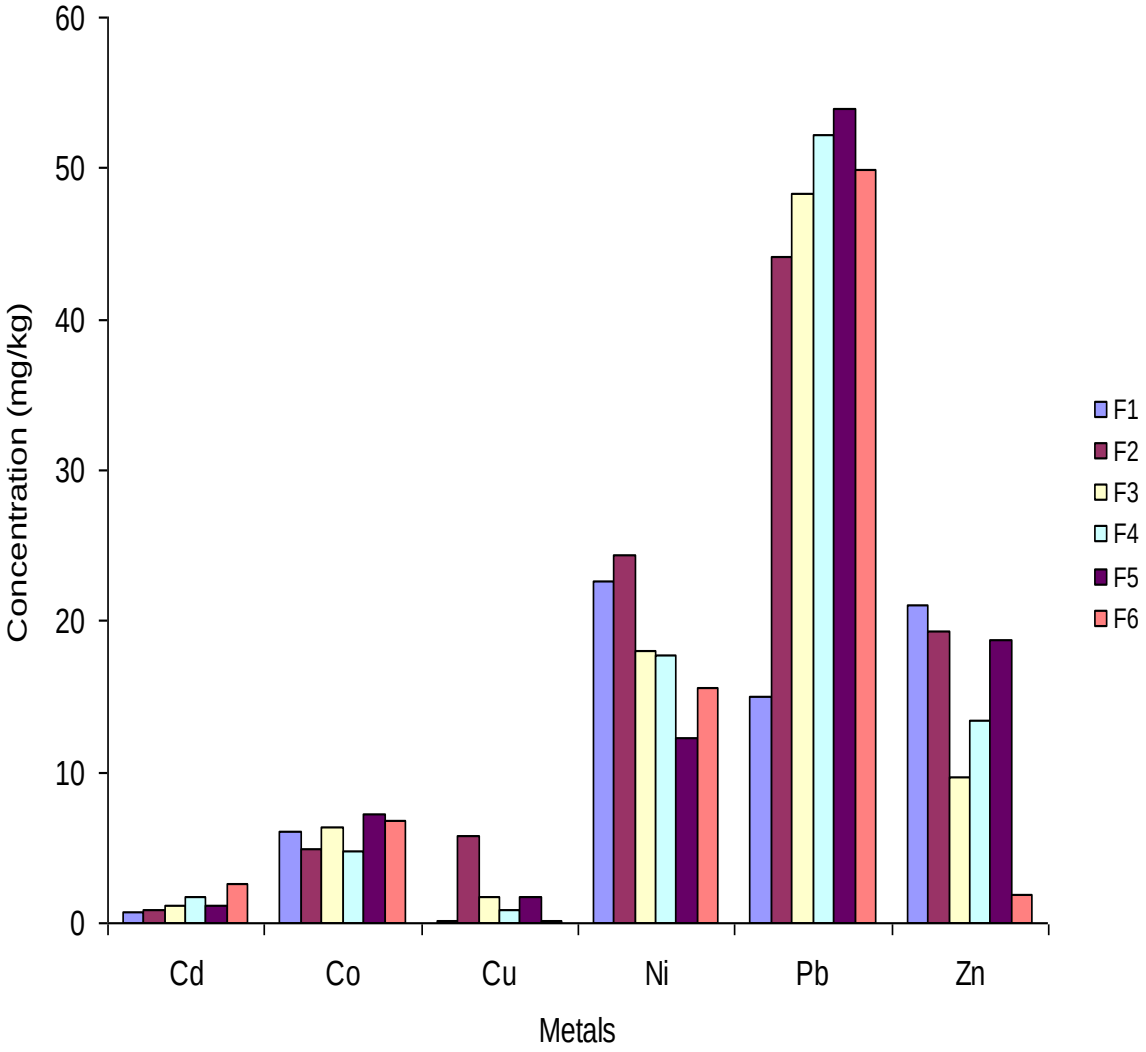


Figure 4.5: Concentrations (mg/kg) of Metals in Different Fractions of the Soil at Gaskiya

F1= water soluble Fraction, F2 = Exchangeable Fraction, F3 = Carbonate bound Fraction, F4 = Fe and Mn oxides bound Fraction, F5 = Organic matter bound Fraction, F6 = Residual Fraction.

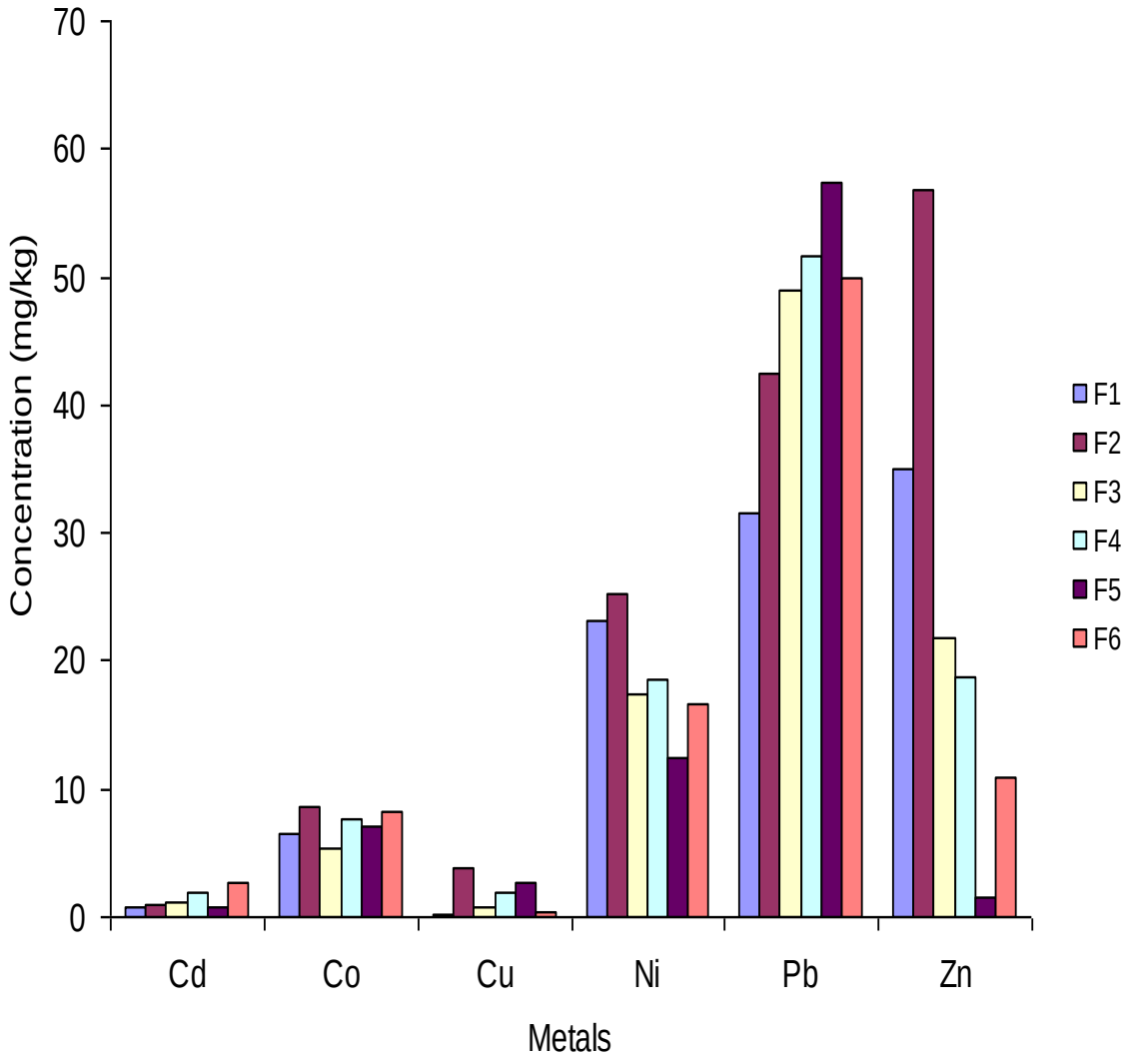


Figure 4.6: Concentrations (mg/kg) of Metals in Different Fractions of the Soil at Hanwa

F1= water soluble Fraction, F2 = Exchangeable Fraction, F3 = Carbonate bound Fraction, F4 = Fe and Mn oxides bound Fraction, F5 = Organic matter bound Fraction, F6 = Residual Fraction

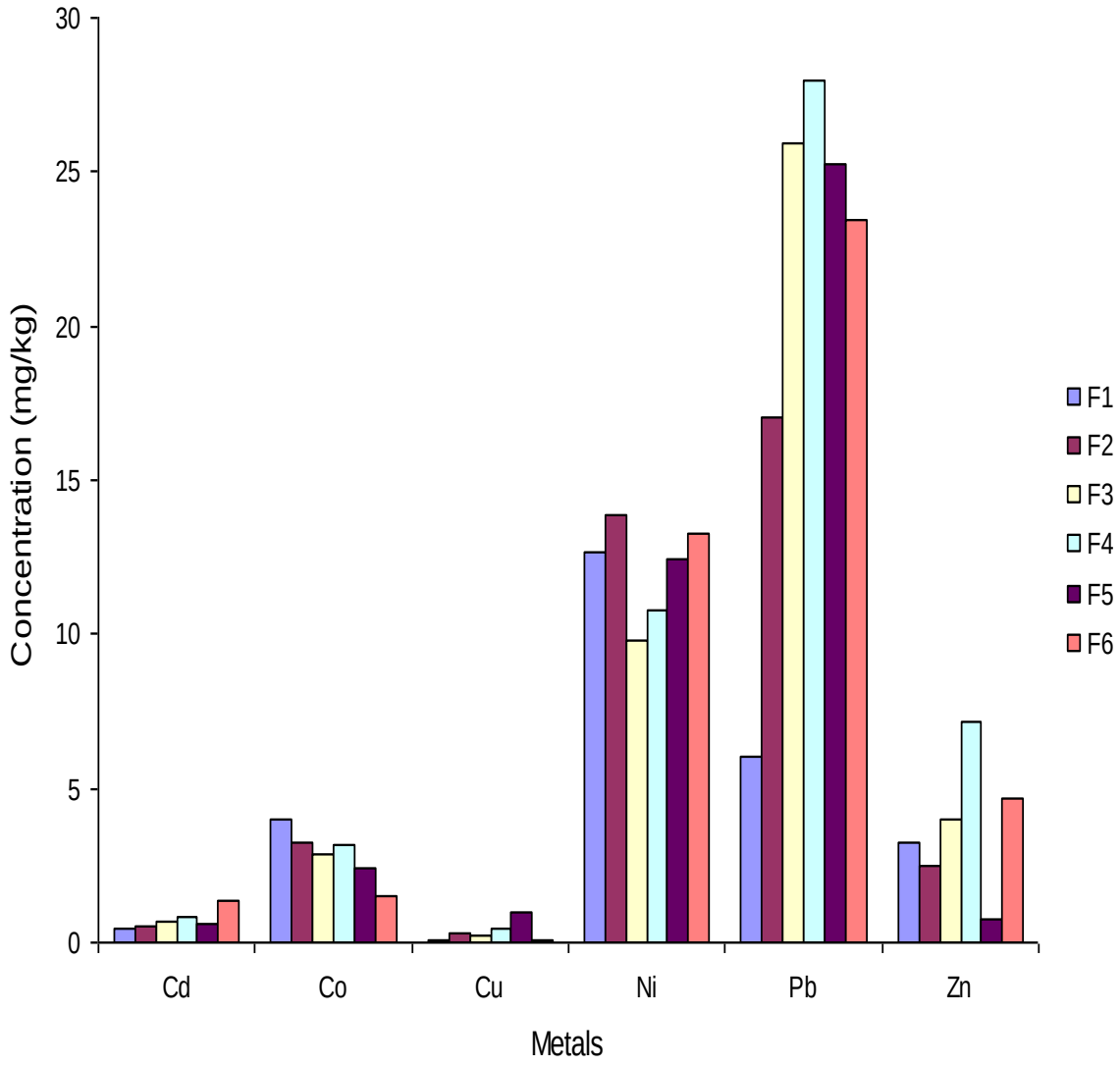


Figure 4.7: Concentrations (mg/kg) of Metals in Different Fractions of the Soil at Control Site

F1= water soluble Fraction, F2 = Exchangeable Fraction, F3 = Carbonate bound Fraction, F4 = Fe and Mn oxides bound Fraction, F5 = Organic matter bound Fraction, F6 = Residual Fraction.

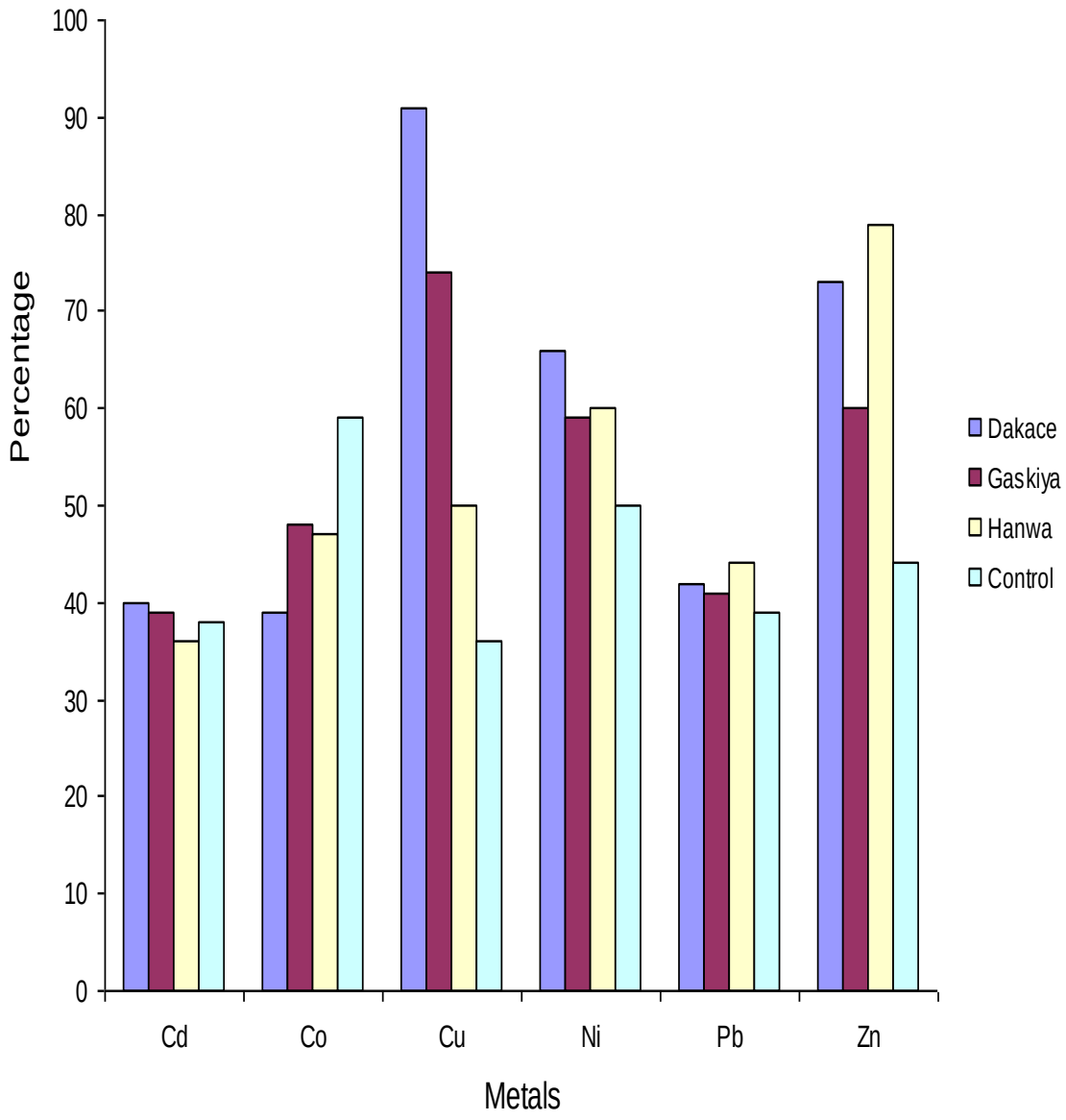


Figure 4.8: Percentage Bioavailability of Metals at the Study Areas

(F5) contain about 1% Zn, while the Fe – Mn oxides (F4) had 33% Zn, the residual (F6) fractions had 21% Zn.

4.5 Bioavailability of the Metals Analysed in the Soils

The percentage bioavailability of the metals analysed in the soils at the three study areas and the control soils was calculated and presented in Figure 4.8 and in Appendix VIII. The water soluble fraction (F1), the exchangeable fraction (F2) and the carbonate fraction (F3) make up the biovailable fraction of the metals in the different soils.

At Dakace, Cu (91%) > Zn (73%) > Ni (66%) > Pb (42%) > Cd (40%) > Co (39%); At Gaskiya, Cu (74%) > Zn (60%) > Ni (59%) > Co (48%) > Pb (41%) > Cd (39%); At Hanwa, Zn (79%) > Ni (60%) > Cu (50%) > Co (47%) > Pb (44%) > Cd (36%); At Control, Cu (59%) > Ni (50%) > Zn (44%) > Pb (39%) > Cd (38%) > Co (36%).

4.6 Metal Content in Different Parts of Plant Species without EDTA Application at Dakace Soil.

4.6.1 Metal concentration in different parts of *Vetivera zizanioide* plant

The result of the metal concentration in different parts of *Vetivera zizanioide* plant harvested from Dakace soil near a metal-scrap dumpsite and the control site is presented in Figure 4.9 and Appendix IX . The results indicated that there was a general increase in metal concentration from the roots to the leaves for all the elements studied for the test and control samples. The leaves contained 2.10±0.01 mg/kg of Cd, 5.30.±0.07 mg/kg of Co, 4.30±0.01 mg/kg of Cu, 9.50±0.02 mg/kg of Ni, 50.50±0.04 mg/kg of Pb and 85.90±0.04 mg/kg of Zn. The roots contained 1.90±0.03 mg/kg of Cd, 5.20±0.03 mg/mg of Co, 3.00±0.04 mg/kg of Cu, 8.10±0.02 mg/kg of Ni, 50.10±0.02 mg/kg of Pb and 20.52±0.06 mg/kg. Both the BF and TF (Figure 4.10) for the metals were greater than 1 except cobalt

and lead had their BF less than 1. The BF of the elements were in the order of Cu > Ni > Cd ≈ Zn > Pb > Co, while the TF was Zn > Cu > Ni > Cd ≈ Co ≈ Pb.

4.6.2 Concentrations of the studied metals in different parts *Cymbopogon citratus* plant

The concentrations of the studied metals in different parts of *Cymbopogon citratus* plant harvested from the test site at Dakace and the control site are presented in Figure 4.11 and Appendix X. The concentrations of the metals in the leaves were as follows: Cd - 2.60±0.03 mg/kg, Co - 6.40±0.04 mg/kg, Cu - 1.60±0.03 mg/kg, Ni - 7.70±0.03 mg/kg, Pb - 46.20±0.01 mg/kg and Zn - 51.41±0.0 mg/kg. The roots contained 2.00±0.02 mg/kg of Cd, 5.00±0.02 mg/kg of Co, 0.90±0.03 mg/kg of Cu, 6.20±0.10 mg/kg of Ni, 42.20±0.01 mg/kg of Pb and 22.54±0.0 of Zn. These concentrations at the test site were higher than those of the control site. The BF of Cd, Ni and Pb were greater than 1 while that of Co, Cu and Zn were less than 1. The TF of all the metals studied were greater than 1. The BF of the studied metals were in the order of Ni > Cd > Pb > Zn > Co ≈ Cu, while the TF followed the order: Cu > Zn > Co > Cd > Ni > Pb and all greater than 1 (Figure 4.12).

4.6.3 Metal concentrations in different parts of *Helianthus annus* (sunflower) plant

The metal concentrations in different parts of *Helianthus annus* (sunflower) plant harvested from Dakace test site and the control soil are presented in Figure 4.13 and Appendix XI. The metal concentrations in the leaves were as follows: Cd - 3.30±0.05 mg/kg, Co - 6.90±0.09 mg/kg, Cu - 28.20±0.02 mg/kg, Ni - 9.60±0.01mg/kg, Pb - 40.50±0.02 mg/kg, Zn - 103.50±0.08 mg/kg; in the stems Cd - 2.40±0.01 mg/kg, Co - 2.40±0.05 mg/kg, Cu - 21.80±0.02 mg/kg, Ni - 9.80±0.02 mg/kg, Pb - 36.00±0.01 mg/kg, Zn - 63.93±0.11 mg/kg; and in the roots Cd - 2.10±0.02 mg/kg, Co - 1.40±0.04 mg/kg, Cu - 13.10±0.05 mg/kg, Ni - 7.80±0.04 mg/kg, Pb - 18.20±0.02 mg/kg and Zn - 54.64±0.05

mg/kg. All the studied metal values were higher than those of the control. Figure 4.14 shows that the BF for Cd, Cu and Zn were greater than 1 while TF for all the metals found to be greater than 1. The BF and TF followed the order: Cu > Cd > Zn > Pb > Co > Ni, and Co > Cu > Zn > Cd ≈ Ni > Pb respectively.

4.6.4 Metal concentrations in different parts of *Ipomoea asarifolia* plant

The metal concentrations in different parts of *Ipomoea asarifolia* plant harvested from Dakace test site and the control soil are presented in Figure 4.15 and Appendix XII. The leaves had highest metal levels for Ni (22.20±0.04 mg/kg), Cu (14.90±0.03 mg/kg), Co (3.60±0.03 mg/kg) and Zn (37.64±0.11 mg/kg), but Cd (1.80±0.05 mg/kg) and Pb (41.00±0.03 mg/kg) were highest in the roots. The test values were higher than the control values. Only Cu had its BF greater than 1 and the TF for the metals were greater than 1 except Cd and Pb (Figure 4.16). The BF and TF followed the order: Cu > Cd > Zn > Pb > Co > Ni and Ni > Cu > Co ≈ Zn > Pb >Cd respectively.

4.6.5 Metal concentrations in different parts of *Ricinus communis* plant

The metal concentrations in different parts of *Ricinus communis* plant harvested from Dakace test site and the control soil are presented in Figure 4.17 and Appendix XIII. The result indicated that there is a variation in the metal levels in the leaves, stems and roots of the plant. The concentrations of metals in levels are: Zn (35.94±0.03mg/kg) > Pb (25.70±0.06mg/kg) > Ni (12.90±0.05mg/kg) > Cu (8.40±0.03mg/kg) > Co (6.20±0.03mg/kg) > Cd (2.30±0.02mg/kg); the stem: Zn (45.73±0.02mg/kg) > Pb (19.90±0.02mg/kg) > Ni (11.80±0.02mg/kg) > Cu (6.80±0.02mg/kg) > Co (6.10±0.02mg/kg) > Cd (2.10±0.02mg/kg); the roots: Zn (39.73±0.16mg/kg) > Pb (22.00±0.04mg/kg) > Ni (7.60±0.08mg/kg) > Co (4.10±0.02mg/kg) >Cu (2.90±0.04mg/kg) > Cd (2.10±0.03mg/kg). The BF for Cd and Ni were greater than 1 while those of Co, Cu, Pb and Zn were less than 1. All the metals had their TF greater than 1 (Figure 4.18). The BF and TF were in the order: Ni > Cd > Cu > Co ≈ Zn > Pb and Cu > Ni > Co > Cd ≈ Zn ≈ Pb respectively.

4.7 Bioaccumulation and Transfer Factors for the Metals in Different Plant Species at Dakace

The BF and TF for the studied metals in different plant species harvested from Dakace soil are presented in Figures 4.19 to 4.24 and Appendex XIV. For Cd, the BF is in the order of *Helianthus annus* (1.4) > *Cymbopogon citratus* (1.3) > *Ricinus communis* (1.2) > *Vetivera zizanioide* (1.1) > *Ipomoea asarifolia* (0.9), TF is in the order of *Helianthus annus* (1.4) > *Cymbopogon citratus* (1.3) > *Vetivera zizanioide* (1.1) > *Ricinus communis* (1.0) > *Ipomoea asarifolia* (0.8). For cobalt, the BF in the order of *Cymbopogon citratus* (0.7) ≈ *Ricinus communis* (0.7) > *Vetivera zizanioide* (0.6) ≈ *Helianthus annus* (0.6) > *Ipomoea asarifolia* (0.4), TF was in the order of *Helianthus annus* (3.3) > *Cymbopogon citratus* (1.3) > *Vetivera zizanioide* (1.1) ≈ *Ipomoea asarifolia* (1.1) > *Ricinus communis* (0.7). The BF for Cu:- *Helianthus annus* (3.2) > *Vetivera zizanioide* (1.9) > *Ipomoea asarifolia* (1.7) > *Cymbopogon citratus* (0.7) ≈ *Ricinus communis* (0.7), the TF was in the order of *Ricinus communis* (2.6) > *Helianthus annus* (1.9) > *Cymbopogon citratus* (1.8) > *Vetivera zizanioide* (1.4) ≈ *Ipomoea asarifolia* (1.4). The BF for Ni:- *Ricinus communis* (2.2) > *Vetivera zizanioide* (1.8) > *Cymbopogon citratus* (1.4) > *Helianthus annus* (0.2) ≈ *Ipomoea asarifolia* (0.2), while TF was indicated that *Ipomoea asarifolia* (2.2) > *Ricinus communis* (1.6) > *Helianthus annus* (1.4) > *Vetivera zizanioide* (1.2) ≈ *Cymbopogon citratus* (1.2). For Pb, BF - *Cymbopogon citratus* (1.0) > *Vetivera zizanioide* (0.7) > *Helianthus annus* (0.6) > *Ipomoea asarifolia* (0.5) > *Ricinus communis* (0.3), TF - *Ricinus communis* (1.1) ≈ *Cymbopogon citratus* (1.1) > *Helianthus annus* (1.0) ≈ *Vetivera zizanioide* (1.0) > *Ipomoea asarifolia* (0.9). The BF for Zn - *Helianthus annus* (1.3) > *Vetivera zizanioide* (1.0) > *Cymbopogon citratus* (0.9) > *Ricinus communis* (0.7) > *Ipomoea asarifolia* (0.6). Then TF was in the order of *Vetivera zizanioide* (4.2) > *Cymbopogon citratus* (2.3) > *Helianthus annus* (1.5) > *Ricinus communis* (1.1) ≈ *Ipomoea asarifolia* (1.1).

4.8 Metal Content in Different Parts of Plant Species without EDTA Application at Gaskiya Soil

4.8.1 Metal concentration in different parts of *Vetivera zizanioide* plant

The result of the metal concentration in different parts of *Vetivera zizanioide* plant harvested from Gaskiya soil near a metal-scrap dumpsite and the control site is presented

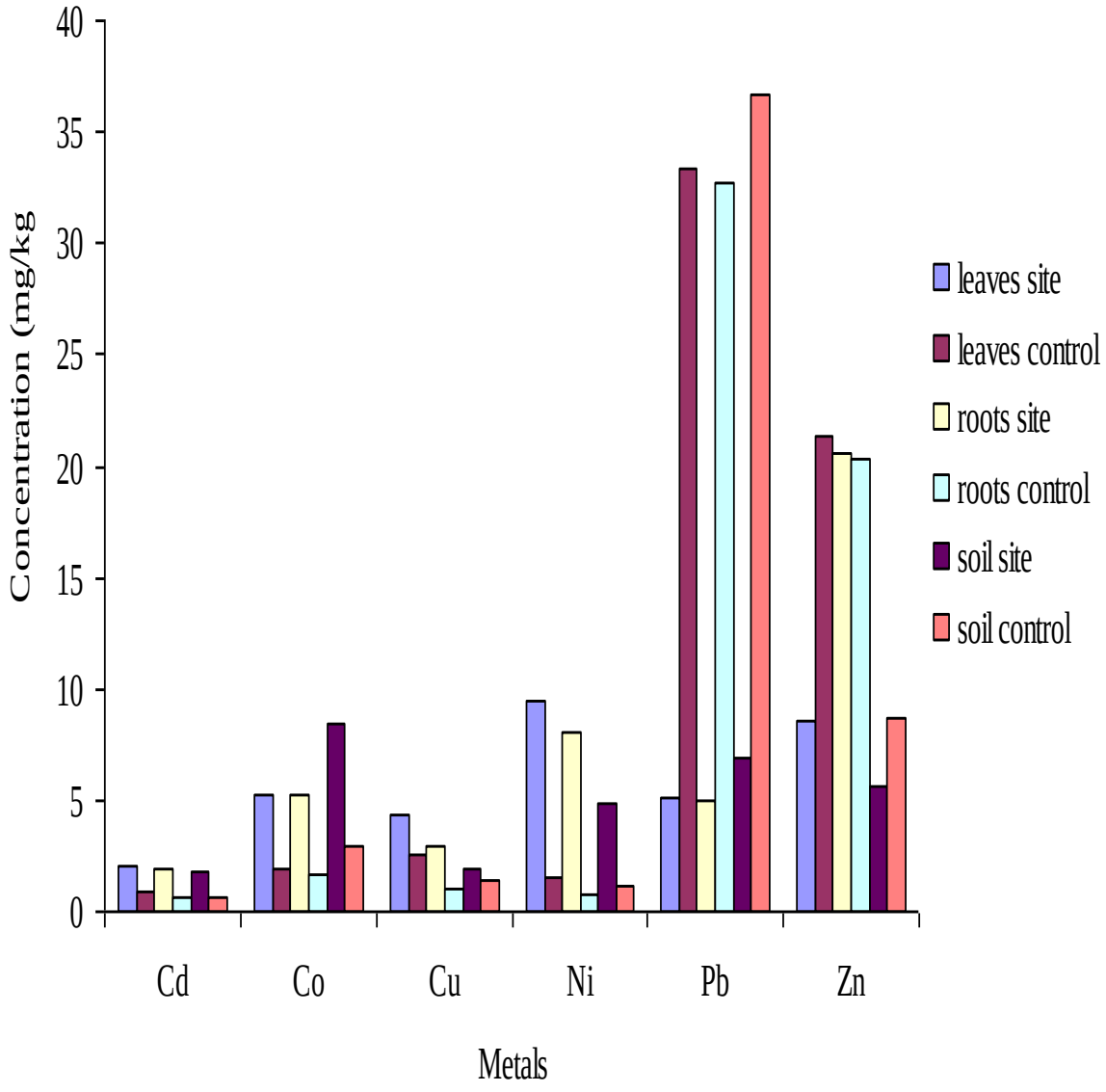


Figure 4.9: Concentrations (mg/kg) of Metals in Different Parts of *Vetivera zizanioide* Plant and the Soil at Dakace

*Pb (soil) = 5.59 x 10, Pb (roots) = 5.01 x 10, Pb (leaves) = 5.05 x 10, Zn (leaves) = 8.59 x 10, Zn (soil)5.93 x 10

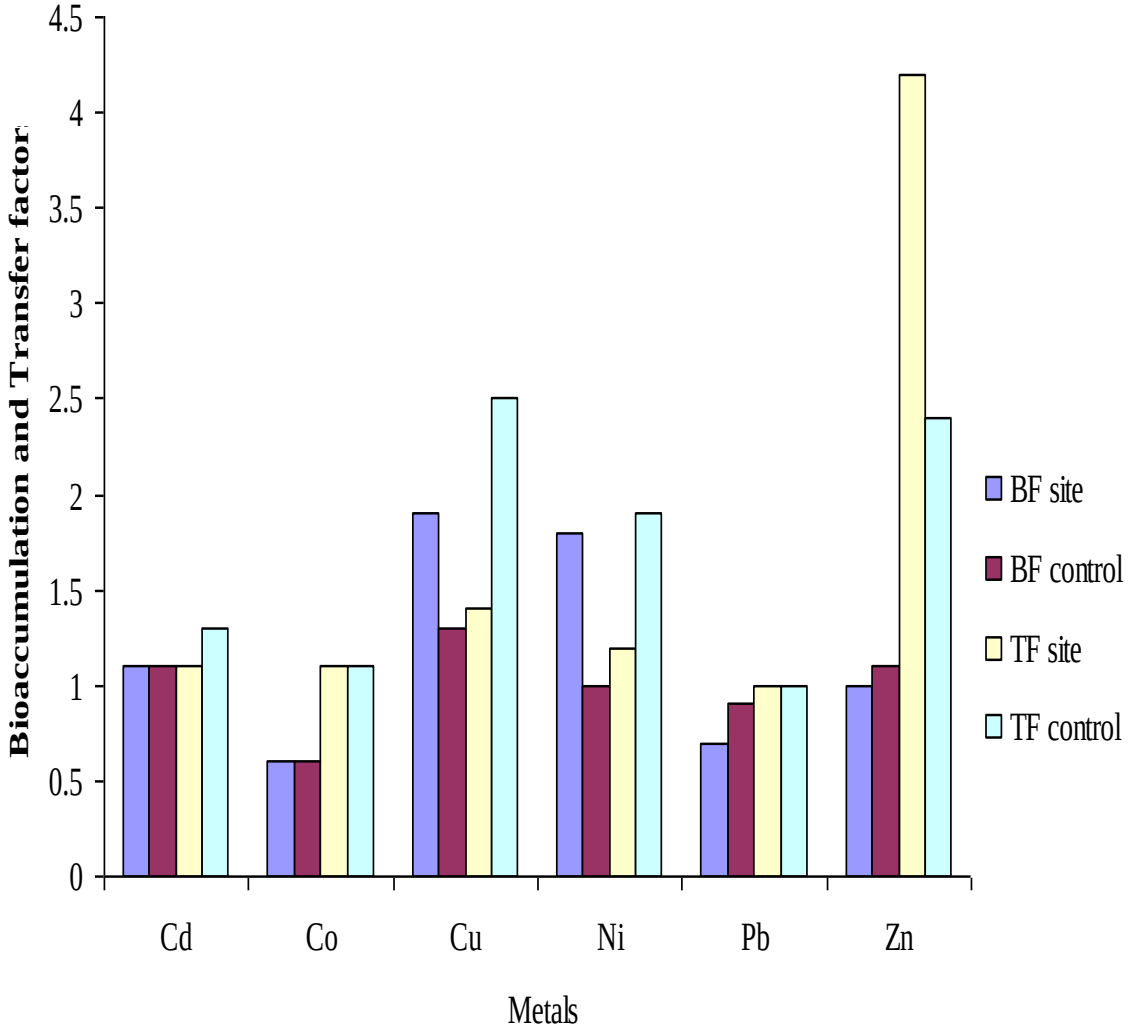


Figure 4.10: Bioaccumulation and Transfer Factors in *Vetivera zizaniodes* Plant at Dakace

BF = Bioaccumulation factor; TF = Translocation factor.

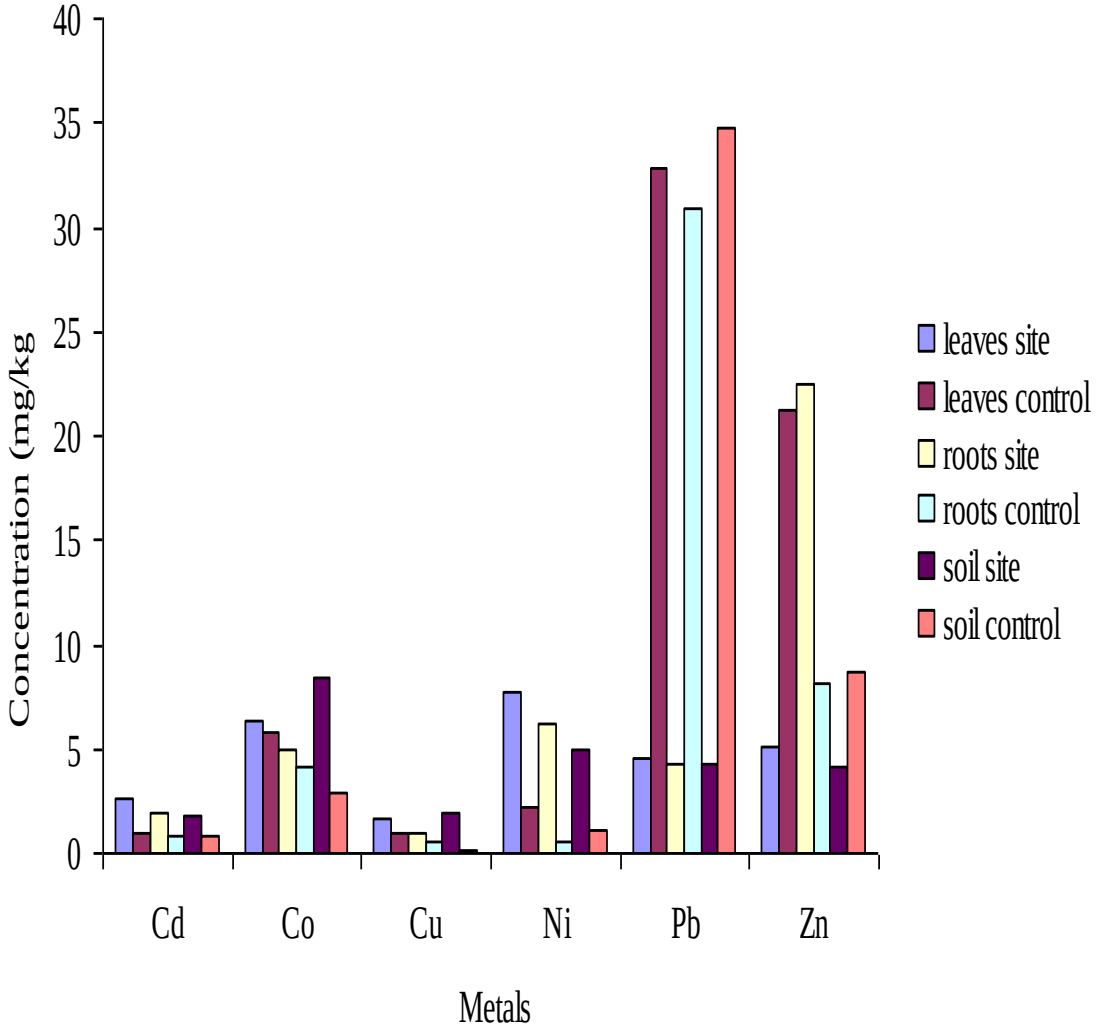


Figure 4.11: Concentrations (mg/kg) of Metals in Different Parts of *Cymbopogon citratus* Plant and the Soil at Dakace

*Pb (leaves) = 4.62 x 10, Pb (roots) = 4.22 x 10, Pb (soil) = 4.28 x 10, Zn (leaves) = 5.141 x10, Zn (soil) = 4.133 x 10

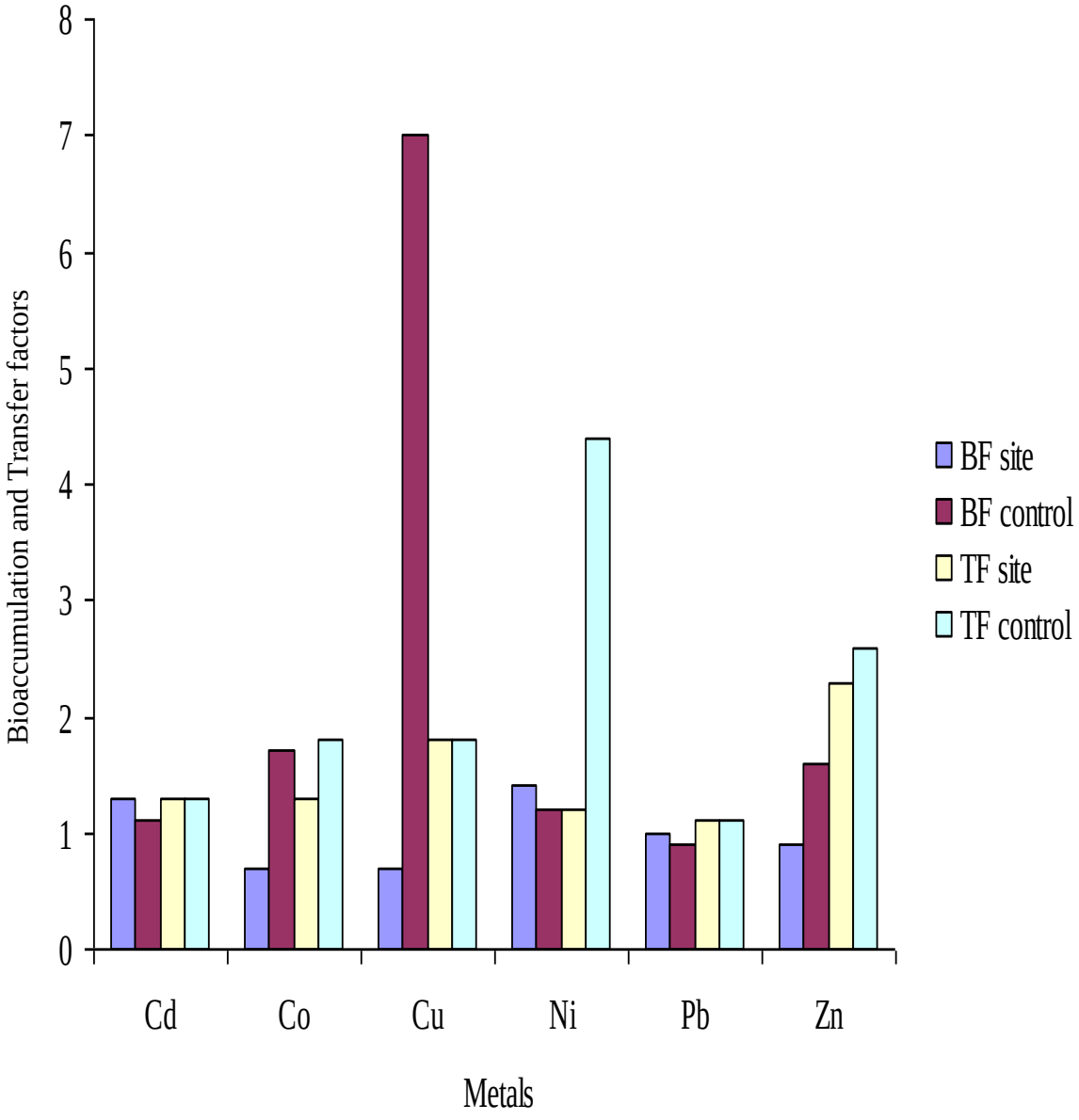


Figure 4.12: Bioaccumulation and Transfer Factors of *Cymbopogon citratus* Plant at Dakace

BF = Bioaccumulation factor; TF = Translocation factor.

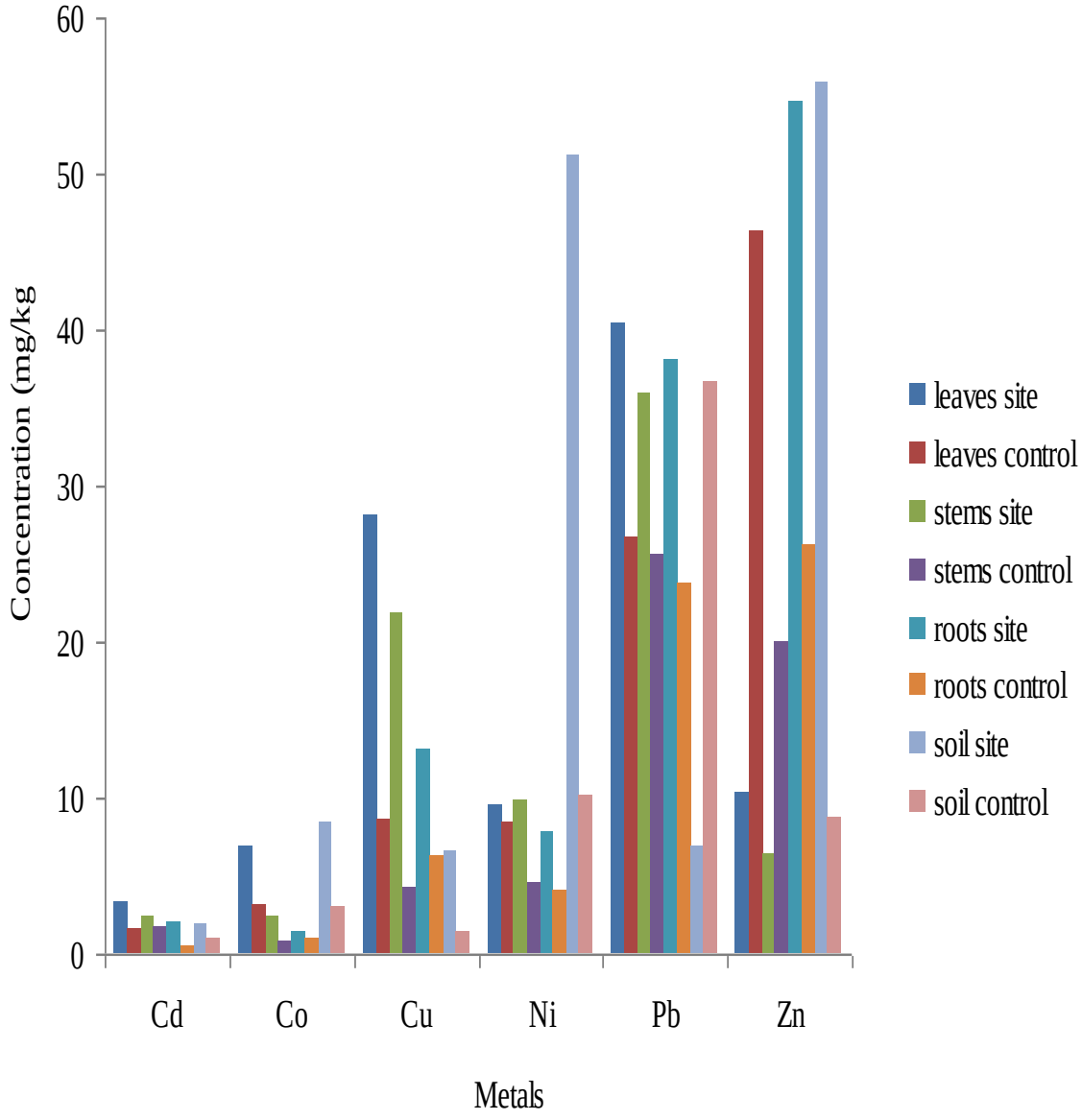


Figure 4.13: Concentrations (mg/kg) of Metals in Different Parts of *Helianthus annus* Plant and Soil at Dakace

* Zn (leaves) = 10.35 x10, Zn (stems) 6.393 x 10, Pb (soil) = 6.93 x 10

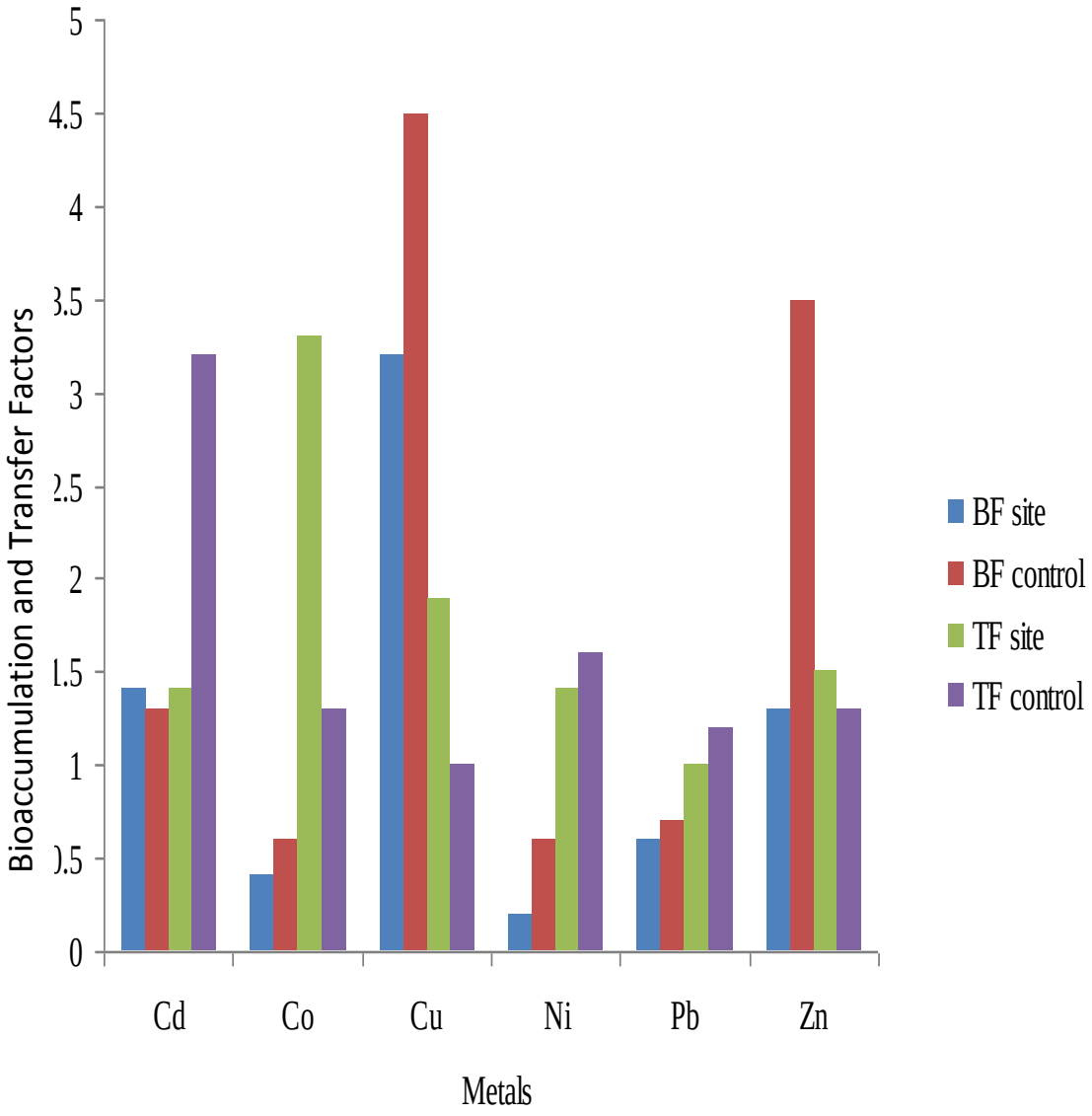


Figure 4.14: Bioaccumulation and Transfer Factors of Metals for *Helianthus annus* at Dakace

BF = Bioaccumulation factor; TF = Translocation factor.

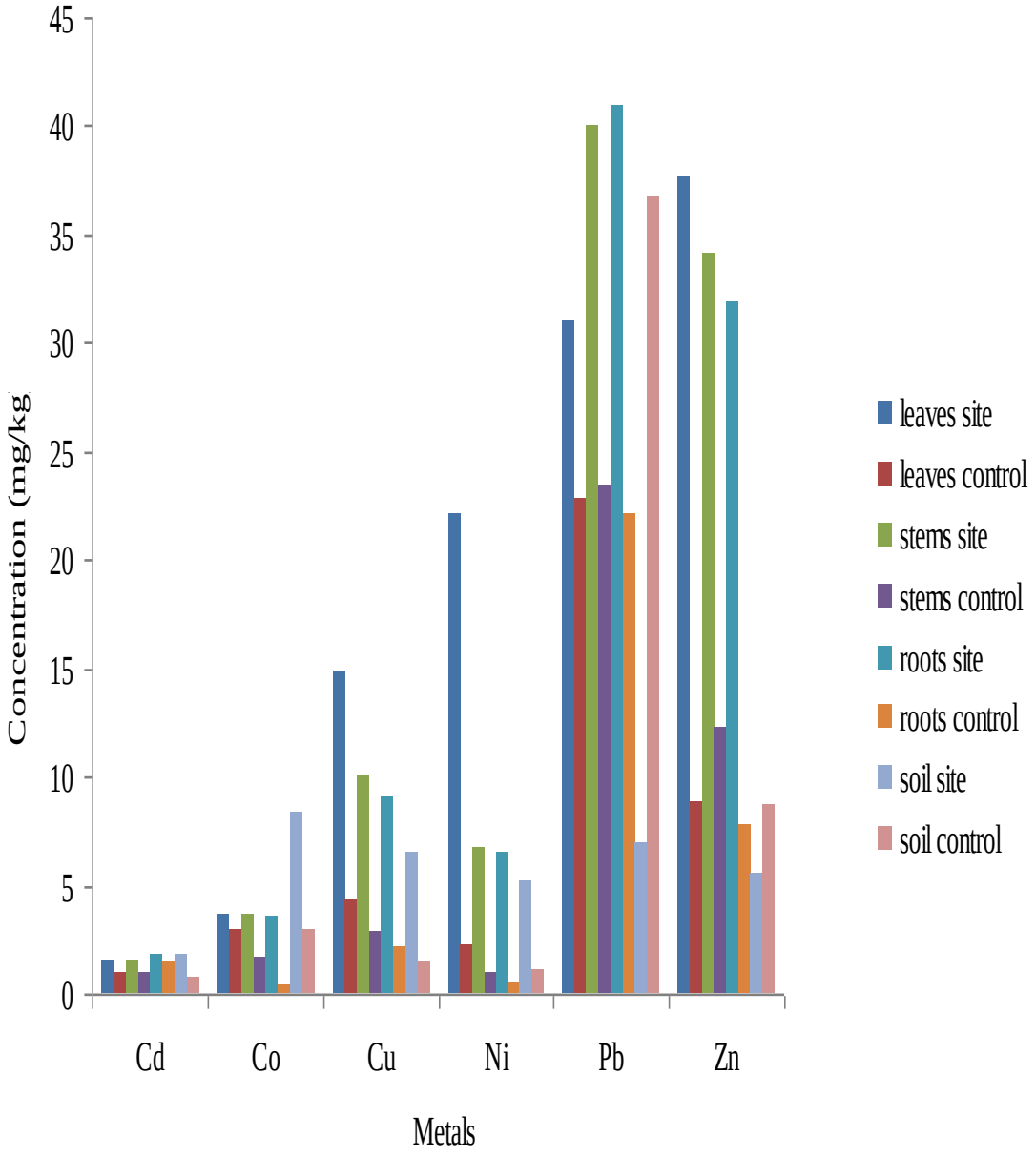


Figure 4.15: Concentrations (mg/kg) of Metals in Different Parts of *Ipomoea asarifolia* Plant and Soil at Dakace

* Ni (soil) = 5.13 x 10; Pb (soil) = 6.93 x 10 ; Zn (soil) = 5.593 x 10

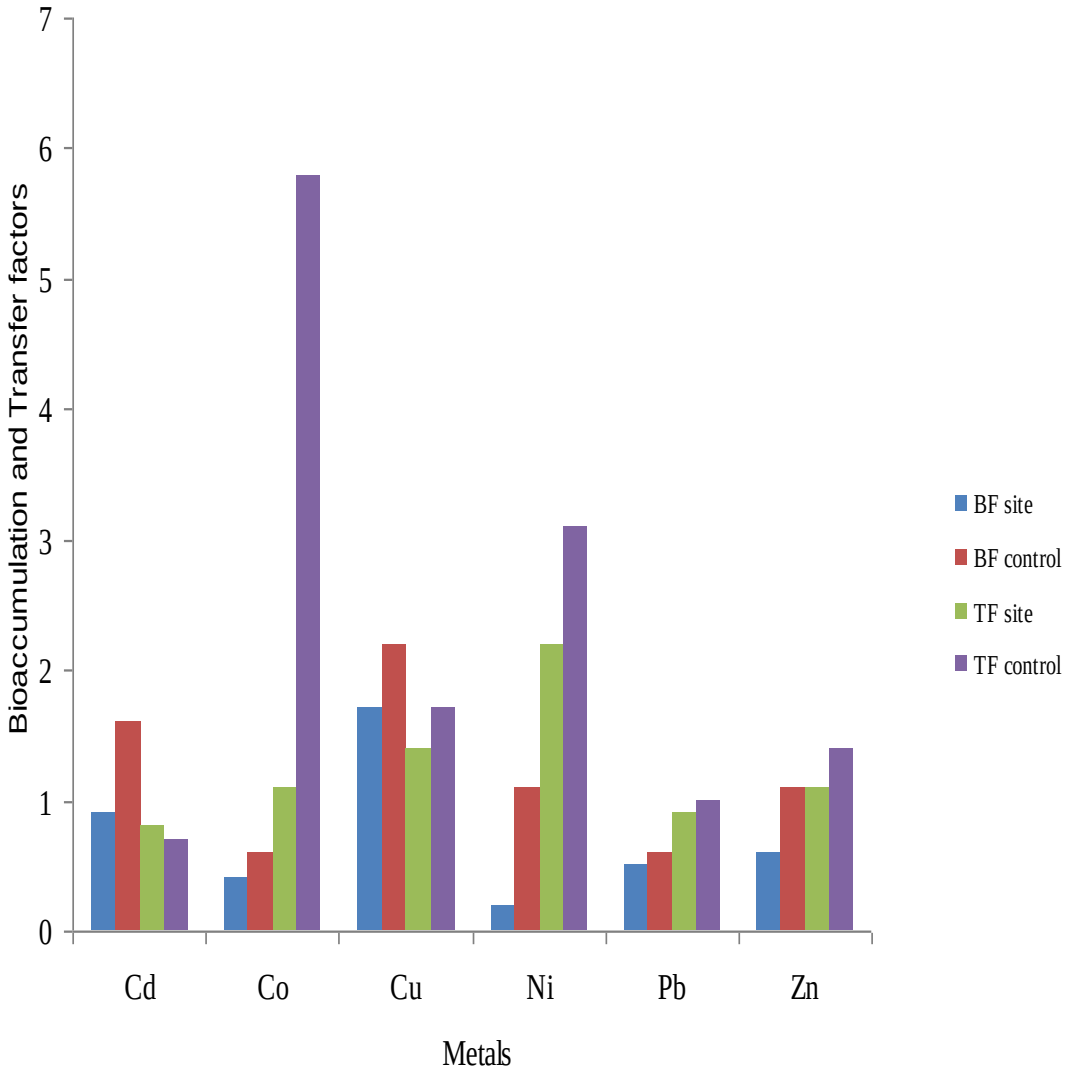


Figure 4.16: Bioaccumulation and Transfer Factors of Metals for *Ipomoea asarifolia* Plant at Dakace

BF = Bioaccumulation factor; TF = Translocation factor.

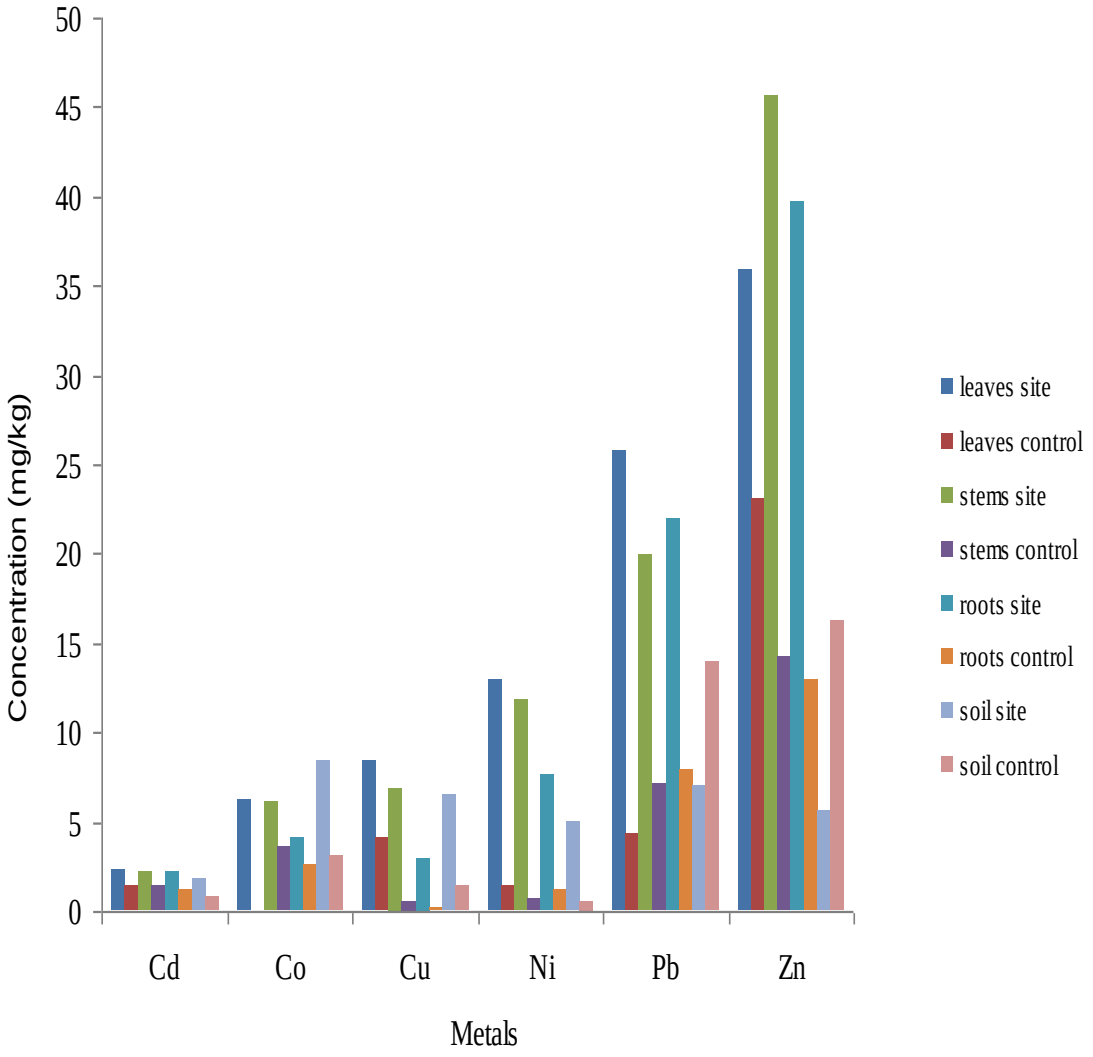


Figure 4.17: Concentrations (mg/kg) of Metals in Different Parts of *Ricinus communis* Plant and Soil at Dakace

* Pb (soil) = 6.93 x 10, Zn (soil) = 5.593 x 10

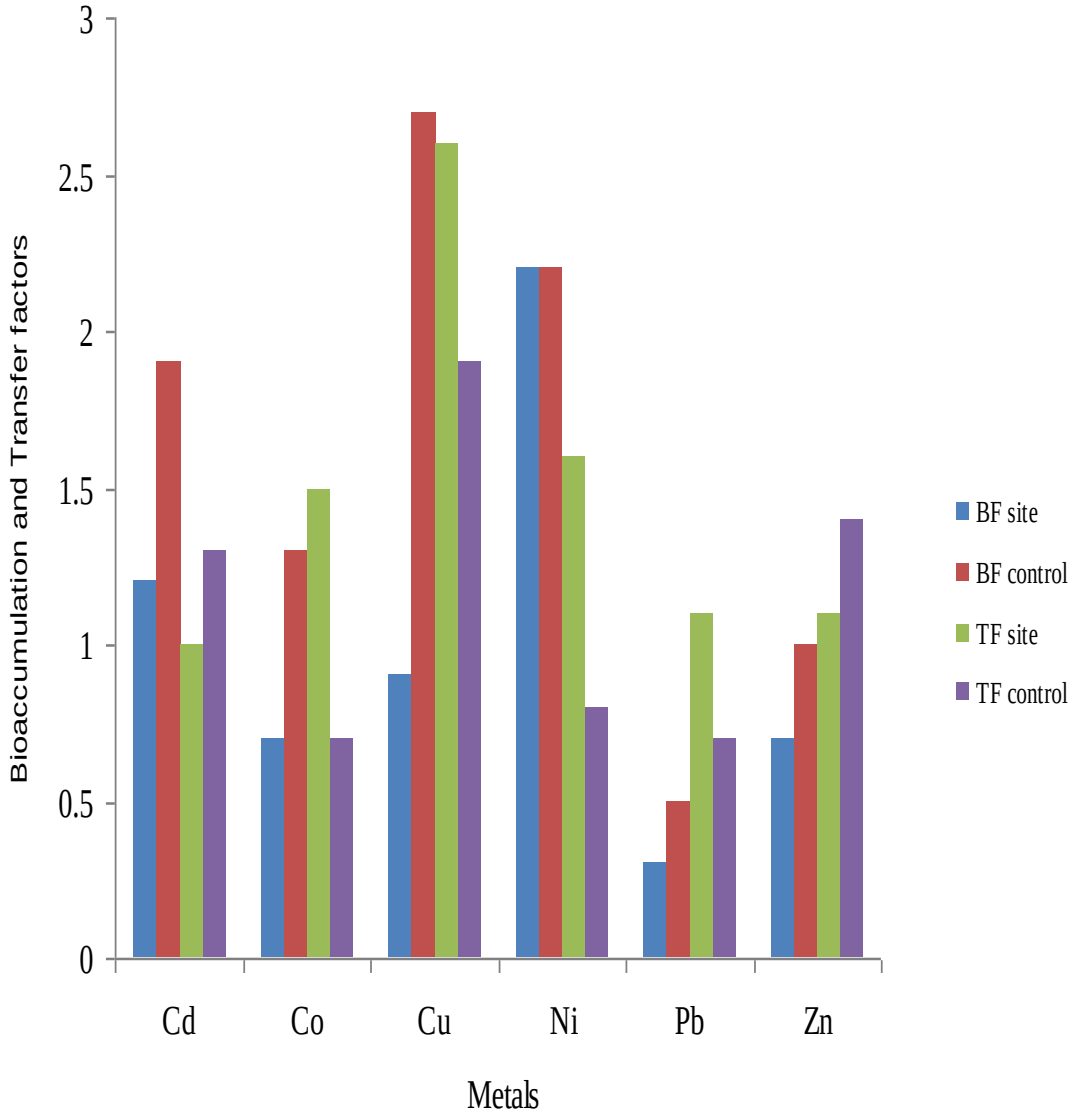


Figure 4.18: Bioaccumulation and Transfer Factors of Metals for *Ricinus communis* Plant at Dakace

BF = Bioaccumulation factor; TF = Translocation factor.

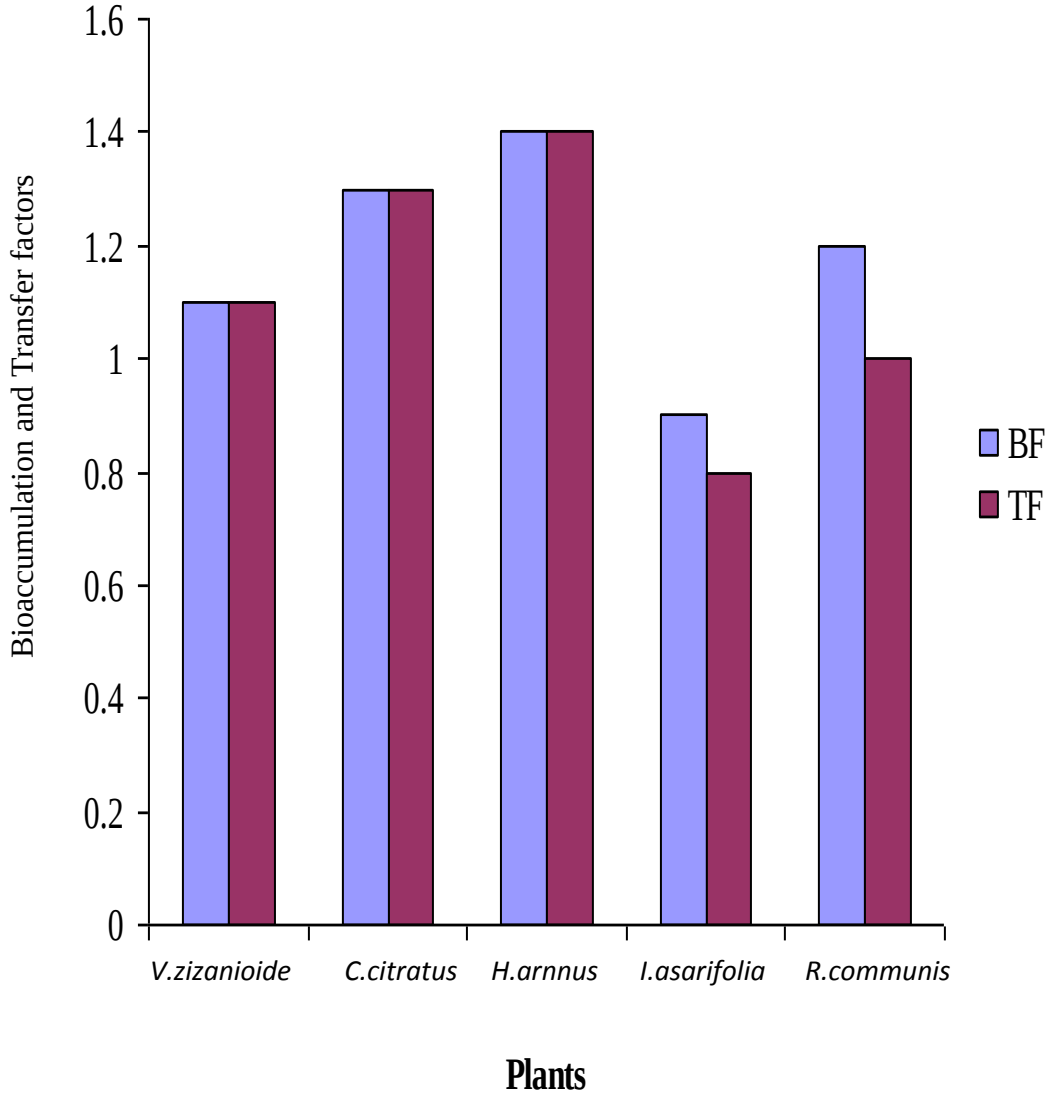


Figure 4.19: Bioaccumulation and Transfer Factors for Cadmium in Different Plant Species at Dakace

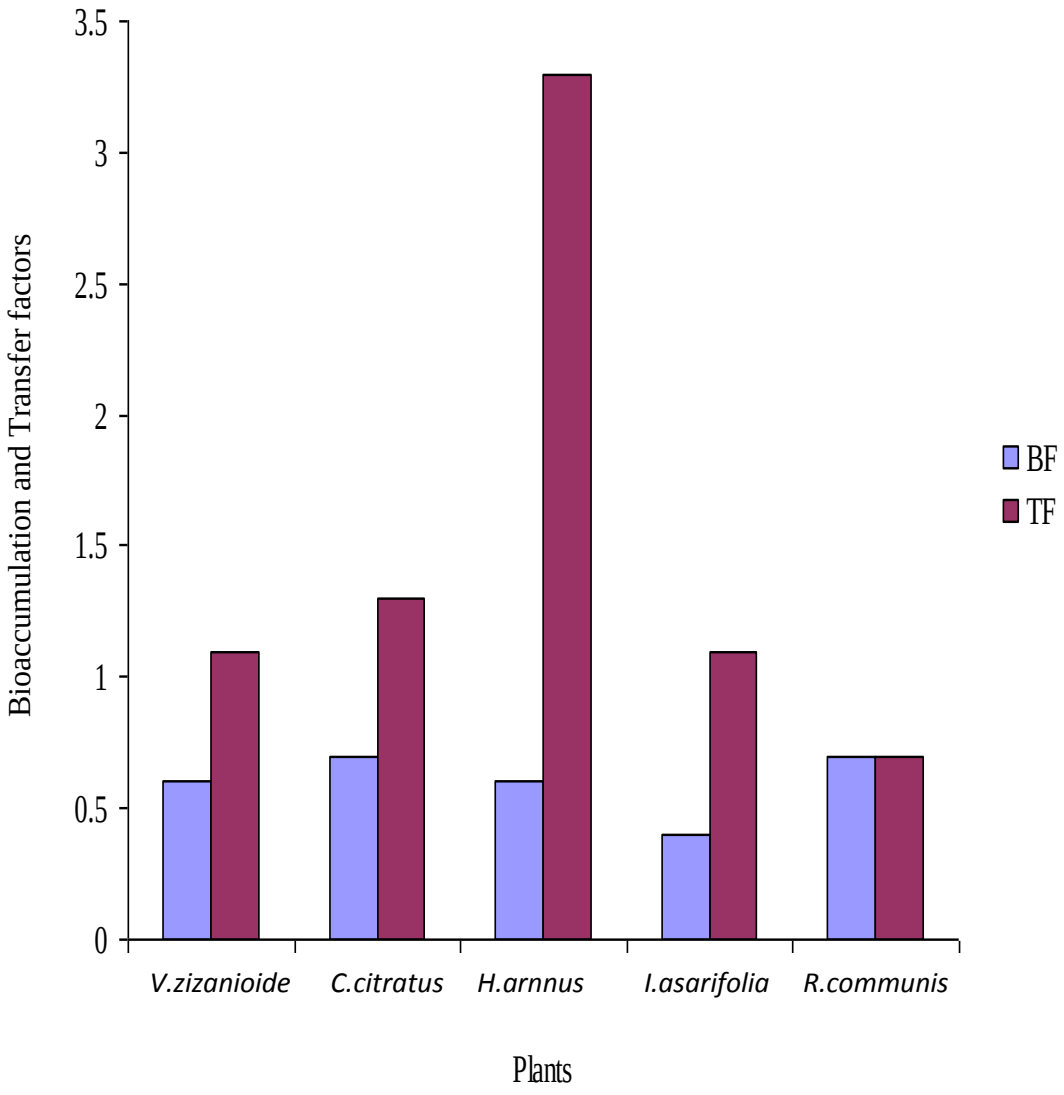


Figure 4.20: Bioaccumulation and Transfer Factors for Cobalt in Different Plant Species at Dakace

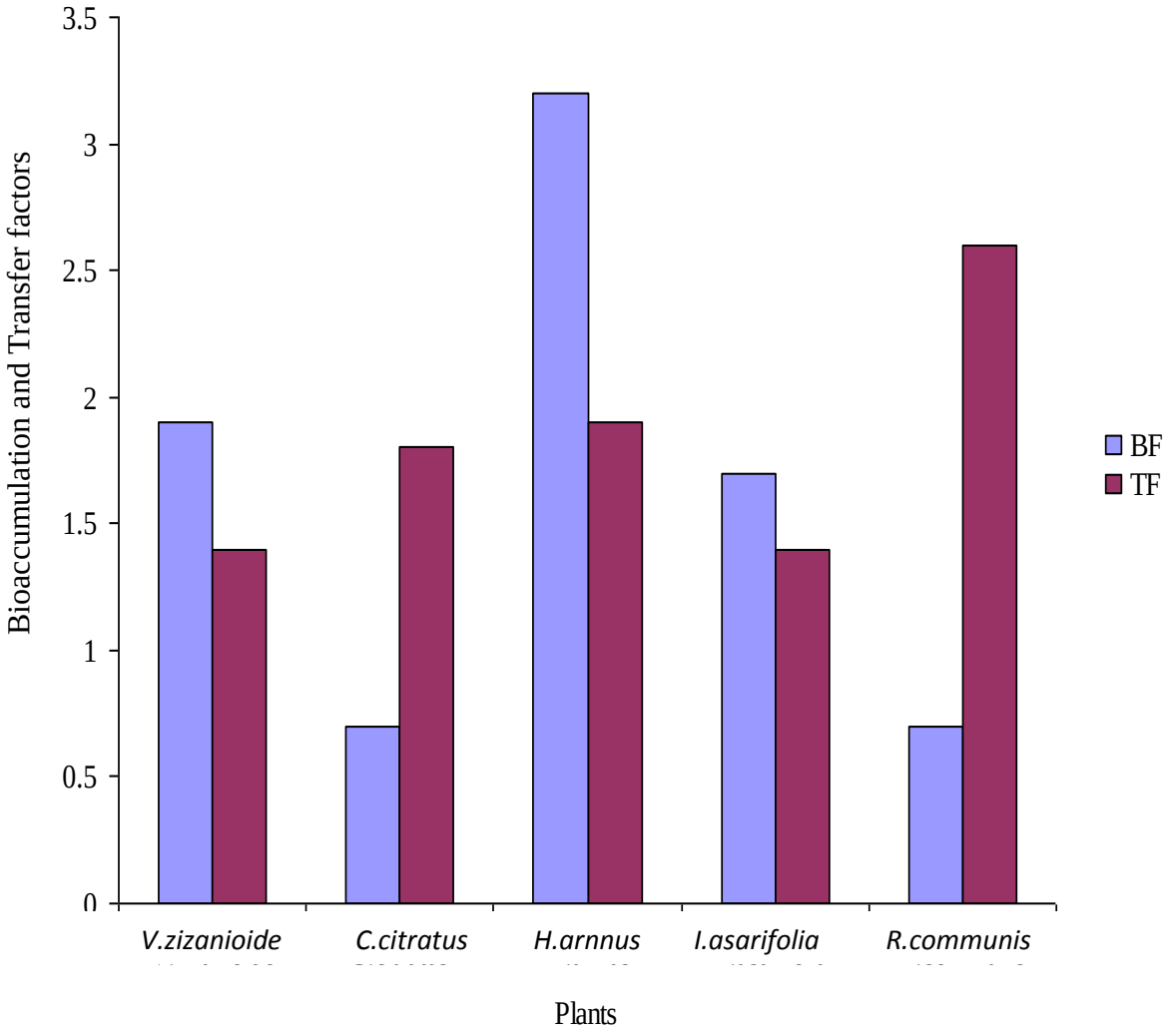


Figure 4.21: Bioaccumulation and Transfer Factors for Copper in Different Plant Species at Dakace

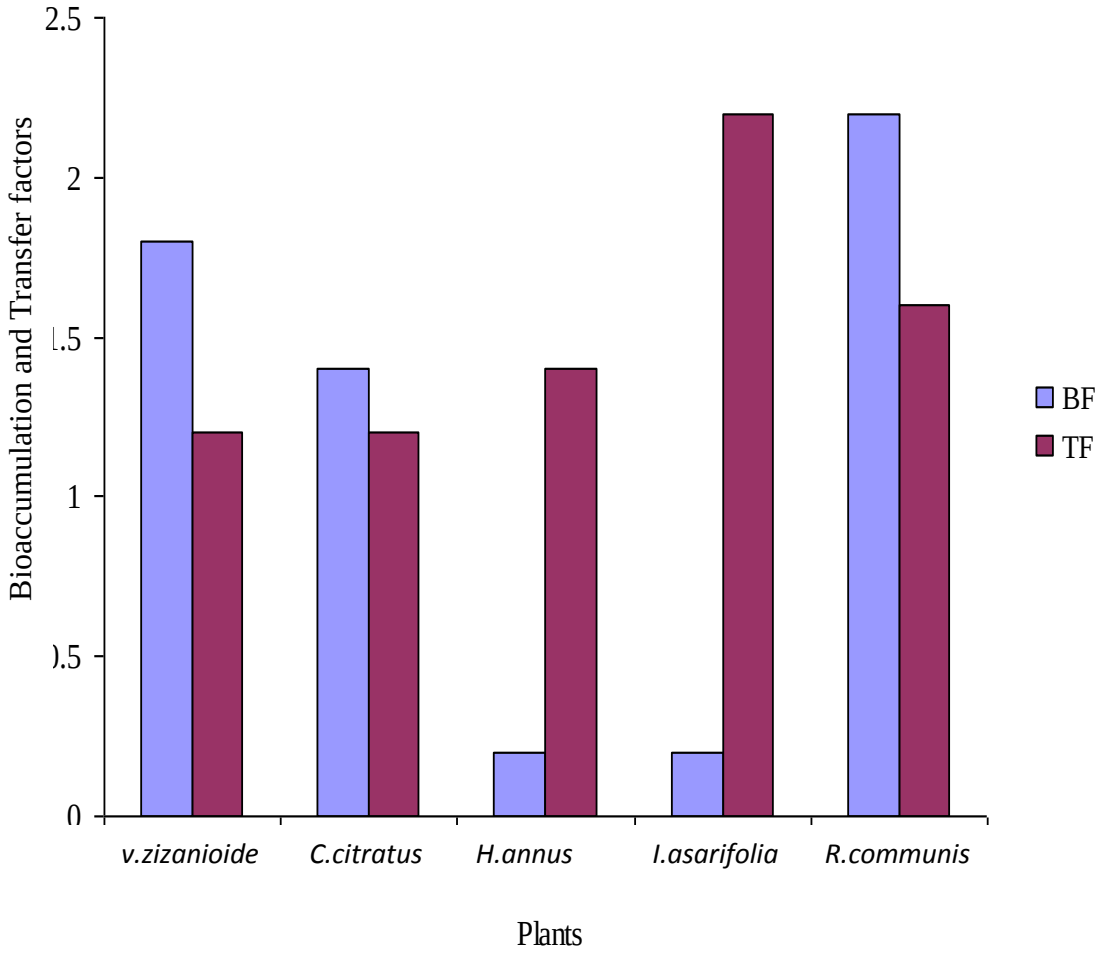


Figure 4.22: Bioaccumulation and Transfer Factors for Nickel in Different Plant Species at Dakace

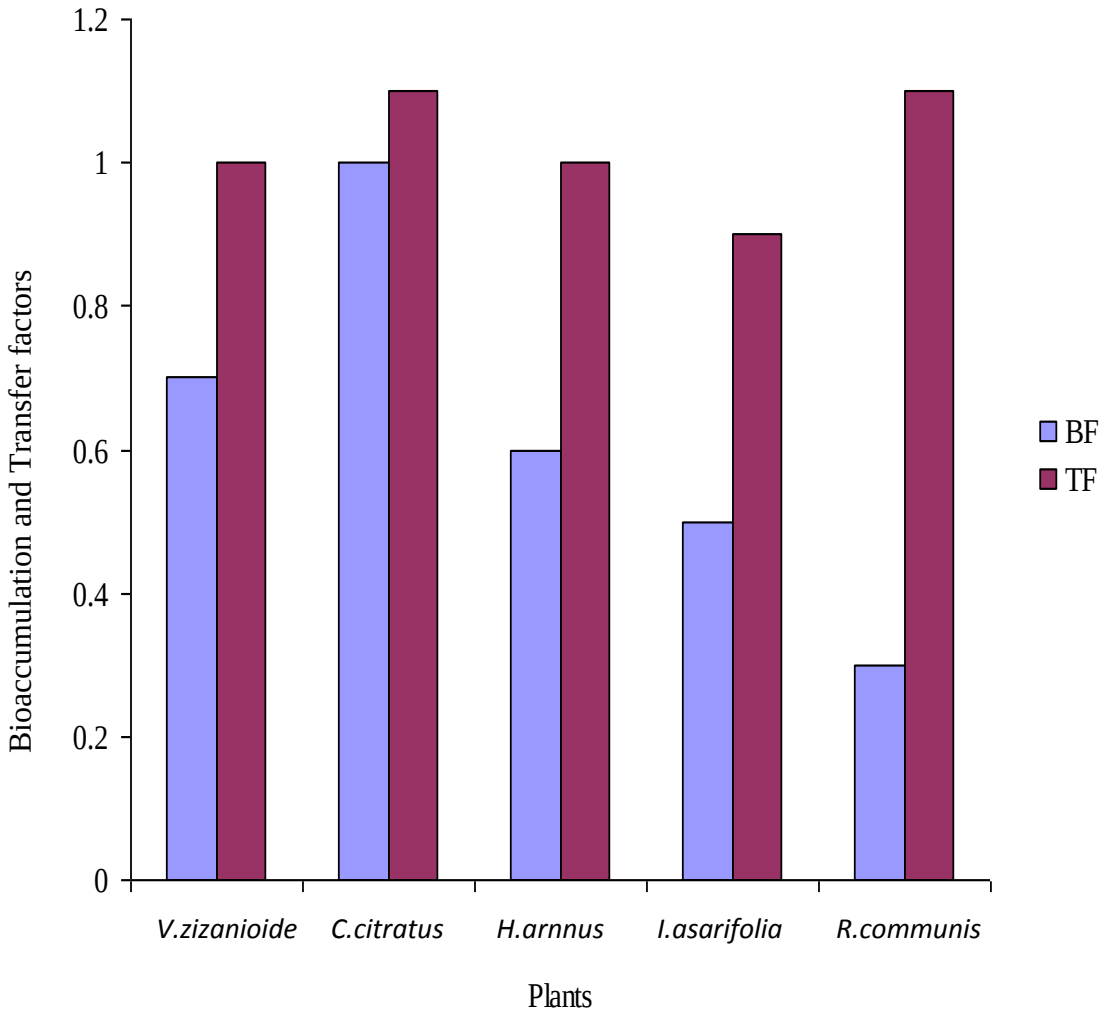


Figure 4.23: Bioaccumulation and Transfer Factors for Lead in Different Plant Species at Dakace

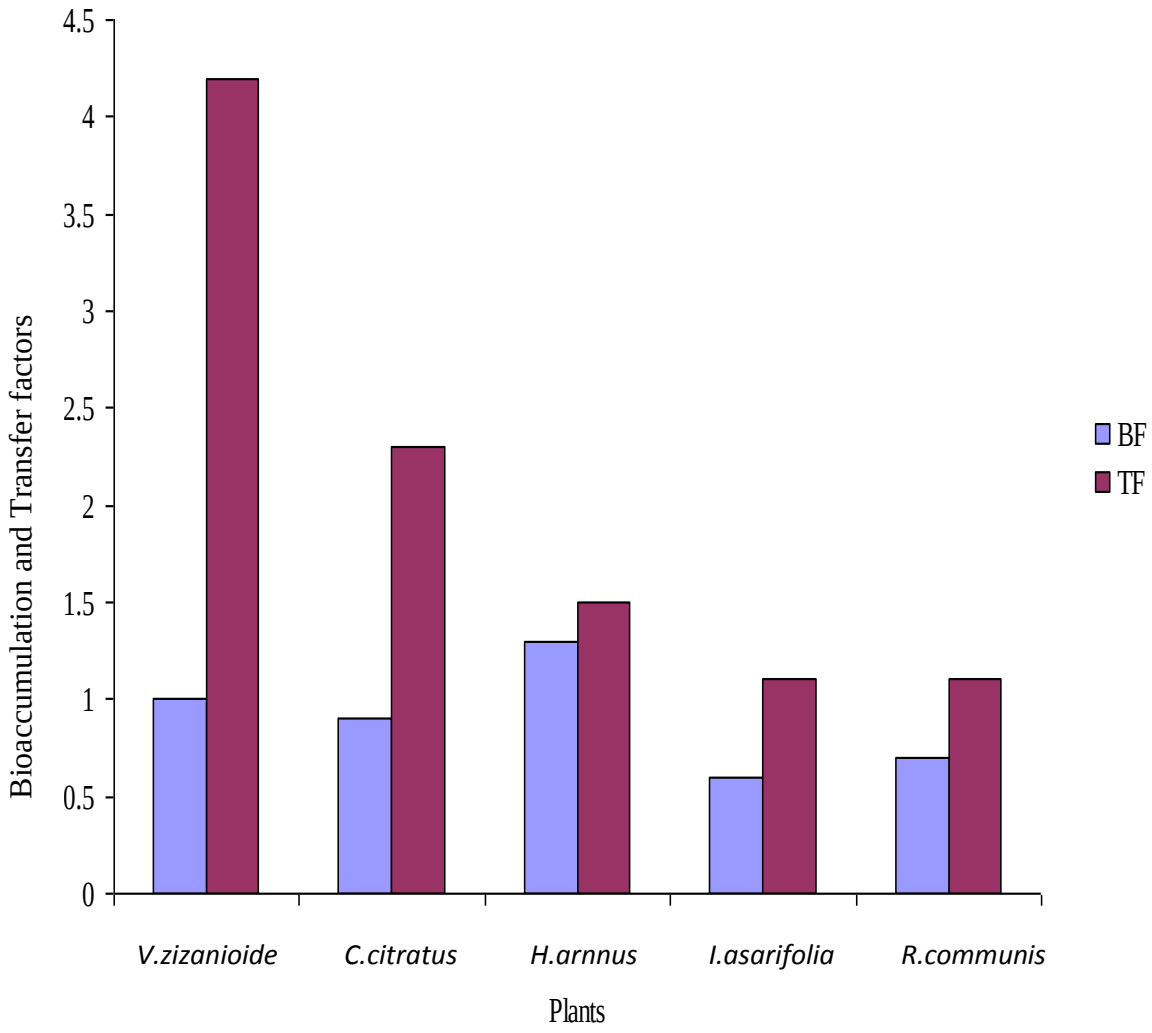


Figure 4.24: Bioaccumulation and Transfer Factors for Zinc in Different Plant Species at Dakace

in Figure 4.25 and Appendix XV. The results indicated that there was a general increase in metal concentration from the roots to the leaves for all the elements studied at the test and control sites. The different metal levels in the leaves were: Cd - 3.00±0.01 mg/kg, Co - 8.60±0.01 mg/kg, Cu - 2.90±0.00 mg/kg, Ni – 9.80±0.06 mg/kg, Pb - 47.00±0.02 mg/kg and Zn - 48.50±0.13 mg/kg; in the roots: Cd - 2.00±0.02 mg/kg, Co - 3.40±0.00 mg/kg, Cu - 1.90±0.02 mg/kg, Ni - 8.80±0.03 mg/kg, Pb - 44.40±0.03 mg/kg and Zn - 30.80±0.17 mg/kg. Both the BF and TF (Figure 4.26) for the metals were greater than 1 except those of lead and Co were their BF was less than 1. The BF of the elements were in the order of Zn > Cd ≈ Cu ≈ Ni > Co > Pb, while the TF followed the order Co > Zn > Cd ≈ Cu > Ni ≈ Pb.

4.8.2 Concentrations of the studied metals in different parts *Cymbopogon citratus* plant

The concentrations of the studied metals in different parts *Cymbopogon citratus* plant harvested from the test site at Gaskiya and the control site are presented in Figure 4.27 and Appendix XVI. The concentrations of the metals in the leaves were as follows: Cd - 2.70±0.01 mg/kg, Co - 5.70±0.02 mg/kg, Cu - 3.10±0.00 mg/kg, Ni - 11.10±0.03 mg/kg, Pb - 43.40±0.01 mg/kg and Zn - 41.40±0.07 mg/kg. The roots contained 2.20±0.03 mg/kg of Cd, 5.70±0.03 mg/kg of Co, 2.90±0.03 mg/kg of Cu, 4.40±0.06 mg/kg of Ni, 41.50±0.01 mg/kg of Pb and 14.23±0.04 of Zn. The BF and TF for all the metals studied (Figure 4.28) were greater than 1 except Co and Pb whose BF was less than 1. The BF of the elements were in the order of Zn > Cu > Cd > Ni > Pb > Co, while TF followed the order Ni > Cd > Co ≈ Cu ≈ Zn > Pb.

4.8.3 Metal concentrations in different parts of *Helianthus annus* (sunflower) plant

The metal concentrations in different parts of *Helianthus annus* **(**sunflower) plant and the soil at the Gaskiya study area and the control site are presented in Figure 4.29 and Appendix XVII. In the leaves, Zn (95.00±0.13 mg/kg) concentration was highest, followed

by Pb (58.50±0.03 mg/kg), Cu (19.10±0.03 mg/kg), Ni (11.70±0.07 mg/kg), Co (7.40±0.03 mg/kg) and Cd (2.40±0.0 mg/kg). The stems were found to contain 51.26±0.09 mg/kg of Zn, 42.40±0.04 mg/kg of Pb, 10.40±0.07 mg/kg of Ni, 14.00±0.0mg/kg of Cu, 2.30±0.02 mg/kg of Cd and 1.20±0.03 mg/kg of Co. The metal levels in the roots were : Pb - 39.10±0.03 mg/kg, Zn - 29.52±0.04 mg/kg, Ni - 10.50±0.05 mg/kg, Cu - 8.80±0.02 mg/kg, Cd - 2.10±0.04 mg/kg and Co - 1.00±0.02 mg/kg. The BF values for Cu, Ni and Zn were greater than 1, TF values for all the metals studied were found to be greater than 1. The BF values for studied metals were in the order of: Cu > Zn > Ni > Pb > Cd > Co. For the TF the trend was: Co > Zn > Cu > Pb > Ni ≈ Cd (Figure 4.30).

4.8.4 Metal concentrations in different parts of *Ipomoea asarifolia* plant

The metal concentrations in different parts of *Ipomoea asarifolia* plant harvested from Gaskiya test site and the control soil are presented in Figure 4.31 and Appendix XVIII. The concentration values in the leaves were: Cd - 2.60±0.04mg/kg, Co - 3.90±0.03mg/kg, Cu - 13.20±0.04 mg/kg, Ni - 8.80±0.04mg/kg, Pb -37.90±0.20mg/kg and Zn - 31.59±0.03mg/kg; In the stems : Cd - 2.10±0.02mg/kg,Co - 5.50±0.05mg/kg, Cu - 10.70±0.01mg/kg, Ni - 7.30±0.06mg/kg, Pb - 36.50±0.04 mg/kg and Zn - 35.75±0.04mg/kg. The roots contained Cd - 1.50±0.02mg/kg, Co - 8.10±0.04mg/kg, Cu - 7.70±0.08mg/kg, Ni - 2.70±0.06mg/kg, Pb - 75.90±0.05mg/kg and Zn - 22.40±0.04mg/kg. Only Cd, Cu and Zn had their BF greater than 1, and the TF for all the studied metals were greater than 1. The BF for the studied metals followed the order: Cu > Zn > Cd > Ni > Co > Pb, while the TF was Ni > Cd ≈ Cu > Zn > Co > Pb (Figure 4.32).

4.8.5 Metal concentrations in different parts of *Ricinus communis* plant

The metal concentrations in different parts of *Ricinus communis* plant harvested from Gaskiya test site and the control are presented in Figure 4.33 and Appendix XIX. The result indicated that there is a variation in the metal levels in the leaves, stems and roots of the plant. The concentrations of metals in leaves were: Zn - 32.00±0.05 mg/kg, Pb - 21.20±0.04 mg/kg, Ni - 12.40±0.05 mg/kg, Cu - 9.00±0.03 mg/kg, Co - 8.00±0.05 mg/kg

and Cd - 2.30±0.02 mg/kg; the stem: Zn - 31.60±0.02 mg/kg, Pb - 21.70±0.04 mg/kg, Ni - 12.80±0.06 mg/kg, Cu - 5.70±0.03 mg/kg, Co - 6.80±0.05 mg/kg and Cd - 2.00±0.01 mg/kg; the roots : Zn (36.40±0.11 mg/kg), Pb - 20.60±0.03 mg/kg, Ni - 7.80±0.03 mg/kg, Co - 5.60±0.03 mg/kg, Cu - 5.50±0.08 mg/kg, Cd - 2.10±0.02 mg/kg. The BF values for studied metals were greater than 1 except Pb and Co (Figure 4.34). All the metals studied have their TF greater than 1. The BF and TF were in the order: Cu > Ni > Zn > Cd > Co > Pb and Zn > Ni > Cu > Co > Cd ≈ Pb respectively.

4.9 Bioaccumulation and Transfer Factors for the Studied Metals in Different Plant Species at Gaskiya

The BF and TF for the studied metals in different plant species harvested from Gaskiya soil are presented in Figures 4.35 to 4.40 and Appendex XX. The BF for Cd was of the order- *Vetivera zizanioide* (1.3) ≈ *Cymbopogon citratus* (1.3) > *Ipomoea asarifolia* (1.1) ≈ *Ricinus communis* (1.1) > *Helianthus annus* (0.6), while the TF was of the order *Ipomoea asarifolia* (1.6) > *Vetivera zizanioide* (1.5) > *Cymbopogon citratus* (1.2) ≈ *Ricinus communis* (1.2) > *Helianthus annus* (1.1). For Co, the BF of *Ricinus communis* (0.8) > *Vetivera zizanioide* (0.7) ≈ *Cymbopogon citratus* (0.7) > *Ipomoea asarifolia* (0.6) > *Helianthus annus* (0.4), while the TF was of the order *Helianthus annus* (4.3) > *Vetivera zizanioide* (2.5) > *Ricinus communis* (1.3) > *Ipomoea asarifolia* (1.2) > *Cymbopogon citratus* (1.0). The BF for Cu was of the order *Helianthus annus* (7.4) > *Ipomoea asarifolia* (5.5) > *Ricinus communis* (1.8) > *Cymbopogon citratus* (1.6) > *Vetivera zizanioide* (1.3), while the TF- *Helianthus annus* (1.9) > *Ipomoea asarifolia* (1.6) > *Vetivera zizanioide* (1.5) ≈ *Ricinus communis* (1.5) > *Cymbopogon citratus* (1.1). The BF and TF for Ni in different plant species were - *Ricinus communis* (1.6) > *Vetivera zizanioide* (1.3) > *Cymbopogon citratus* (1.1) > *Ipomoea asarifolia* (0.9) > *Helianthus annus* (0.6) and *Ipomoea asarifolia* (3.0) > *Cymbopogon citratus* (2.5) > *Ricinus communis* (1.6) > *Vetivera zizanioide* (1.1) ≈ *Helianthus annus* (1.1) respectively. BF and TF for Pb - *Helianthus annus* (0.9) > *Cymbopogon citratus* (0.8) > *Vetivera zizanioide* (0.6) > *Ipomoea asarifolia* (0.5) > *Ricinus communis* (0.3) and *Ricinus communis* (1.3) ≈ *Helianthus annus* (1.3) > *Ipomoea asarifolia* (1.1) ≈ *Vetivera zizanioide* (1.1) > *Cymbopogon citratus* (1.0) respectively. The BF and TF for Zn in different plant species indicated that *Cymbopogon citratus* (2.9) > *Helianthus annus* (2.3) > *Vetivera zizanioide* (1.4) > *Ipomoea asarifolia*

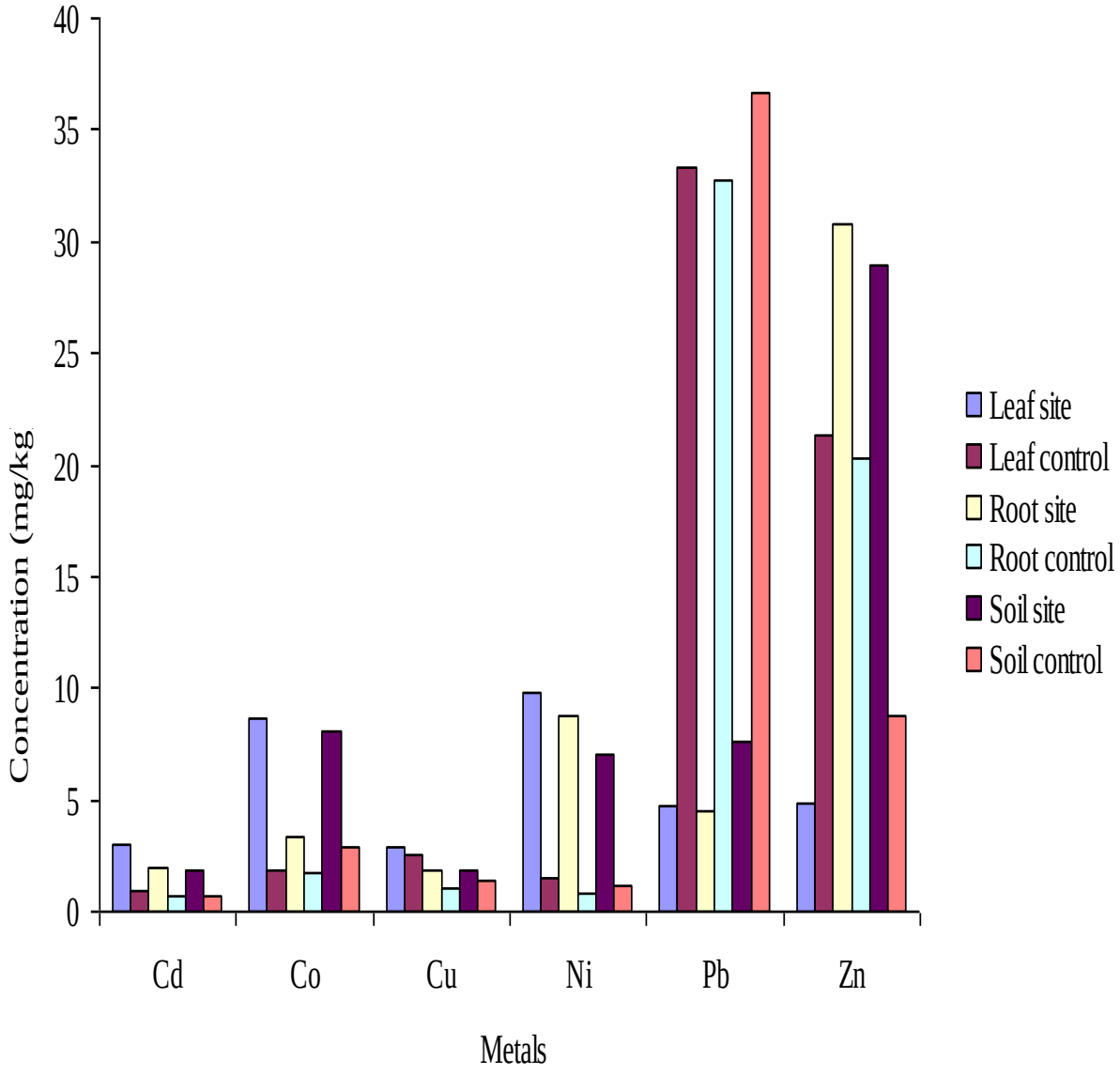


Figure 4.25: Concentrations (mg/kg) of Metals in Different Parts of *Vetivera zizanioide* Plant at Gaskiya

*Pb (leaves) = 4.7 x 10. Pb (roots) = 4.44 x 10, Pb (soil) = 7.59 x 10, Zn (leaves) = 4.85 x 10

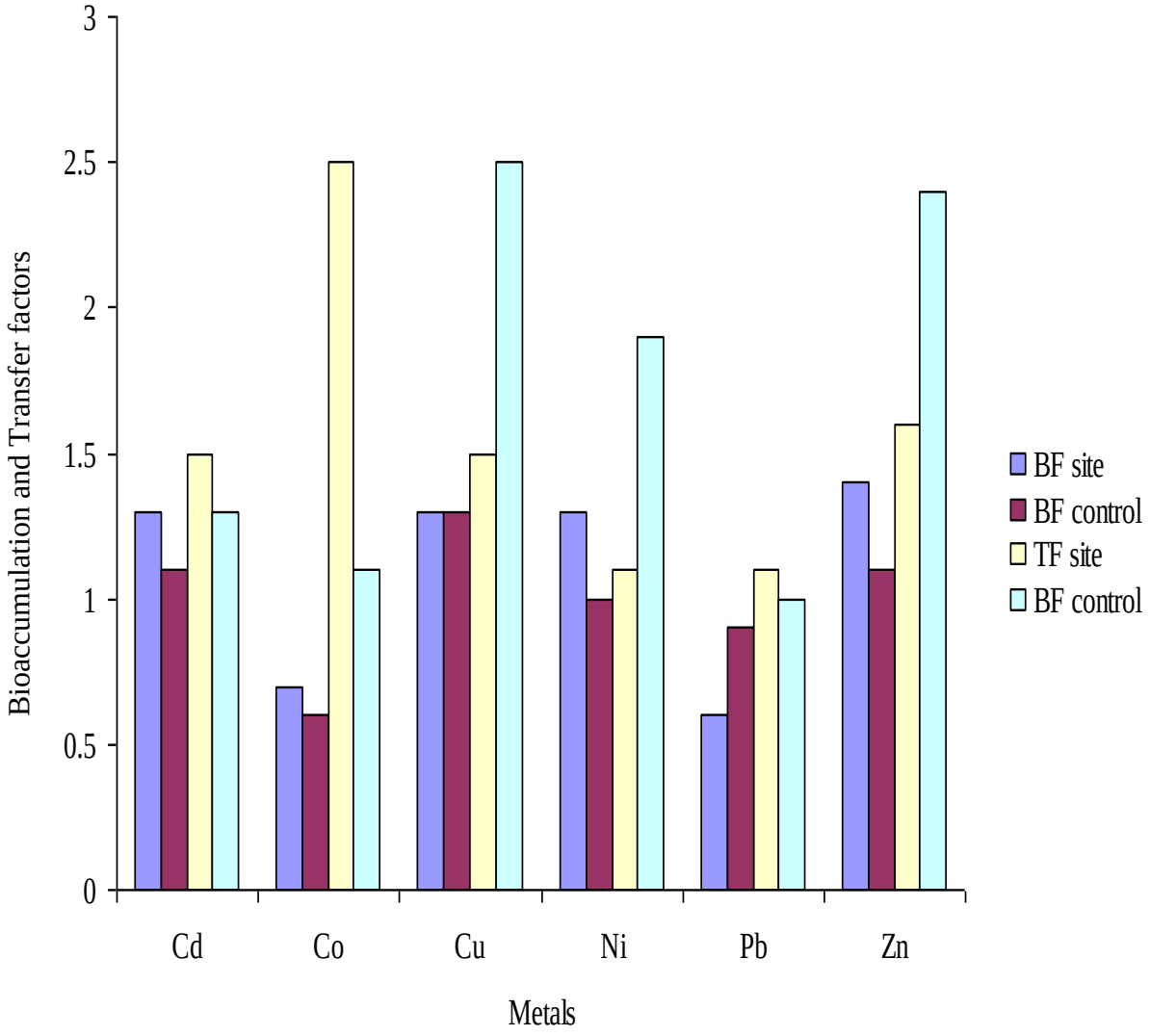


Figure 4.26: Bioaccumulation and Transfer Factors of Metals for *Vetivera zizanioide* Plant at Gaskiya

BF = Bioaccumulation factor; TF = Translocation factor.

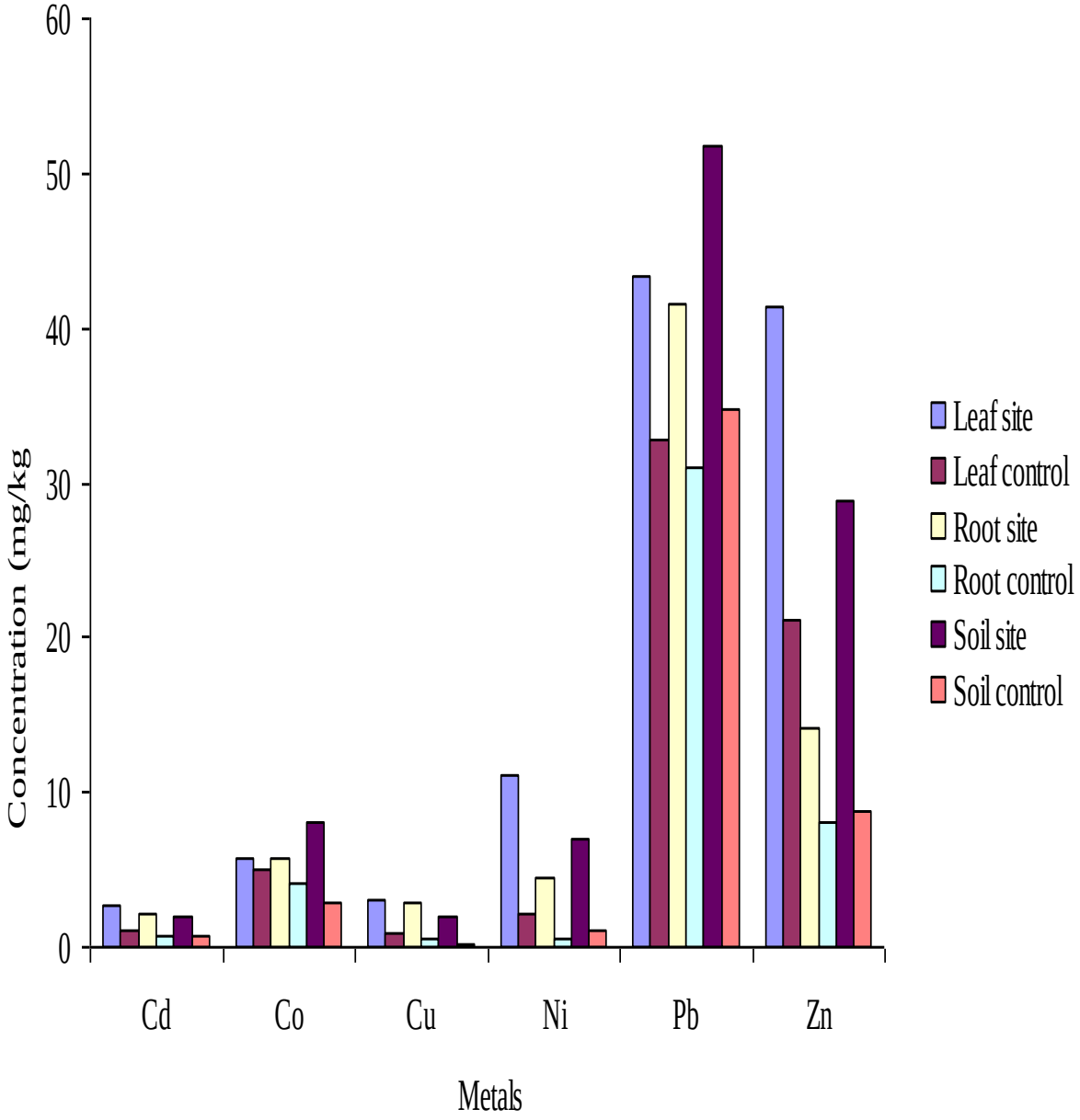


Figure 4.27: Concentrations (mg/kg) of Metals in Different Parts of *Cymbopogon citratus* at Gaskiya

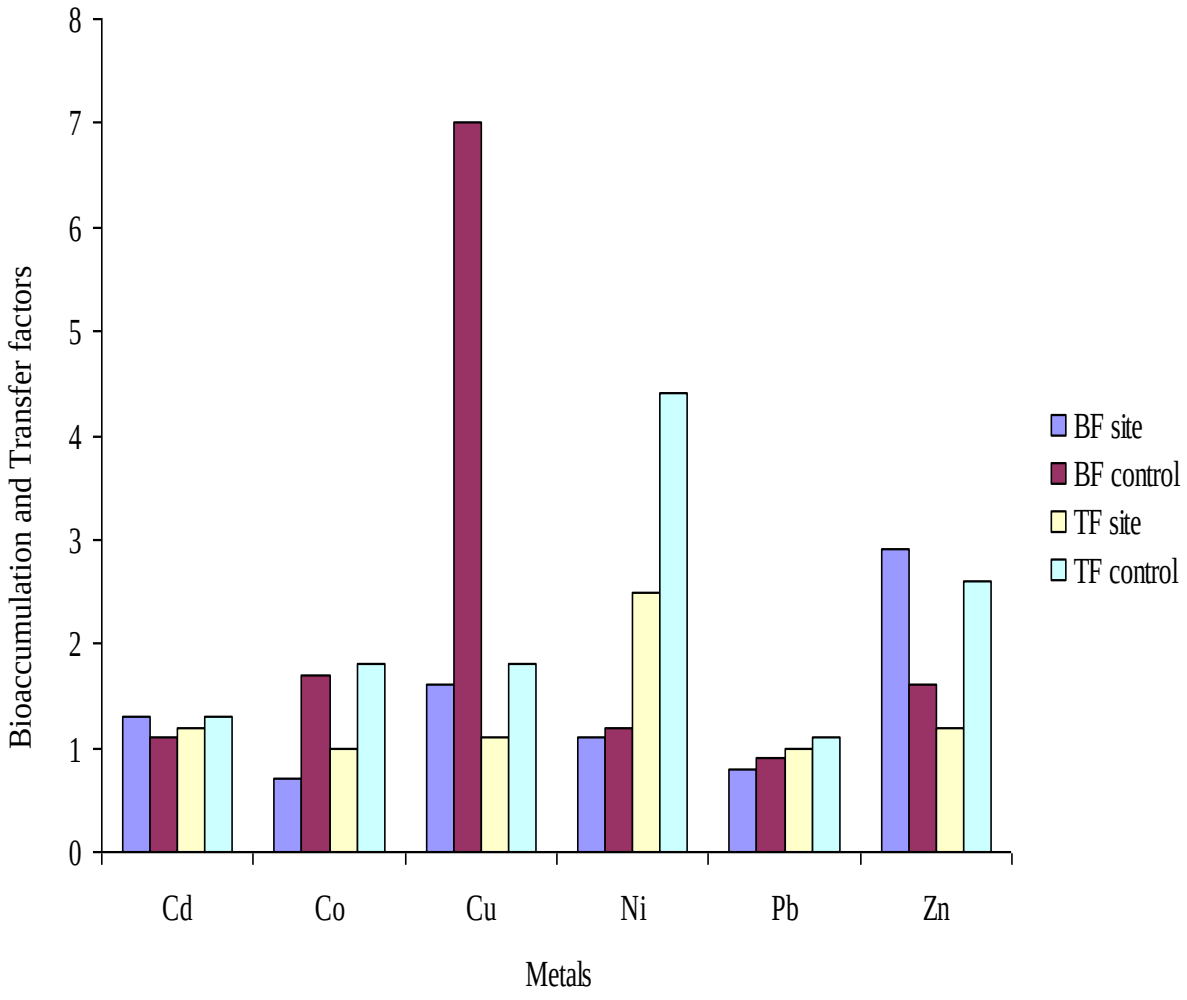


Figure 4.28: Bioaccumulation and Transfer Factors of Metals for *Cymbopogon citratus* at Gaskiya

BF = Bioaccumulation factor; TF = Translocation factor.

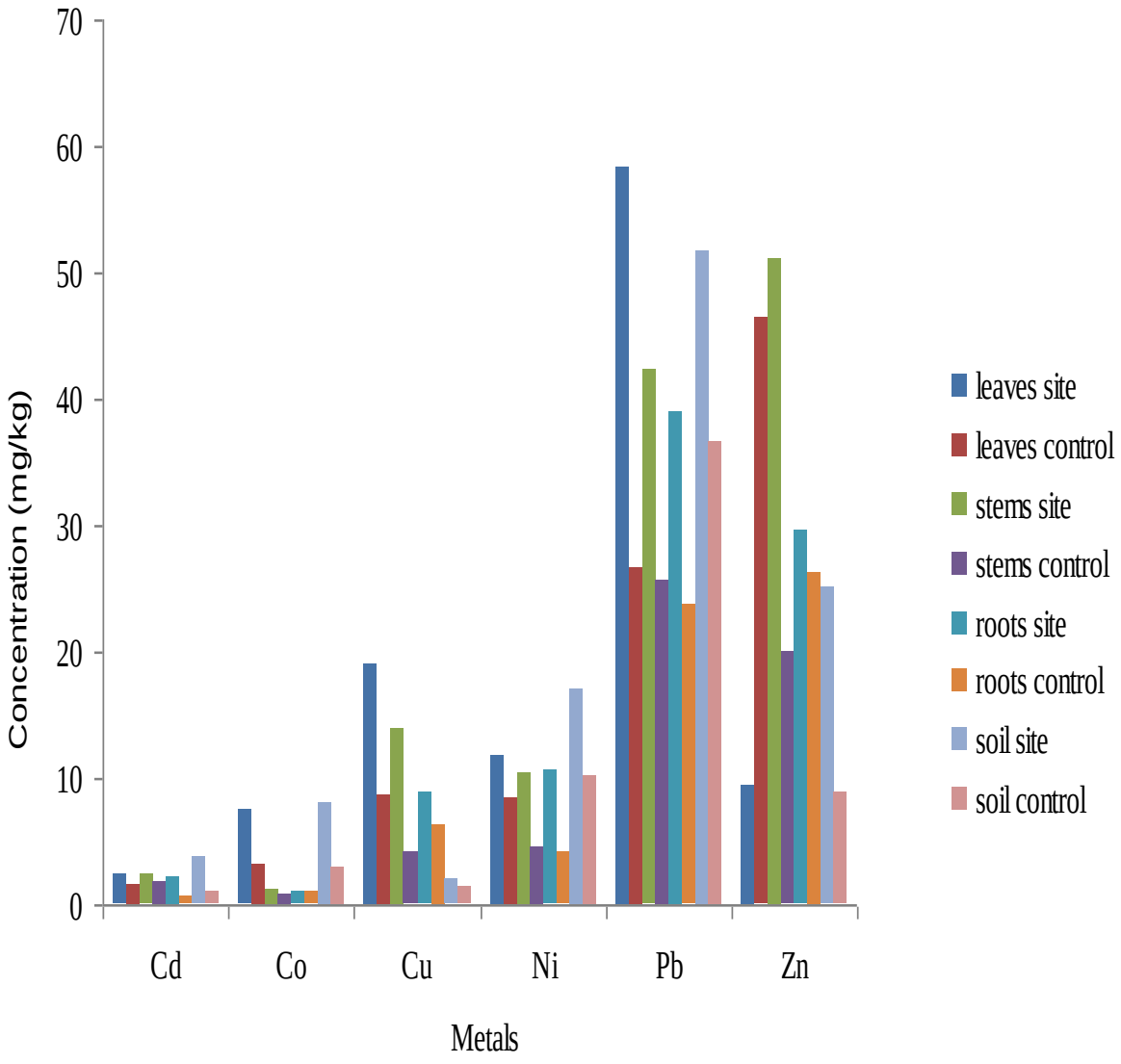


Figure 4.29: Concentrations (mg/kg) of Metals in Different Parts of *Helianthus annus* Plant at Gaskiya

* Zn (leaves) = 9.5 x 10

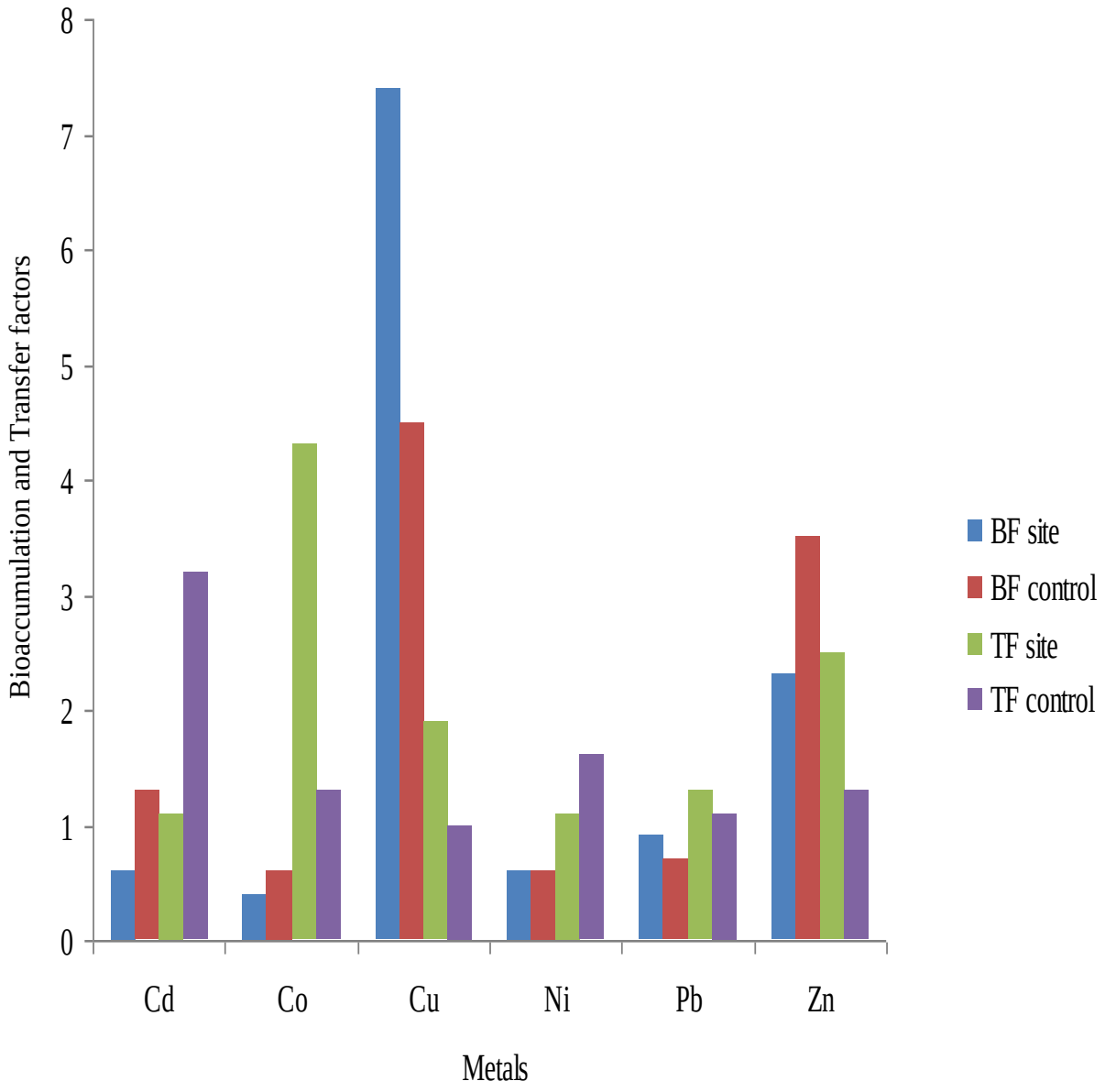


Figure 4.30: Bioaccumulation and Transfer Factors of Metals for *Helianthus annus* Plant at Gaskiya

BF = Bioaccumulation factor; TF = Translocation factor.

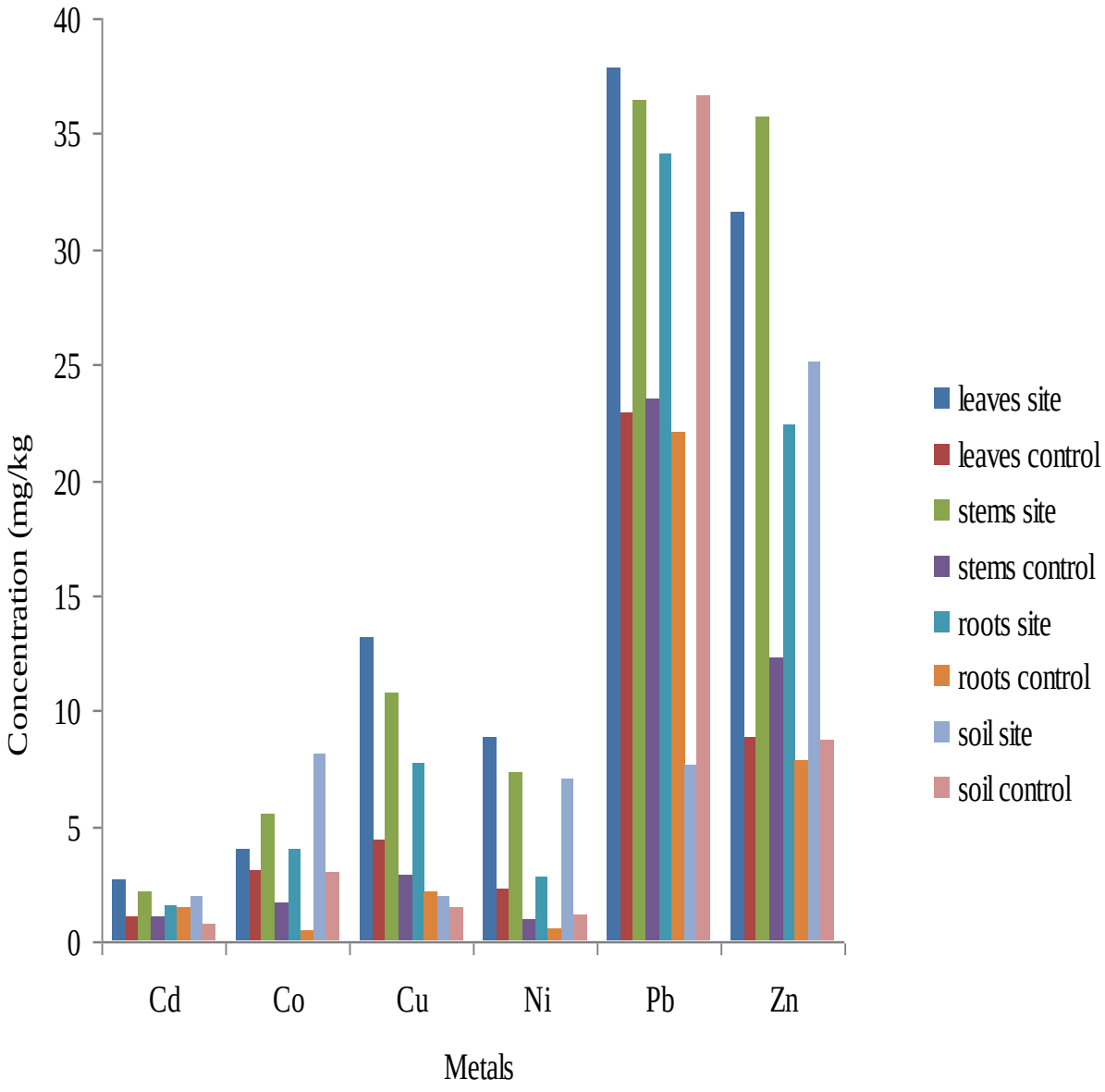


Figure 4.31: Concentrations (mg/kg) of Metals in Different Parts of *Ipomoea asarifolia* Plant and Soil at Gaskiya

*Pb (soil) = 7.59 x 10

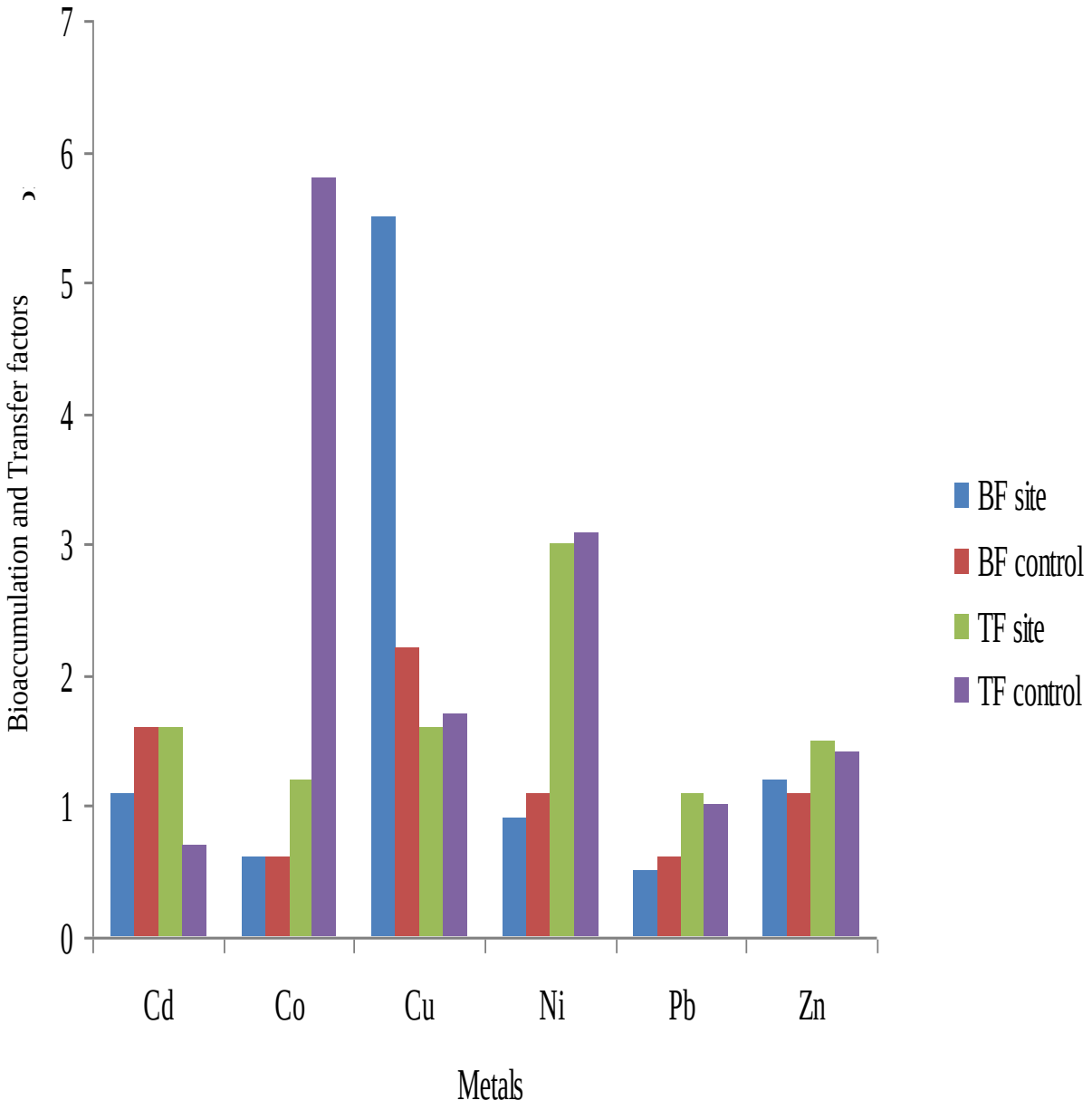


Figure 4.32: Bioaccumulation and Transfer Factors of Metals for *Ipomoea asarifolia* Plant at Gaskiya

BF = Bioaccumulation factor; TF = Translocation factor

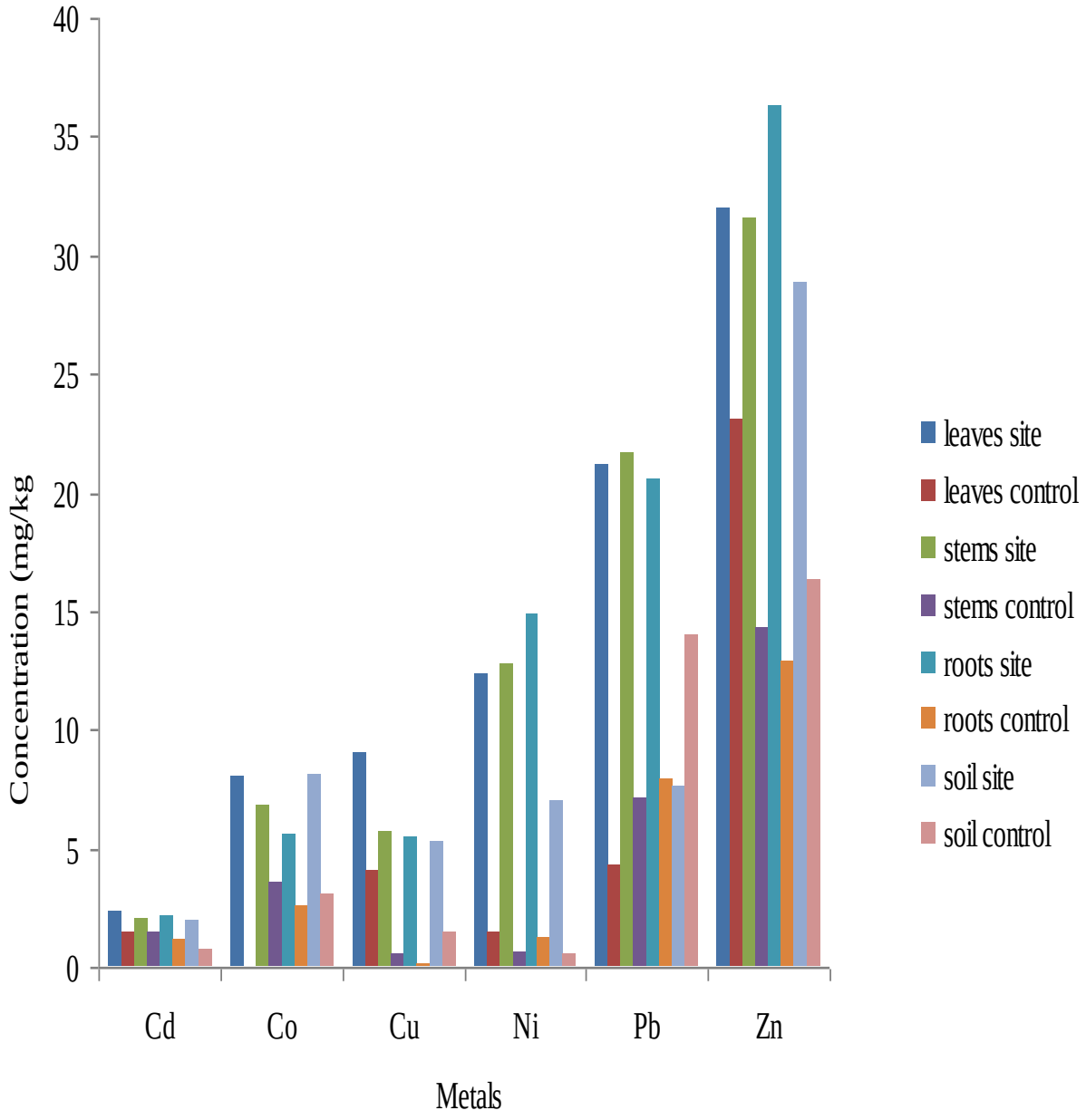


Figure 4.33: Concentrations (mg/kg) of Metals in Different Parts of *Ricinus communis* Plant at Gaskiya

*Pb (soil) = 7.59 x 10

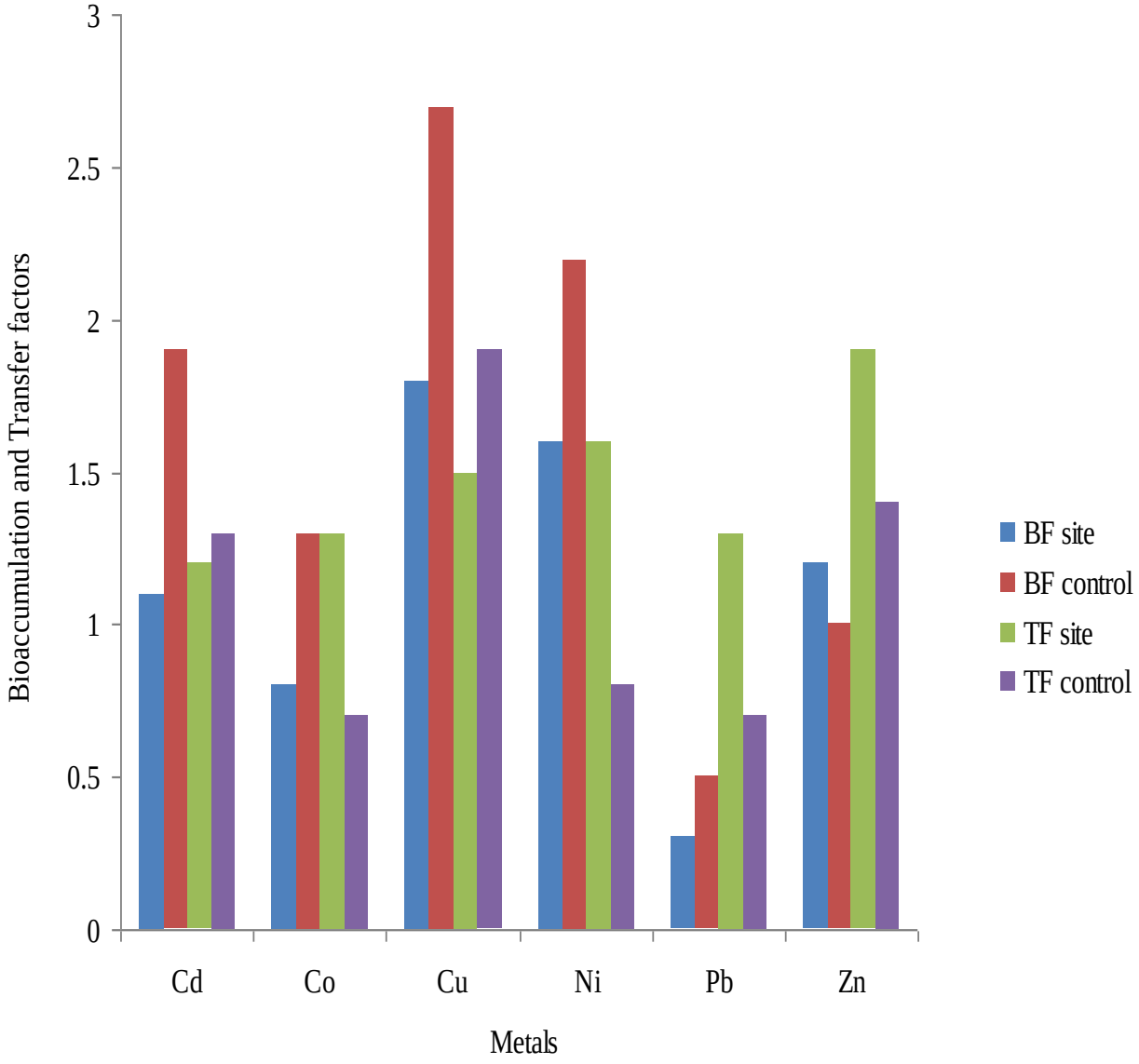


Figure 4.34: Bioaccumulation and Transfer Factors of Metals for *Ricinus communis* Plant at Gaskiya

BF = Bioaccumulation factor; TF = Translocation factor.

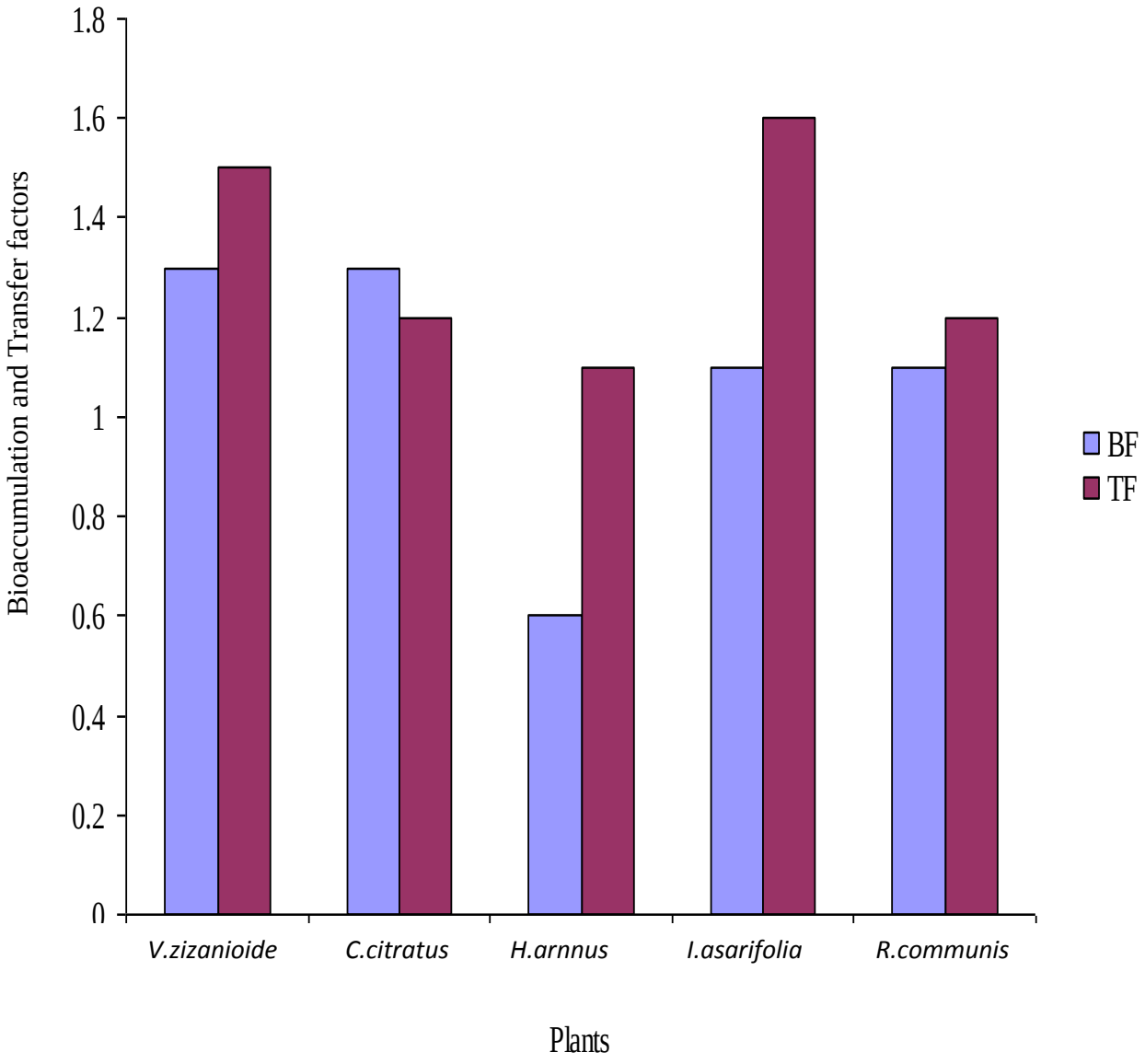


Figure 4.35: Bioaccumulation and Transfer Factors for Cadmium in Different Plant Species at Gaskiya

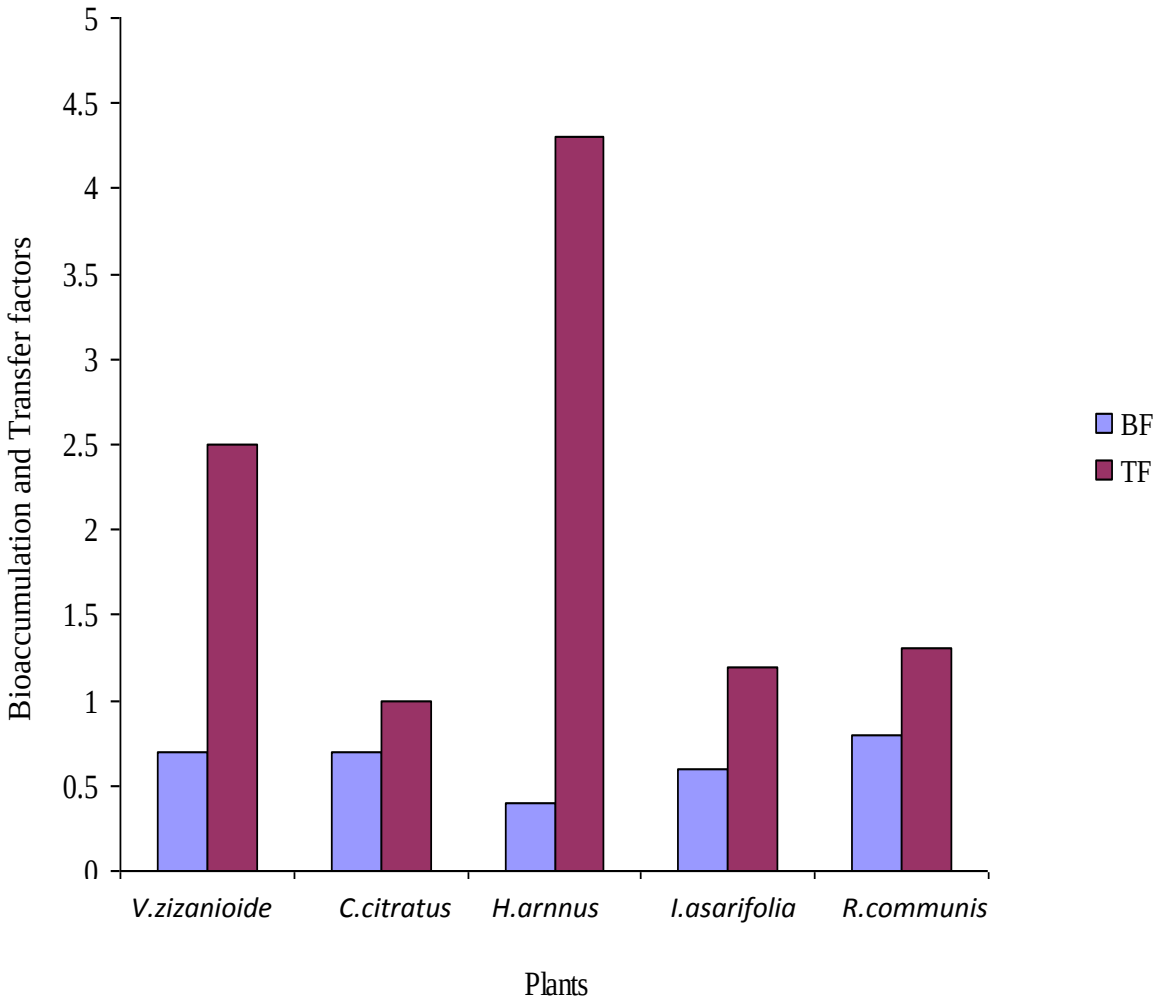


Figure 4 36: Bioaccumulation and Transfer Factors for Cobalt in Different Plant Species at Gaskiya

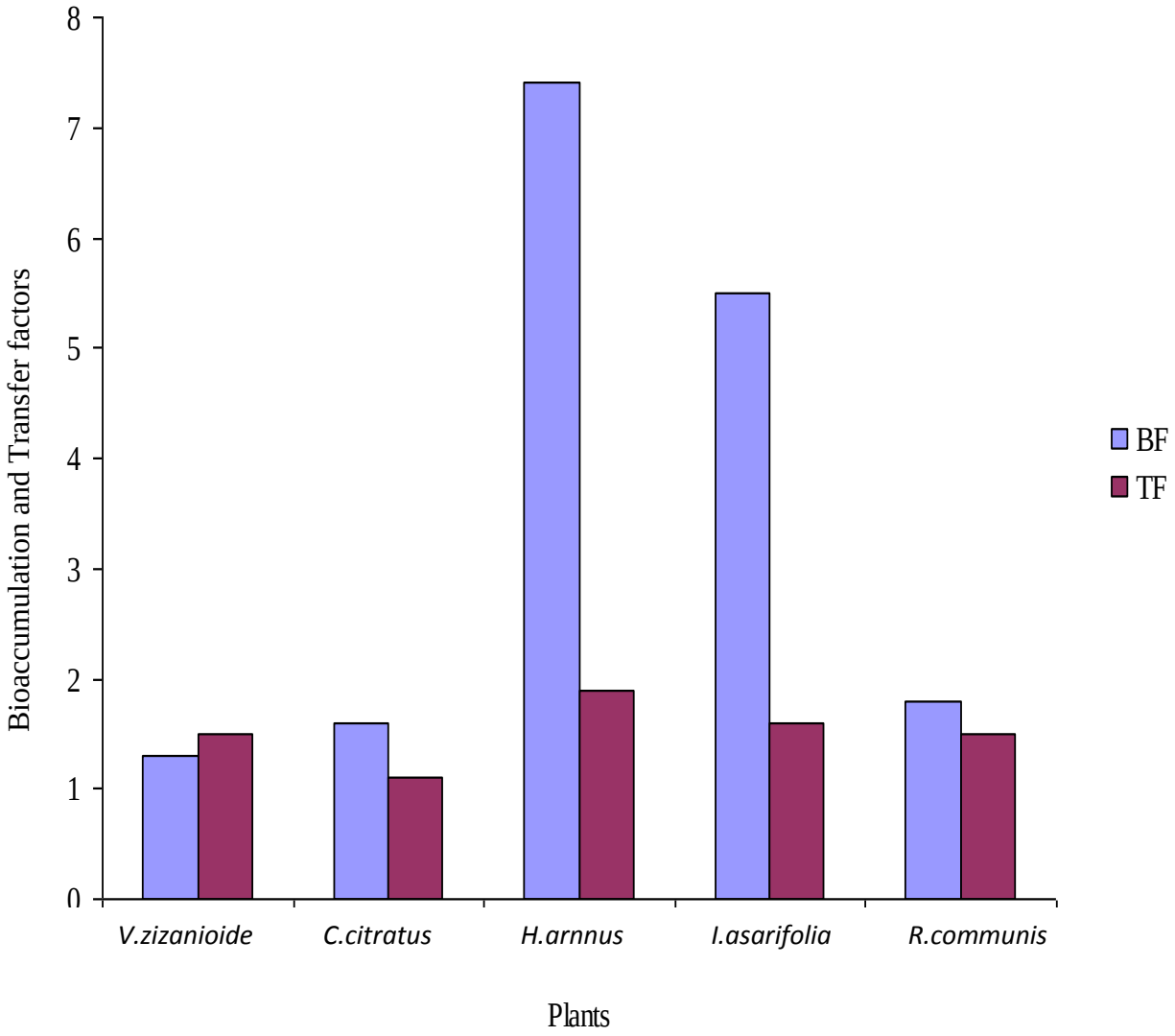


Figure 4.37: Bioaccumulation and Transfer Factors for Copper in Different Plant Species at Gaskiya

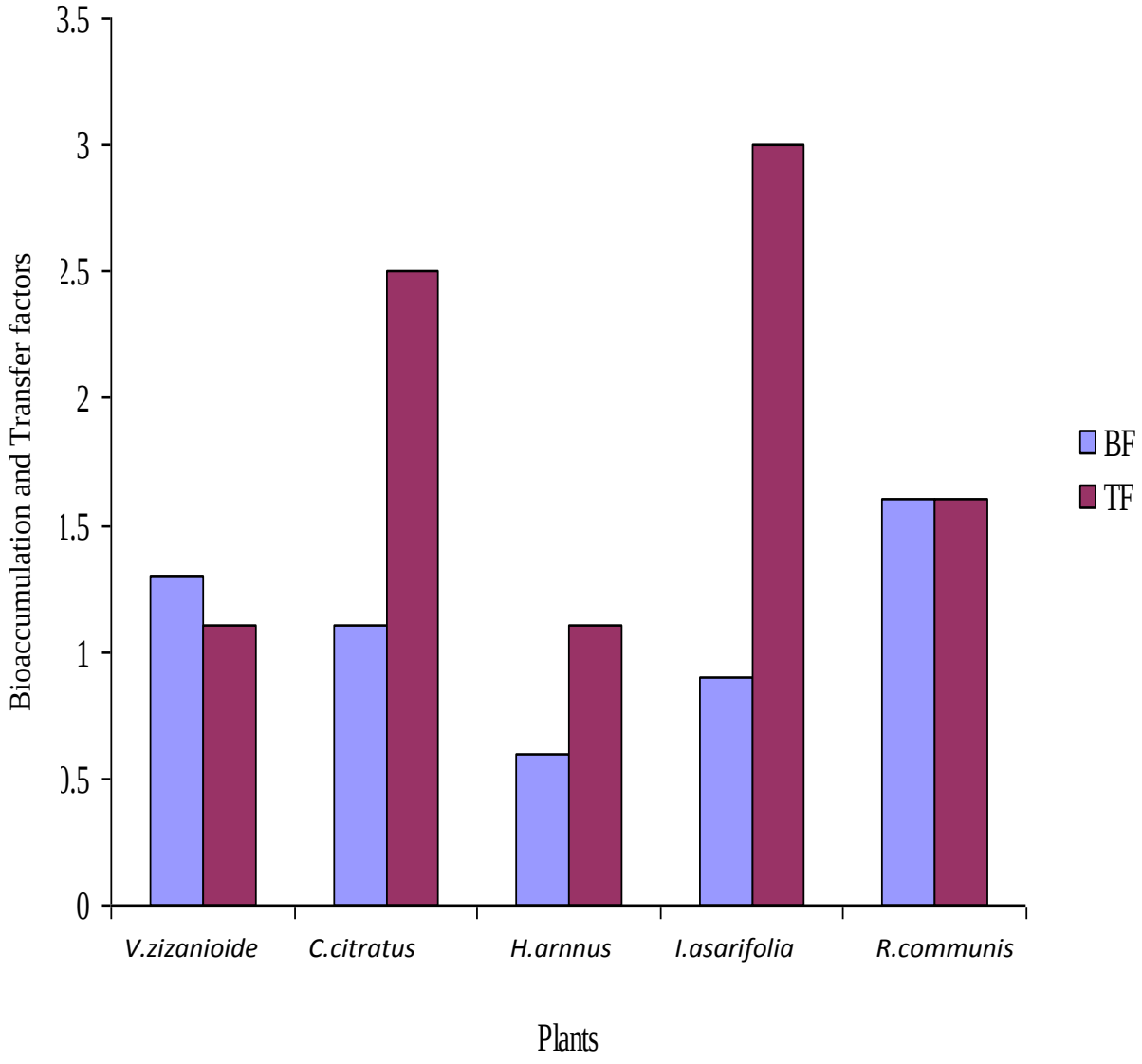


Figure 4.38: Bioaccumulation and Transfers Factors for Nickel in Different Plant Species at Gaskiya

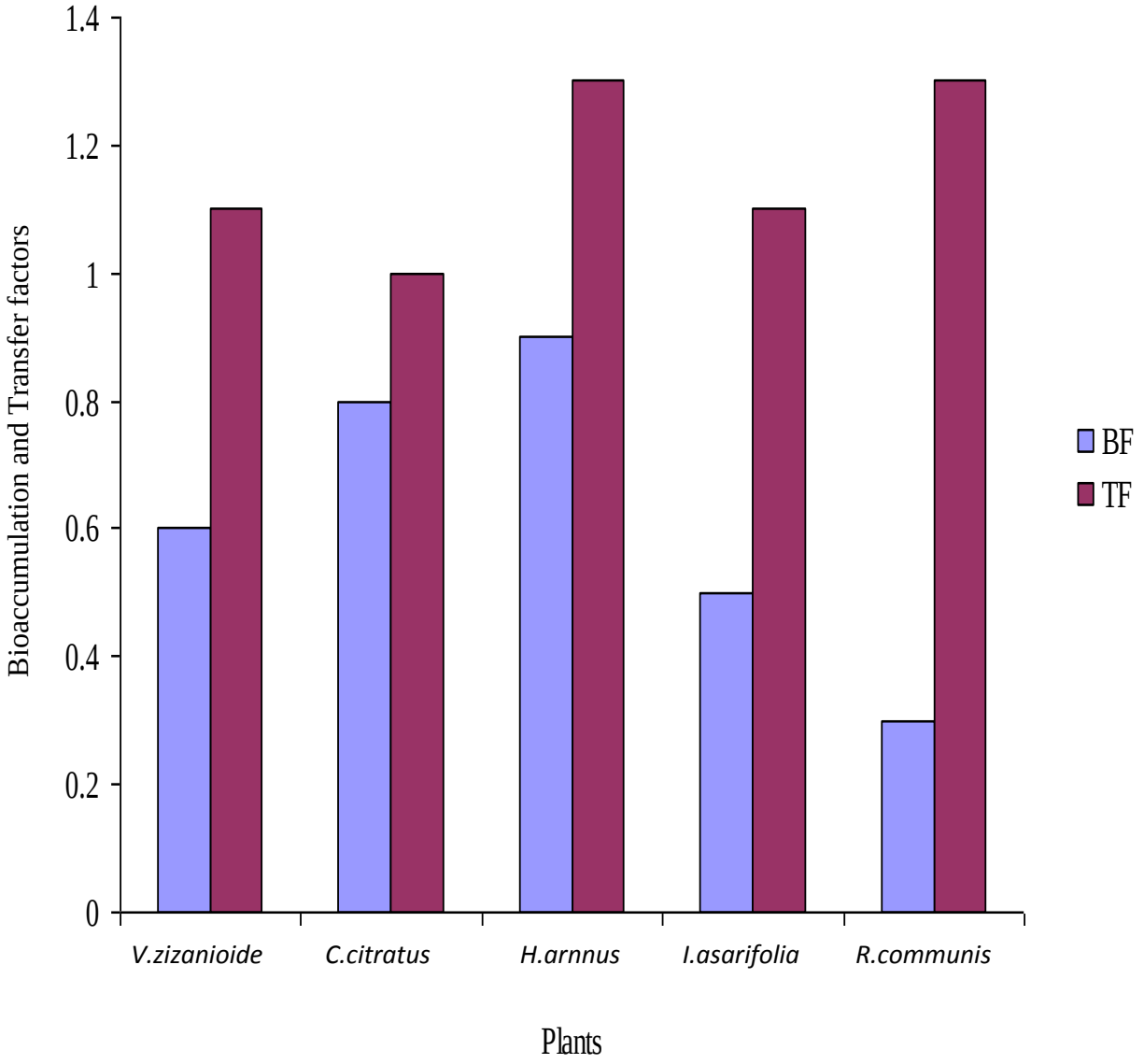


Figure 4.39: Bioaccumulation and Transfer Factors for Lead in Different Plant Species at Gaskiya

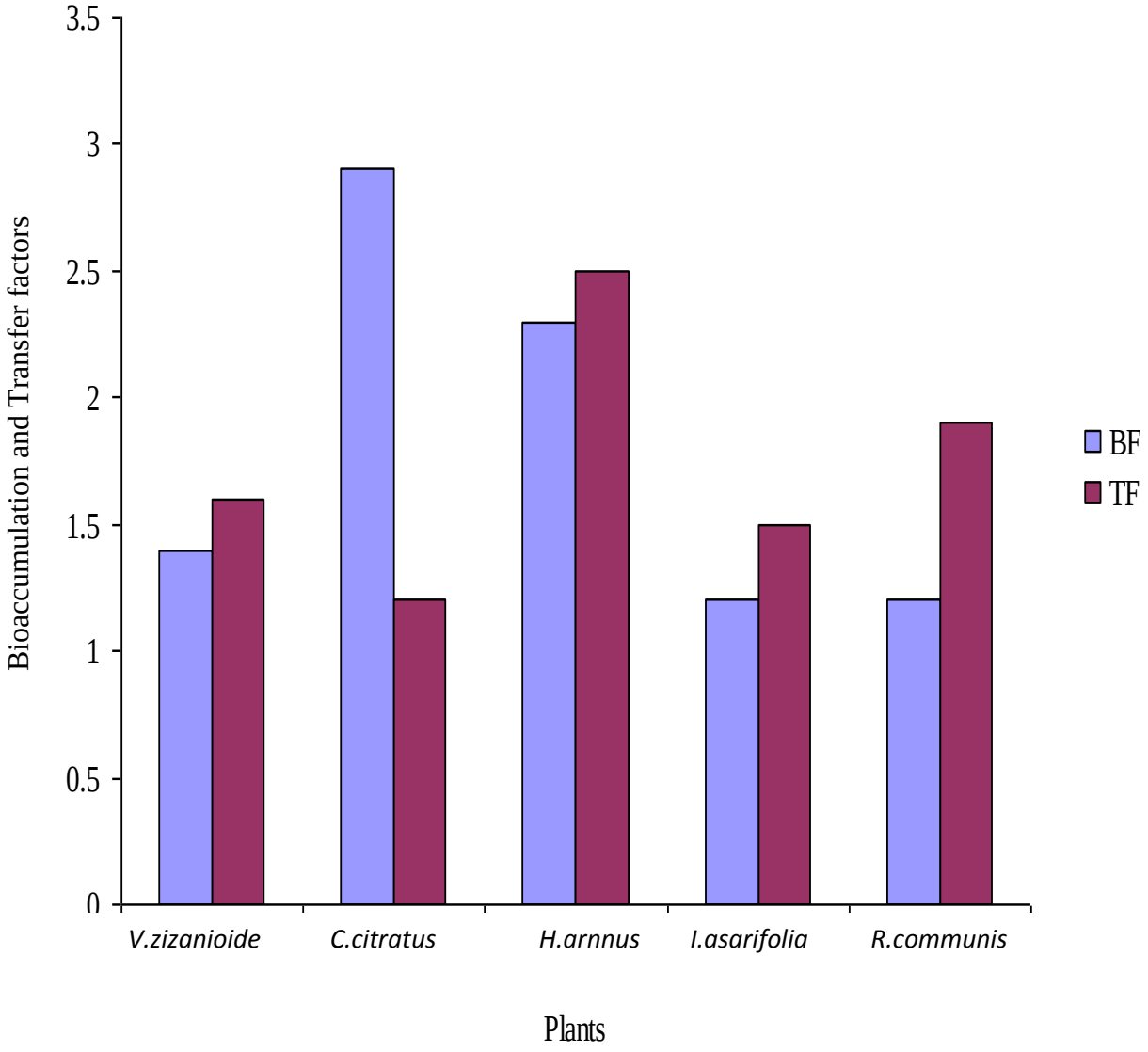


Figure 4.40: Bioaccumulation and Transfer Factors for Zinc in Different Plant Species at Gaskiya

(1.2) ≈ *Ricinus communis* (1.2) and *Helianthus annus* (2.5) > *Ricinus communis* (1.9) > *Vetivera zizanioide* (1.6) > *Ipomoea asarifolia* (1.5) > *Cymbopogon citratus* (1.2) respectively.

4.10 Metal Content in Different Parts of Plant Species without EDTA Application at Hanwa Soil

4.10.1 Metal concentrations in different parts of *Vetivera zizanioide* plant

The result of the metal concentrations in different parts of *Vetivera zizanioide* plant grown at Hanwa soil near a metal-scrap dumpsite is presented in Figure 4.41 and Appendix XXI. The test values for the Cd level in leasves (2.20±0.03 mg/kg) were higher than in the roots (1.80±0.02 mg/kg) and the soil (1.90±0.00 mg/kg). Co level in the soil (8.60±0.04 mg/kg) was higher than levels in the leaves (5.80±0.03 mg/kg) and the roots (5.30±0.04 mg/kg). Cu also showed a similar trend as that of Co, that is, higher in the soil (5.60±0.03 mg/kg) when compared to the values in the leaves (3.30±0.05 mg/kg) and the roots (2.90±0.01 mg/kg). For Ni, its concentration in the leaves (10.60±0.06 mg/kg) was higher than in the roots (10.10±0.07 mg/kg), which in turn was higher than in the soil (4.90±0.08 mg/kg). The concentration of Pb in the leaves (46.30±0.04 mg/kg was higher than in the roots (42.80±0.05 mg/kg) and the soil (42.30±0.06 mg/kg). The concentration of Zn in the plant was of the order in leaves (46.00±0.03 mg/kg) > roots (26.54±0.03 mg/kg) > soil (20.49±0.03 mg/kg). The concentrations of the studied metals in the plant at the control site did not follow the same trend but were lower than than those at the test site. The BF for Cd, Pb and Zn were greater 1 while those of Co, Cu and Ni were less than 1. TF (Figure 4.42) for the metals were greater than 1. The BF and TF of the elements were of the order Zn > Pb≈ Cd > Co ≈ Cu >Ni and Zn > Cd > Co ≈ Ni ≈ Cu ≈ Pb.

4.10.2 Metal concentrations in different parts of *Cymbopogon citratus* plant

The concentrations of the studied metals in different parts of *Cymbopogon citratus* plant and the soil at Hanwa and their corresponding values at the control site are presented in Figure 4.43 and Appendix XXII. The test values for the metal levels in the leaves were: Cd - 3.00±0.01 mg/kg, Co - 7.40±0.06 mg/kg, Cu - 4.80±0.00 mg/kg, Ni - 8.70±0.05 mg/kg, Pb - 45.70±0.03 mg/kg and Zn - 66.41±0.07 mg/kg; in the roots: Cd - 2.20±0.02 mg/kg, Co - 4.50±0.07 mg/kg, Cu - 2.30±0.11 mg/kg, Ni - 8.50±0.06 mg/kg, Pb - 43.60±0.01 mg/kg and Zn - 37.33±0.02 mg/kg. The soil also showed variations in metal concentrations: : Cd - 3.80±0.03 mg/kg, Co - 8.60±0.04 mg/kg, Cu - 5.60±0.03 mg/kg, Ni - 4.90±0.08 mg/kg, Pb - 76.90±0.06 mg/kg and Zn - 20.49±0.03 mg/kg. The BF and TF for all the metals studied were greater than 1 except Pb whose BF (0.8) was less than 1. The BF and TF of the elements were of the order Zn > Cu > Ni > Cd > Co > Pb and Zn > Cu > Cd > Ni ≈ Co > Pb (Figure 4.44).

4.10.3 Metal concentrations in different parts of *Helianthus annus* (sunflower) plant

The metal concentrations in different parts of *Helianthus annus* **(**sunflower) plant harvested at Hanwa and those of the corresponding values at the control site are presented in Figure 4.45 and Appendix XXIII. The results for the test values showed that the level of Cd was highest in the stems (2.80±0.03 mg/kg), followed by the leaves (2.70±0.02 mg/kg) then the roots (2.50±0.03 mg/kg). For Co, concentration in the leaves (5.80±0.05 mg/kg) was highest, followed by the stems (3.90±0.01 mg/kg) and then the roots (2.20±0.06 mg/kg). The highest Cu content was in the leaves (14.30±0.02 mg/kg), followed by the roots (11.50±0.01 mg/kg) then the stems (4.30±0.01 mg/kg). For Ni, the order was as follows: stems (11.40±0.10 mg/kg) > leaves (11.10±0.03 mg/kg) > roots (11.50±0.01

mg/kg). Pb also followed the order: leaves (47.90±0.04 mg/kg) > stems (42.80±0.02 mg/kg) > roots (39.80±0.04 mg/kg). Zn content was highest in leaves (65.81±0.09 mg/kg), followed by the roots (50.40±0.07 mg/kg) then in the stems (43.03±0.02 mg/kg). The concentrations of the metals studied were more in the soil than in the plant, except Zn which was less in the soil (20.49±0.03 mg/kg). The BF values for only Cu and Zn were greater than 1. TF values for all the metals studied (except Cu) were greater than 1. The BF and TF values for studied metals were of the order : Zn > Cu > Cd > Pb >Co >Ni. For the TF the trend is: Co >Ni > Cd≈ Zn ≈ Pb >Cu (Figure 4.46).

4.10.4 Metal concentrations in different parts of *Ipomoea asarifolia* plant

Metal concentrations in different parts of *Ipomoea asarifolia* plant and soil at Hanwa study area and control site are presented in Figure 4.47 and Appendix XXIV. The test values for the metal concentration in the leaves were: Cd - 1.50±0.02 mg/kg, Co - 4.20±0.11 mg/kg, Cu- 8.00±0.03 mg/kg, Ni - 35.30±0.03 mg/kg, Pb - 43.00±0.03 mg/kg and Zn - 27.63±0.01 mg/kg; concentrations in stems: Cd - 1.60±0.03 mg/kg, Co - 3.90±0.11 mg/kg, Cu - 7.10±0.01 mg/kg, Ni - 7.80±0.05 mg/kg, Pb - 36.10±0.05 mg/kg and Zn - 24.69±0.03 mg/kg; while the roots had Cd -2.50±0.01 mg/kg, Co - 4.40±0.01 mg/kg, Cu - 3.40±0.02 mg/kg, Ni - 6.80±0.14 mg/kg, Pb - 33.00±0.01 mg/kg and Zn - 13.79±0.03 mg/kg. The concentrations in the soil were: Cd - 1.90±0.00 mg/kg, Co - 8.70±0.03 mg/kg, Cu - 5.60±0.03 mg/kg, Ni - 42.10±0.04 mg/kg, Pb - 76.90±0.04 mg/kg and Zn - 20.49±0.03 mg/kg. Only Co (0.5) and Pb (0.5) had their BF less than 1. The TF for Cd and Co were less than 1, while those of Cd (0.6), Co (0.9) and Cu (0.9) were less than 1. The BF and TF were in the order Cd ≈ Cu ≈ Zn > Co≈ Pb > Ni and Ni > Cu > Zn > Pb > Co > Cd respectively (Figure 4.48).

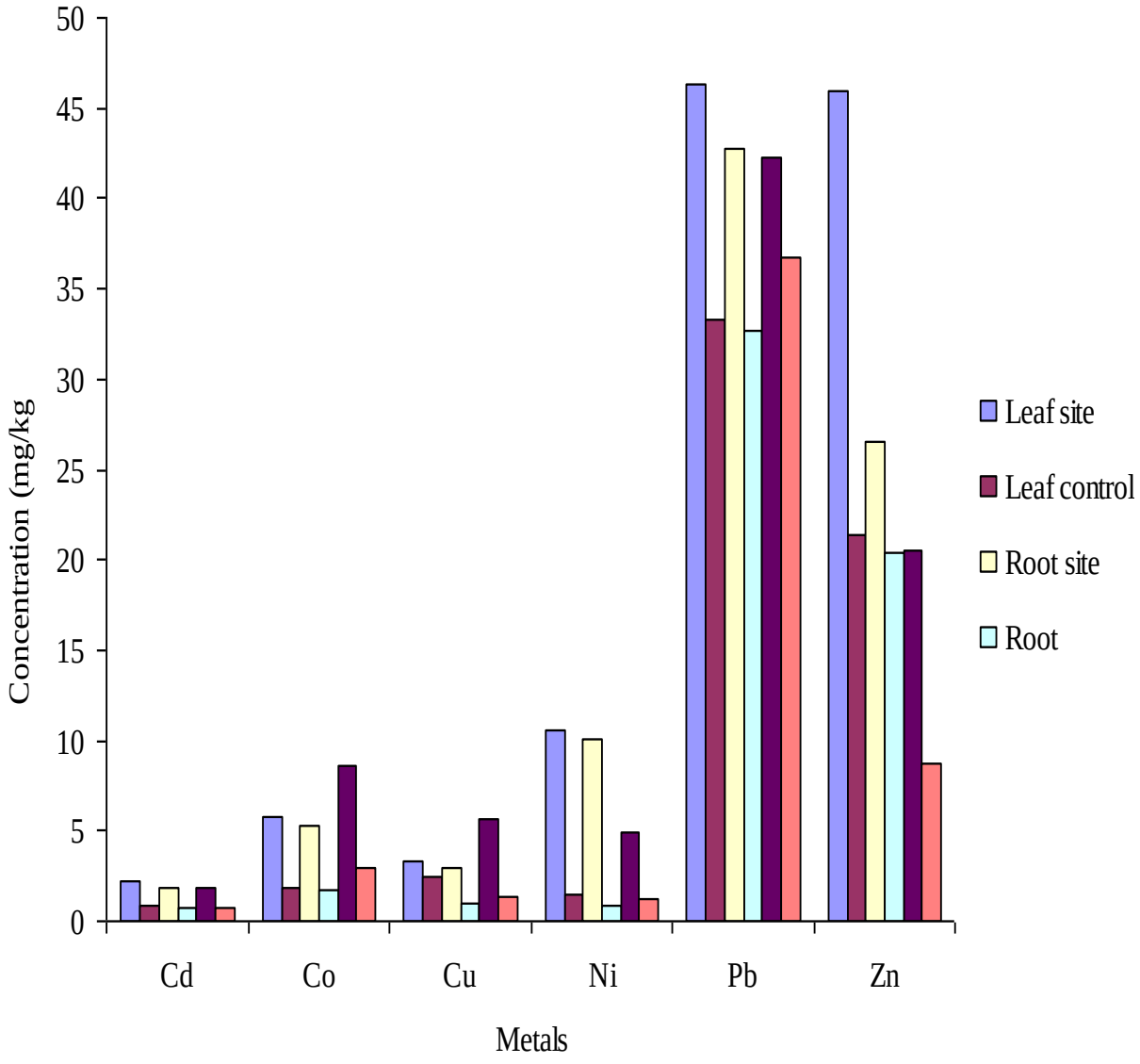


Figure 4.41: Concentrations (mg/kg) of Metals in Different Parts of *Vetivera zizanioide* Plant and Soil at Hanwa

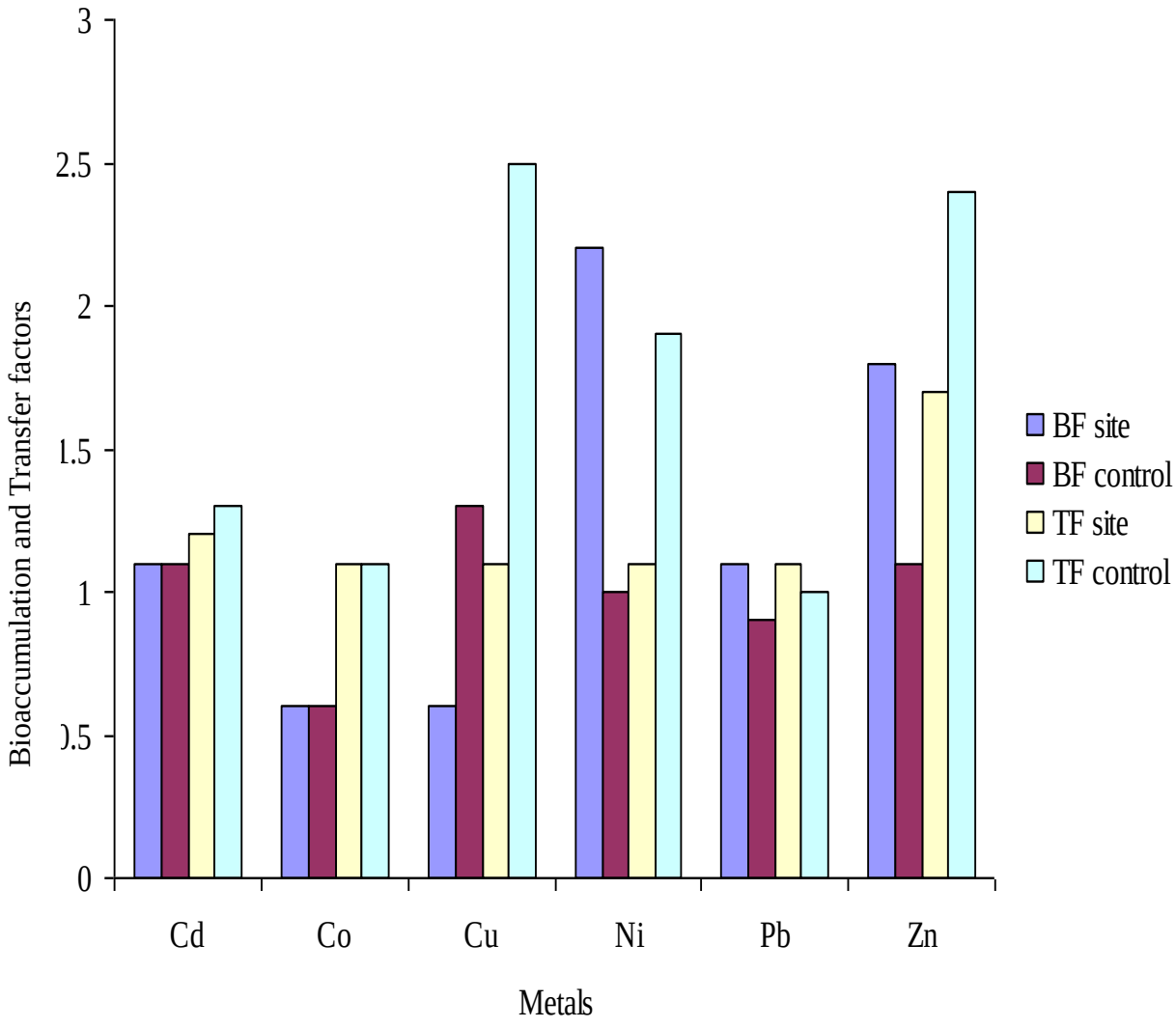


Figure 4.42: Bioaccumulation and Transfer Factors of Metals for *Vetivera zizanioide* Plant at Hanwa

BF = Bioaccumulation factor; TF = Translocation factor.

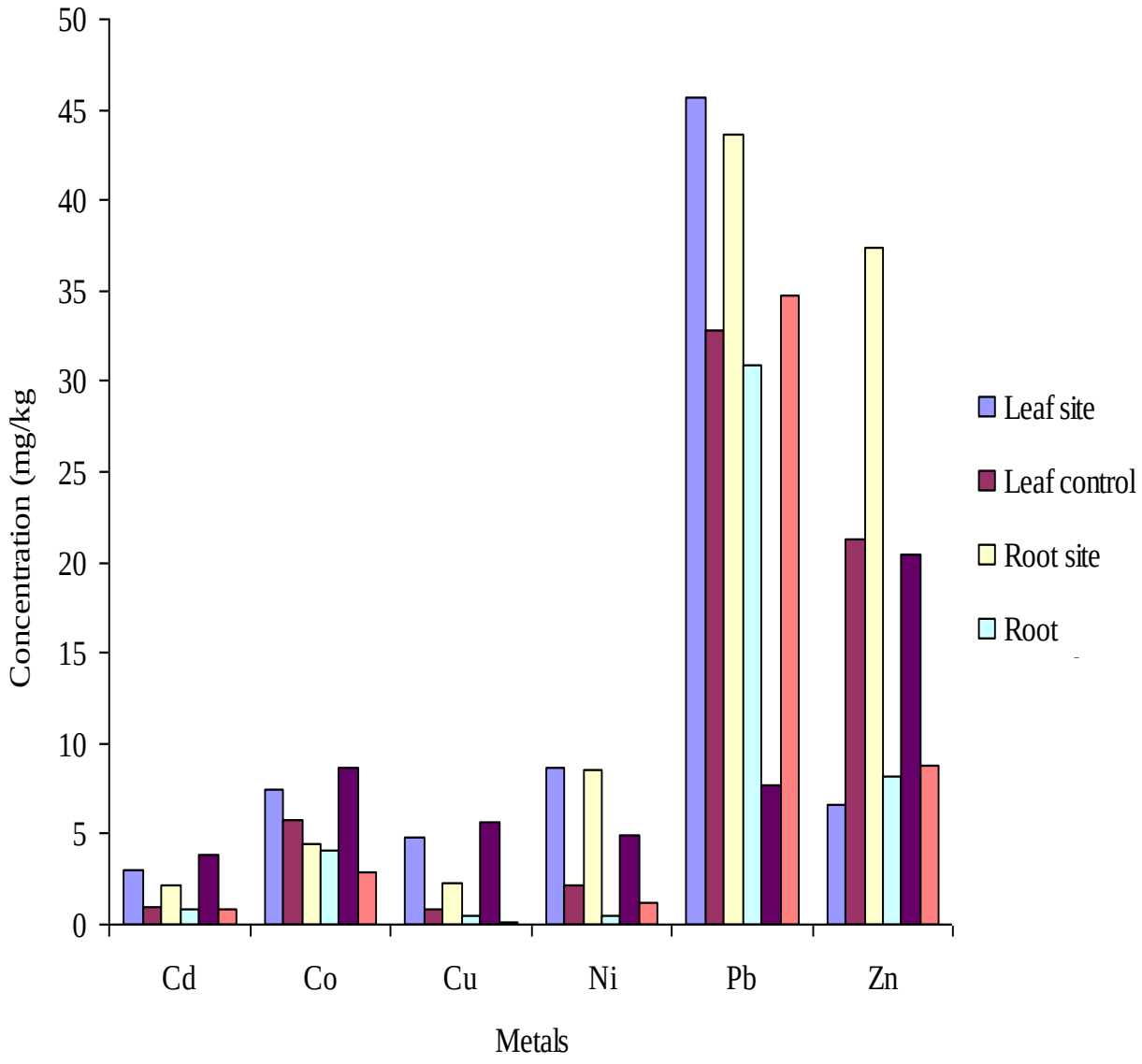


Figure 4.43: Concentrations (mg/kg) of Metals in Different Parts of *Cymbopogon citratus* Plant and the Soil at Hanwa

*Pb (soil) = 7.69 x 10, Zn (leaves) = 6.64 x 10

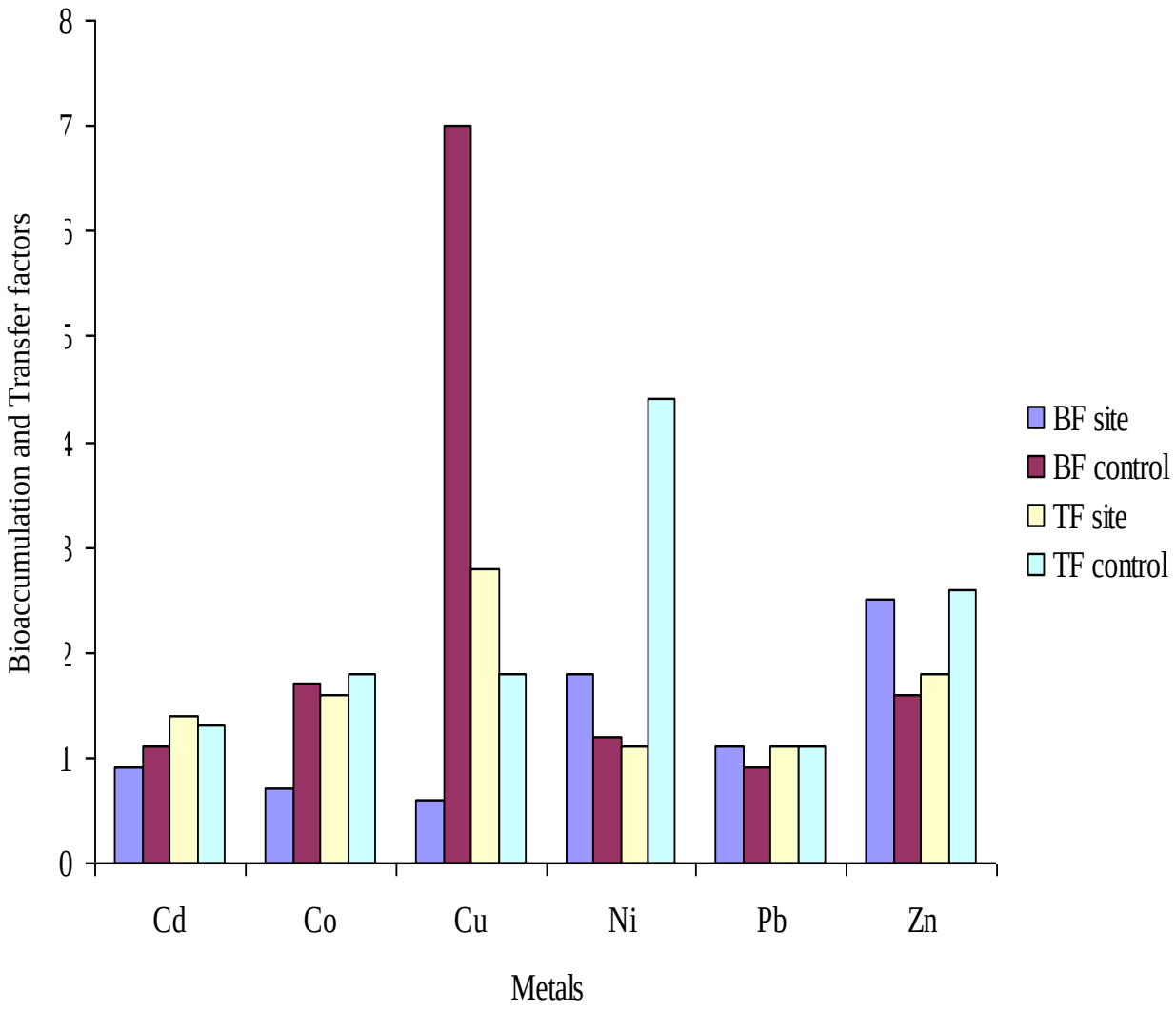


Figure 4.44: Bioaccumulation and Transfer Factors of Metals for *Cymbopogon citratus* Plant at Hanwa

BF = Bioaccumulation factor; TF = Translocation factor.

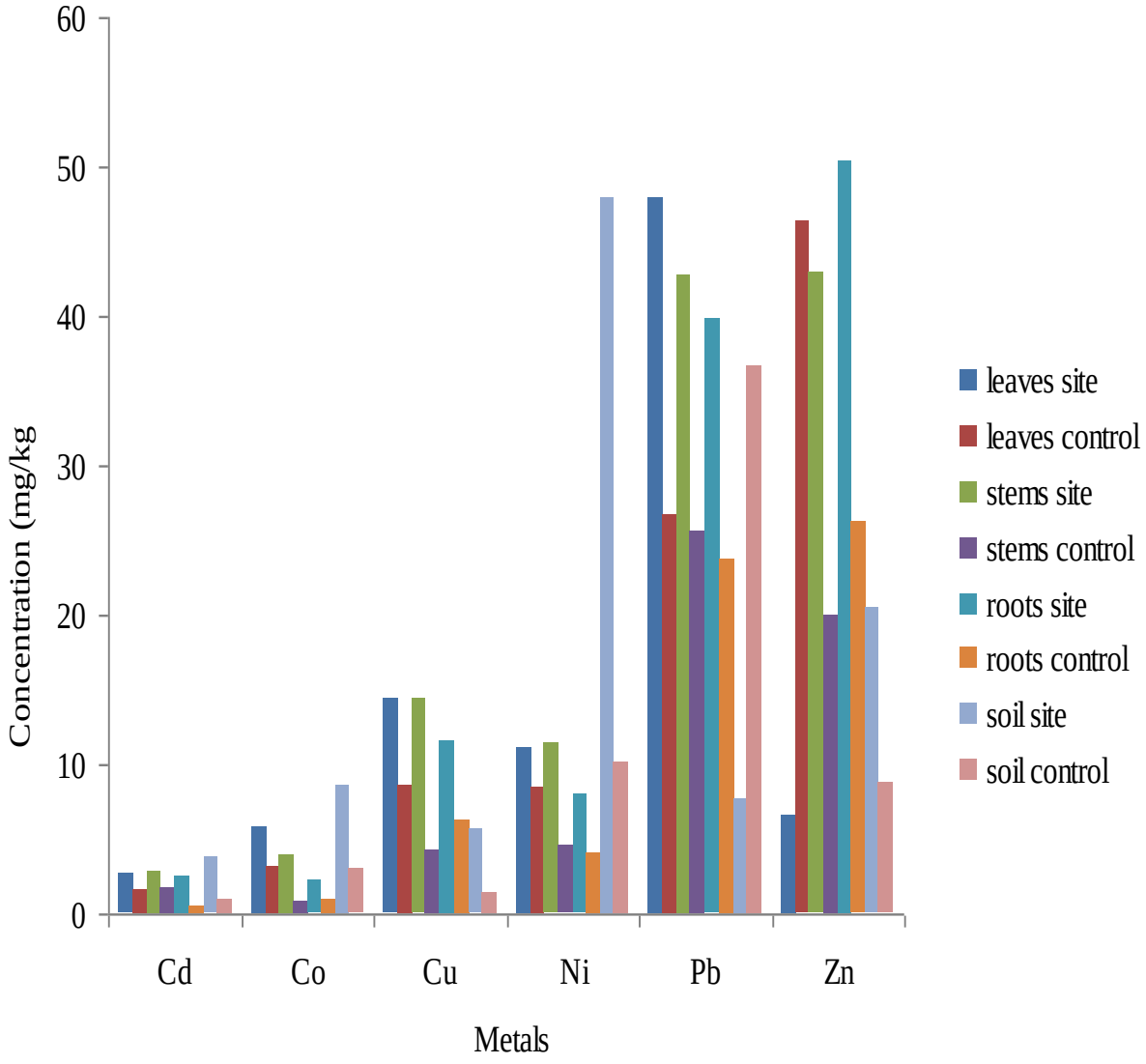


Figure 4.45: Concentrations (mg/kg) of Metals in Different Parts of *Helianthus annus* Plant at Hanwa

* Pb (soil) = 7.69 x 10, Zn (leaves) = 6.581 x 10

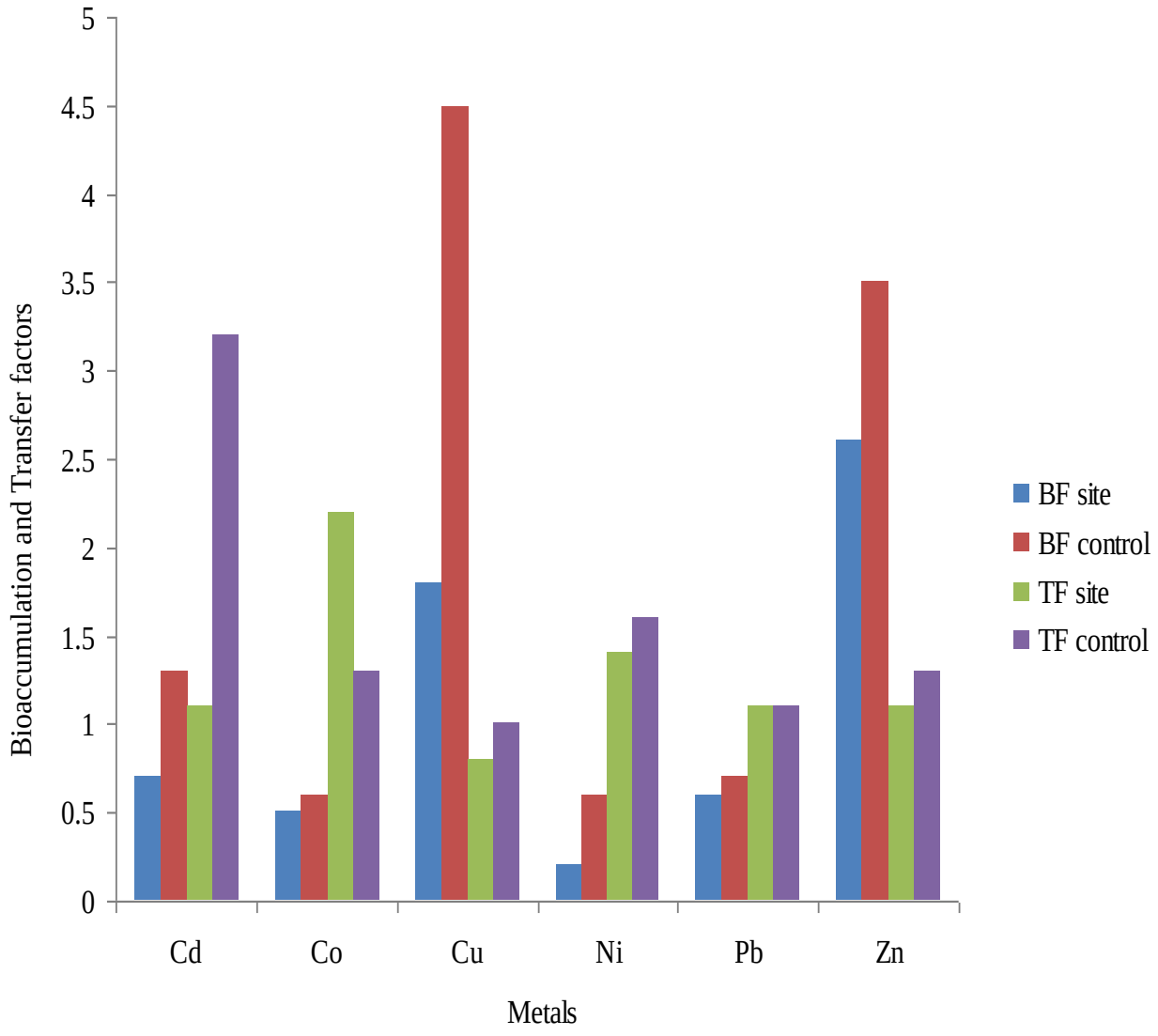


Figure 4.46: Bioaccumulation and Transfer Factors of Metals for *Helianthus annus* Plant at Hanwa

BF = Bioaccumulation factor; TF = Translocation factor.

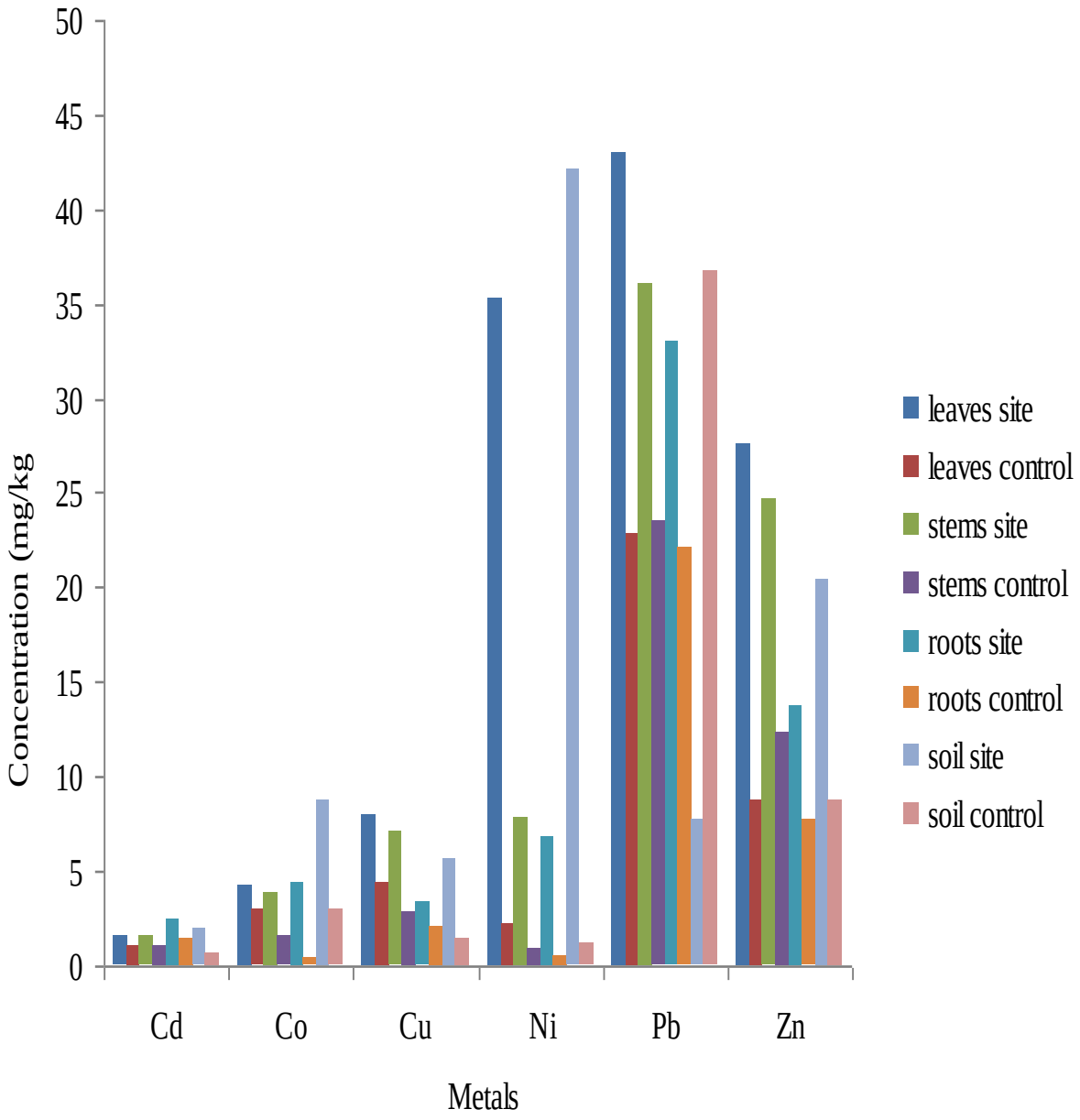


Figure 4.47: Concentrations (mg/kg) of Metals in Different Parts of *Ipomoea asarifolia* Plant at Hanwa

* Pb (soil) = 7.69 x 10

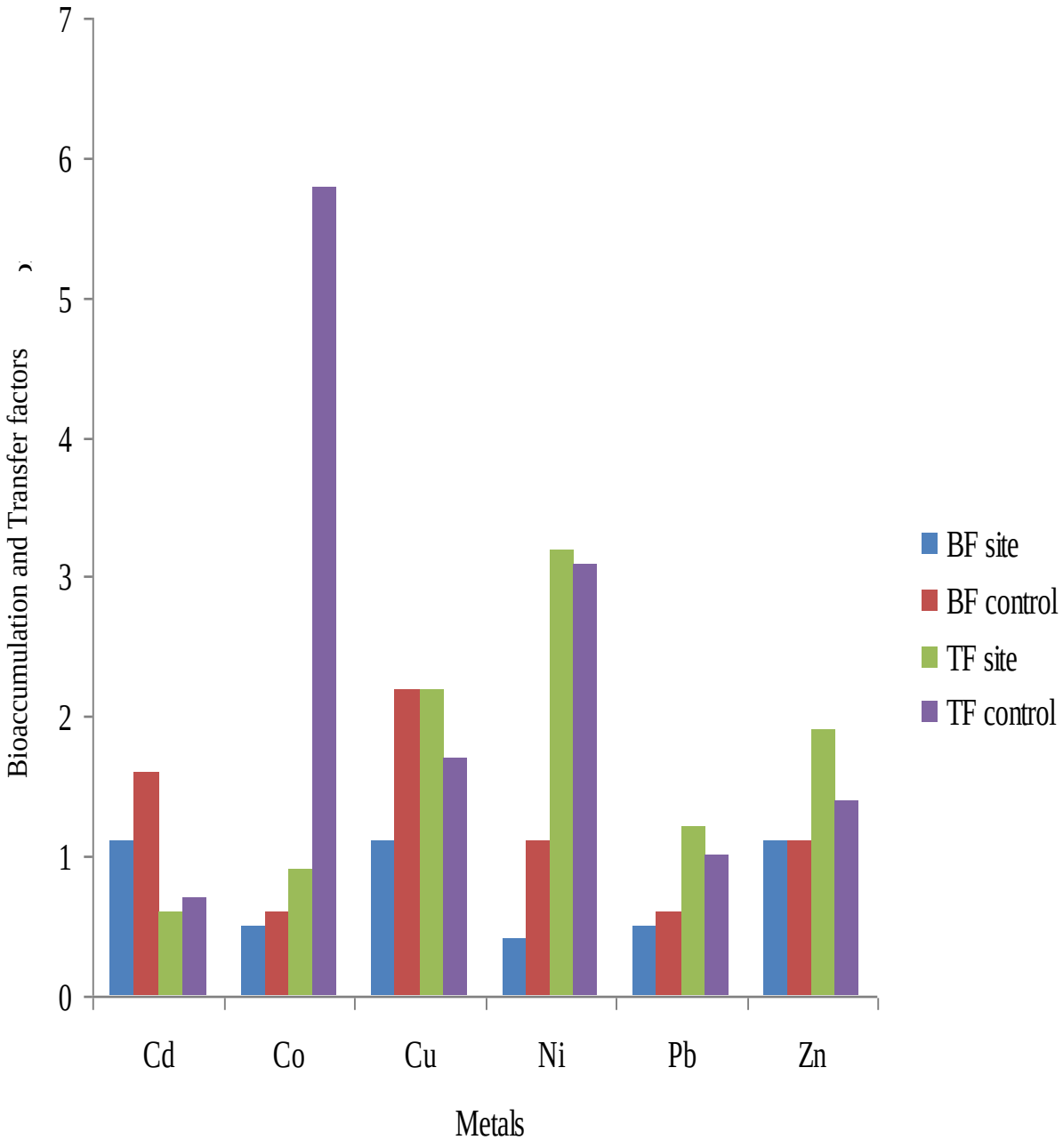


Figure 4.48: Bioaccumulation and Transfer Factors of Metals for *Ipomoea asarifolia* Plant at Hanwa

BF = Bioaccumulation factor; TF = Translocation factor

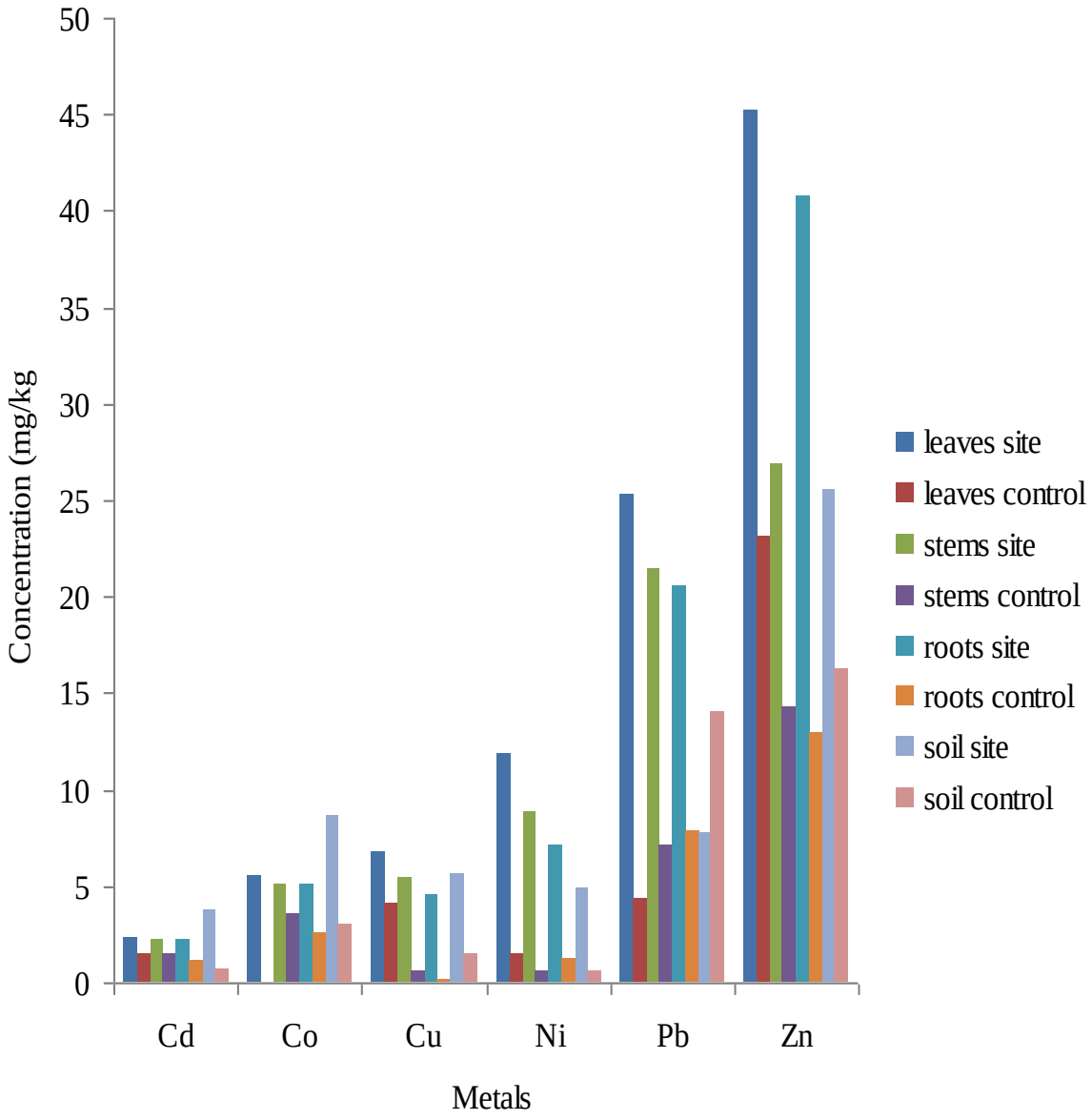


Figure 4.49: Concentrations (mg/kg) of Metals in Different Parts of *Ricinus communis* Plant at Hanwa

* Pb (soil) = 7.69 x 10

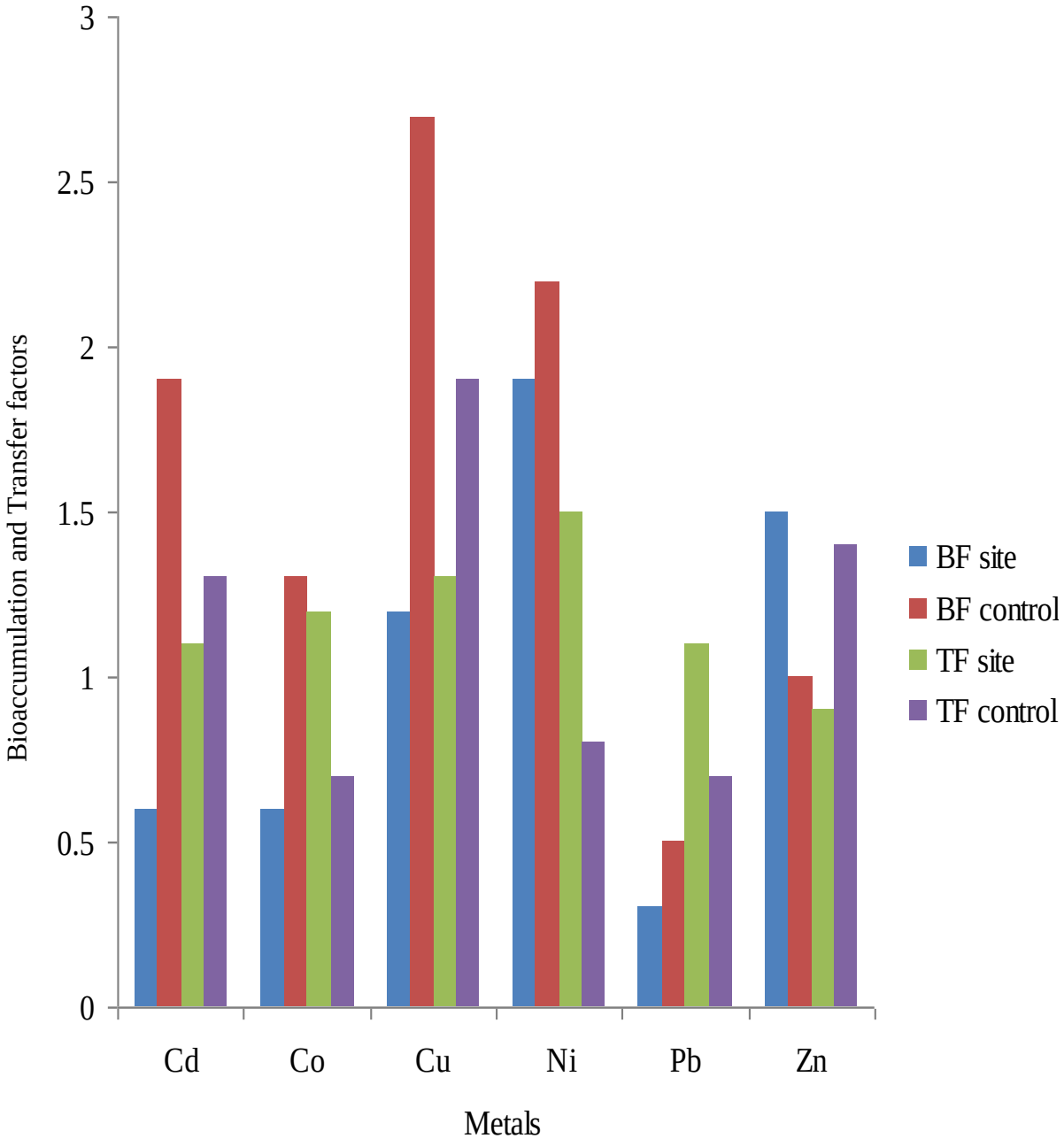


Figure 4.50: Bioaccumulation and Transfer Factors of Metals for *Ricinus communis* Plant at Hanwa

BF = Bioaccumulation factor; TF = Translocation factor

4.10.5 Metal concentrations in different parts of *Ricinus communis* plant

The metal concentrations in different parts of *Ricinus communis* plant harvested from the Hanwa and the control sites are presented in Figure 4.49 and Appendix XXV. The leaves contained highest values of all the studied metals Cd (2.30±0.03 mg/kg), Co (5.50±0.05 mg/kg), Cu (6.70±0.01 mg/kg), Ni (11.80±0.04 mg/kg), Pb (25.30±0.04 mg/kg) and Zn (45.19±0.02 mg/kg). The metal levels in the stems were as follows: Cd (2.20±0.01 mg/kg), Co (5.10±0.03 mg/kg), Cu (5.40±0.03 mg/kg), Ni (8.90±0.02 mg/kg), Pb (21.50±0.03 mg/kg) and Zn (26.90±0.07 mg/kg). The metal contents in the roots were Cd (2.20±0.04 mg/kg), Co (5.10±0.03 mg/kg), Cu (4.50±0.02 mg/kg), Ni (7.10±0.01 mg/kg), Pb (20.60±0.01 mg/kg) and Zn (40.81±0.11 mg/kg). The metal concentrations in the different parts of the *Ricinus communis* plant harvested from the test site were higher than those in the plant harvested from the control site. The metal concentrations in the soil were Cd - 3.80±0.03 mg/kg, Co - 8.60±0.04 mg/kg, Cu - 5.60±0.03 mg/kg, Ni - 4.90±0.08 mg/kg, Pb - 76.90±0.04 mg/kg and Zn - 25.58±0.06 mg/kg. Only Cu and Zn had their BF greater than 1 and the TF value for Zn (0.9) was less than 1 while other studied metals had their TF values greater than 1. The BF and TF were in the following order: Zn > Cu >Co ≈ Cd > Pb > Ni and Ni > Cu > Co > Cd ≈ Pb > Zn respectively (Figure 4.50).

4.11 Bioaccumulation and Transfer Factors for the Metals in Different Plant Species at Hanwa

The BF and TF for Cd in different plant species harvested from Hanwa soil is presented in Figures 4.51 to 4.56 and Appendex XXVI. The BF for Cd indicated the trend *Vetivera zizanioide* (1.1) ≈ *Ipomoea asarifolia* (1.1) > *Cymbopogon citratus* (0.9) > *Helianthus*

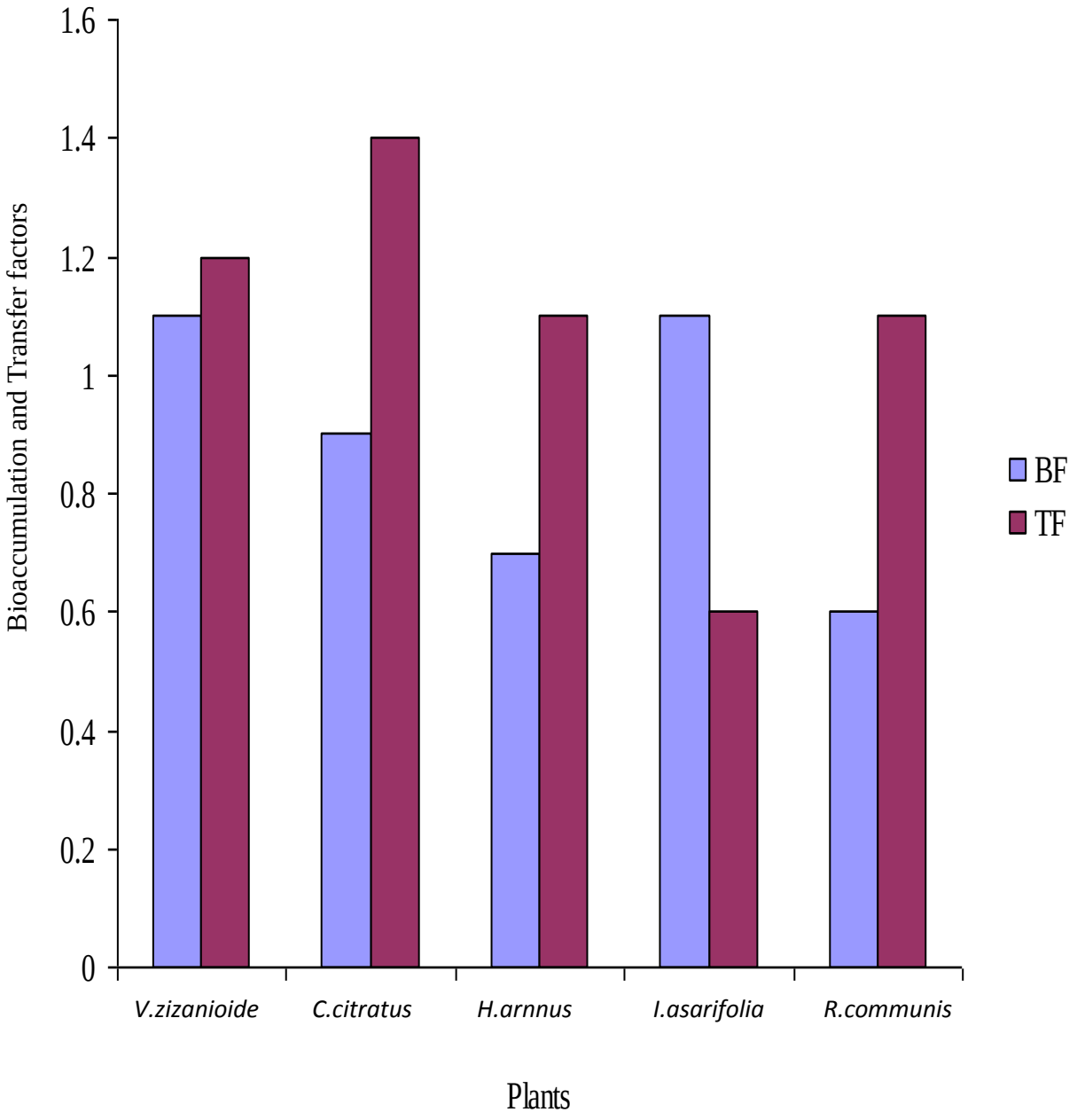


Figure 4.51: Bioaccumulation and Transfer Factors for Cadmium in Different Plant Species at Hanwa

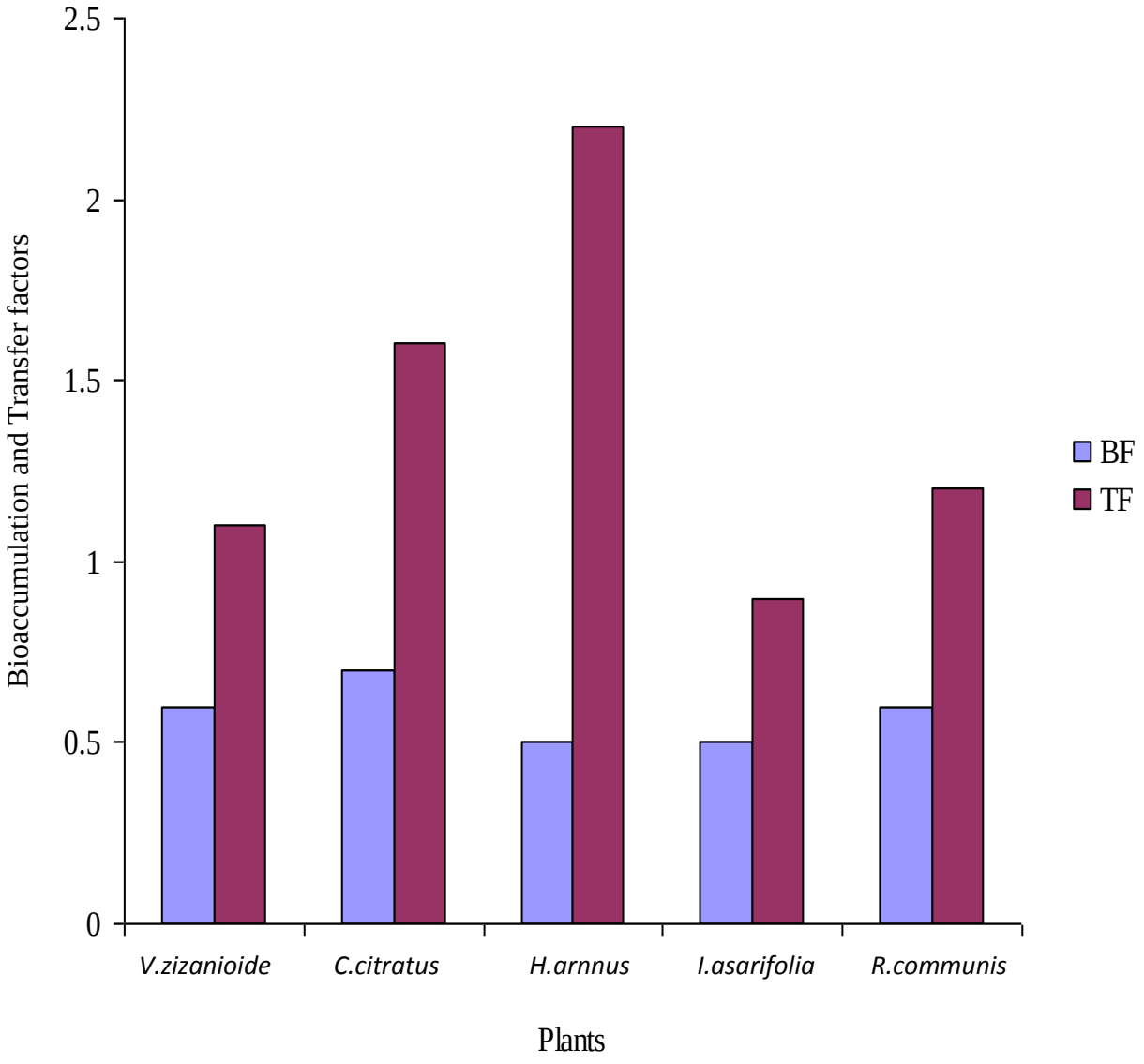


Figure 4.52: Bioaccumulation and Transfer Factors for Cobalt in Different Plant Species at Hanwa

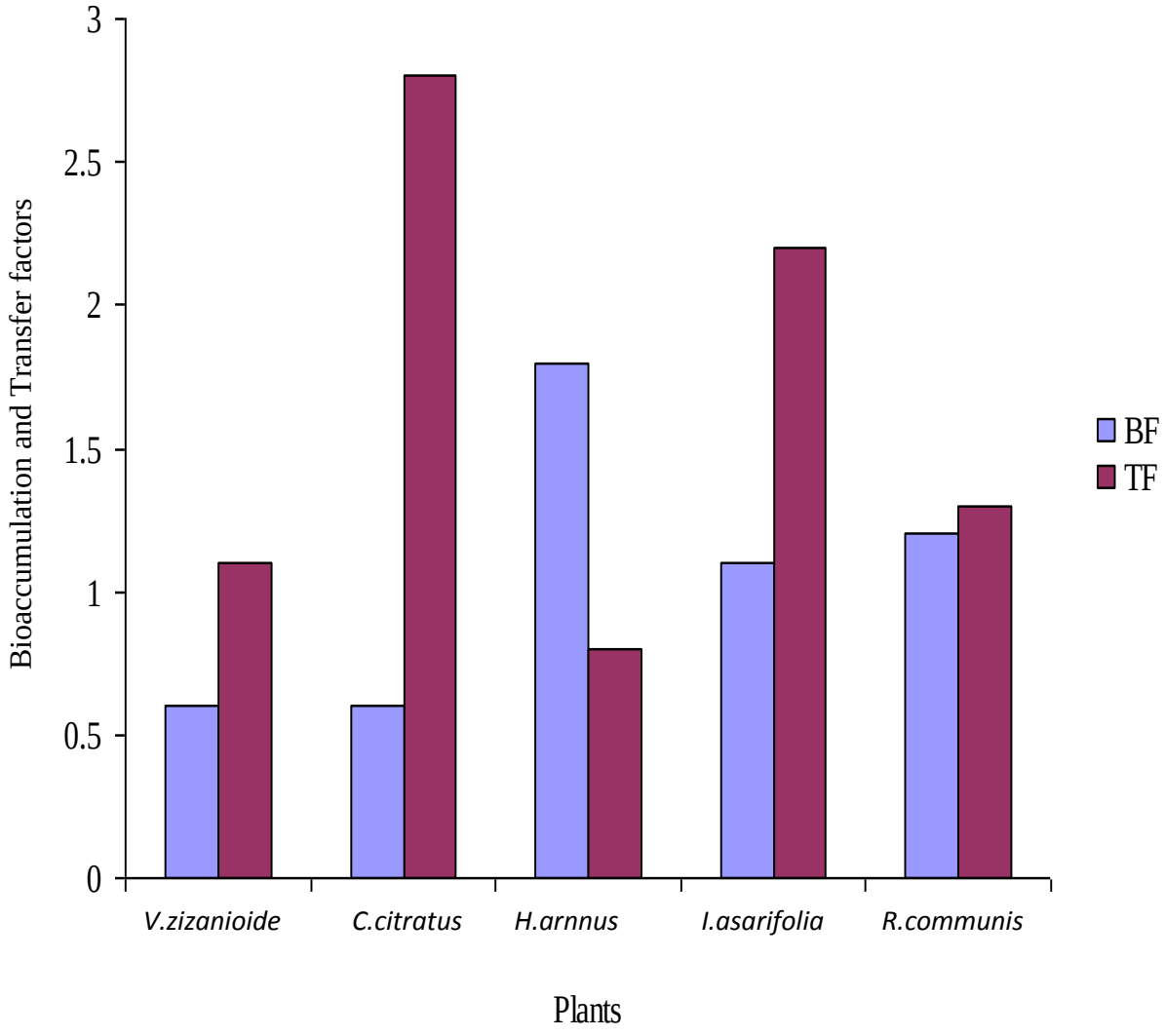


Figure 4.53: Bioaccumulation and Transfer Factors for Copper in Different Plant Species at Hanwa

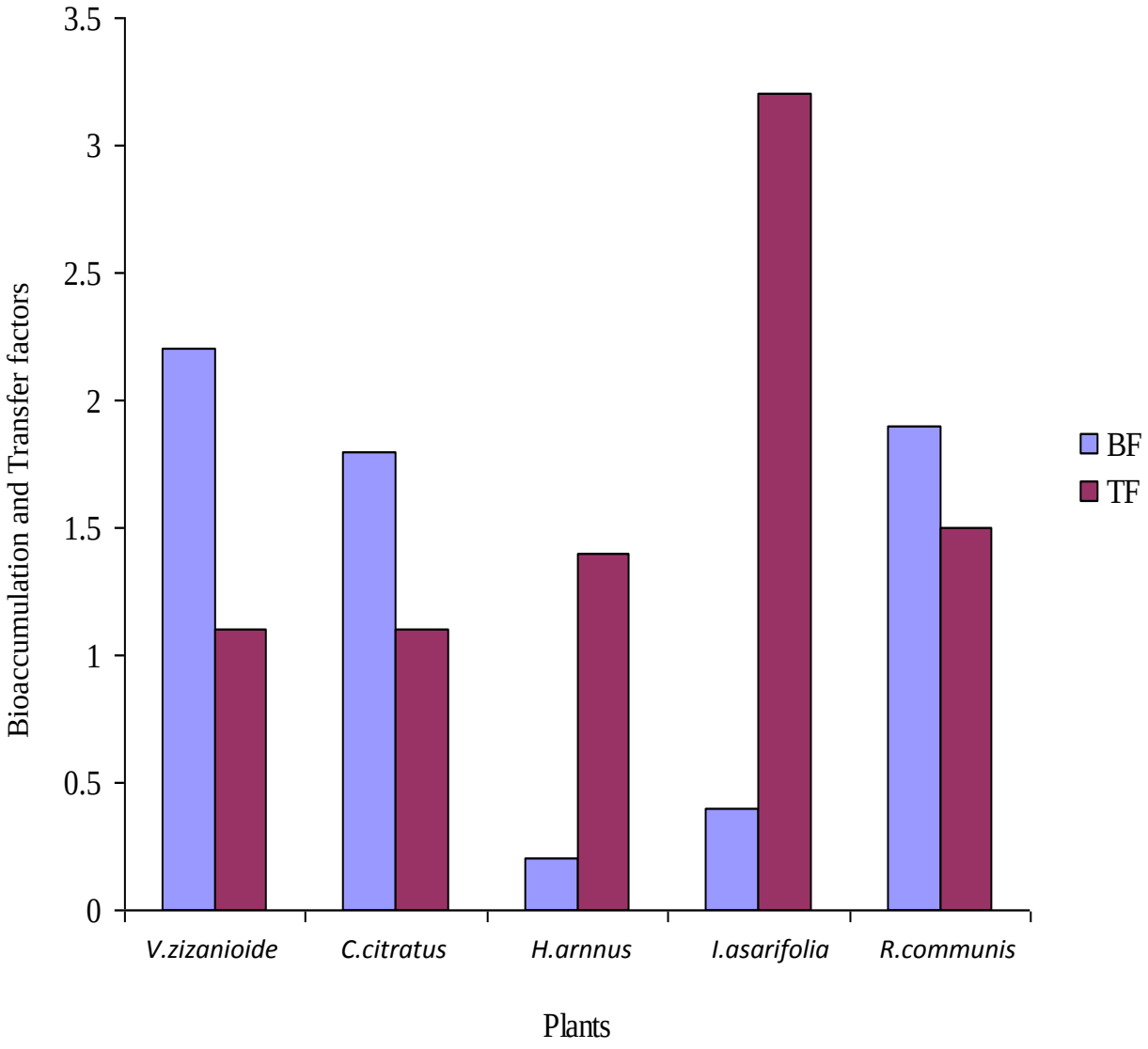


Figure 4.54: Bioaccumulation and Transfer Factors for Nickel in Different Plant Species at Hanwa

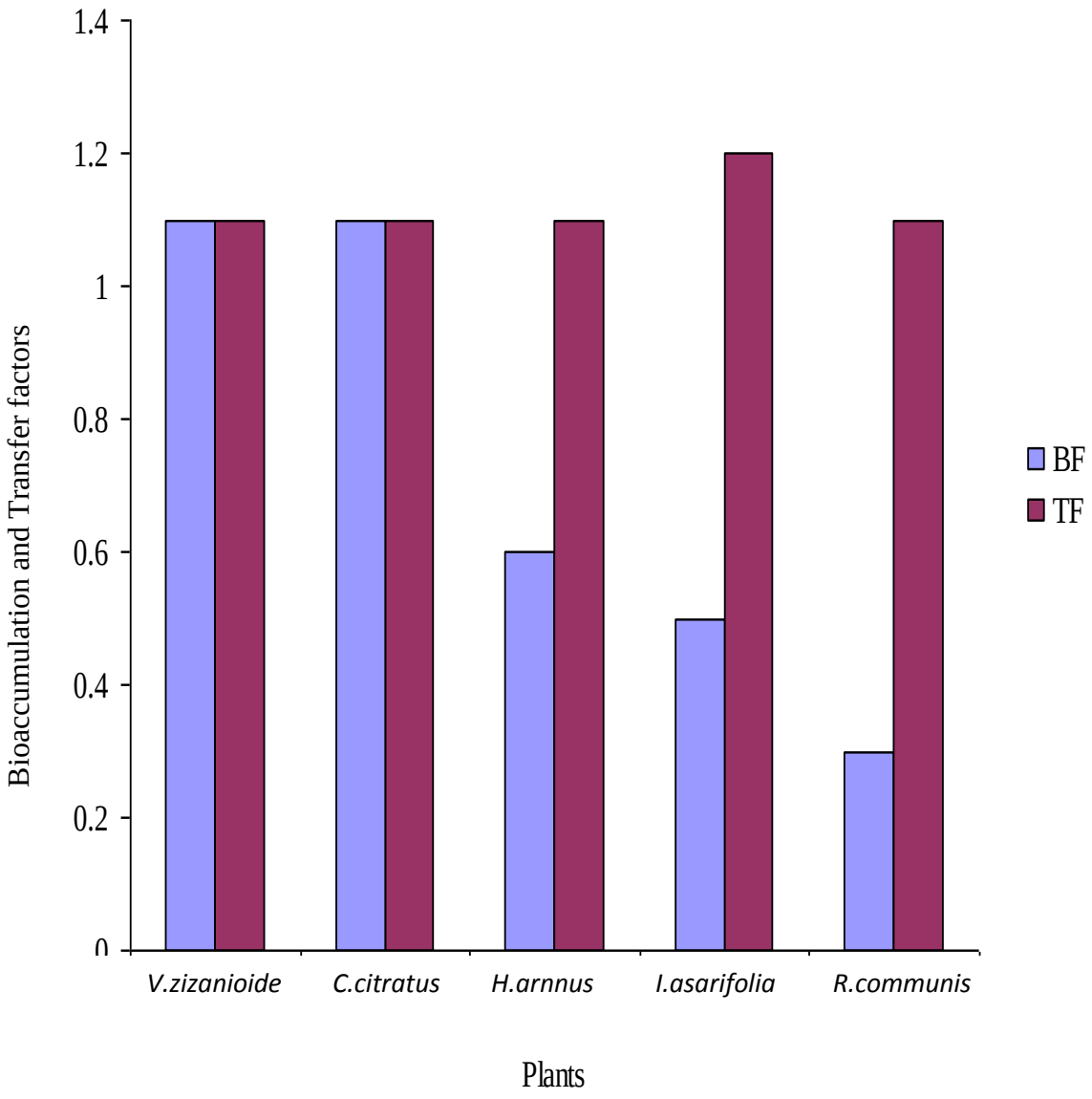


Figure 4.55: Bioaccumulation and Transfer Factors for Lead in Different Plant Species at Hanwa

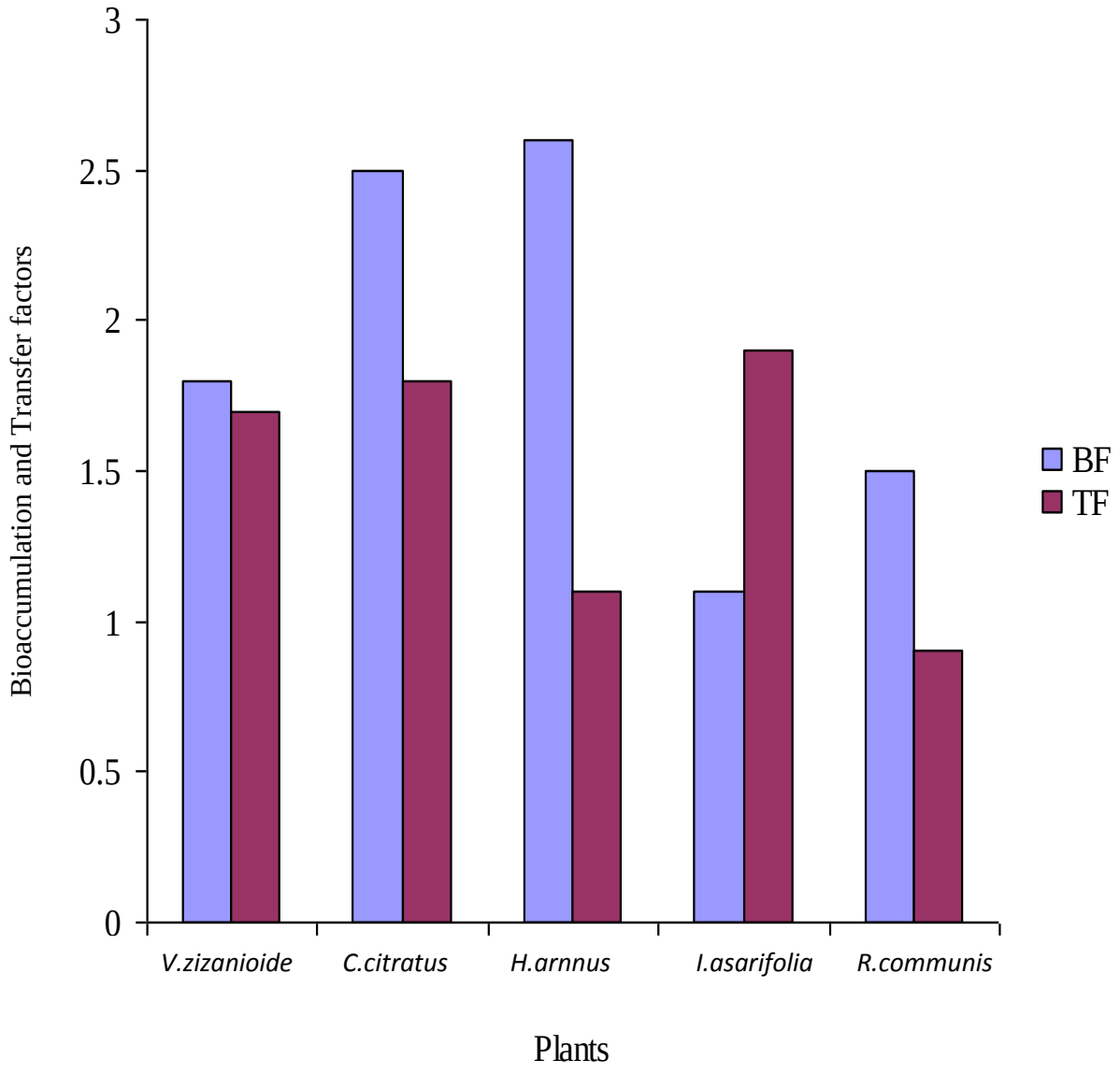


Figure 4.56: Bioaccumulation and Transfer Factors for Zinc in Different Plant Species at Hanwa

annus (0.7) > *Ricinus communis* (0.6), while the TF in *Cymbopogon citratus* (1.4) > *Vetivera zizanioide* (1.2) > *Ricinus communis* (1.1) ≈ *Helianthus annus* (1.1) > *Ipomoea asarifolia* (0.6). The BF and TF for Co in different plant species showed that *Cymbopogon citratus* (0.7) > *Vetivera zizanioide* (0.6) ≈ *Ricinus communis* (0.6) > *Helianthus annus* (0.5) ≈ *Ipomoea asarifolia* (0.5) and *Helianthus annus* (2.2) > *Cymbopogon citratus* (1.6) > *Ricinus communis* (1.2) > *Vetivera zizanioide* (1.1) > *Ipomoea asarifolia* (0.9) respectively. The the BF F for Cu indicated that *Helianthus annus* (1.8) > *Ricinus communis* (1.2) > *Ipomoea asarifolia* (1.1) > *Cymbopogon citratus* (0.6) ≈ *Vetivera zizanioide* (0.6), while the TF followed the order of *Cymbopogon citratus* (2.8) > *Ipomoea asarifolia* (2.2) > *Ricinus communis* (1.3) > *Vetivera zizanioide* (1.1) > *Helianthus annus* (0.8). For Ni, the BF and TF followed the order *Vetivera zizanioide* (2.2) > *Ricinus communis* (1.9) > *Cymbopogon citratus* (1.8) > *Ipomoea asarifolia* (0.4) > *Helianthus annus* (0.2) and *Ipomoea asarifolia* (3.2) > *Ricinus communis* (1.5) > *Helianthus annus* (1.4) > *Vetivera zizanioide* (1.1) ≈ *Cymbopogon citratus* (1.1) respectively. The BF for Pb indicated that *Vetivera zizanioide* (1.1) ≈ *Cymbopogon citratus* (1.1) > *Helianthus annus* (0.6) > *Ipomoea asarifolia* (0.5) > *Ricinus communis* (0.3), while the TF was *Ipomoea asarifolia* (1.2) > *Ricinus communis* (1.1) ≈ *Helianthus annus* (1.1) ≈ *Vetivera zizanioide* (1.1) ≈ *Cymbopogon citratus* (1.1). The BF and TF for Zn in different plant species were *Helianthus annus* (2.6) > *Cymbopogon citratus* (2.5) > *Vetivera zizanioide* (1.8) > *Ricinus communis* (1.5) > *Ipomoea asarifolia* (1.1) and *Ipomoea asarifolia* (1.9) > *Cymbopogon citratus* (1.8) > *Vetivera zizanioide* (1.7) > *Helianthus annus* (1.1) > *Ricinus communis* (0.9) respectively.

4.12 Metal Content in Different Fractions of the Soil with EDTA Application at the Study Areas and Control

The metal concentrations (mg/kg) in different fractions of the soil after the addition of EDTA at the Dakace study area are presented in Figure 4.57 and Appendix XXVII. The concentrations of the studied metals in different fractions of the soil followed the trend: for Cd, Residual Fraction (F6) > Fe and Mn oxides bound Fraction (F4) > Carbonate bound Fraction (F3) > Exchangeable Fraction (F2) > water soluble Fraction (F1) > Organic matter bound Fraction (F5); for Co, Exchangeable Fraction (F2) > water soluble Fraction (F1) > Fe and Mn oxides bound Fraction (F4) > Residual Fraction (F6) > Organic matter bound Fraction (F5) > Carbonate bound Fraction (F3); for Cu, Exchangeable Fraction (F2) > Organic matter bound Fraction (F5) > Carbonate bound Fraction (F3) > water soluble Fraction (F1) > Residual Fraction (F6) > Fe and Mn oxides bound Fraction (F4); for Ni, Residual Fraction (F6) > Organic matter bound Fraction (F5) > Carbonate bound Fraction (F3) > Exchangeable Fraction (F2) > Fe and Mn oxides bound Fraction (F4) > water soluble Fraction (F1); for Pb, Organic matter bound Fraction (F5) > Carbonate bound Fraction (F3) > Fe and Mn oxides bound Fraction (F4) > Exchangeable Fraction (F2) > water soluble Fraction (F1) > Residual Fraction (F6); and for Zn, water soluble Fraction (F1) > Carbonate bound Fraction (F3) > Residual Fraction (F6) > Fe and Mn oxides bound Fraction (F4) > Exchangeable Fraction (F2) > Organic matter bound Fraction (F5).

The result of the metal concentrations (mg/kg) in different fractions of the soil after the addition of EDTA at the Gaskiya study area is presented in Figure 4.58 and Appendix XXVIII. The results showed that in the water soluble Fraction (F1), Zn (8.97±0.02 mg/kg) > Ni (5.70±0.07 mg/kg) > Pb (5.20±0.02 mg/kg) > Co (3.70±0.07 mg/kg) > Cd (0.90±0.05

mg/kg) > Cu (0.60±0.02 mg/kg); Exchangeable Fraction (F2) – Pb (24.50±0.01 mg/kg) > Ni (6.65±0.11 mg/kg) > Zn (4.80±0.03 mg/kg) > Co (4.50±0.03 mg/kg) > Cd (1.10±0.03 mg/kg) > Cu (0.75±0.04 mg/kg); Carbonate bound Fraction (F3) – Pb (22.65±0.01 mg/kg) > Ni (8.90±0.09 mg/kg) > Co (2.35±0.03 mg/kg) > Zn(1.74±0.03m mg/kg) > Cd (1.20±0.02 mg/kg) > Cu (0.25±0.01 mg/kg); Fe and Mn oxides bound Fraction (F4) – Pb (25.05±0.03 mg/kg) > Ni (8.30±0.05 mg/kg) > Zn (4.13±0.04 mg/kg) > Co (2.25±0.06 mg/kg) > Cd (1.50±0.03 mg/kg) > Cu (0.15±0.03 mg/kg); Organic matter bound Fraction (F5) – Pb (26.75±0.05 mg/kg) > Ni (10.55±0.02 mg/kg) > Co (3.45±0.11mg/kg) > Cd (1.00±0.00 mg/kg) > Zn (0.83±0.01mg/kg) > Cu (0.15±0.00 mg/kg); Residual Fraction (F6) – Pb (19.95±0.02 mg/kg) > Ni (11.45±0.00 mg/kg) > Cd (2.40±0.03 mg/kg) > Co (1.50±0.07 mg/kg) > Zn (0.94±0.04 mg/kg) > Cu (0.05±0.03 mg/kg).

The result for the metal concentrations (mg/kg) in different fractions of the soil after the addition of EDTA at the Hanwa study area is presented in Figure 4.59 and Appendix XXIX. The results showed that in the water soluble Fraction (F1), Zn (10.84±0.07 mg/kg) > Pb (5.60±0.03 mg/kg) > Ni (5.00±0.01 mg/kg) > Co (4.10±0.02 mg/kg) > Cd (0.70±0.02 mg/kg) > Cu (0.15±0.03 mg/kg); Exchangeable Fraction (F2) – Pb (18.70±0.03 mg/kg) > Zn (12.21±0.01 mg/kg) > Ni (8.00±0.07 mg/kg) > Co (4.40±0.03 mg/kg) > Cu (1.70±0.02 mg/kg) > Cd (1.00±0.05 mg/kg); Carbonate bound Fraction (F3) – Pb (23.55±0.05 mg/kg) > Ni (8.55±0.07 mg/kg) > Zn (6.68±0.07mg/kg) > Co (2.50±0.03 mg/kg) > Cd (1.20±0.01 mg/kg) > Cu (0.15±0.02 mg/kg); Fe and Mn oxides bound Fraction (F4) – Pb (22.90±0.03 mg/kg) > Zn (9.27±0.17 mg/kg) > Ni (8.95±0.04 mg/kg) > Co (2.80±0.05 mg/kg) > Cd (1.20±0.01 mg/kg) > Cu (0.05±0.01 mg/kg); Organic matter bound Fraction (F5) – Pb (24.85±0.03 mg/kg) > Ni (9.10±0.03 mg/kg) > Co (2.90±0.05

mg/kg) > Cu (1.20±0.02 mg/kg) > Cd (0.80±0.05 mg/kg) > Zn (0.68±0.04 mg/kg); Residual Fraction (F6) – Pb (22.60±0.03 mg/kg) > Ni (12.10±0.02 mg/kg) > Zn (2.77±0.0 mg/kg) > Cd (2.50±0.03 mg/kg) > Co (2.00±0.09 mg/kg) > Cu (0.10±0.01 mg/kg).

The results of the metal concentrations (mg/kg) in different fractions of the soil after the addition of EDTA at the control area is presented in Figure 4.60 and Appendix XXX. The results showed that in the water soluble Fraction (F1), Pb (7.42±0.0 mg/kg) > Ni (6.55±0.05 mg/kg) > Co (4.40±0.05 mg/kg) > Zn (3.83±0.04 mg/kg) >Cd (0.43±0.02 mg/kg) > Cu (0.34±0.02 mg/kg); Exchangeable Fraction (F2) – Pb (23.32±0.03 mg/kg) > Zn (9.22±0.04m g/kg) > Ni (8.00±0.05 mg/kg) > Co (3.27±0.05 mg/kg) > Cu (0.57±0.03 mg/kg) > Cd (0.52±0.02 mg/kg); Carbonate bound Fraction (F3) – Pb (24.90±0.02 mg/kg) > Ni (9.22±0.04 mg/kg) > Zn (3.94±0.03 mg/kg) > Co (2.80±0.03 mg/kg) > Cd (0.62±0.03 mg/kg) > Cu (0.17±0.03 mg/kg); Fe and Mn oxides bound Fraction (F4) – Pb (26.42±0.05 mg/kg) > Ni (10.18±0.07 mg/kg) > Zn (3.15±0.04 mg/kg) > Co (2.97±0.03 mg/kg) > Cd (0.81±0.01 mg/kg) > Cu (0.10±0.01 mg/kg); Organic matter bound Fraction (F5) – Pb (23.95±0.04 mg/kg) > Ni (12.40±0.04 mg/kg) > Co (2.12±0.05 mg/kg) > Cu (0.62±0.01 mg/kg) > Cd (0.52±0.02 mg/kg) > Zn (0.29±0.03 mg/kg); Residual Fraction (F6) – Pb (23.13±0.03 mg/kg) > Ni (13.30±0.06 mg/kg) > Zn (1.50±0.02 mg/kg) > Co (1.45±0.03 mg/kg) > Cd (1.32±0.02 mg/kg) > Cu (0.08±0.01 mg/kg).

4.13 Metal Content in Different Parts of Plant Species with EDTA Application at Dakace Site

4.13.1 Concentrations of metals in different parts of *Vetivera zizanioide* plant

The concentrations of metals in different parts of *Vetivera zizanioide* plant for the various metals studied after the application of EDTA at Dakace and the control study areas are

presented in Figure 4.61 and Appendix XXXI. At the test site, metal levels in the leaves were:Cd - 3.60±0.05 mg/kg, Co - 23.50±0.05 mg/kg, Cu - 13.90±0.10 mg/kg, Ni - 99.14±0.22 mg/kg, Pb - 50.20±0.06 mg/kg and Zn - 100.56±0.08 mg/kg; Roots: Cd - 3.40±0.04 mg/kg, Co - 8.50±0.02 mg/kg, Cu - 7.30±0.01 mg/kg, Ni - 36.00±0.06 mg/kg, Pb - 45.50±0.05 mg/kg and Zn - 36.46±0.07 mg/kg. the concentration of the metals in the soil were: Cd - 3.80±0.02 mg/kg, Co - 8.40±0.03 mg/kg, Cu - 6.50±0.03 mg/kg, Ni - 51.30±0.05 mg/kg, Pb - 42.80±0.02 mg/kg and Zn - 41.33±0.04 mg/kg. The values for the test samples were higher than the control values. The bioaccumulation factor (BF) and the translocation factor (TF) for all the studied metals (except BF for Cd) were greater than 1 (Figure 4.45b). The order in the BF and TF of the metals were: Co > Cu > Zn > Ni > Pb > Cd and Co ≈ Ni ≈ Zn > Cu > Cd ≈ Pb respectively (Figure 4.62).

4.13.2 Concentrations of metals in different parts of *Cymbopogon citratus* (Lemon grass) plant

The concentrations of metals in different parts of *Cymbopogon citratus* (Lemon grass) plant for the various metals studied after the application of EDTA at Dakace and the control study areas are presented in Figure 4.63 and Appendix XXXII. At the test site, the metal level in the leaves were: Cd - 5.97±0.05 mg/kg, Co - 12.00±0.04 mg/kg, Cu - 11.67±0.04 mg/kg, Ni - 99.90±0.07 mg/kg, Pb - 63.90±0.02 mg/kg and Zn - 73.50±0.11 mg/kg. for the roots, Cd - 3.20±0.05 mg/kg, Co - 11.80±0.11 mg/kg, Cu - 4.60±0.04 mg/kg, Ni - 38.00±0.08 mg/kg, Pb - 58.60±0.04 mg/kg, Zn - 37.30±0.15 mg/kg; metal concentrations in the soil: Cd - 3.80±0.02 mg/kg, Co - 38.40±0.05 mg/kg, Cu - 6.50±0.03 mg/kg, Ni - 51.30±0.05 mg/kg, Pb - 69.30±0.11 mg/kg and Zn - 55.93±0.05 mg/kg. The test values were higher than the control values. The bioaccumulation factor (BF) and the translocation factor (TF) for all the studied metals (except BF for Pb) were greater than 1 (Figure 4.64).

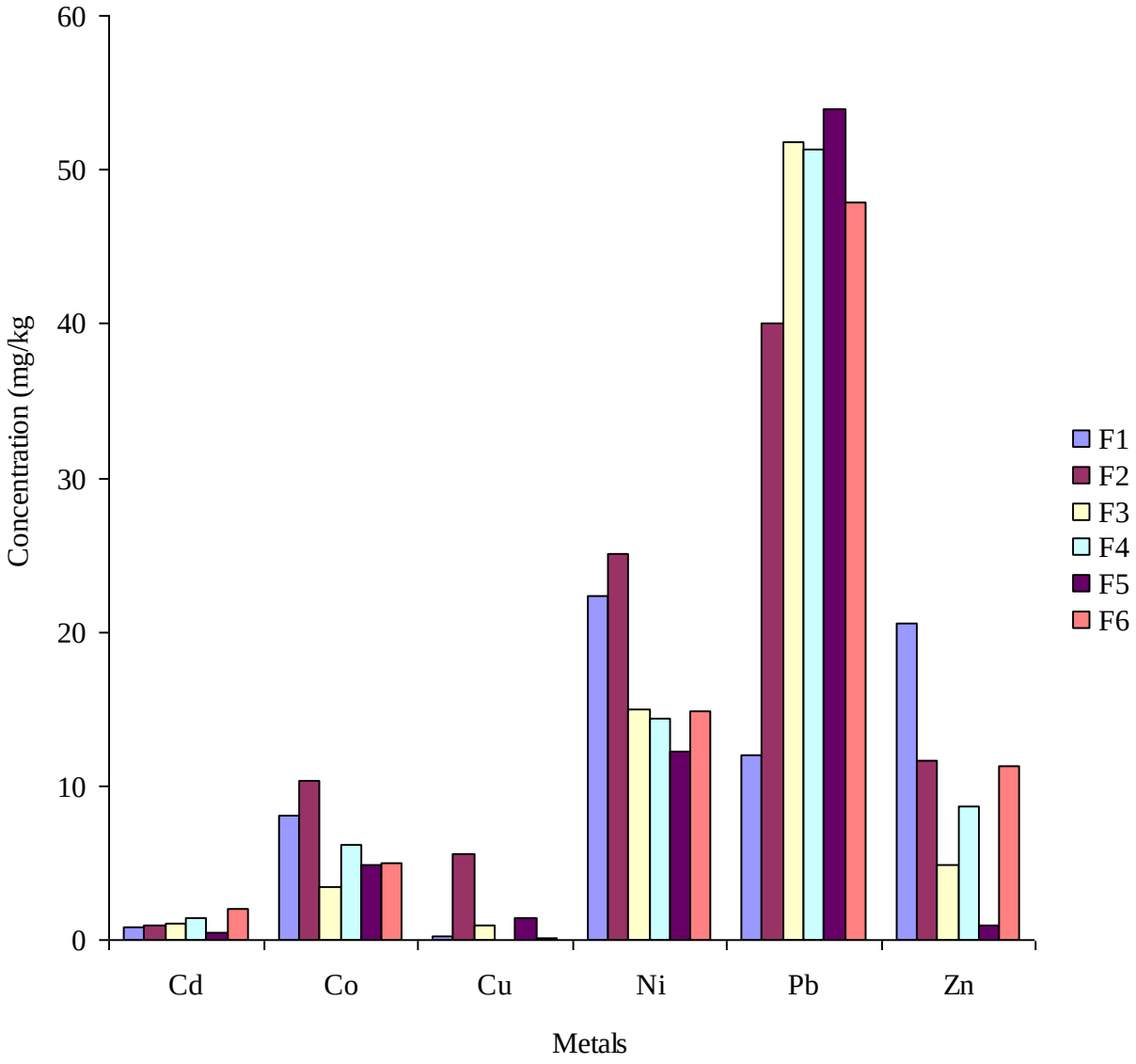


Figure 4.57: Concentrations (mg/kg) of Metals in Different Fractions of the Soil with EDTA at Dakace

F1= water soluble Fraction, F2 = Exchangeable Fraction, F3 = Carbonate bound Fraction,

F4 = Fe and Mn oxides bound Fraction, F5 = Organic matter bound Fraction, F6 = Residual Fraction.

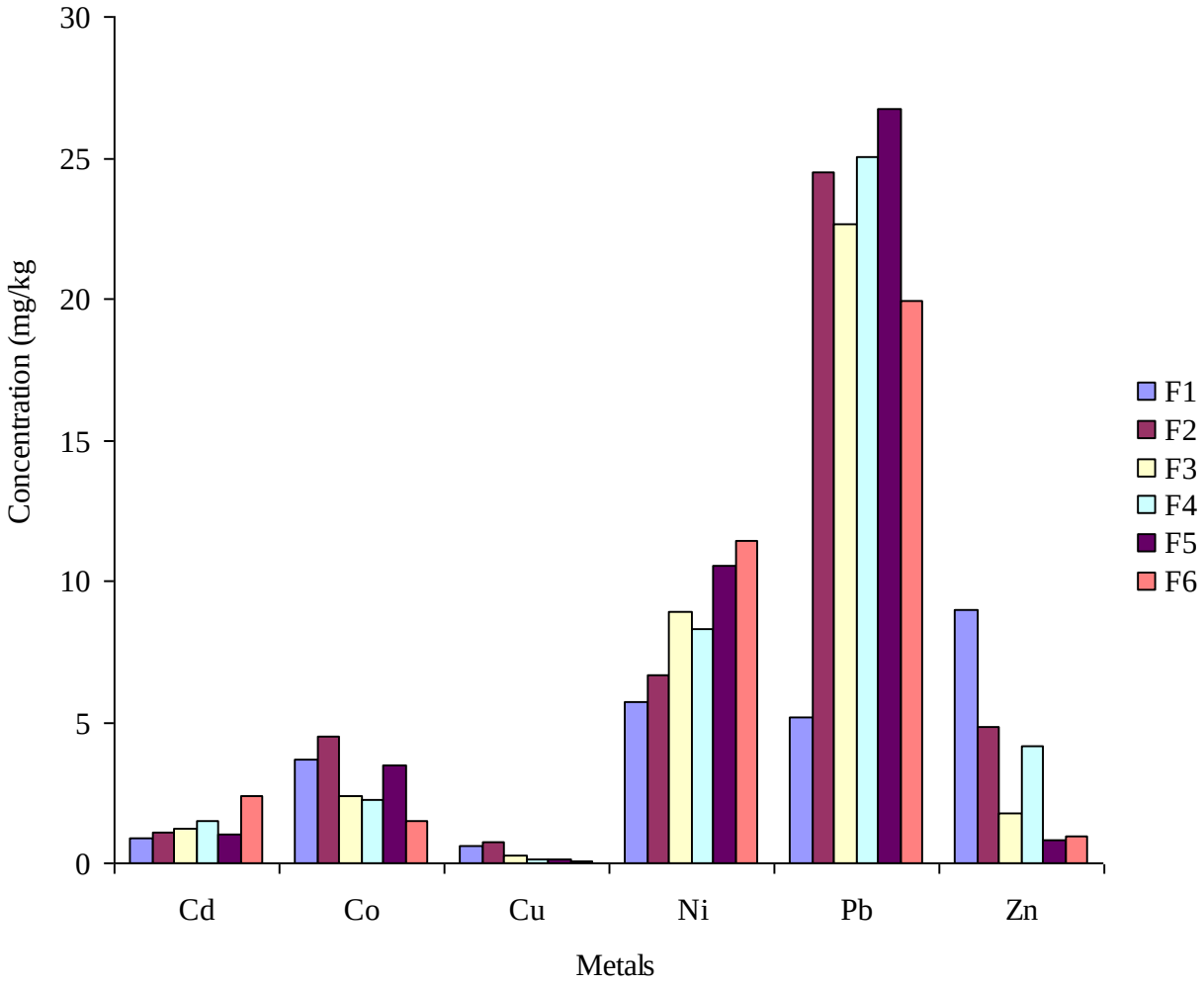


Figure 4.58: Concentrations (mg/kg) of Metals in Different Fractions of the Soil with EDTA at Gaskiya

F1= water soluble Fraction, F2 = Exchangeable Fraction, F3 = Carbonate bound Fraction,

F4 = Fe and Mn oxides bound Fraction, F5 = Organic matter bound Fraction, F6 = Residual Fraction.

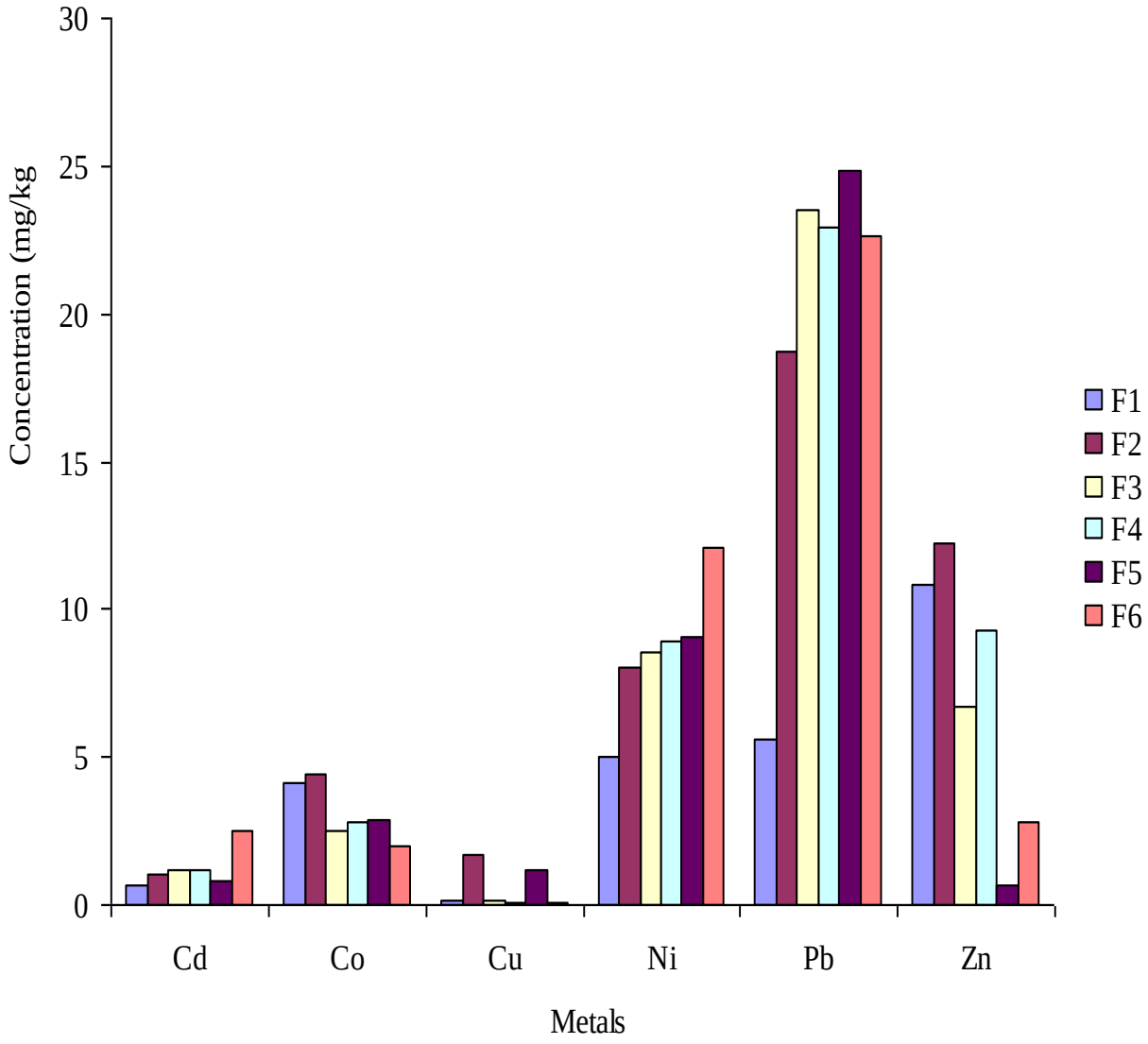


Figure 4.59: Concentrations (mg/kg) of Metals in Different Fractions of the Soil with EDTA at Hanwa

F1= water soluble Fraction, F2 = Exchangeable Fraction, F3 = Carbonate bound Fraction,

F4 = Fe and Mn oxides bound Fraction, F5 = Organic matter bound Fraction, F6 = Residual Fraction.

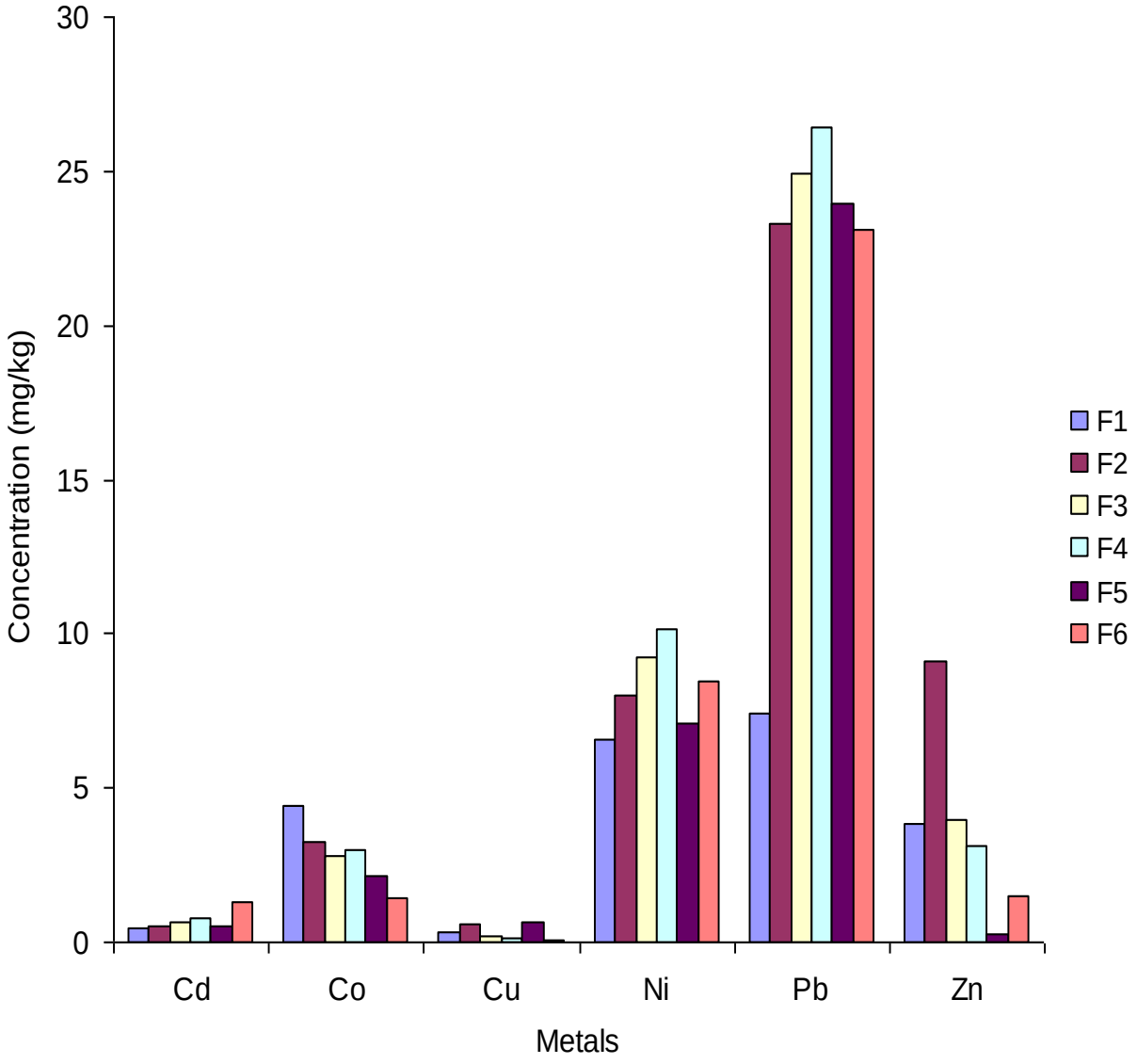


Figure 4.60: Concentrations (mg/kg) of Metals in Different Fractions of the Soil at the Control Site with EDTA

F1= water soluble Fraction, F2 = Exchangeable Fraction, F3 = Carbonate bound Fraction,

F4 = Fe and Mn oxides bound Fraction, F5 = Organic matter bound Fraction, F6 = Residual Fraction.

The order in the BF and TF of the metals were: Co > Cu ≈ Ni > Cd > Zn > Pb and Ni > Cu > Zn > Cd > Co ≈ Pb respectively.

4.13.3 Concentrations of metals in different parts of *Helianthus annus* (Sunflower) plant

The concentrations of metals in different parts of *Helianthus annus* (Sunflower) plant for the various metals studied after the application of EDTA at Dakace and the control study areas are presented in Figure 4.65 and Appendix XXXIII. At the test site, the leaves contained highest concentration of Zn (150.05±0.06mg/kg) > Pb (63.90±0.06 mg/kg) > Cu (40.50±0.03 mg/kg) > Ni (23.80±0.12 mg/kg) > Co (13.10±0.09 mg/kg) > Cd (5.10±0.01 mg/kg). In the stem: Ni (96.30±0.04 mg/kg) > Zn (58.80±0.06 mg/kg) > Pb (39.60±0.00 mg/kg) > Co (13.10±0.02 mg/kg) > Cu (3.90±0.06 mg/kg) > Cd (2.80±0.03 mg/kg). For the roots: Pb (35.40±0.06 mg/kg) > Zn (16.45±0.04 mg/kg) > Ni (14.70±0.04 mg/kg) > Co (9.00±0.04 mg/kg) > Cd (2.60±0.01 mg/kg) > Cu (2.50±0.02 mg/kg). The concentrations of the studied metals in the soil: Pb (42.80±0.02 mg/kg) > Zn (41.33±0.04 mg/kg) > Co (8.40±0.03 mg/kg) > Ni (4.90±0.08 mg/kg) > Cd (3.80±0.02 mg/kg) > Cu (1.90±0.03 mg/kg). The test values wer higher than the control values. The bioaccumulation factor (BF) and the translocation facor (TF) for the studied metals (excpt the BF for Cd) at the test site were greater than 1 (Figure 4.66). The BF and the TF followed the order: Ni > Cu > Zn > Co > Pb > Cd and Cu > Zn > Ni > Co ≈ Pb ≈ Cd. For the control, only the BF for Pb and Co were less than 1 but the TF for all the metals were greater than 1.

4.13.4 Concentrations of metals in different parts of *Ipomoea asarifolia* plant

The concentrations of metals in different parts of *Ipomoea asarifolia* plant for the various metals studied after the application of EDTA at Dakace and the control study areas

are presented in Figure 4.67 and Appendix XXXIV. At the test site, concentrations of Co (11.50±0.09 mg/kg), Cu (17.80±0.02 mg/kg), Ni (116.70±0.08 mg/kg), Zn (52.52±0.10 mg/kg), Cd (3.90±0.04 mg/kg) and Pb (31.90±0.03 mg/kg) were in the leaves; Cd (4.10±0.02 mg/kg), Co (6.20±0.07 mg/kg), Cu (15.80±0.01 mg/kg), Ni (25.90±0.13 mg/kg), Pb (35.50±0.05 mg/kg) and Zn (41.40±0.13 mg/kg) in the stems; while Pb (36.90±0.04 mg/kg), Zn (34.18±0.03 mg/kg), Ni (21.90±0.07 mg/kg), Cu (11.90±0.01 mg/kg), Cd (4.00±0.01 mg/kg) and Co (3.70±0.07 mg/kg) in the roots. The concentrations of the metals in the soil: Pb (42.80±0.02 mg/kg), Zn (41.33±0.04 mg/kg), Co (8.40±0.04 mg/kg), Cd (3.80±0.02 mg/kg), Ni (4.90±0.08 mg/kg) and Cu (1.90±0.03 mg/kg). The BF for the studied metals were greater than 1 except Co and Pb. The TF for the metals were also greater than 1 except that of Pb which was less than 1 (Figure 4.68).

4.13.5 Metal concentrations in different parts of *Ricinus communis* (Castor Oil) plant

The concentrations of the studied metals in different parts of *Ricinus communis* (Castor Oil) plant and soil after the application of EDTA to the soil at the Dakace and control study areas are presented in Figures 4.69 and Appendix XXXV. The metal levels in the leaves at test site: Cd - 3.60±0.01 mg/kg, Co - 12.10±0.00 mg/kg, Cu - 12.10±0.06 mg/kg, Ni - 231.30±0.06 mg/kg, Pb - 43.70±0.02 mg/kg and Zn - 40.34±0.04 mg/kg; the stems contain: Cd - 3.30±0.03 mg/kg, Co - 12.70±0.05 mg/kg, Cu - 10.90±0.01 mg/kg, Ni - 70.40±0.06 mg/kg, Pb (47.30±0.03 mg/kg) and Zn (43.64±0.06 mg/kg); the roots of plant: Cd - 3.00±0.04 mg/kg, Co - 11.60±0.06 mg/kg, Cu - 6.80±0.02 mg/kg, Ni - 19.80±0.06 mg/kg, Pb - 44.20±0.04 mg/kg and Zn - 40.34±0.04 mg/kg. The concentrations of the metals in the soil were: Pb (42.80±0.02 mg/kg), Zn (41.33±0.04 mg/kg), Co (8.40±0.04 mg/kg), Cd (3.80±0.02 mg/kg), Ni (51.30±0.05 mg/kg) and Cu (1.90±0.03 mg/kg).The biaccumulation

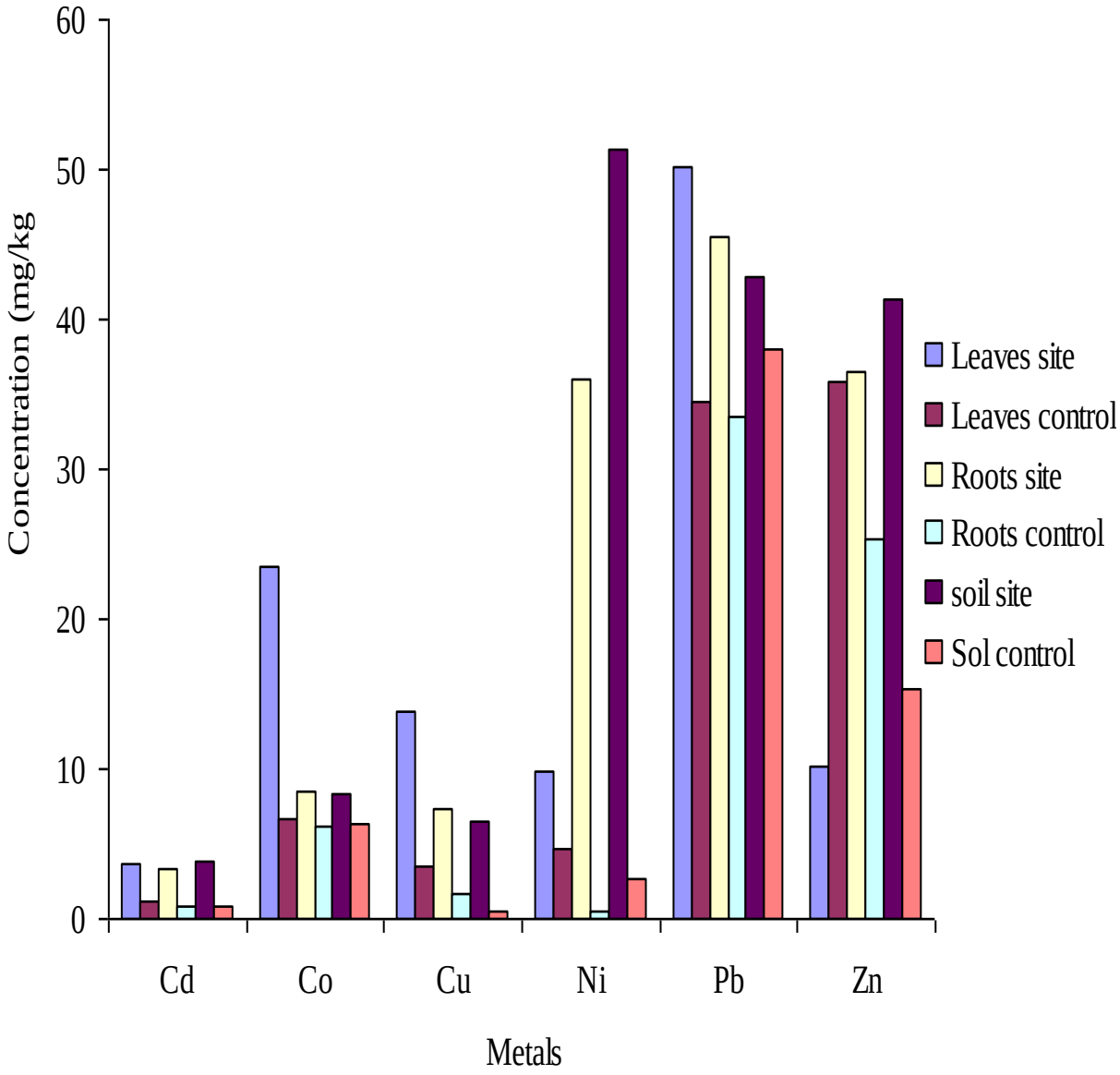


Figure 4.61: Concentrations (mg/kg) of Metals in Different Parts of *Vetivera zizanioide* Plant and Soil with EDTA at Dakace

* Ni (leaves) = 9.91 x 10, Zn (leaves) = 10.1 x 10

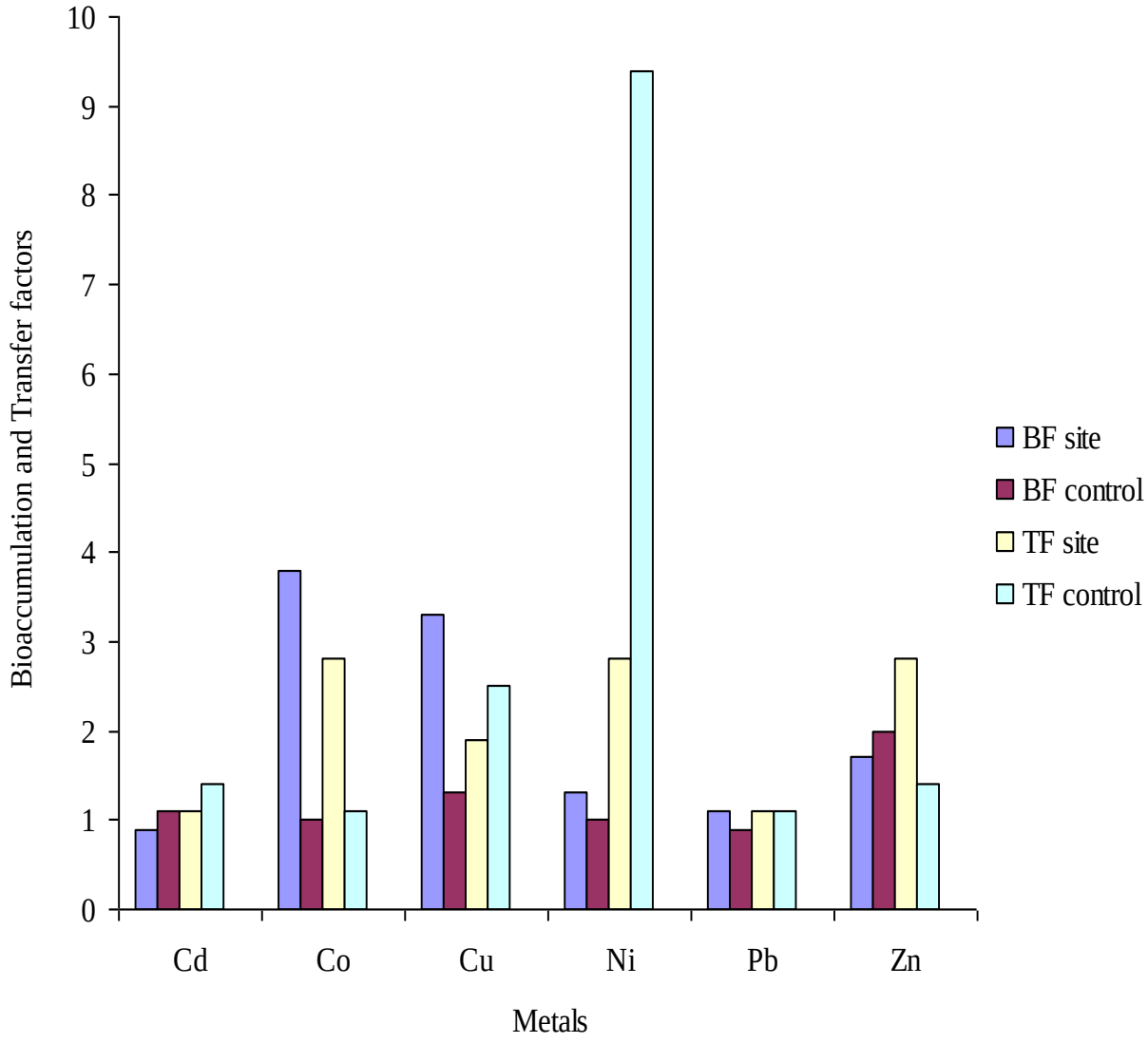


Figure 4.62: Bioaccumulation and Transfer Factors for *Vetivera zizanioide* Plant after Addition of EDTA at Dakace

BF = Bioaccumulation factor; TF = Translocation factor.

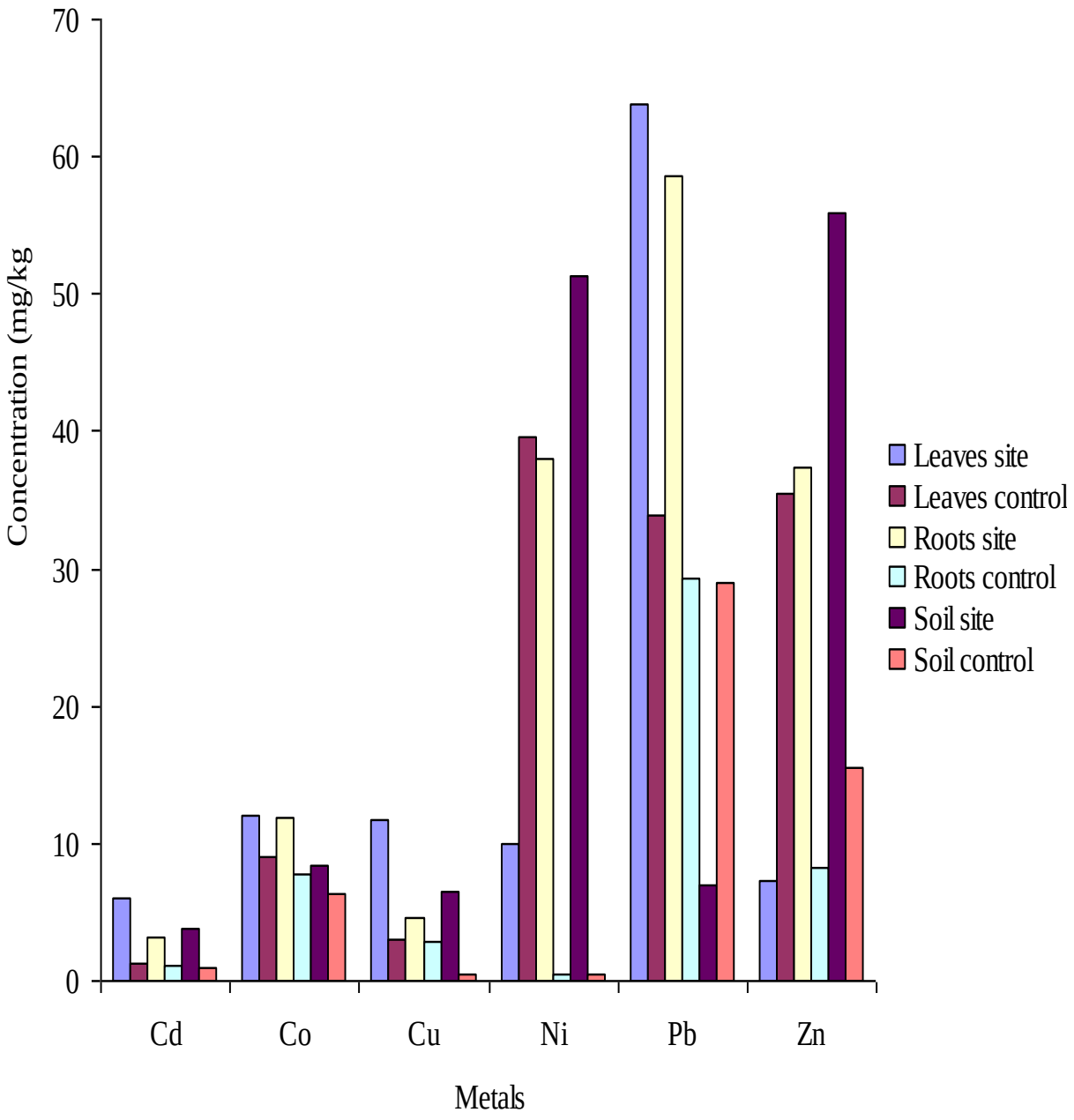


Figure 4.63: Concentrations (mg/kg) Metals in Different Parts of *Cymbopogon citratus* Plant and Soil at Dakace after Addion of EDTA

* Ni (leaves) = 9.99 x 10, Pb (soil) = 6.93 x 10, Zn (leaves) = 7.35 x 10

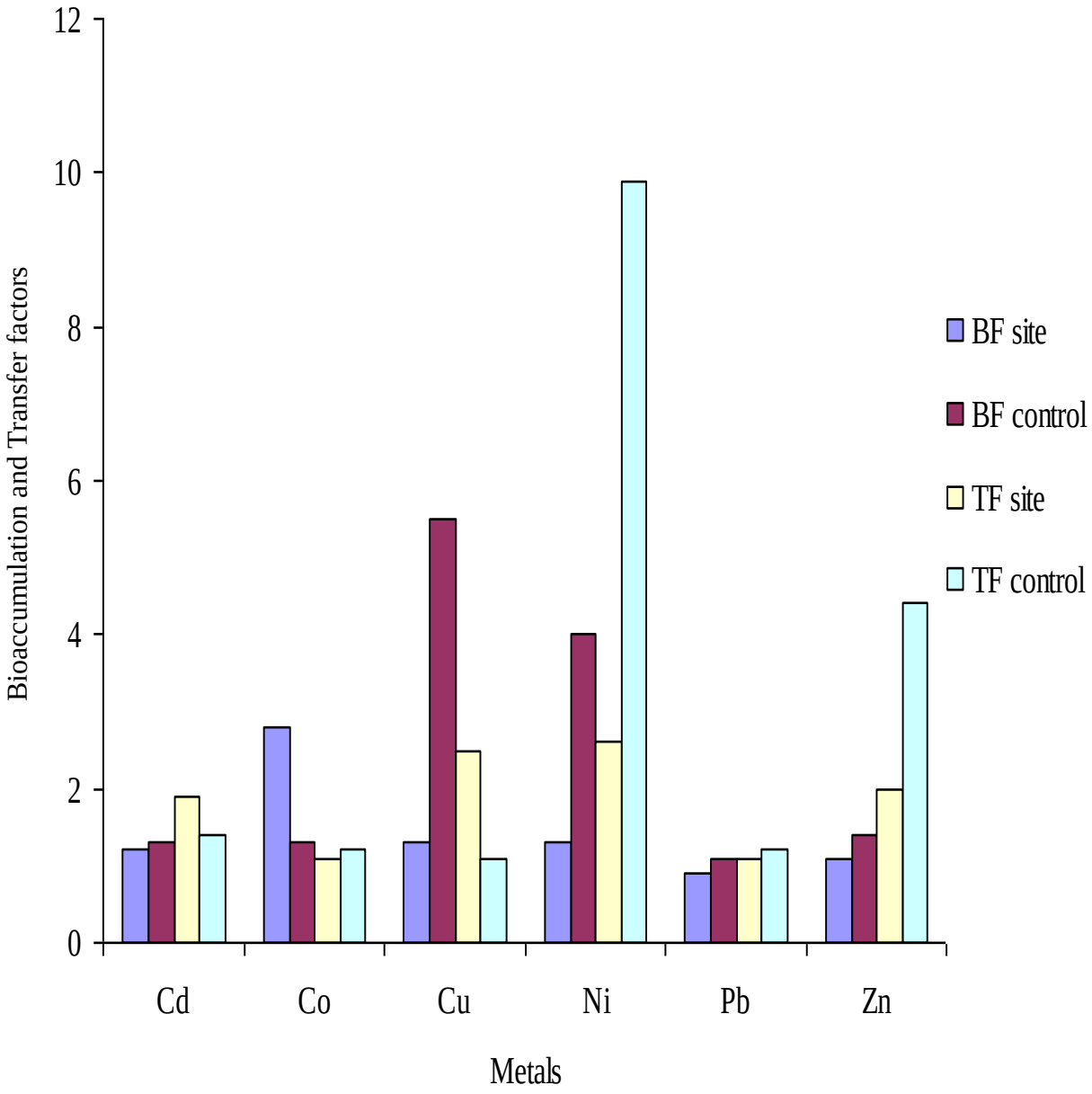


Figure 4.64: Bioaccumulation and Transfer Factors for *Cymbopogon citratus* Plant at Dakace after Addition of EDTA

BF = Bioaccumulation factor; TF = Translocation factor

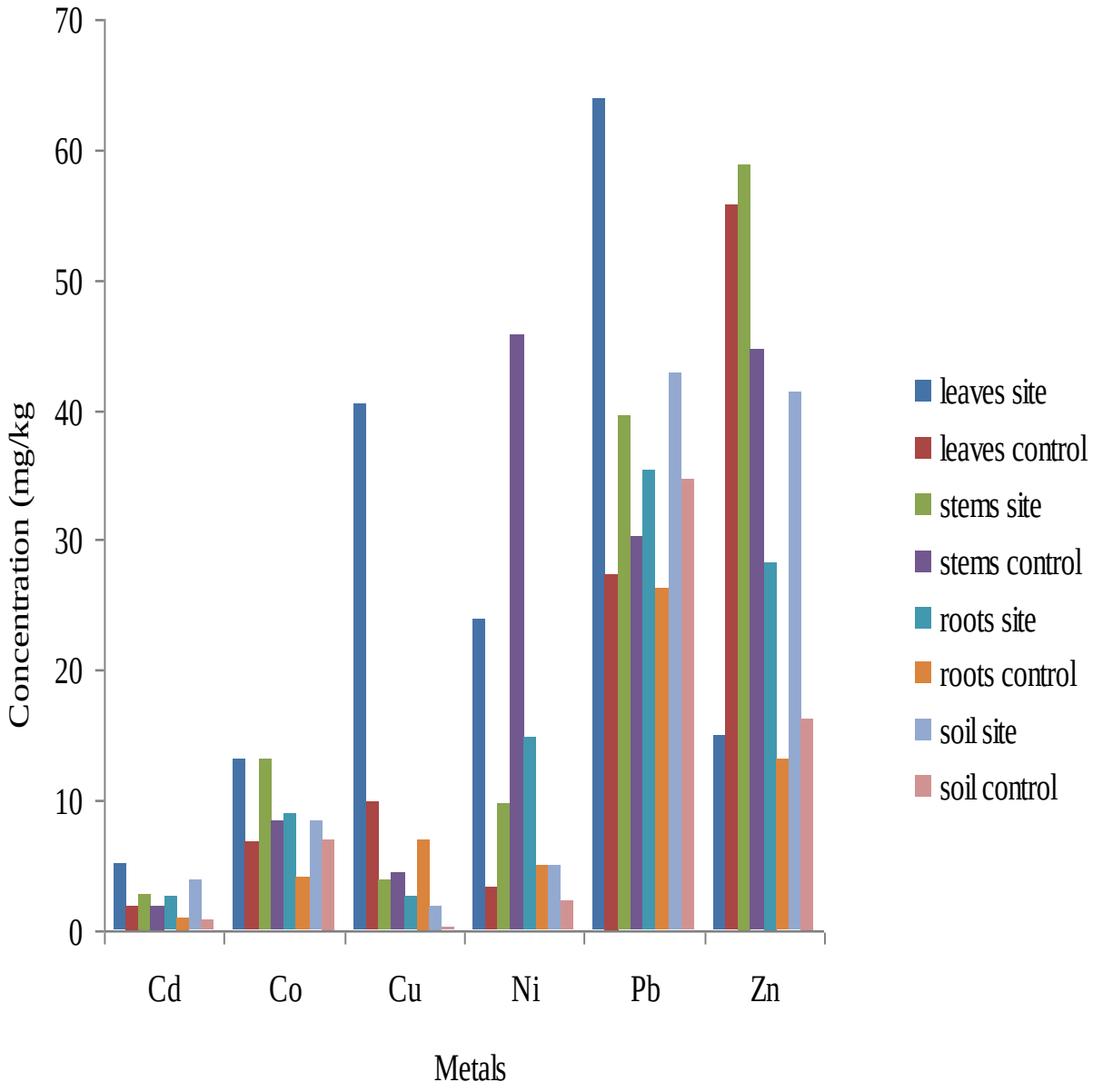


Figure 4.65: Concentrations (mg/kg) of Metals in Different Parts of *Helianthus annus* Plant after Addition of EDTA at Dakace

* Ni (stems) = 9.63 x 10, Zn (leaves) = 15.005 x 10

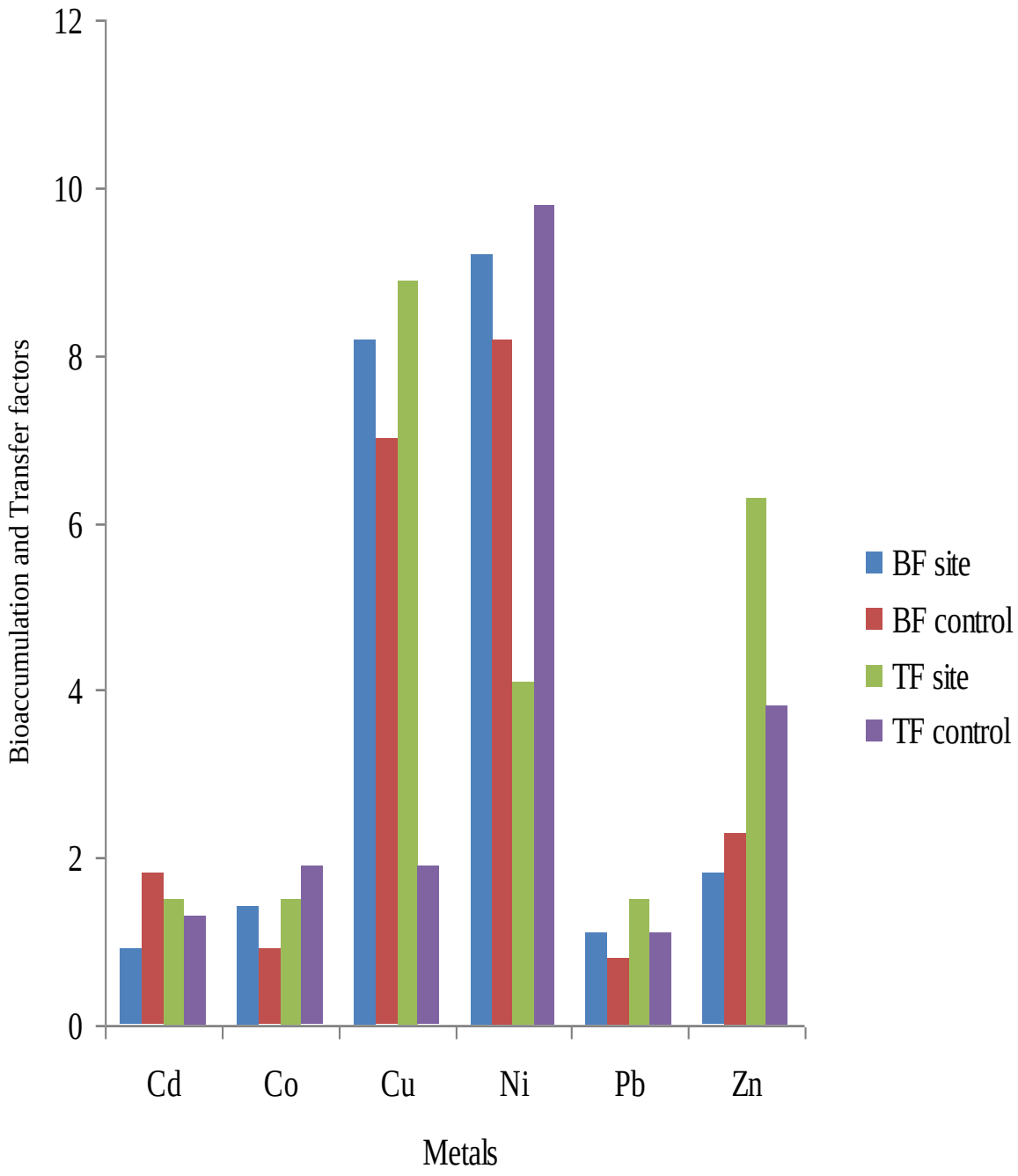


Figure 4.66: Bioaccumulation and Transfer Factors of Metals for *Helianthus annus* Plant after Addition of EDTA at Dakace

BF = Bioaccumulation factor; TF = Translocation factor.

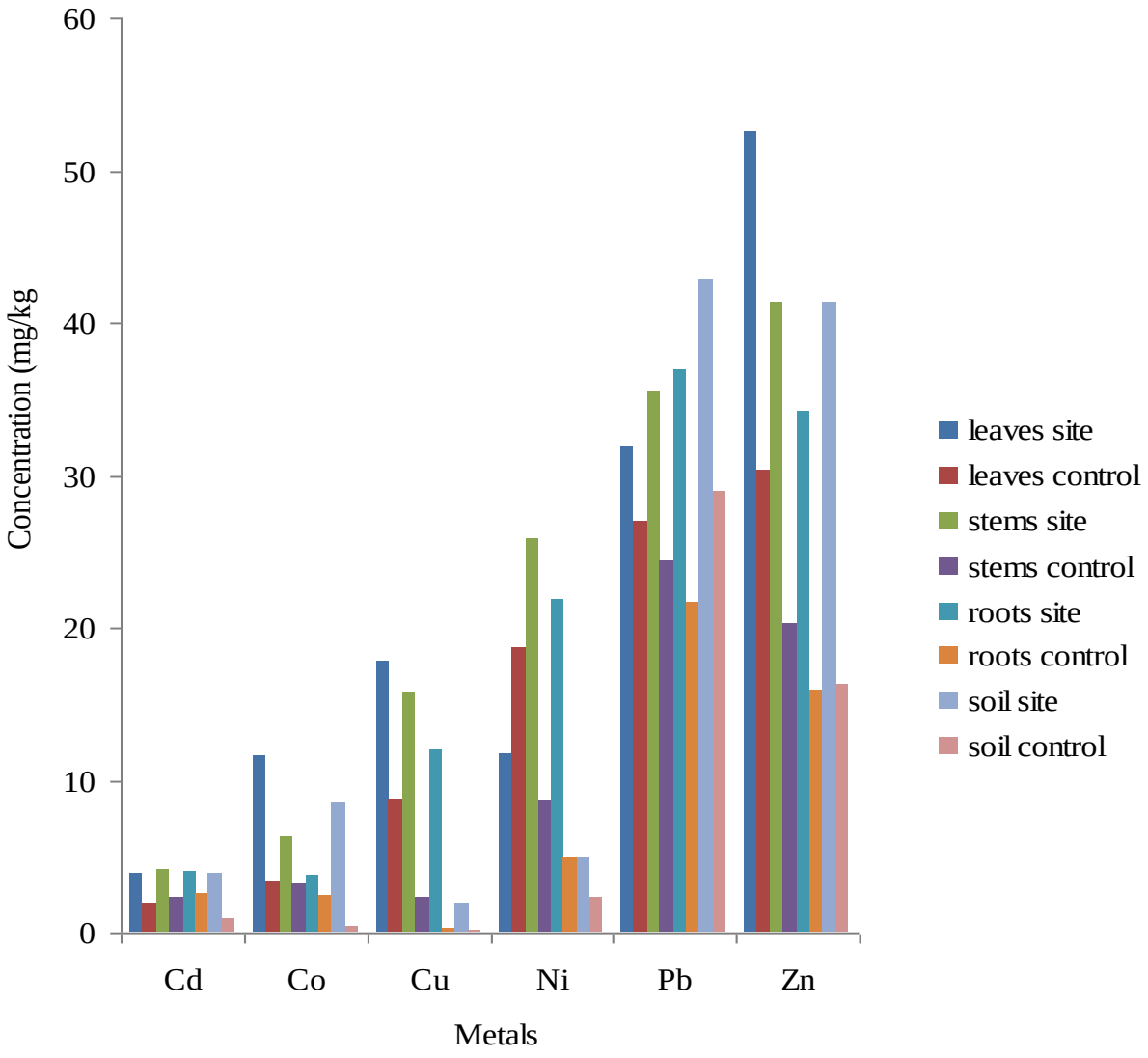


Figure 4.67: Concentrations (mg/kg) of Metals in Different Parts of *Ipomoea asarifolia* Plant after Addition of EDTA at Dakace

* Ni (leaves) = 11.67 x 10

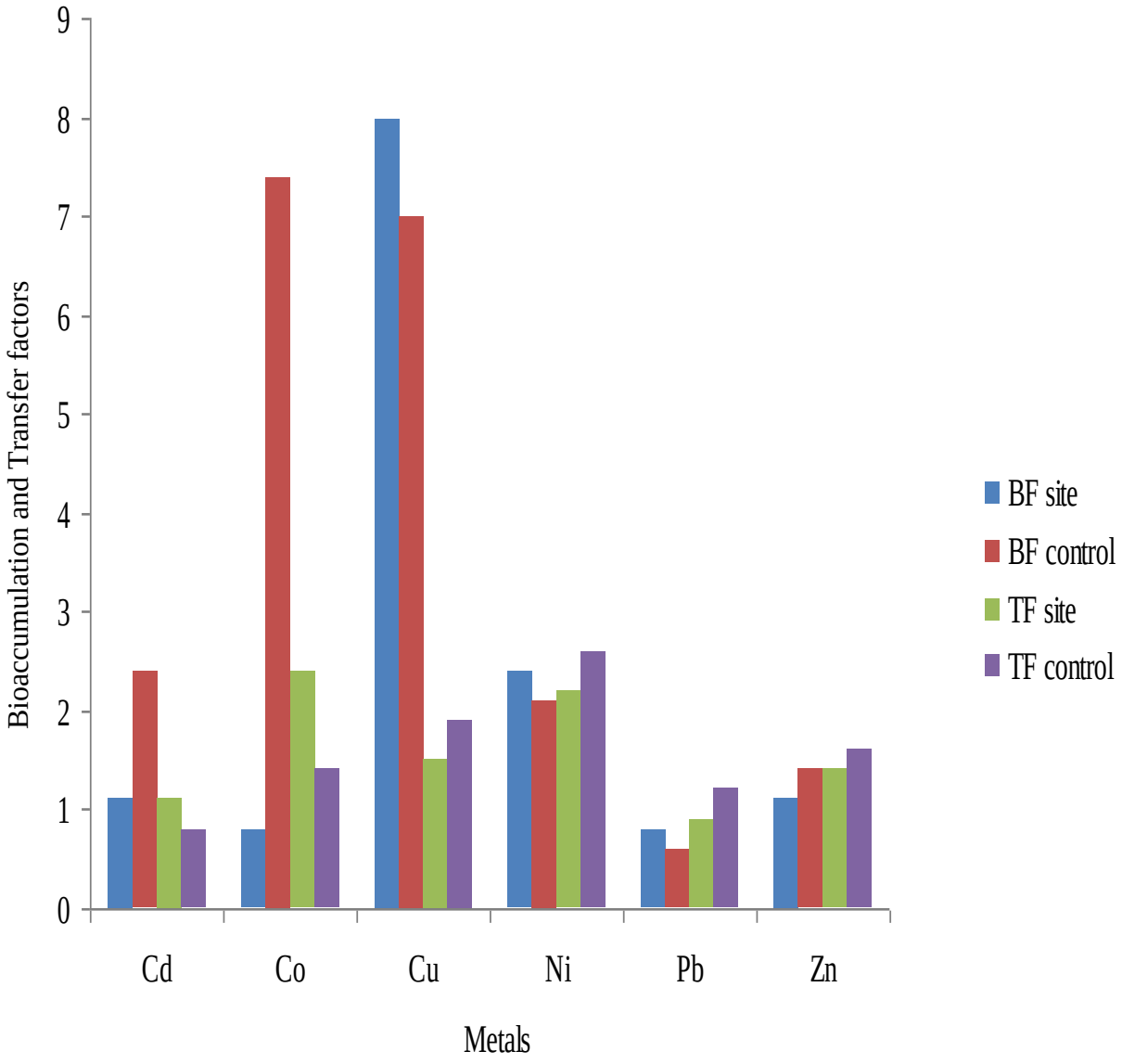


Figure 4.68: Bioaccumulation and Transfer Factors of Metals for *Ipomoea asarifolia* Plant after Addition of EDTA at Dakace

BF = Bioaccumulation factor; TF = Translocation factor.

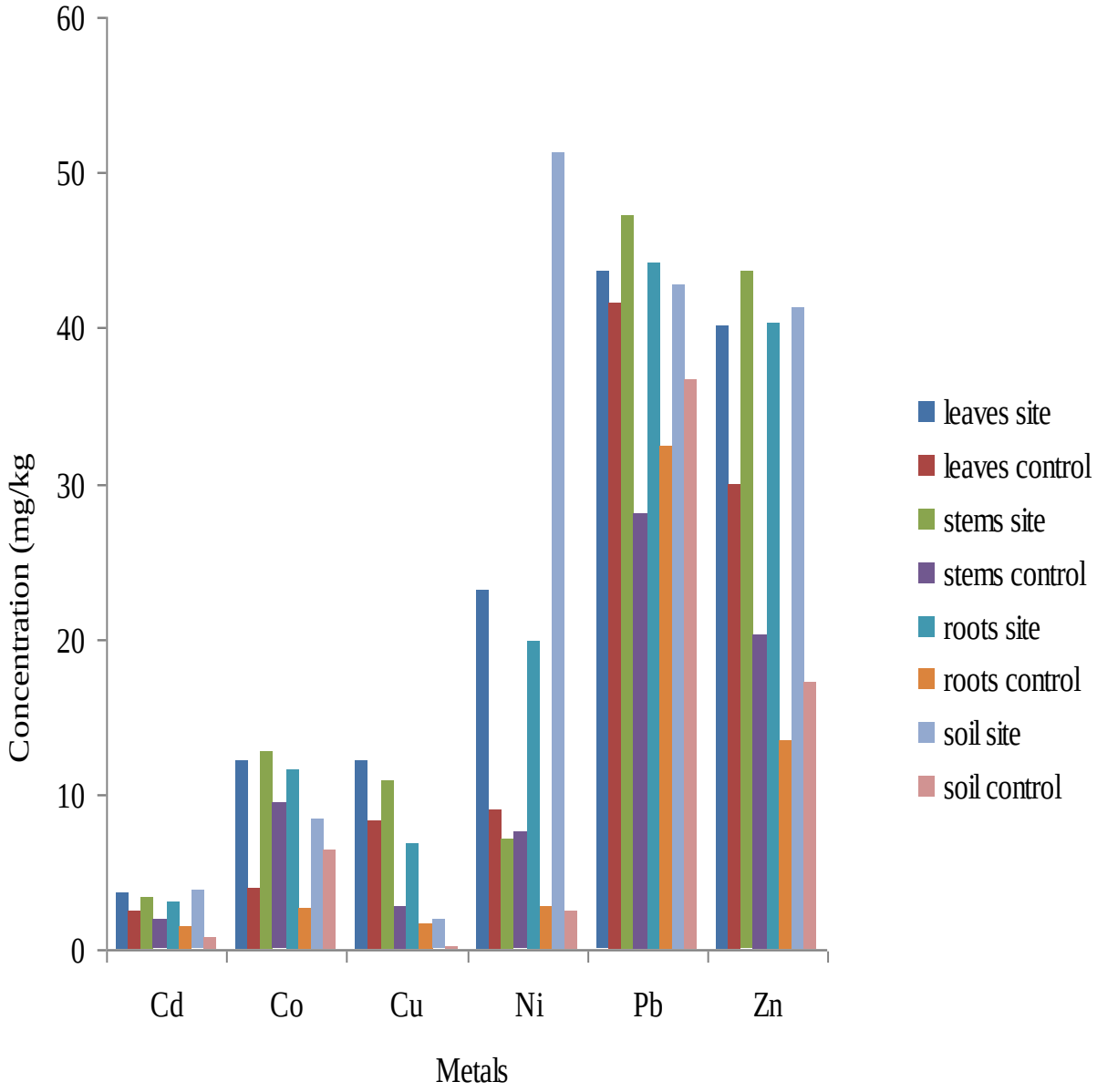


Figure 4.69: Concentrations (mg/kg) of Metals in Different Parts of *Ricinus communis* Plant after Addition of EDTA at Dakace

* Ni (leaves) = 23.13 x 10, Ni (stem) = 7.04 x 10

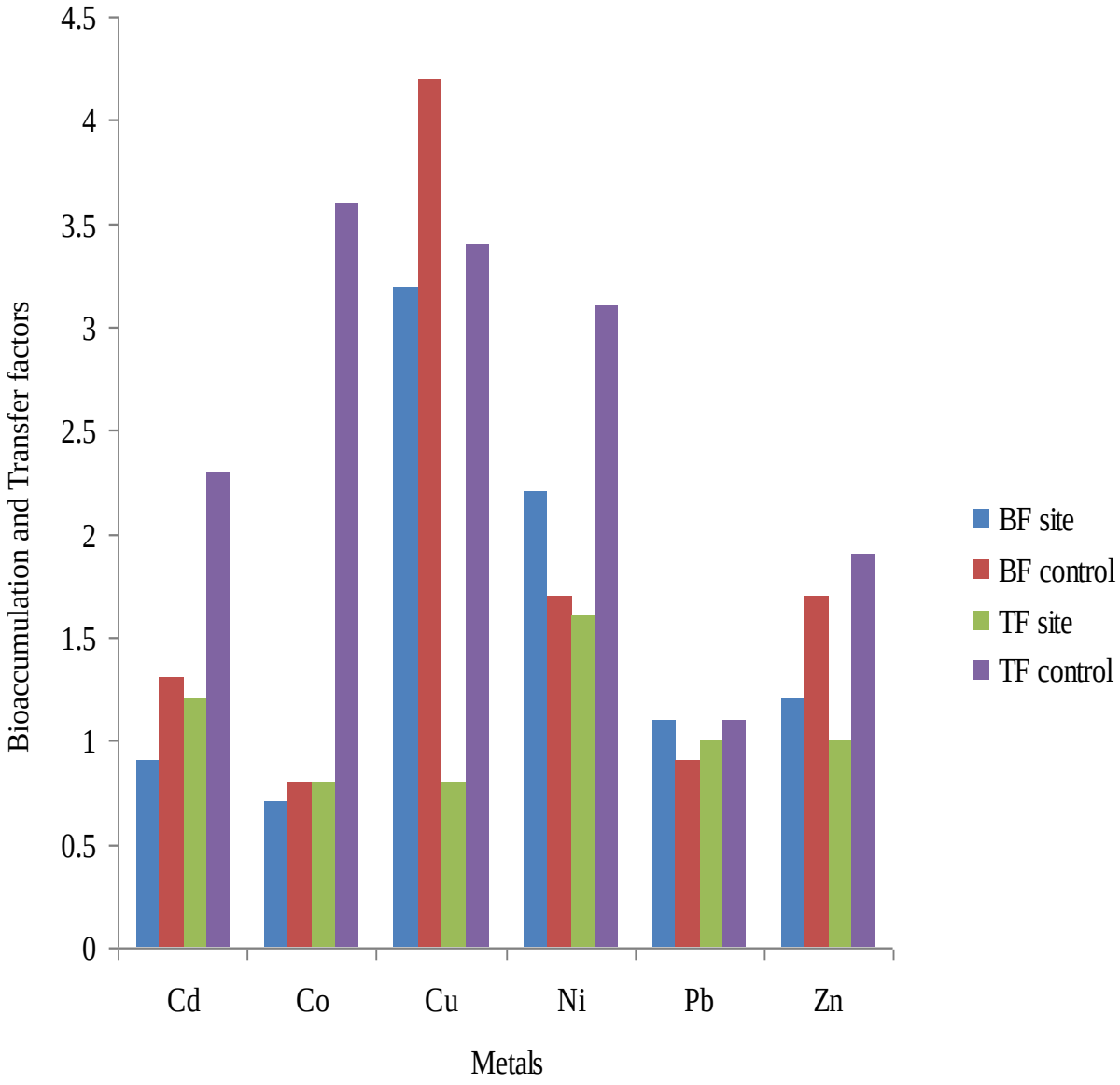


Figure 4.70: Bioaccumulation and Transfer Factors of Metals for *Ricinus communis* Plant at Dakace after Addition of EDTA

BF = Bioaccumulation factor; TF = Translocation factor.

factor (BF) and the translocation factor (TF) for the various metals studied at the test site were greater than 1, except the BF for Cd which was less than 1. For the control, only the BF and TF for Pb were less than 1 (Figure 4.70).

4.14 Bioaccumulation and Transfer Factors for the Metals in Different Plant Species at Dakace Soil Treated with EDTA

The results for the BF and TF for the studied metals in different plant species harvested from Dakace soil treated with EDTA are presented in Figures 4.71 to 4.76 and Appendix XXXVI. The BF for Cd was in the order of *Cymbopogon citratus* (1.2) > *Ipomoea asarifolia* (1.1) > *Vetivera zizanioide* (0.9) ≈ *Helianthus annus* (0.9) ≈ *Ricinus communis* (0.9), while the TF was *Cymbopogon citratus* (1.9) > *Helianthus annus* (1.5) > *Ricinus communis* (1.2) > *Vetivera zizanioide* (1.1) ≈ *Ipomoea asarifolia* (1.1). The BF for Co followed the order of *Cymbopogon citratus* (2.8) > *Ipomoea asarifolia* (0.8) > *Vetivera zizanioide* (3.8) ≈ *Helianthus annus* (1.4) ≈ *Ricinus communis* (0.7), while the TF was *Vetivera zizanioide* (2.8) > *Ipomoea asarifolia* (2.4) > *Helianthus annus* (1.5) > *Cymbopogon citratus* (1.1) > *Ricinus communis* (0.8). BF for Cu:- *Helianthus annus* (8.2) > *Ipomoea asarifolia* (8.0) > *Vetivera zizanioide* (3.3) > *Ricinus communis* (3.2) > *Cymbopogon citratus* (1.3), while the TF - *Vetivera zizanioide* (1.9) > *Ipomoea asarifolia* (1.5) > *Helianthus annus* (8.9) > *Cymbopogon citratus* (2.5) > *Ricinus communis* (0.8). The BF for Ni - *Helianthus annus* (9.2) > *Ipomoea asarifolia* (2.4) > *Ricinus communis* (2.2) > *Vetivera zizanioide* (1.3) ≈ *Cymbopogon citratus* (1.3), while the TF for Ni - *Helianthus annus* (4.2) > *Vetivera zizanioide* (2.8) > *Cymbopogon citratus* (2.4) > *Ipomoea asarifolia* (2.2) > *Ricinus communis* (1.6). The BF and TF for Pb in different plant species indicated that *Helianthus annus* (1.1) ≈ *Ricinus communis* (1.1) ≈ *Vetivera zizanioide* (1.1) > *Cymbopogon citratus* (0.9) > *Ipomoea asarifolia* (0.8) and *Helianthus annus* (1.5) >

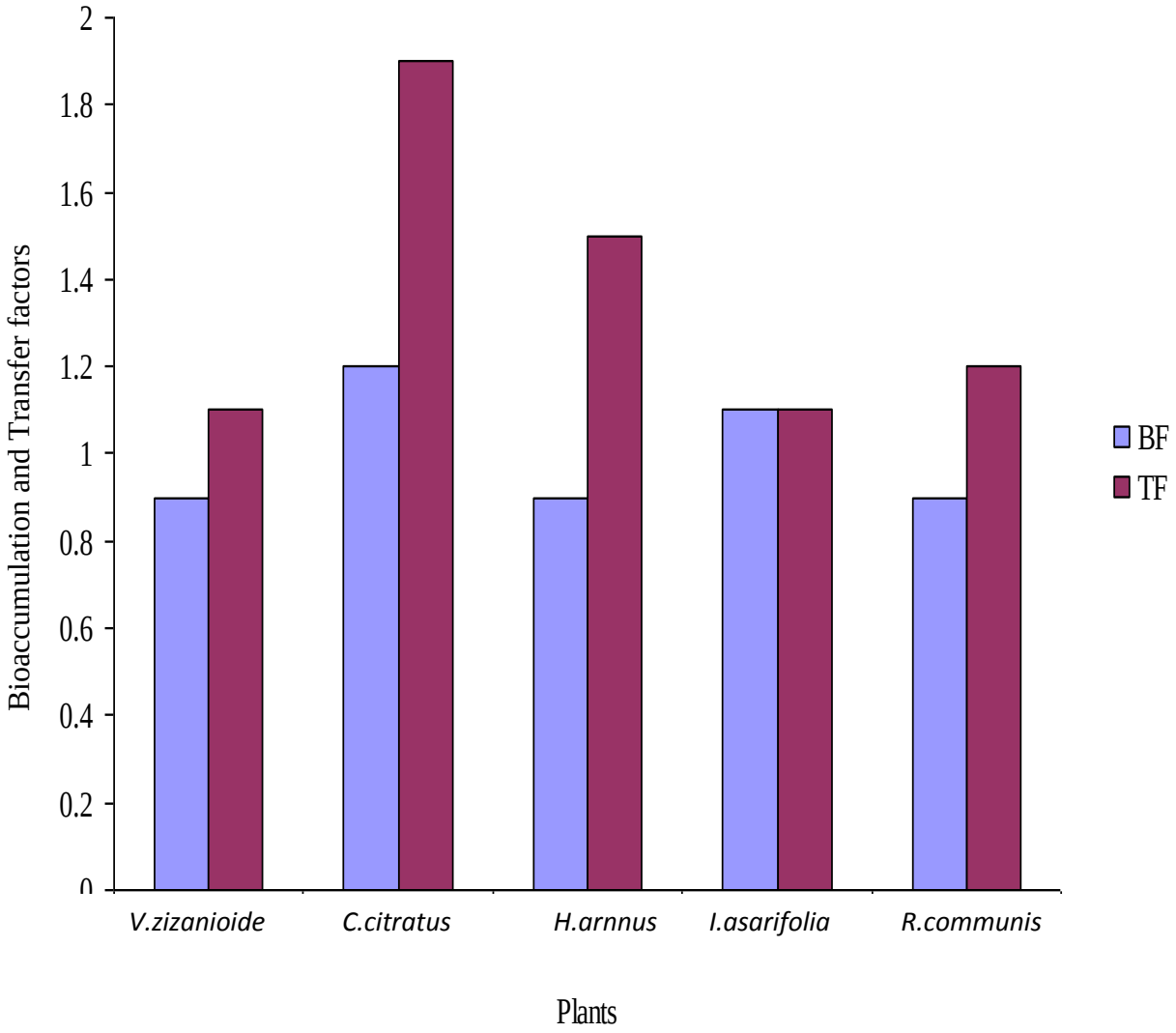


Figure 4.71: Bioaccumulation and Transfer Factors for Cadmium in Different Plant Species at Dakace Soil Treated with EDTA

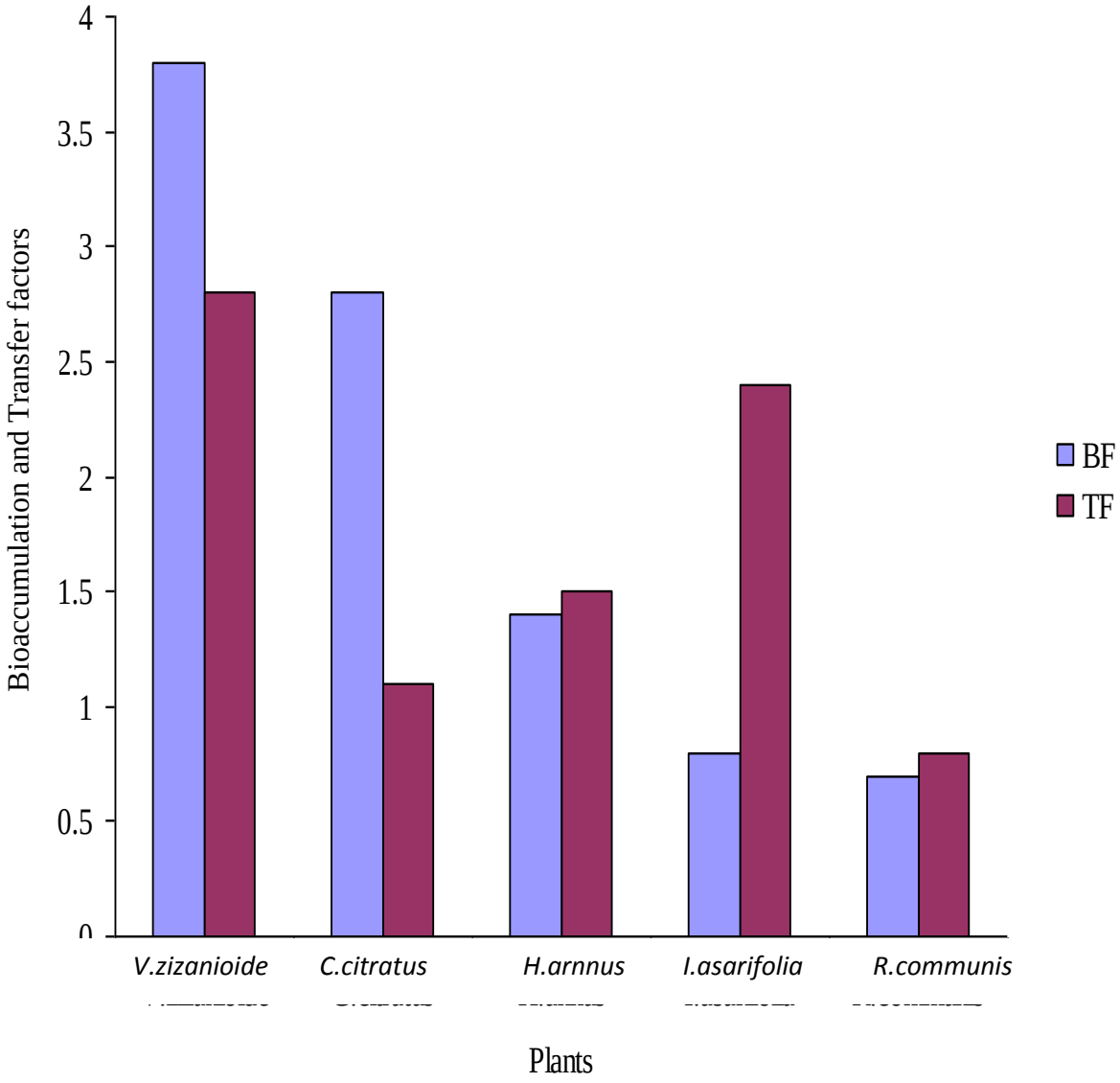


Figure 4.72: Bioaccumulation and Transfer Factors for Cobalt in Different Plant Species at Dakace Soil Treated with EDTA

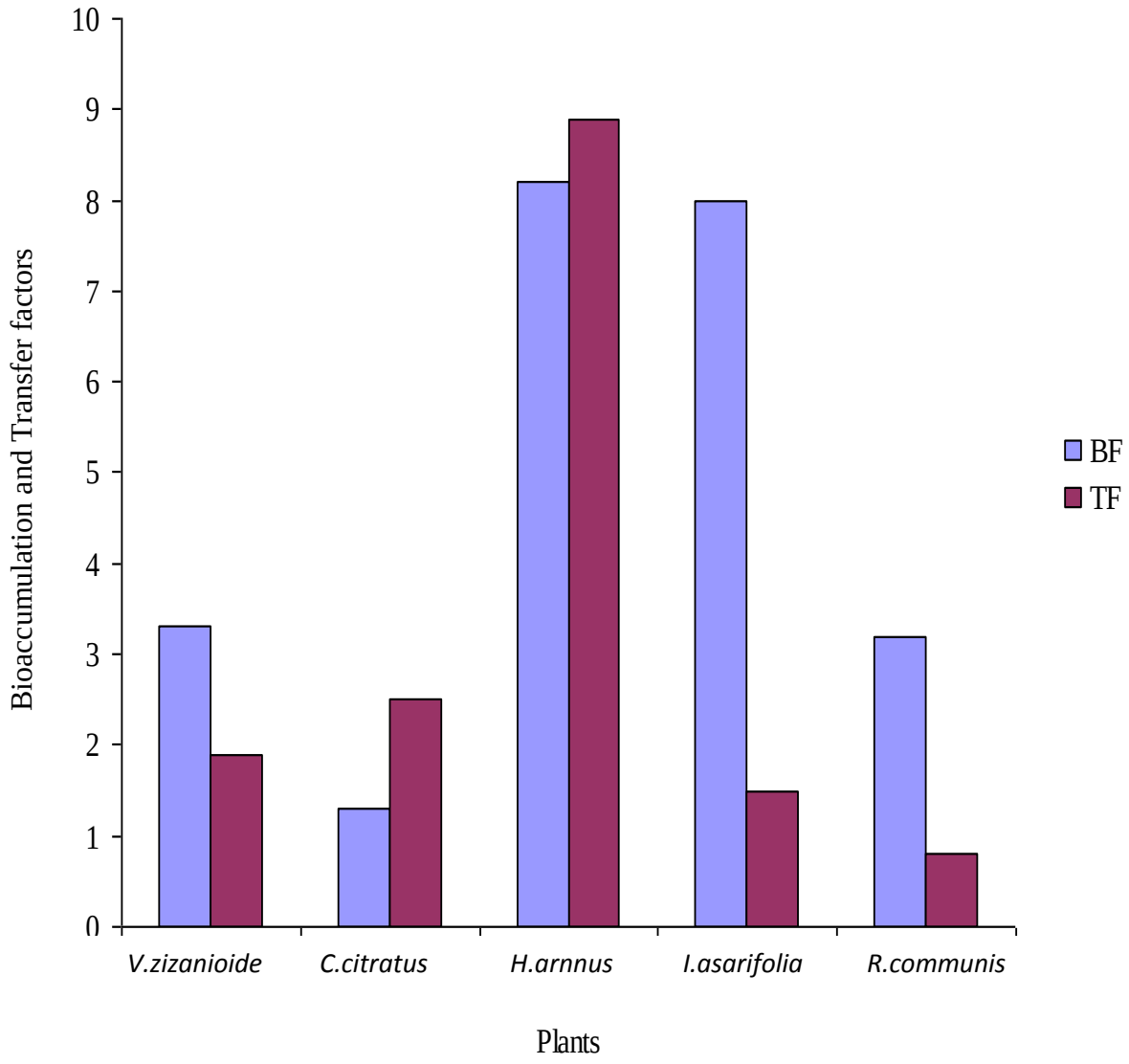


Figure 4.73: Bioaccumulation and Transfer Factors for Copper in Different Plant Species at Dakace Soil Treated with EDTA

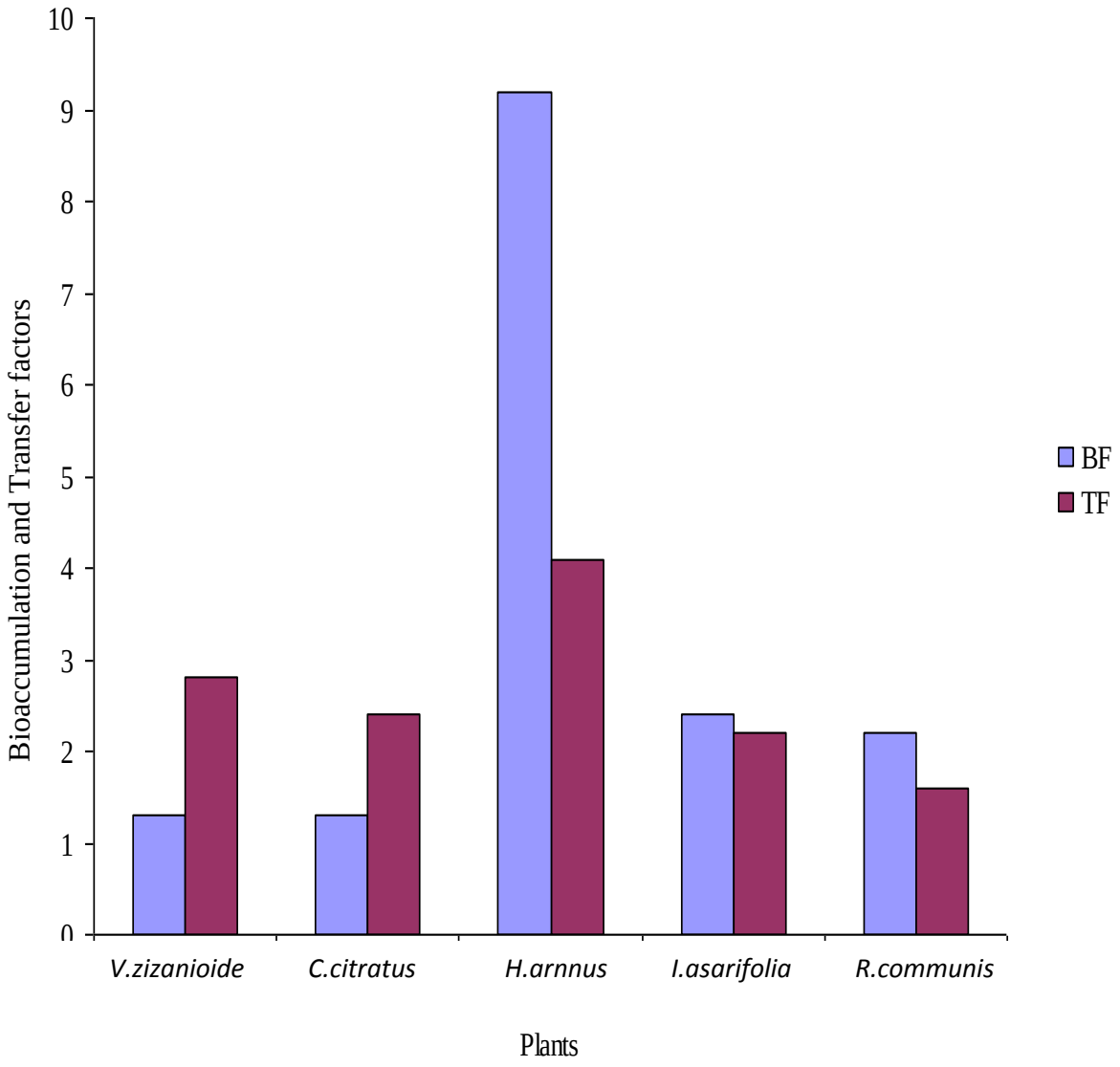


Figure 4.74: Bioaccumulation and Transfer Factors for Nickel in Different Plant Species at Dakace Soil Treated with EDTA

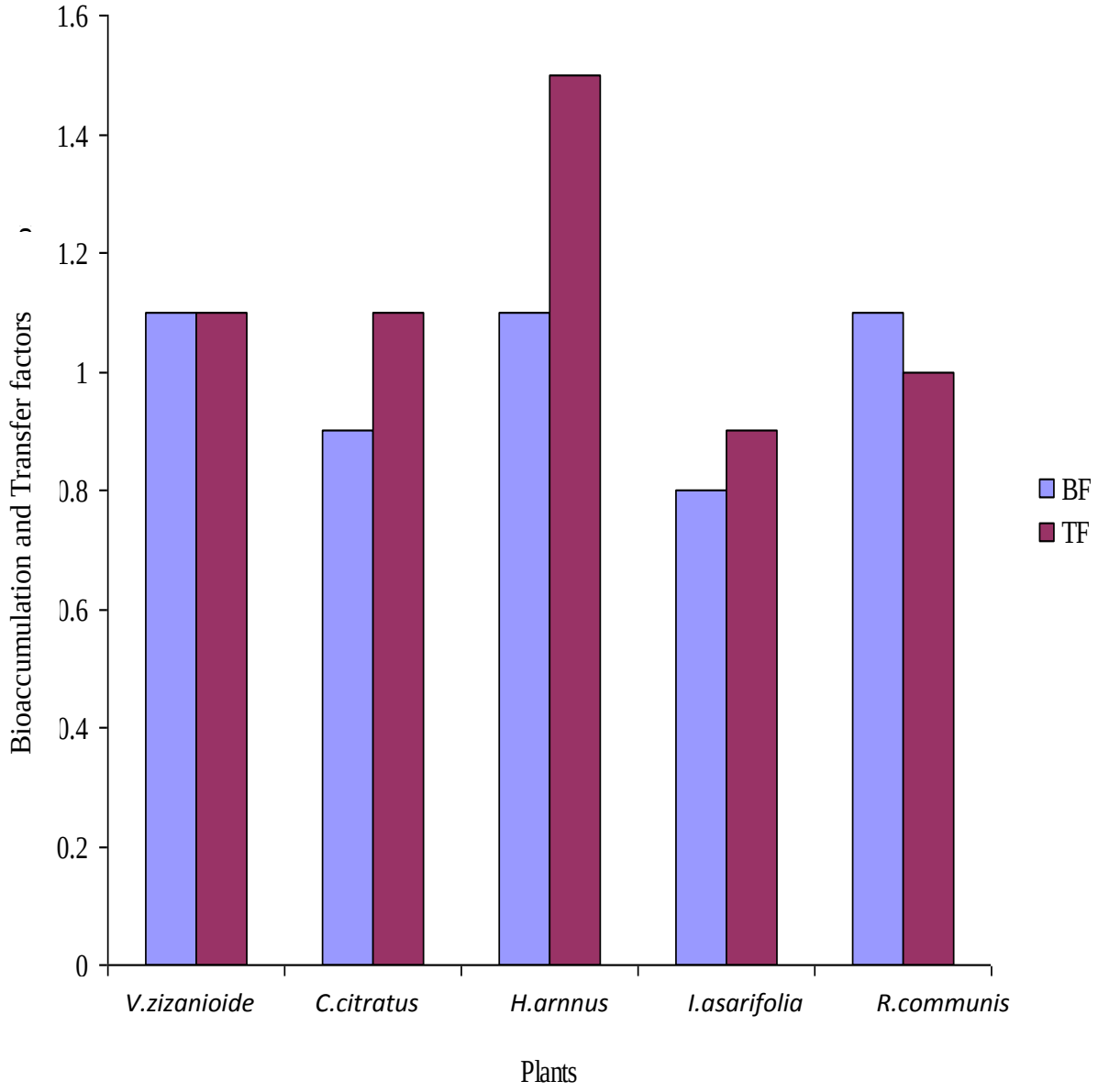


Figure 4.75: Bioaccumulation and Transfer Factors for Lead in Different Plant Species at Dakace Soil Treated with EDTA

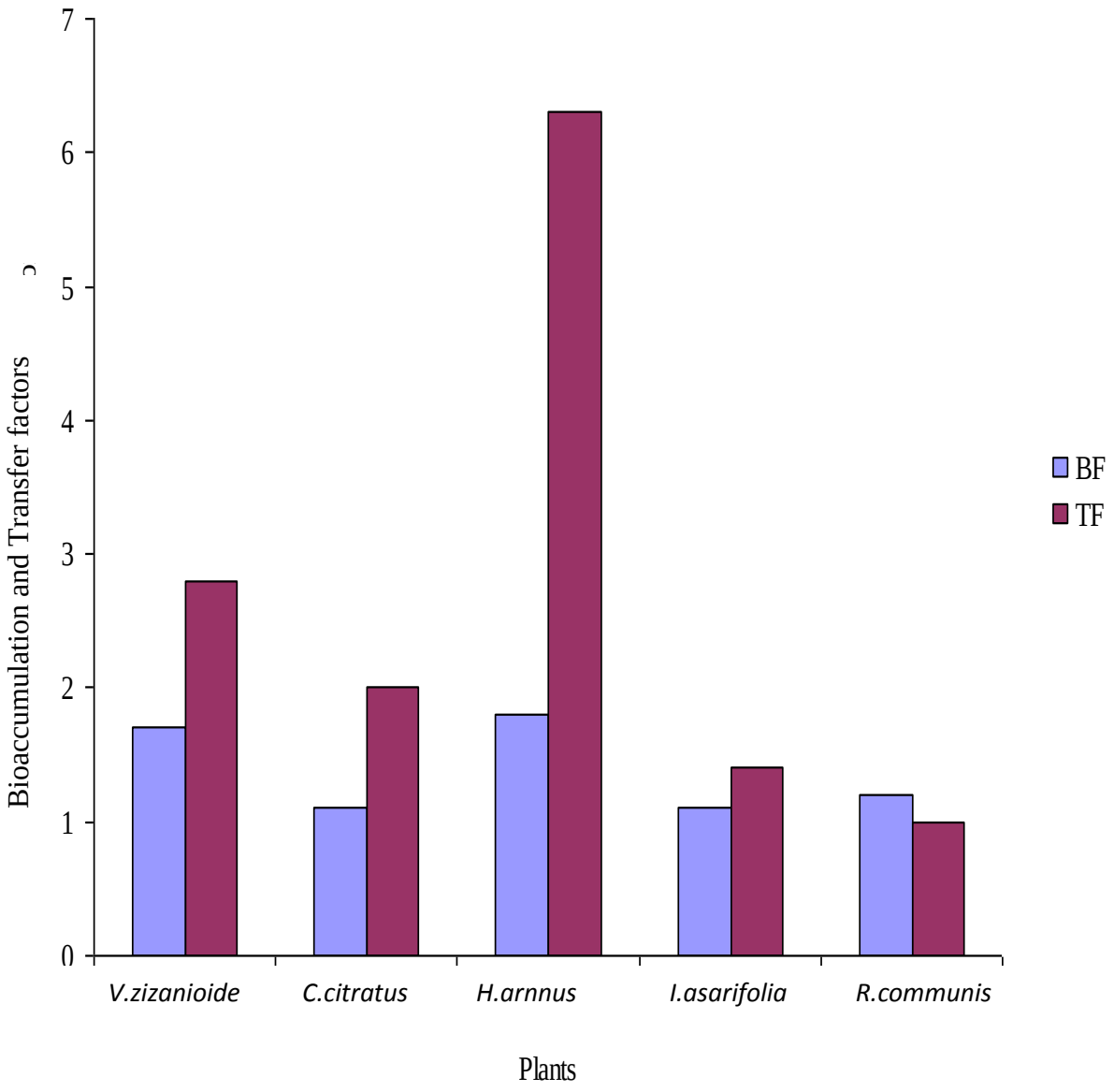


Figure 4.76: Bioaccumulation and Transfer Factors for Znc in Different Plant Species at Dakace Soil Treated with EDTA

Vetivera zizanioide (1.1) ≈ *Cymbopogon citratus* (1.1) > *Ricinus communis* (1.0) > *Ipomoea asarifolia* (0.9) respectively. The BF for Zn was in the order of *Helianthus annus* (1.8) > *Vetivera zizanioide* (1.7) > *Ricinus communis* (1.2) > *Cymbopogon citratus* (1.1) ≈ *Ipomoea asarifolia* (1.1), while the TF was *Helianthus annus* (6.3) > *Vetivera zizanioide* (2.8) > *Cymbopogon citratus* (2.0) > *Ipomoea asarifolia* (1.4) > *Ricinus communis* (1.0).

4.15 Metal Content in Different Parts of Plant Species with EDTA Application at Gaskiya Site

4.15.1 Metal concentrations in different parts of *Vetivera zizanioide* plant

The concentrations of metals in different parts of *Vetivera zizanioide* plant for the various metals studied after the application of EDTA at Gaskiya and the control study areas are presented in Figure 4.77 and Appendix XXXVII. The concentrations of all the studied metals in the leaves from the test site were of the order: Cd (3.80±0.04 mg/kg) < Cu (6.90±0.00 mg/kg) < Co (12.20±0.03 mg/kg) < Ni (54.10±0.12 mg/kg) < Pb (56.40±0.07 mg/kg) < Zn (66.96±0.08 mg/kg). The concentrations of the metals in the roots were: Cd (3.60±0.00 mg/kg) < Cu (4.40±0.02 mg/kg) < Co (7.70±0.01mg/kg) < Ni (43.30±0.06 mg/kg) < Zn (29.29±0.03 mg/kg) < Pb (48.80±0.04 mg/kg). The metal levels in soil at the test site were: Cd (3.80±0.01 mg/kg) < Cu (5.30±0.03 mg/kg) < Co (9.90±0.03 mg/kg) < Zn (25.15±0.06 mg/kg) < Pb (51.70±0.05 mg/kg) < Ni (84.90±0.06 mg/kg). All the concentrations of the metals at the test site were higher than corresponding values at the control site. The bioaccumulation factor (BF) and the translocation factor (TF) for all the studied metals (except BF for Ni) were greater than 1 (Figure 4.78). The order in the BF and TF of the metals were: Zn > Pb ≈ Cd ≈ Co ≈Cu > Ni and Co ≈ Zn ≈ Cu > Ni≈ Pb > Cd respectively. For the control, only the BF for Co and Ni were less than 1 but the TF for all the studied metals were greater than 1.

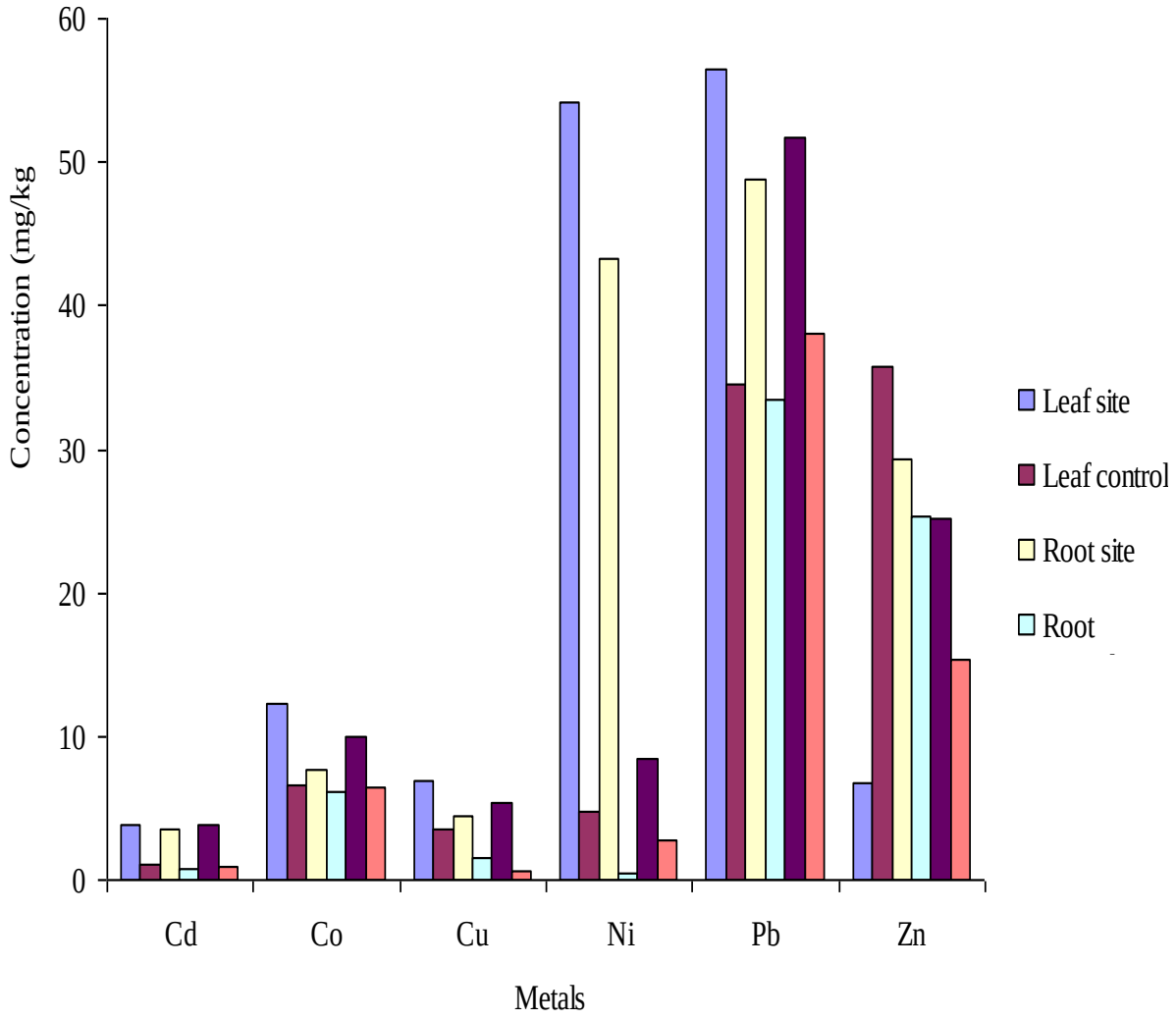


Figure 4.77: Concentrations of Metals in Different Parts of *Vetivera zizanioide* Plant and the Soil at Gaskiya after Addition of EDTA

* Ni (soil) = 8.49 x 10, Zn(leaves) = 6.696 x 10

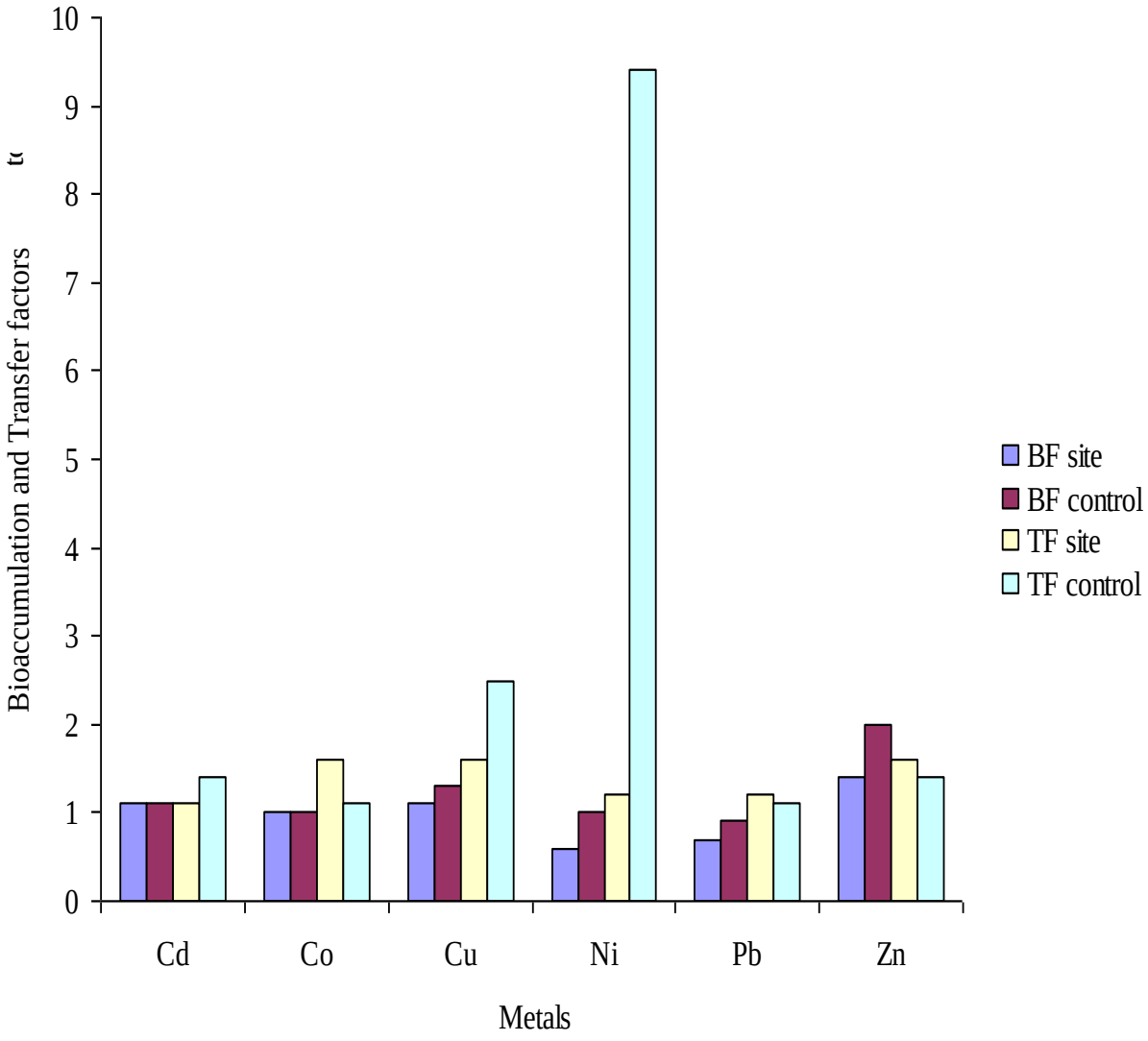


Figure 4.78: Bioaccumulation and Transfer Factors of Metals for *Vetivera zizanioide* Plant at Gaskiya after Addition of EDTA

BF = Bioaccumulation factor; TF = Translocation factor.

4.15.2 Metals concentrations in different parts of *Cymbopogon citratus* (Lemon grass) plant

The concentrations of metals in different parts of *Cymbopogon citratus* (Lemon grass) plant for the various metals studied after the application of EDTA at Gaskiya and the control study areas are presented in Figure 4.79 and Appendix XXXVIII. The concentrations of all the studied metals in the leaves at the test site were Cd - 3.70±0.06 mg/kg, Co - 21.10±0.06 mg/kg, Cu - 12.90±0.02 mg/kg, Ni - 324.70±0.10 mg/kg, Pb - 67.40±0.02 mg/kg and Zn - 46.60±0.02 mg/kg; the roots Cd - 3.40±0.02 mg/kg, Co - 11.10±0.03 mg/kg, Cu - 7.00±0.02 mg/kg, Ni - 99.20±0.58 mg/kg, Pb - 62.10±0.02 mg/kg and Zn - 38.80±0.06 mg/kg; while the soil contained Cd - 3.80±0.01 mg/kg, Co - 9.90±0.03 mg/kg, Cu - 5.30±0.03 mg/kg, Ni - 84.90±0.06 mg/kg, Pb - 75.90±0.05 mg/kg and Zn - 25.15±0.02. the metal concentrations at the test site were higher than their corresponding values at the control site. The bioaccumulation factor (BF) and the translocation factor (TF) for all the studied metals (except BF for Cd and Pb) were greater than 1 (Figure 4.80). The order in the BF and TF of the metals were: Ni > Cu > Co > Zn > Cd ≈ Pb and Zn ≈ Ni > Co > Cu > Cd > Pb respectively.

4.15.3 Metals concentrations in different parts of *Helianthus annus* (Sunflower) plant

The concentrations of metals in different parts of *Helianthus annus* (Sunflower) plant for the various metals studied after the application of EDTA at Gaskiya and the control study areas are presented in Figure 4.81 and Appendix XXXIX. At the test site, the concentrations of metals in the leaves followed the trend Zn (107.34±0.16 mg/kg) > Pb (87.00±0.07 mg/kg) > Ni (64.30±0.08 mg/kg) > Cu (30.10±0.02 mg/kg) > Co (13.20±0.06 mg/kg) > Cd (2.90±0.03 mg/kg). The concentrations in the stem indicated the trend Ni (107.20±0.04 mg/kg) > Zn (44.41±0.06 mg/kg) > Pb (33.80±0.05 mg/kg) > Co (9.10±0.02 mg/kg) > Cu (8.10±0.02 mg/kg) > Cd (2.70±0.03 mg/kg). The concentrations in the roots followed the trend Ni (51.66±0.11 mg/kg) > Zn (28.29±0.04 mg/kg) > Pb (25.50±0.03 mg/kg) > Co (7.80±0.09 mg/kg) > Cu (7.60±0.01 mg/kg) > Cd (2.70±0.04 mg/kg). The soil

showed that Ni (84.90±0.06 mg/kg) > Pb (75.90±0.05 mg/kg) > Zn (28.91±0.06 mg/kg) > Co (9.90±0.03 mg/kg) > Cu (5.30±0.03 mg/kg) > Cd (1.90±0.01 mg/kg). The concentrations of the studied metals in the plant tissues and soil at the test site were higher than at the control site. The bioaccumulation factor (BF) and the translocation facor (TF) for the studied metals (excpt the BF for Ni and Pb) at the test site were greater than 1 (Figure 4.82). The BF and the TF followed the order: Cu > Zn > Cd > Co > Ni > Pb and Zn > Cu > Pb > Ni > Co > Cd respectively. For the control, only the BF for Pb and Co were less than 1 but the TF for all the metals were greater than 1.

4.15.4 Metals concentrations in different parts of *Ipomoea asarifolia* plant

The concentrations of metals in different parts of *Ipomoea asarifolia* plant for the various metals studied after the application of EDTA at Gaskiya and the control study areas are presented in Figure 4.83 and Appendix XL. At the test site, concentrations of the metals in the leaves showed that Ni (391.90±0.06 mg/kg) > Zn (117.77±0.00 mg/kg) > Pb (43.70±0.02 mg/kg) > Cu (21.30±0.02 mg/kg) > Co (7.10±0.01 mg/kg) > Cd (3.90±0.01 mg/kg); in the stems, Ni (95.90±0.14 mg/kg) > Zn (88.10±0.06 mg/kg) > Pb (40.60±0.03 mg/kg) > Cu (18.50±0.07 mg/kg) > Co (14.50±0.08 mg/kg) > Cd (4.10±0.02 mg/kg); in the roots: Zn (44.71±0.06 mg/kg) > Ni (30.40±0.02 mg/kg) > Pb (30.00±0.08 mg/kg) > Cu (9.70±0.04 mg/kg) > Co (4.70±0.02 mg/kg) > Cd (4.00±0.02) mg/kg); while in the soil Ni (84.90±0.06 mg/kg) > Pb (51.70±0.01 mg/kg) > Zn (28.91±0.06 mg/kg) > Co (9.90±0.03 mg/kg) > Cu (5.30±0.03 mg/kg) > Cd (3.80±0.01 mg/kg). The BF for the studied metals were greater than 1 except Co and Pb. The TF for the metals were also greater than 1 except that of Pb which was less than 1 (Figure 4.84). the BF and the TF followed the order: Cu > Zn > Ni > Cd > Co > Pb and Ni > Zn ≈ Co > Cu > Pb > Cd respectively.

4.15.5 Metals concentrations in different parts of *Ricinus communis* (Castor Oil) plant

The concentrations of the studied metals in different parts of *Ricinus communis* (Castor Oil) plant and soil after the application of EDTA to the soil at the Gaskiya and control study areas are presented in Figures 4.85 and Appendix XLI. At the test site, the leaves contained levels of the studied metals as Cd - 3.30±0.03 mg/kg, Co - 14.90±0.02 mg/kg, Cu - 12.20±0.05 mg/kg, Ni - 276.00±0.12 mg/kg, Pb - 45.70±0.03 mg/kg, Zn - 52.98±0.05 mg/kg; in the stems, Cd - 3.70±0.02 mg/kg, Co - 12.20±0.02 mg/kg, Cu - 11.00±0.02 mg/kg, Ni - 64.40±0.09 mg/kg, Pb - 44.50±0.05 mg/kg, Zn - 46.00±0.05 mg/kg; in the roots, Cd - 2.90±0.03 mg/kg, Co - 11.70±0.05 mg/kg, Cu - 6.90±0.03 mg/kg, Ni - 14.90±0.10 mg/kg, Pb - 44.50±0.02 mg/kg, Zn - 43.39±0.03 mg/kg; in the soil, Cd - 3.80±0.01 mg/kg, Co - 9.90±0.03 mg/kg, Cu - 1.90±0.04 mg/kg, Ni - 84.90±0.06 mg/kg, Pb - 51.70±0.01 mg/kg, Zn - 25.15±0.02 mg/kg. The metal concentrations for the test site were higher than their corresponding values for the control site. The bioaccumulation factor (BF) and the translocation factor (TF) (Figure 4.86) for the various metals studied at the test site were greater than 1, except the BF for Cd and Pb were less than 1. For the control, only the BF for Co, Pb and Zn were less than 1. The order in the BF values for metals was: Cu > Zn > Ni > Co > Cd ≈ Pb, while that of the TF was Ni > Cu > Pb > Cd ≈ Co > Zn.

4.16 Bioaccumulation and Transfer Factors for Metals in Different Plant Species at Gaskiya Soil Treated with EDTA

The result for the BF and TF for Cd in different plant species harvested from Gaskiya soil treated with EDTA is presented in Figures 4.87 to 4.92 and Appendix XLII. The BF for Cd followed the order *Helianthus annus* (1.5) > *Ipomoea asarifolia* (1.1) ≈ *Vetivera zizanioide* (1.1) > *Cymbopogon citratus* (0.9) ≈ *Ricinus communis* (0.9), while the TF

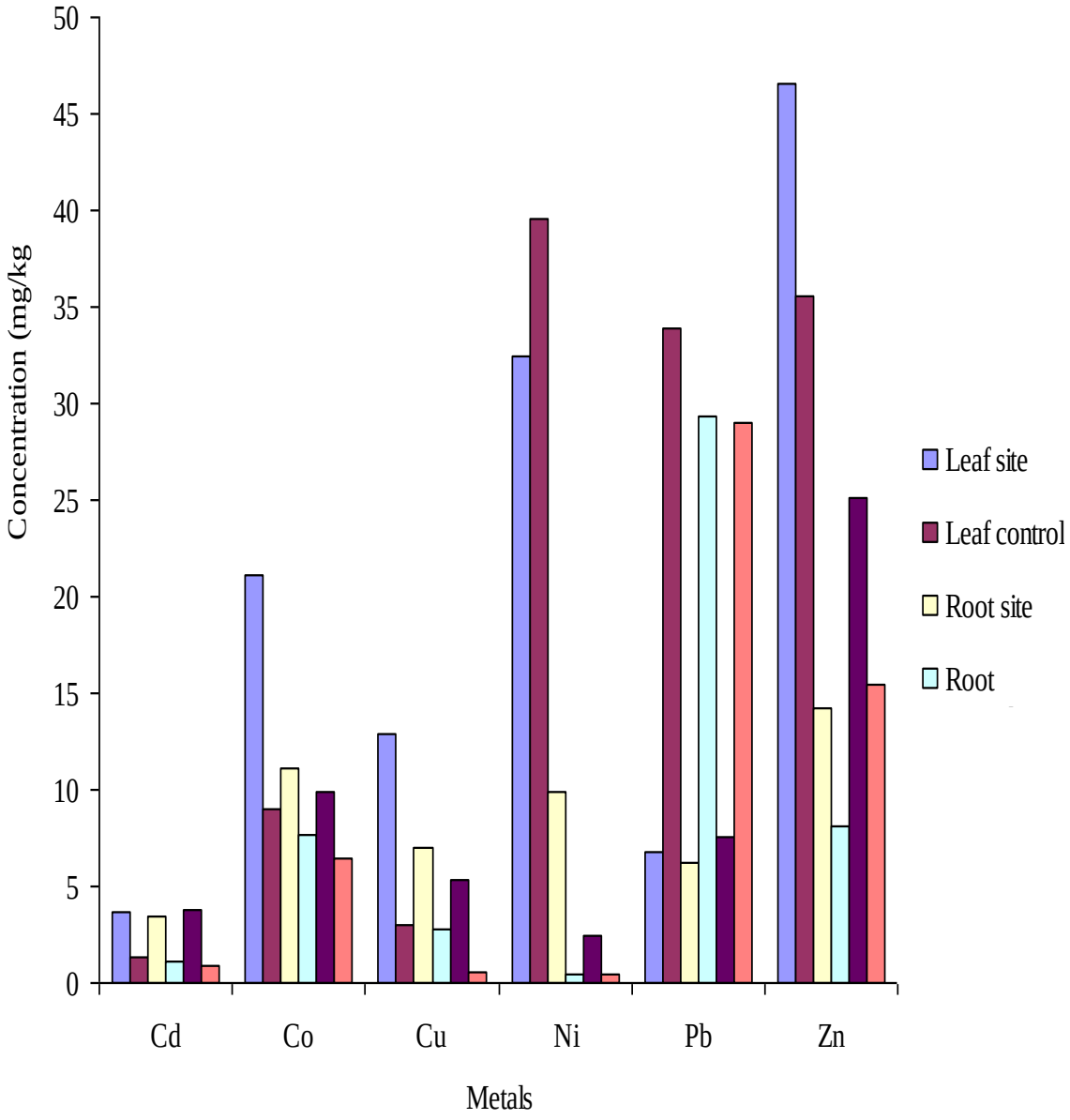


Figure 4.79: Concentrations of Metals in Different Parts of *Cymbopogon citratus* Plant and the Soil at Gaskiya after Addition of EDTA

* Ni (roots) =9.92 x 10, Ni (leaves) = 32.5 x10, Ni (soil) = 8.49 x 10, Pb (leaves) = 6.74 x 10, Pb (roots) = 6.21 x 10, Pb (soil) = 7.59 x 10

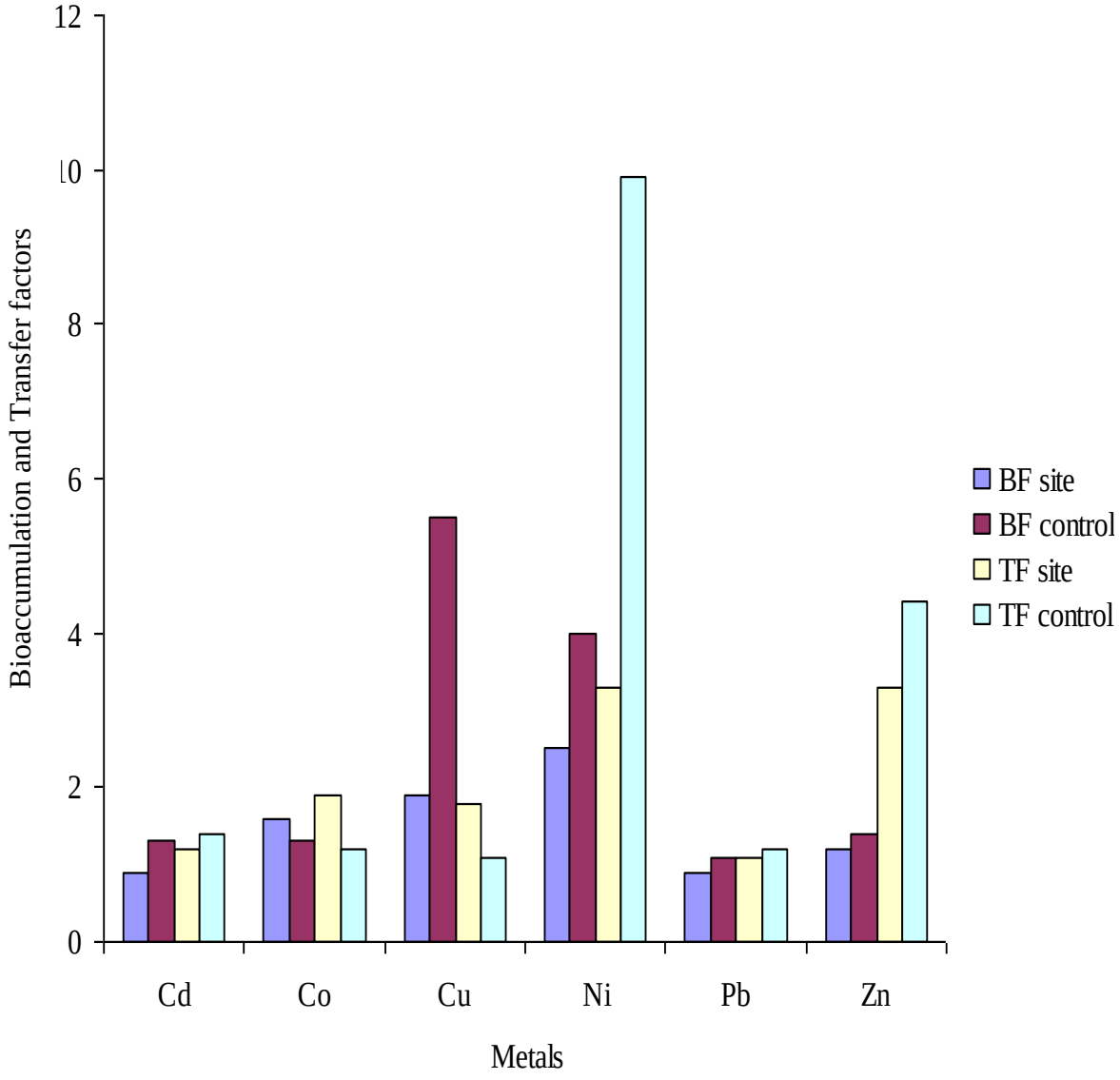


Figure 4.80: Bioaccumulation and Transfer Factors of Metals for *Cymbopogon citratus* Plant at Gaskiya after Addition of EDTA

BF = Bioaccumulation factor; TF = Translocation factor.

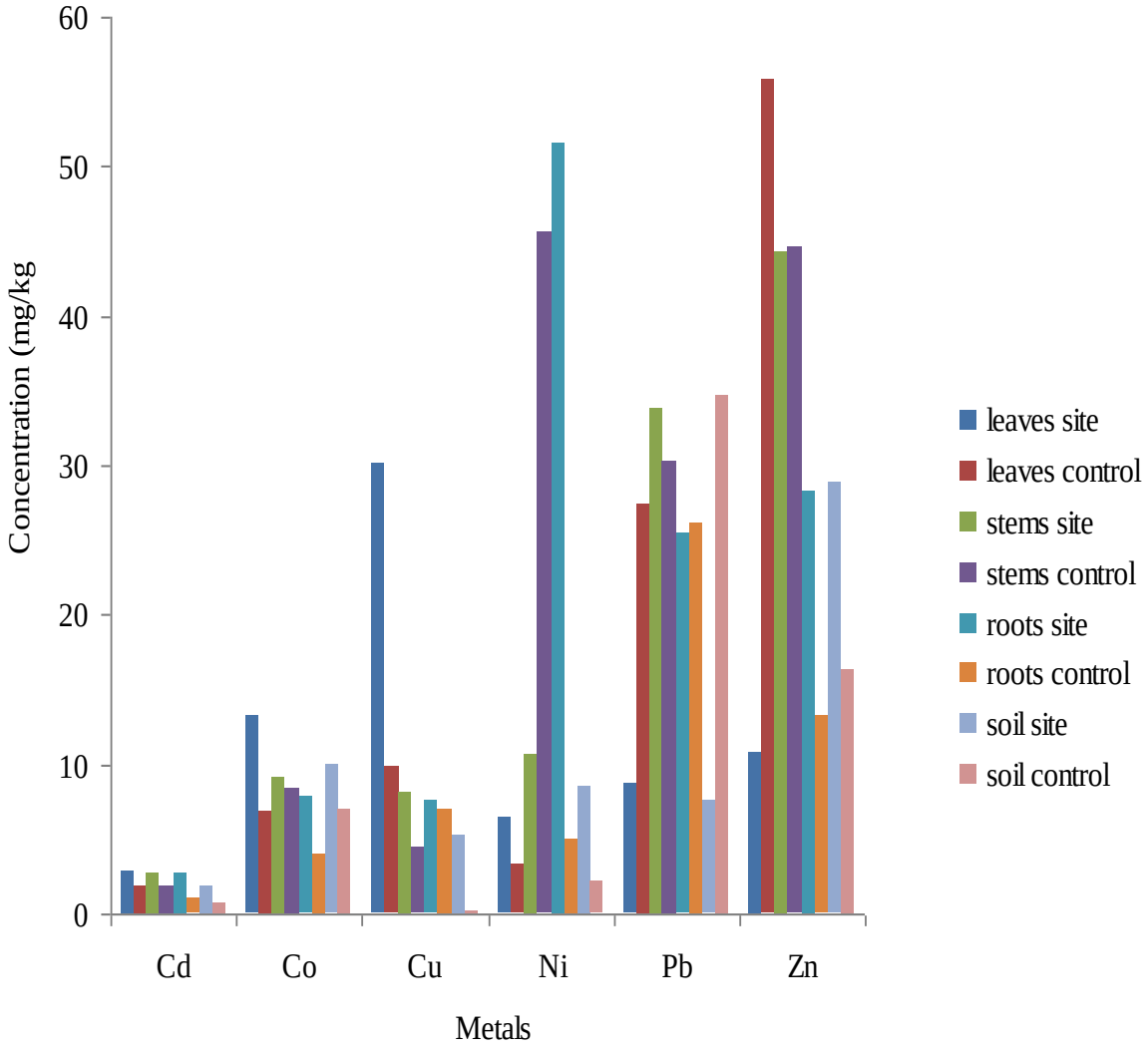


Figure 4.81: Concentrations of Metals in Different Parts of *Heliathus annus* Plant after Addition of EDTA at Gaskiya

* Ni (leaves) =6.43 x 10, Ni (stems) = 10.72 x 10, Ni (soil) = 8.49 x 10, Zn (leaves) = 10.74 x 10, Pb (leaves) = 8.7 x 10, Pb (soil) = 7.59 x 10

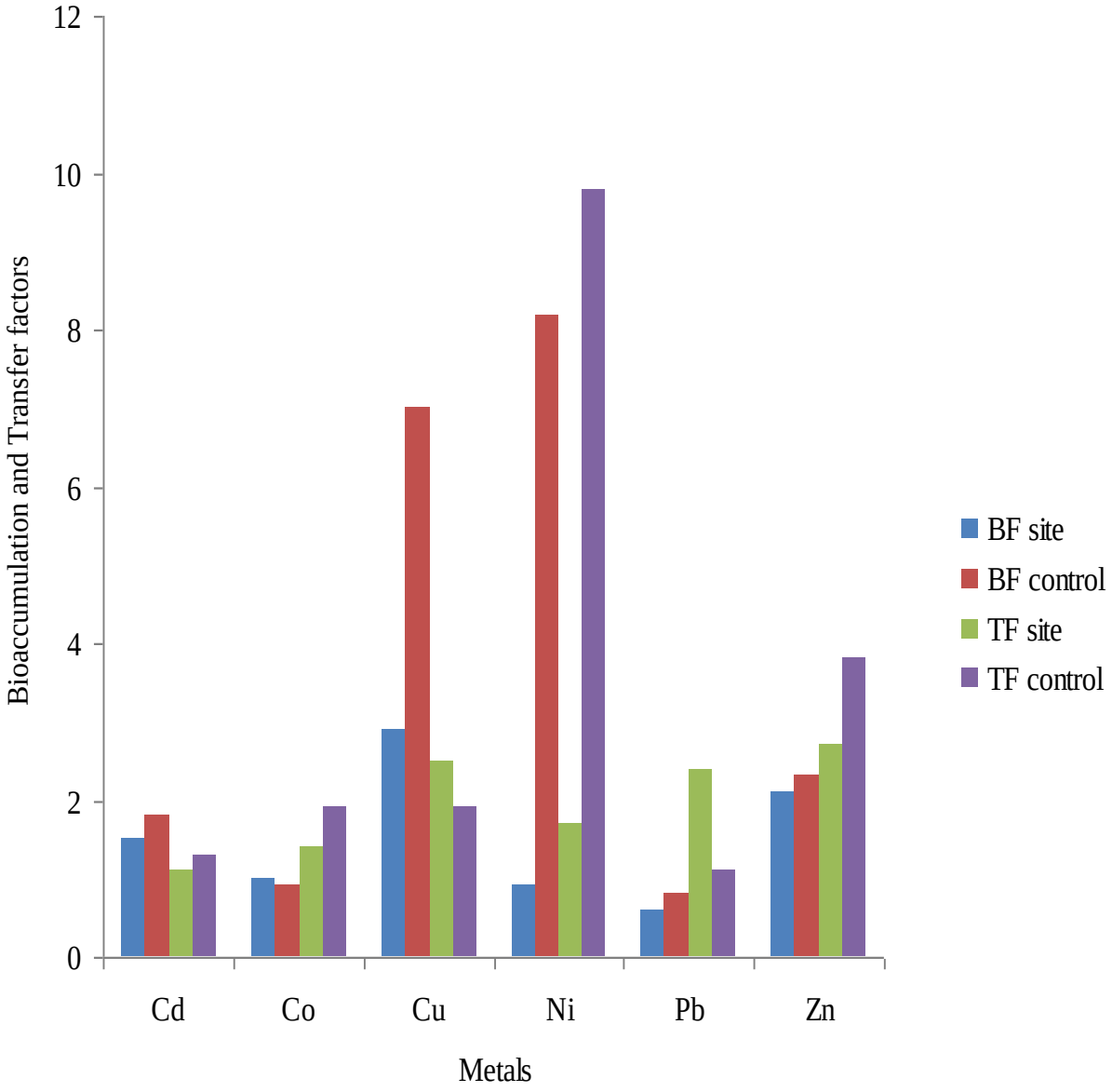


Figure 4.82: Bioaccumulation and Transfer Factors of Metals for *Heliathus annus* Plant after Addition of EDTA at Gaskiya

BF = Bioaccumulation factor; TF = Translocation factor

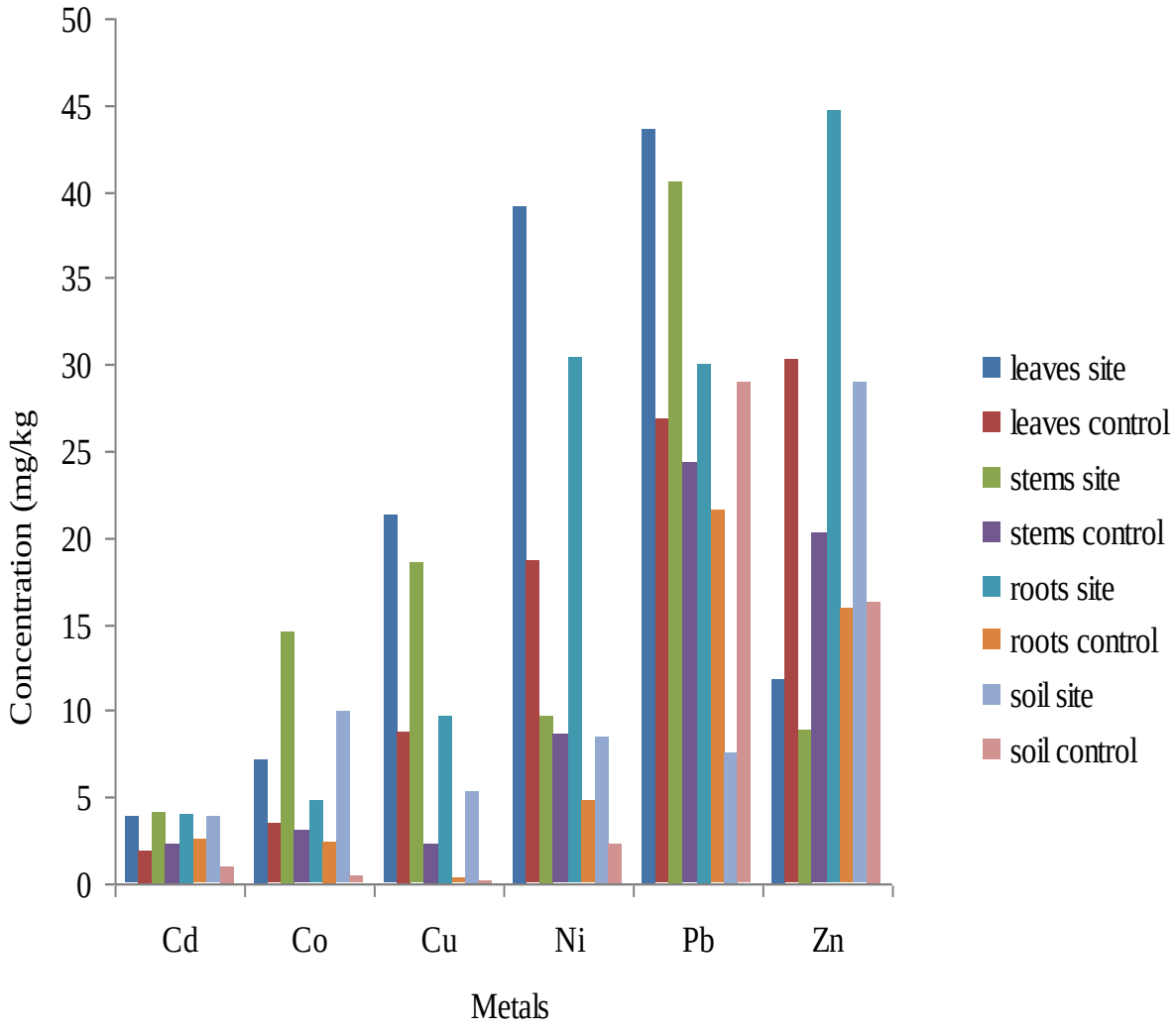


Figure 4.83: Concentrations of Metals in Different Parts of *Ipomoea asarifolia* Plant after Addition of EDTA at Gaskiya

* Ni (leaves) = 39.19 x 10, Ni (stems) = 9.59 x 10, Ni (soil) 8.49 x 10, Pb (soil) = 7.59, Zn (leaves) = 11.78 x 10, Zn (stems) = 8.81 x 10

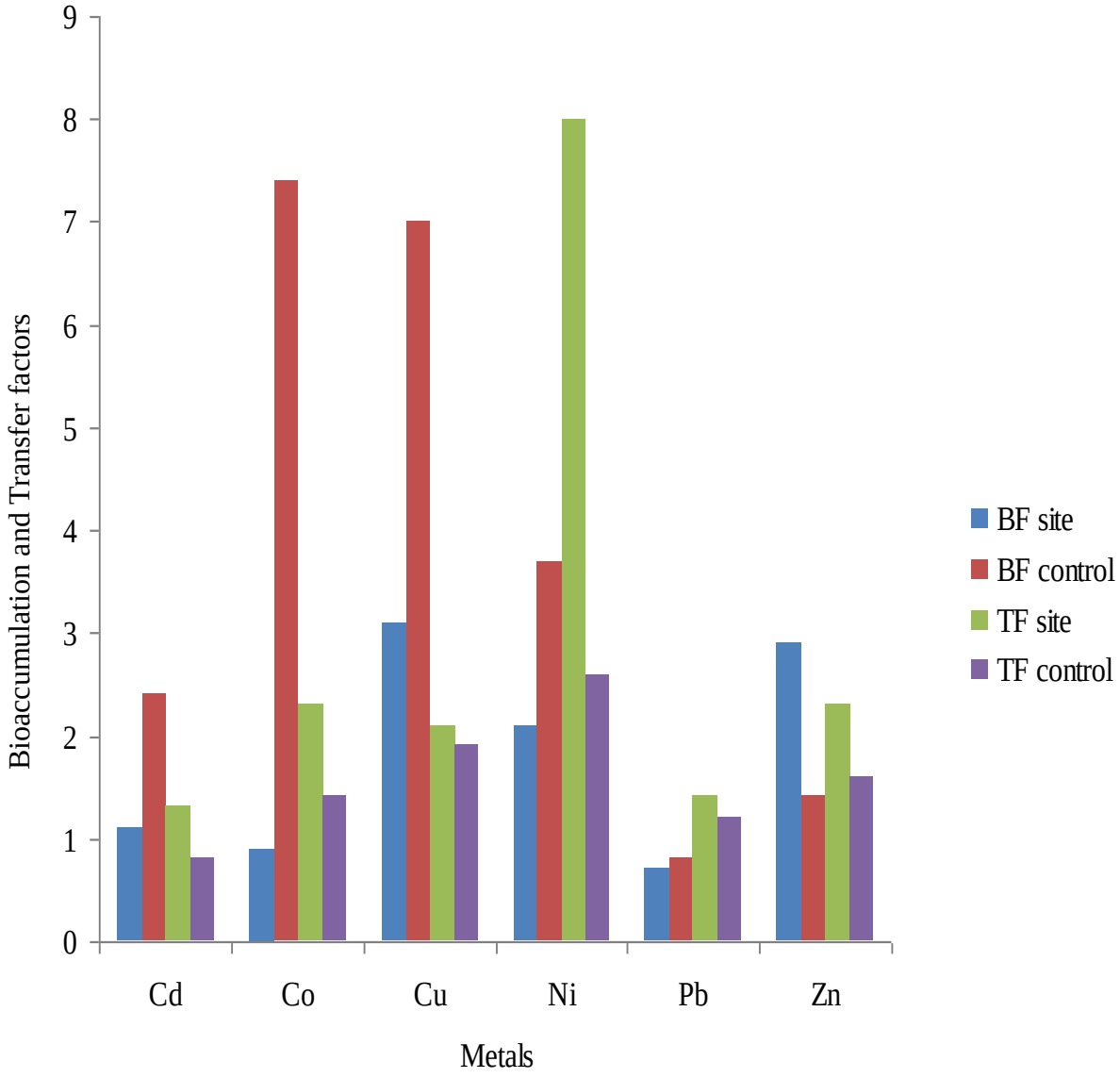


Figure 4.84: Bioaccumulation and Translocation Factors of Metals for *Ipomoea asarifolia* Plant at Gaskiya after Addition of EDTA

BF = Bioaccumulation factor; TF = Translocation factor.

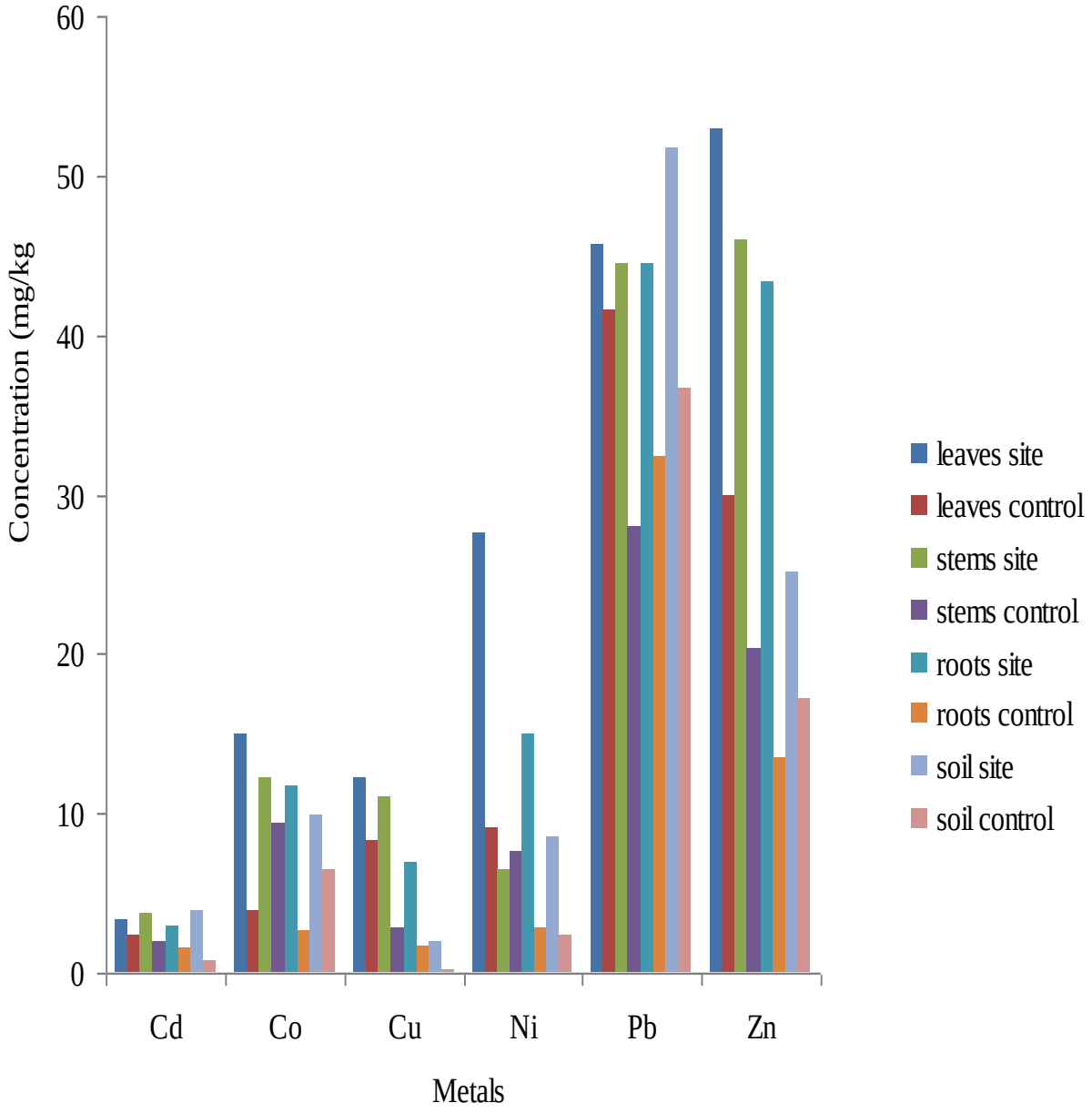


Figure 4.85: Concentrations of Metals in Different Parts of *Ricinus communis* Plant after Addition of EDTA at Gaskiya

* Ni (leaves) = 27.6 x 10, Ni (stems) = 6.44 x 10, Ni (soil) = 8.49 x 10

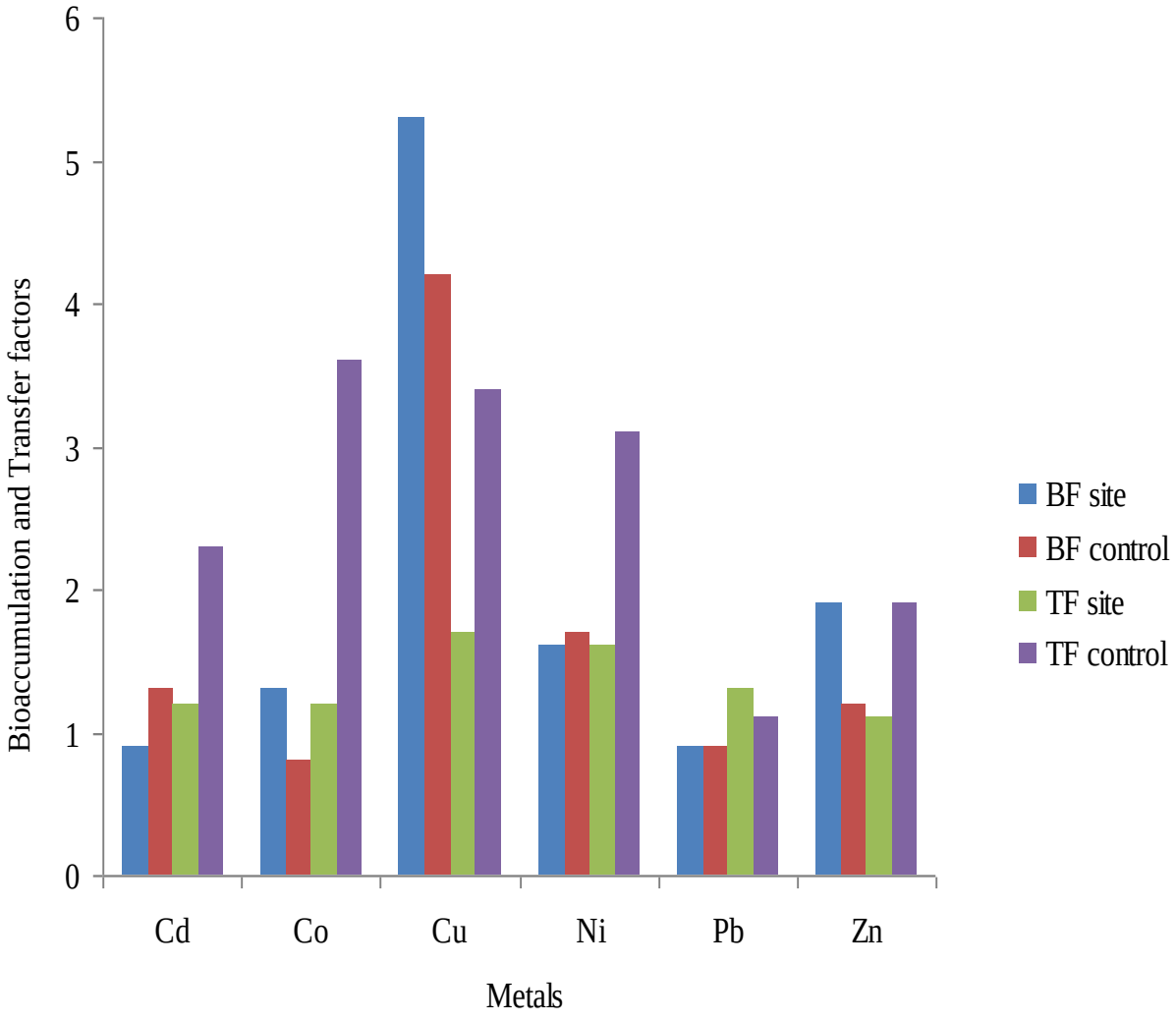


Figure 4.86: Bioaccumulation and Transfer Factors of Metals for *Ricinus communis* Plant at Gaskiya after Addition of EDTA

BF = Bioaccumulation factor; TF = Translocation factor.

showed that *Ipomoea asarifolia* (1.3) > *Cymbopogon citratus* (1.2) ≈ *Ricinus communis* (1.2) > *Helianthus annus* (1.1) ≈ *Vetivera zizanioide* (1.1). The BF and TF for Co in different plant species were *Cymbopogon citratus* (1.6) > *Ricinus communis* (1.3) > *Vetivera zizanioide* (1.0) ≈ *Helianthus annus* (1.0) > *Ipomoea asarifolia* (0.9) and *Ipomoea asarifolia* (2.3) > *Cymbopogon citratus* (1.9) > *Vetivera zizanioide* (1.6) > *Helianthus annus* (1.4) > *Ricinus communis* (1.2) respectively. For Cu, the BF and TF were in the order of *Ricinus communis* (5.3) > *Ipomoea asarifolia* (3.1) > *Helianthus annus* (2.9) > *Cymbopogon citratus* (1.9) > *Vetivera zizanioide* (1.1) and *Helianthus annus* (2.5) > *Ipomoea asarifolia* (2.1) > *Cymbopogon citratus* (1.8) > *Ricinus communis* (1.7) > *Vetivera zizanioide* (1.6) respectively. The BF and TF for Ni in different plant species were in the order of *Cymbopogon citratus* (2.5) > *Ipomoea asarifolia* (2.1) > *Ricinus communis* (1.6) > *Helianthus annus* (0.9) > *Vetivera zizanioide* (0.6) and *Ipomoea asarifolia* (8.0) > *Cymbopogon citratus* (3.3) > *Helianthus annus* (1.7) > *Ricinus communis* (1.6) > *Vetivera zizanioide* (1.2) respectively. For Pb, BF and TF followed the order of *Cymbopogon citratus* (0.9) ≈ *Ricinus communis* (0.9) > *Ipomoea asarifolia* (0.7) ≈ *Vetivera zizanioide* (0.7) > *Helianthus annus* (0.6) and *Helianthus annus* (2.4) > *Ipomoea asarifolia* (1.4) >*Ricinus communis* (1.3) > *Vetivera zizanioide* (1.2) > *Cymbopogon citratus* (1.1) respectively. Zn in different plant species indicated that the BF was in the order *Ipomoea asarifolia* (2.9) > *Helianthus annus* (2.1) > *Ricinus communis* (1.9) > *Vetivera zizanioide* (1.4) >*Cymbopogon citratus* (1.2), while the TF was *Cymbopogon citratus* (3.3) > *Helianthus annus* (2.7) > *Ipomoea asarifolia* (2.3) > *Vetivera zizanioide* (1.6) > *Ricinus communis* (1.1).

4.17 Metal Content in Different Parts of Plant Species with EDTA Application at Hanwa Site

4.17.1 Metals concentrations in different parts of *Vetivera zizanioide* plant

The concentrations of metals in different parts of *Vetivera zizanioide* plant after the application of EDTA at Hanwa and the control study areas are presented in Figure 4.93 and Appendix XLIII. At the test site, the metal levels in the leaves were: Cd - 3.80±0.01mg/kg, Co -10.30±0.01mg/kg, Cu - 6.80±0.06mg/kg, Ni - 39.00±0.04mg/kg, Pb - 56.80±0.02mg/kg, Zn - 90.50±0.25mg/kg; in the roots, Cd - 3.70±0.06 mg/kg, Co -

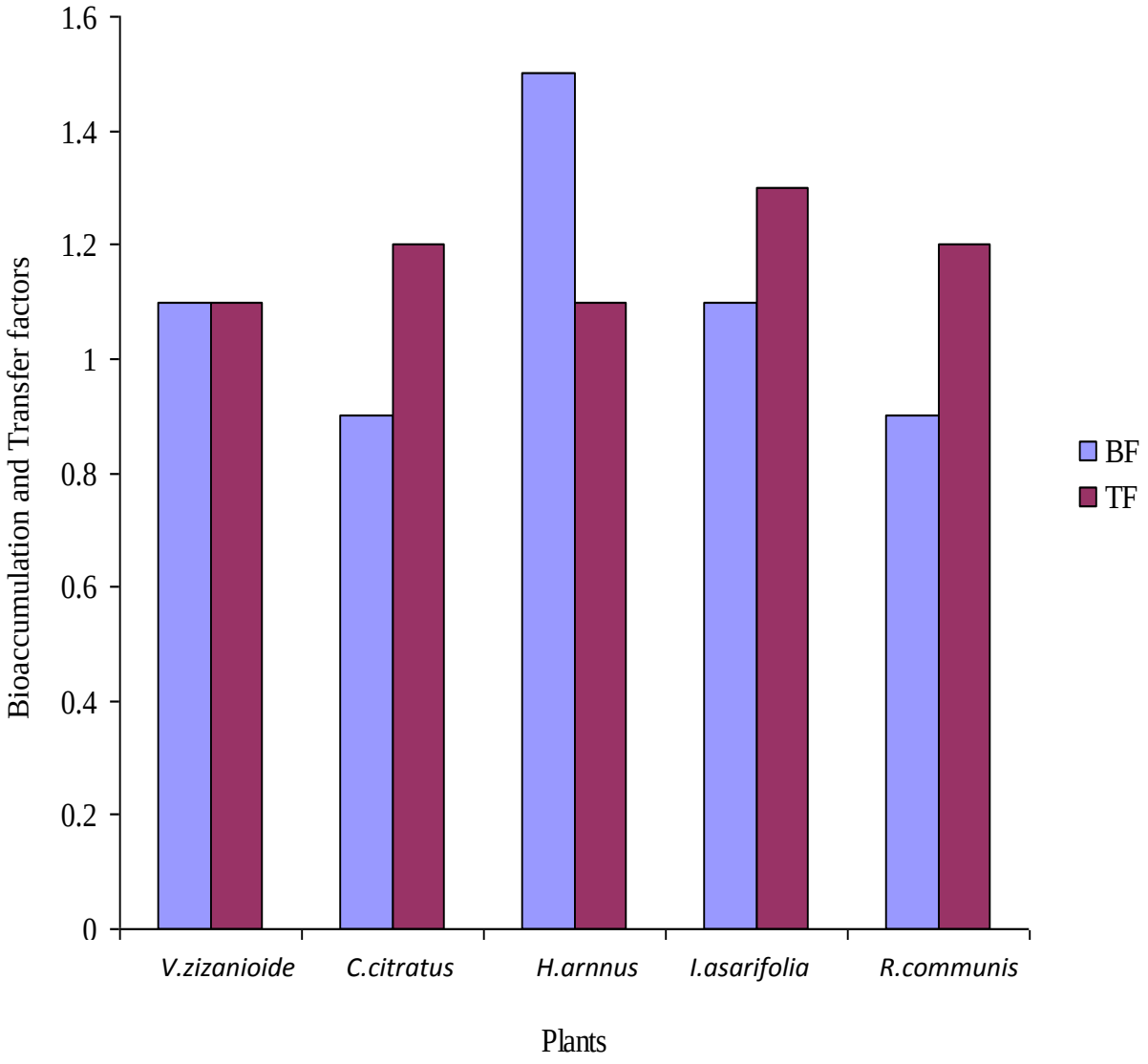


Figure 4.87: Bioaccumulation and Transfer Factors for Cadmium in Different Plant Species at Gaskiya Soil Treated with EDTA

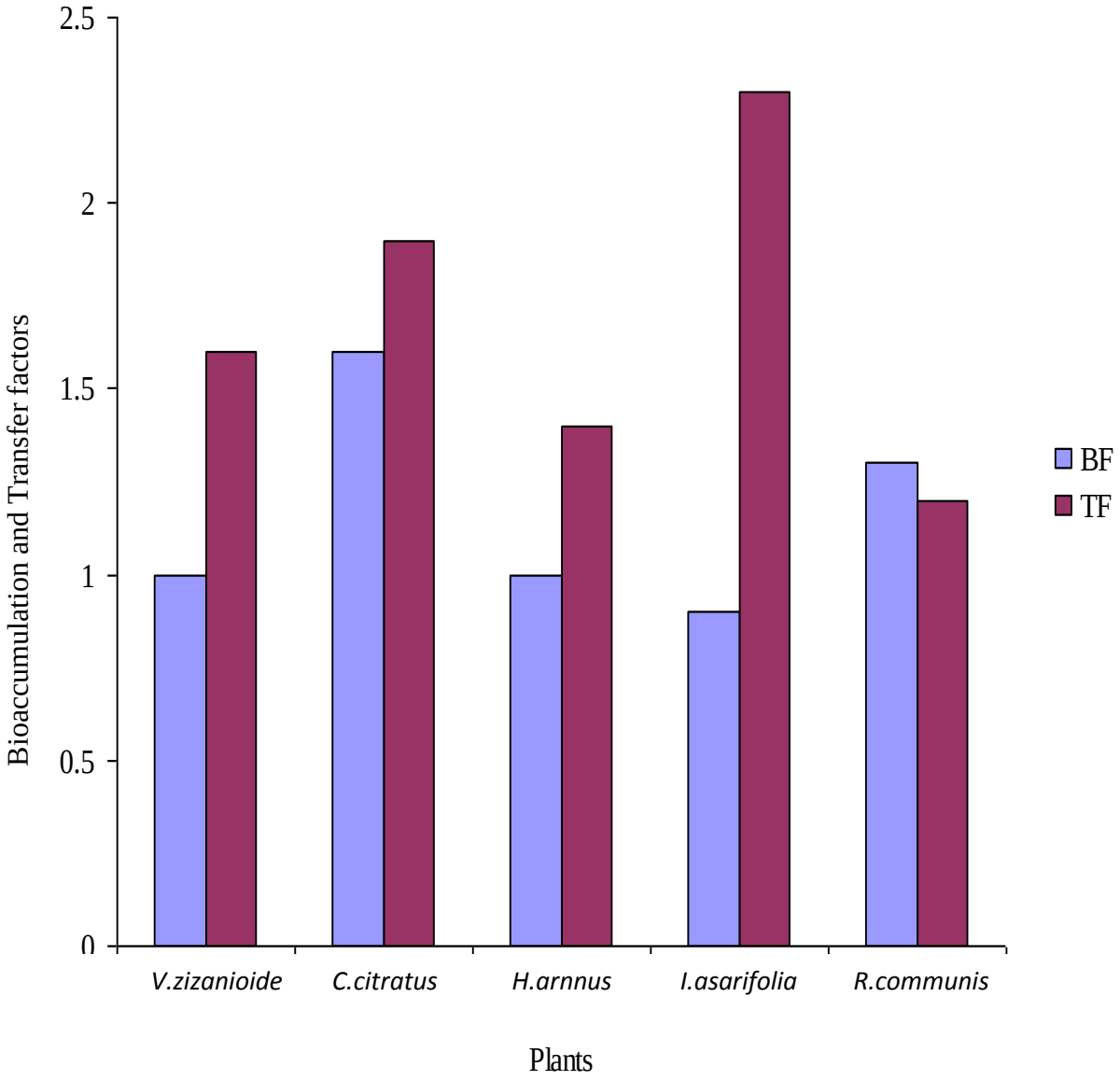


Figure 4.88: Bioaccumulation and Transfer Factors for Cobalt in Different Plant Species at Gaskiya Soil Treated with EDTA

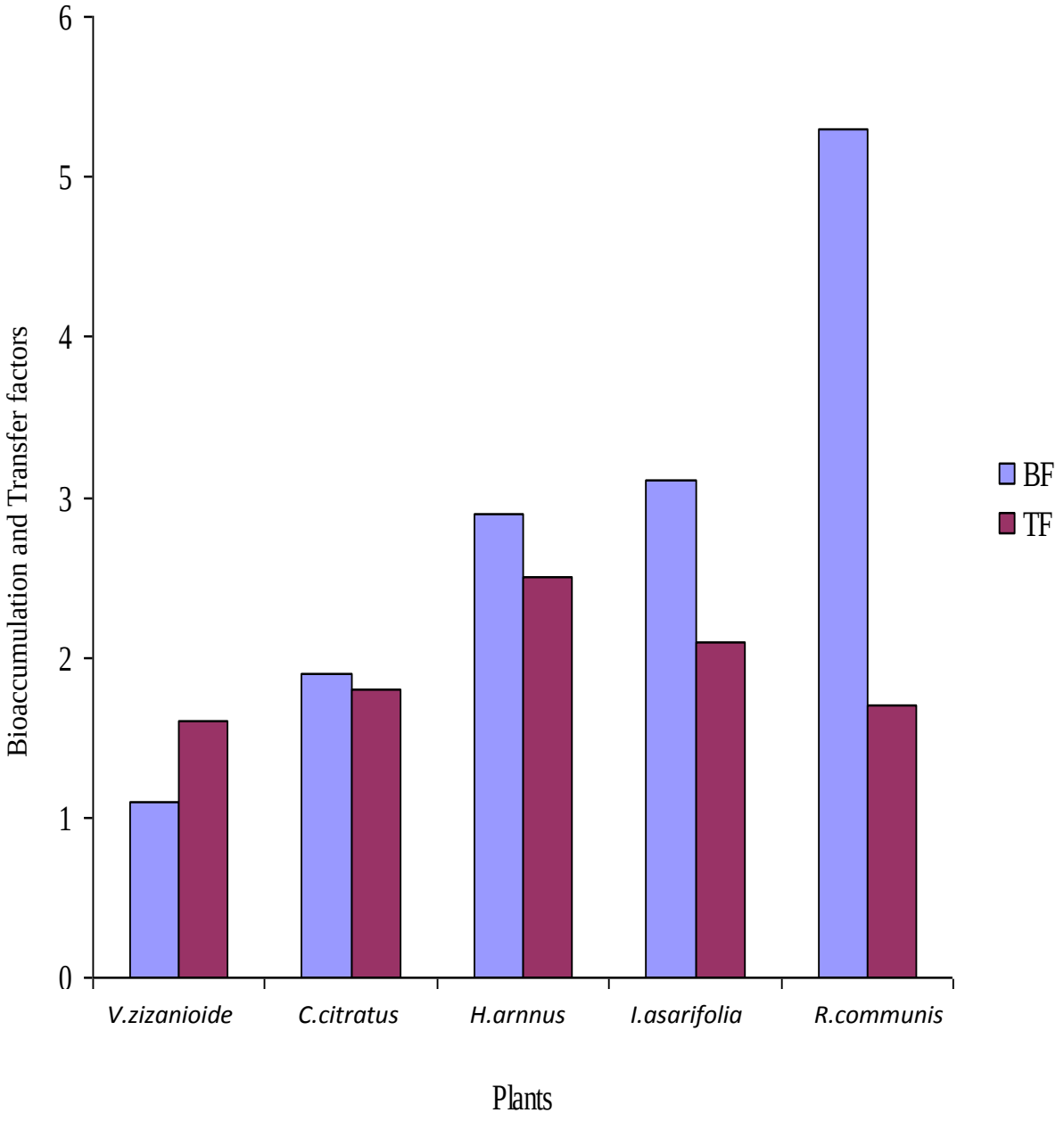


Figure 4.89: Bioaccumulation and Transfer Factors for Copper in Different Plant Species at Gaskiya Soil Treated with EDTA

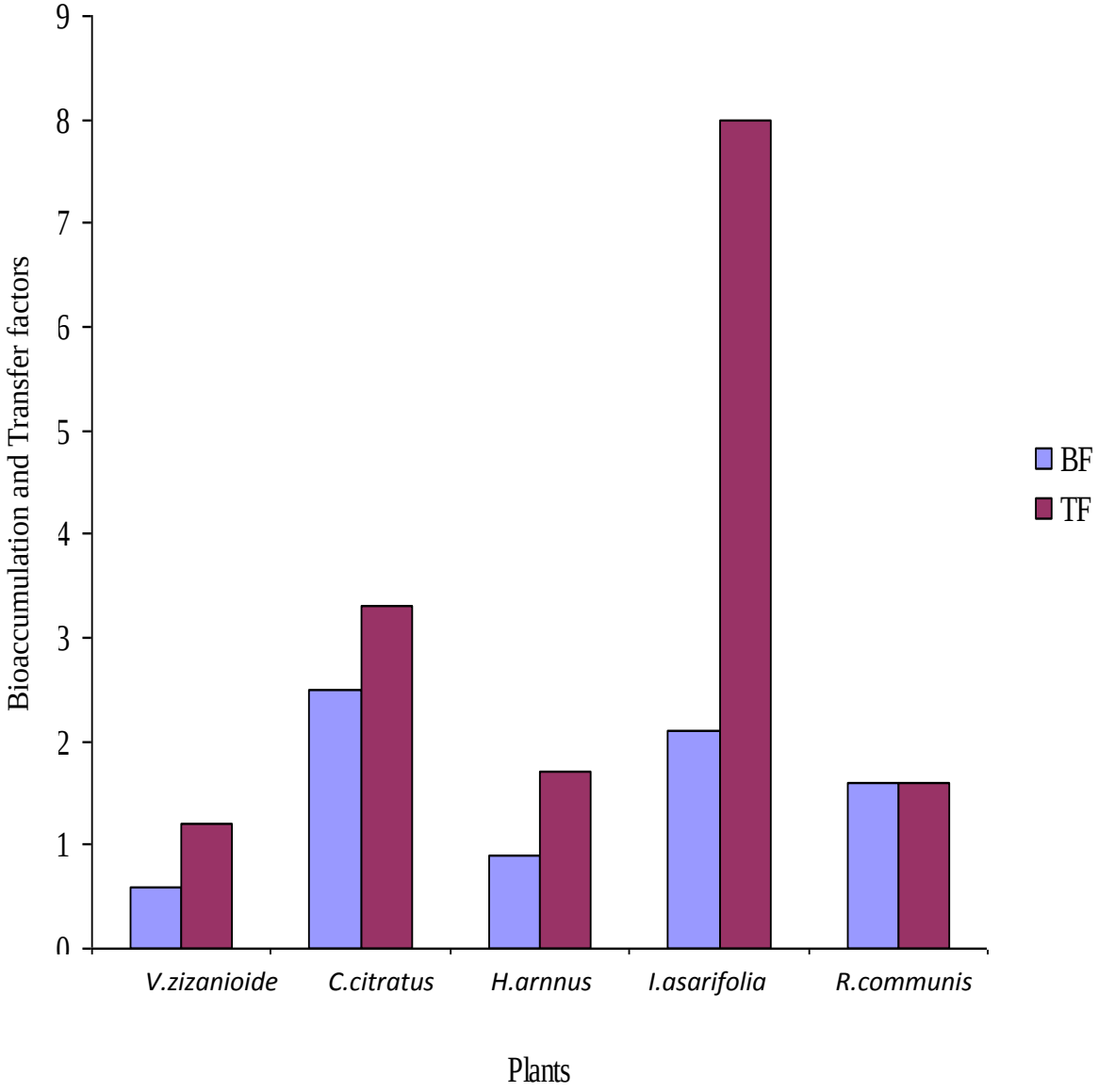


Figure 4.90: Bioaccumulation and Transfer Factors for Nickel in Different Plant Species at Gaskiya Soil Treated with EDTA

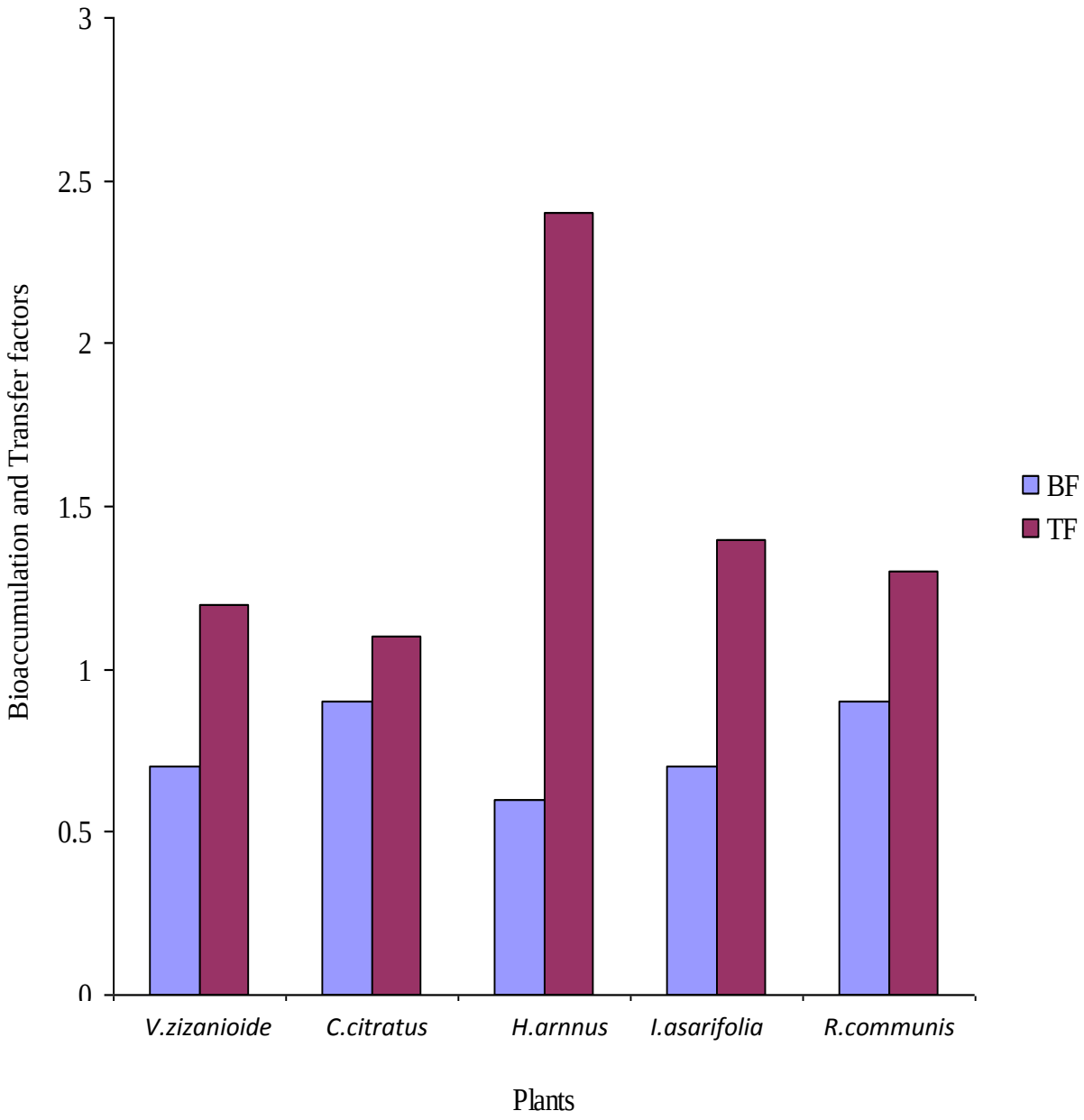


Figure 4.91: Bioaccumulation and Transfer Factors for Lead in Different Plant Species at Gaskiya Soil Ttreated with EDTA

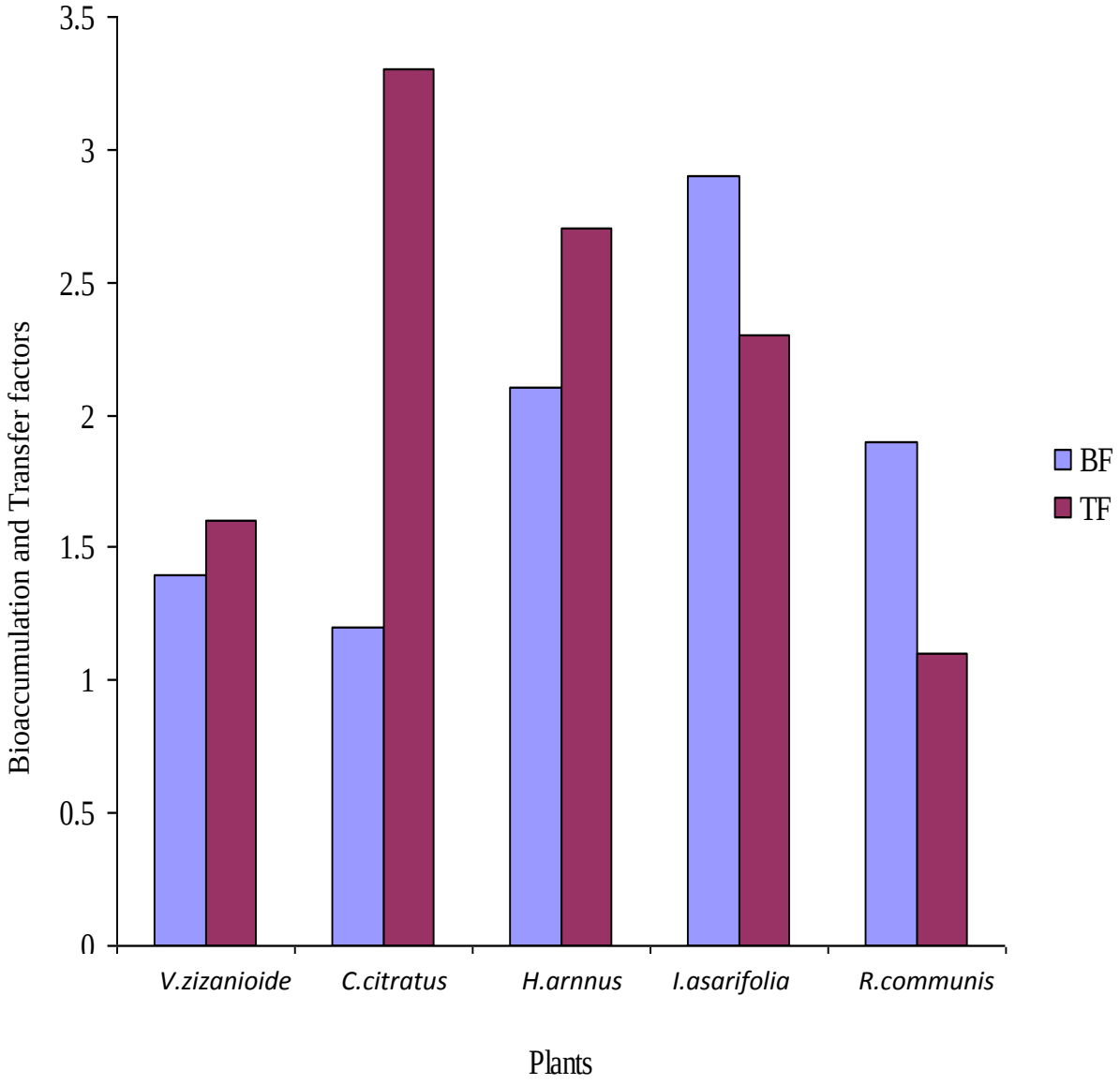


Figure 4.92: Bioaccumulation and Transfer Factors for Zinc in Different Plant Species at Gaskiya Soil Treated with EDTA

8.50±0.02 mg/kg, Cu - 6.70±0.04 mg/kg, Ni - 32.10±0.09 mg/kg, Pb - 56.30±0.03 mg/kg, Zn - 32.70±0.13 mg/kg; in the soil, Cd - 3.80±0.03 mg/kg, Co - 8.70±0.03 mg/kg, Cu - 3.80±0.05 mg/kg, Ni - 42.10±0.04 mg/kg, Pb - 76.90±0.04 mg/kg, Zn - 25.58±0.06 mg/kg. The concentrations of the studied metals were higher at the test site than their corresponding values at the control site.

The BF and the TF (Figure 4.94) for the studied metals at the test and the control sites were greater than 1, except the BF for Ni and Pb at the test site and that for Pb at the control site. The BF and the TF at the test site followed the order: Zn > Cu > Cd ≈ Co > Ni > Pb and Zn > Co ≈ Ni > Cd ≈ Pb > Cu.

4.17.2 Metals concentrations in different parts of *Cymbopogon citratus* (Lemon grass) Plant

The concentrations of metals in different parts of *Cymbopogon citratus* (Lemon grass) plant after the application of EDTA at Hanwa and the control study areas are presented in Figure 4.95 and Appendix XLIV. At the test site,the metal levels in the leaves were: Cd - 3.60±0.01 mg/kg, Co - 12.20±0.02 mg/kg, Cu - 9.20±0.01 mg/kg, Ni - 78.20±0.11 mg/kg, Pb - 65.70±0.03 mg/kg, Zn - 84.40±0.11 mg/kg; in the roots, Cd - 3.40±0.02 mg/kg, Co - 9.50±0.02 mg/kg, Cu - 5.60±0.06 mg/kg, Ni - 59.80±0.02 mg/kg, Pb - 64.20±0.07 mg/kg, Zn - 29.80±0.07 mg/kg; in the soil, Cd - 1.90±0.00 mg/kg, Co - 8.70±0.03 mg/kg, Cu - 3.80±0.05 mg/kg, Ni - 42.10±0.04 mg/kg, Pb - 42.30±0.04 mg/kg, Zn - 25.58±0.06 mg/kg. The concentrations of the studied metals were higher at the test site than their corresponding values at the control site. The BF and TF for the studied metals at the test and control sites were all greater than 1 (Figure 4.96). The decreasing order in the BF and TF was Zn > Cu > Cd > Ni > Pb > Co and Zn > Cu > Co ≈ Ni > Cd ≈ Pb respectively.

4.17.3 Metals concentrations in different parts of *Helianthus annus* (Sunflower) plant

The concentrations of the studied metals in different parts of *Helianthus annus* (Sunflower) plant and soil after the application of EDTA to the soil at the Hanwa and control study areas are presented in Figure 4.97 and Appendix XLV. At the test site, the leaves contained levels of the studied metals as Cd - 3.00±0.03 mg/kg, Co - 16.00±0.0 mg/kg, Cu - 39.90±0.02 mg/kg, Ni - 285.00±0.13 mg/kg, Pb - 81.60±0.04 mg/kg, Zn - 182.24±0.01 mg/kg; in the stems, Cd - 3.10±0.04 mg/kg, Co - 8.90±0.05 mg/kg, Cu - 10.70±0.01 mg/kg, Ni - 50.30±0.04 mg/kg, Pb - 55.70±0.02 mg/kg, Zn - 62.80±0.27 mg/kg; in the roots, Cd - 2.80±0.01 mg/kg, Co - 8.10±0.03 mg/kg, Cu - 15.00±0.01 mg/kg, Ni - 25.70±0.04 mg/kg, Pb - 34.00±0.03 mg/kg, Zn - 51.99±0.06 mg/kg; in the soil, Cd - 1.90±0.00 mg/kg, Co - 8.70±0.03 mg/kg, Cu - 3.80±0.05 mg/kg, Ni - 42.10±0.04 mg/kg, Pb - 42.30±0.04 mg/kg, Zn - 25.58±0.06 mg/kg. The metal concentrations for the test site were higher than their corresponding values for the control site. The BF and TF for the studied metals at the test and control sites were greater than 1 except the BF for Pb at the control site (Figure 4.98). BF for Cu > Zn > Ni > Cd > Co ≈ Pb and TF for Ni > Zn > Pb > Cu > Co > Cd.

4.17.4 Metals concentrations in different parts of *Ipomoea asarifolia* plant

The concentrations of the studied metals in different parts of *Ipomoea asarifolia* plant after the application of EDTA at Hanwa and the control study areas are presented in Figure 4.99 and Appendix XLVI. At the test site, the leaves contained levels of the studied metals as Cd - 4.50±0.11 mg/kg, Co - 5.10±0.09 mg/kg, Cu - 21.90±0.04 mg/kg, Ni - 133.10±0.03 mg/kg, Pb - 40.30±0.03 mg/kg, Zn - 99.31±0.10 mg/kg; in the stems, Cd - 4.00±0.02

mg/kg, Co - 3.80±0.02 mg/kg, Cu - 17.30±0.02 mg/kg, Ni - 92.20±0.05 mg/kg, Pb - 34.30±0.02 mg/kg, Zn - 34.36±0.04 mg/kg; in the roots, Cd - 5.10±0.02 mg/kg, Co - 3.20±0.03 mg/kg, Cu - 10.90±0.01 mg/kg, Ni - 79.10±0.07 mg/kg, Pb - 34.50±0.04 mg/kg, Zn - 29.76±0.02 mg/kg; in the soil, Cd - 3.80±0.01 mg/kg, Co - 8.60±0.04 mg/kg, Cu - 3.80±0.05 mg/kg, Ni - 47.90±0.08 mg/kg, Pb - 42.30±0.06 mg/kg, Zn - 25.58±0.06 mg/kg. The metal concentrations for the test site were higher than their corresponding values for the control site. The BF for Cd, Cu, Ni and Zn were greater than 1, and the TF for all the studied metals were greater than 1(except that for Cd). The BF for Cu > Zn ≈ Ni > Cd > Pb > Co and the TF for Zn > Cu > Co ≈ Ni >Pb > Cd (Figure 4.100).

4.17.5 Metals concentrations in different parts of *Ricinus communis* (Castor Oil) plant

The concentrations of the studied metals in different parts of *Ricinus communis* (Castor Oil) plant and soil after the application of EDTA at Hanwa and the control study areas are presented in Figure 4.101 and Appendix XLVII. At the test site,the leaves contained levels of the studied metals as Cd - 3.40±0.01 mg/kg, Co - 11.60±0.03 mg/kg, Cu - 12.70±0.01 mg/kg, Ni - 85.60±0.02 mg/kg, Pb - 45.60±0.03 mg/kg, Zn - 41.73±0.06 mg/kg; in the stems, Cd - 3.10±0.02 mg/kg, Co - 12.40±0.02 mg/kg, Cu - 3.20±0.03 mg/kg, Ni - 10.80±0.06 mg/kg, Pb - 40.10±0.04 mg/kg, Zn - 30.28±0.02 mg/kg; in the roots, Cd - 3.10±0.01 mg/kg, Co - 11.90±0.01 mg/kg, Cu - 7.90±0.01 mg/kg, Ni - 24.10±0.07 mg/kg, Pb - 42.50±0.01 mg/kg, Zn - 31.19±0.04 mg/kg; in the soil, Cd - 1.90±0.00 mg/kg, Co - 8.70±0.03 mg/kg, Cu - 3.80±0.05 mg/kg, Ni - 42.10±0.04 mg/kg, Pb - 42.30±0.06 mg/kg, Zn - 20.49±0.03 mg/kg. The metal concentrations for the test site were higher than their corresponding values for the control site. The BF for Cd, Co, Cu, Pb and Zn were greater

than 1 at the test site. The translocation factors (TF) for all the studied metals at the test site were greater than 1 (Figure 4.102).

4.18 Bioaccumulation and Transfer Factors for Metals in Different Plant Species at Hanwa Soil Treated with EDTA

The BF and TF for the studied metals in different plant species harvested from Hanwa soil treated with EDTA are presented in Figures 4.103 to 4.108 and Appendix XLVIII. The BF for Cd was in the order of *Cymbopogon citratus* (1.8) > *Ricinus communis* (1.7) > *Helianthus annus* (1.6) > *Ipomoea asarifolia* (1.2) > *Vetivera zizanioide* (1.1), while TF was in the order of *Vetivera zizanioide* (1.1) ≈ *Cymbopogon citratus* (1.1) ≈ *Ricinus communis* (1.1) ≈ *Helianthus annus* (1.1) > *Ipomoea asarifolia* (0.8). The BF and TF for Co in different plant species followed the order of *Ricinus communis* (1.4) > *Helianthus annus* (1.3) > *Cymbopogon citratus* (1.2) > *Vetivera zizanioide* (1.1) > *Ipomoea asarifolia* (0.5) and *Helianthus annus* (1.5) > *Ipomoea asarifolia* (1.4) > *Cymbopogon citratus* (1.3) > *Vetivera zizanioide* (1.2) > *Ricinus communis* (1.1) respectively. The BF for Cu was in the order of *Helianthus annus* (5.8) > *Ipomoea asarifolia* (4.4) > *Ricinus communis* (2.1) > *Cymbopogon citratus* (1.9) > *Vetivera zizanioide* (1.8), while TF was in the order of *Ipomoea asarifolia* (1.8) > *Helianthus annus* (1.7) > *Cymbopogon citratus* (1.6) > *Ricinus communis* (1.3) > *Vetivera zizanioide* (1.1). Ni in different plant species showed that the BF was in the order of *Helianthus annus* (2.9) > *Ipomoea asarifolia* (2.1) > *Cymbopogon citratus* (1.6) > *Ricinus communis* (0.9) > *Vetivera zizanioide* (0.8), while TF was in the order of *Helianthus annus* (6.4) > *Ricinus communis* (2.0) > *Ipomoea asarifolia* (1.4) > *Cymbopogon citratus* (1.3) > *Vetivera zizanioide* (1.2). The BF for Pb was in the order of *Cymbopogon citratus* (1.5) > *Helianthus annus* (1.3) > *Ricinus communis* (1.1) > *Ipomoea asarifolia* (0.9) >*Vetivera zizanioide* (0.7), while TF was in the order of *Helianthus annus*

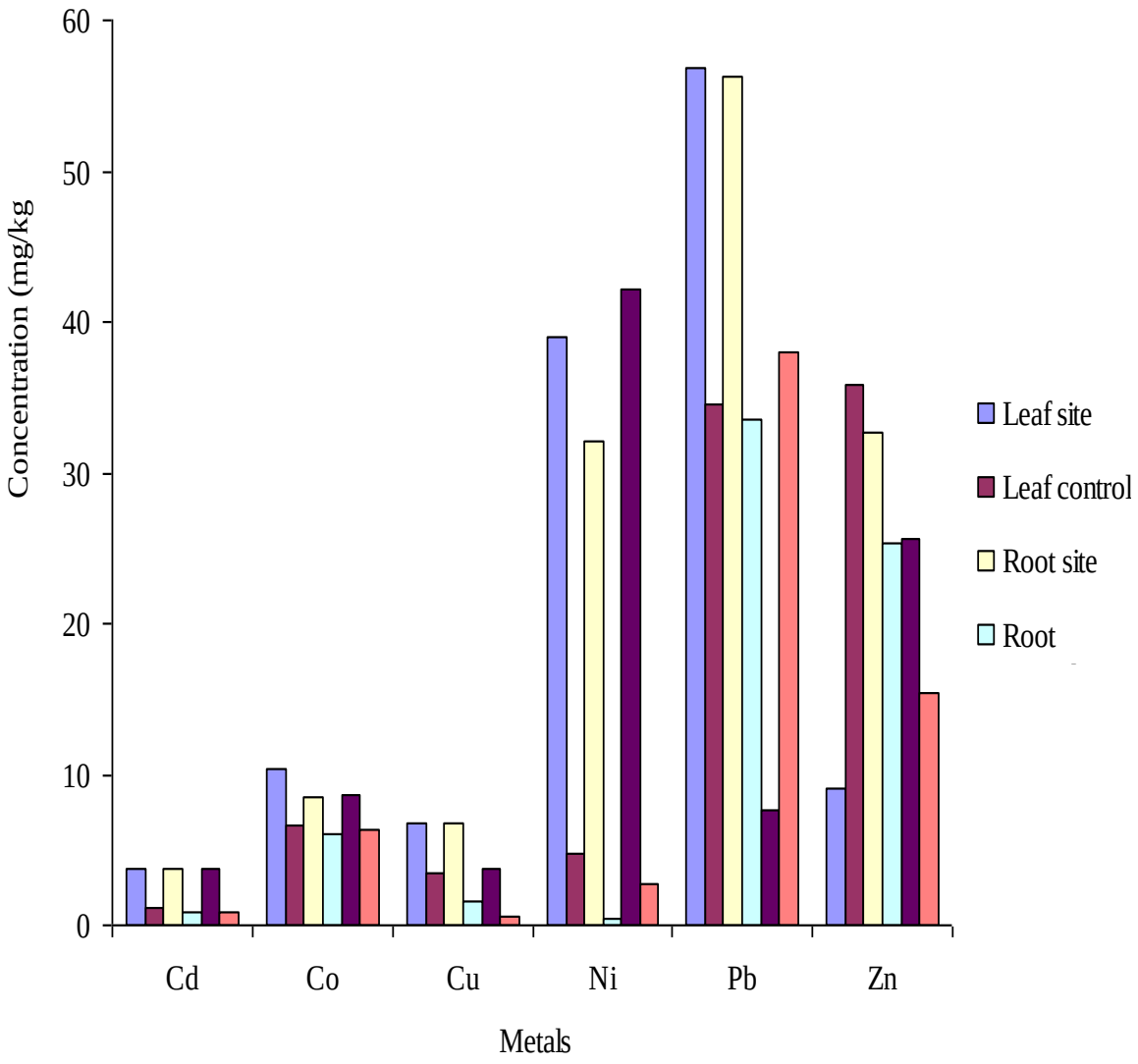


Figure 4.93: Concentrations of Metals in Different Parts of *Vetivera zizanioide* Plant and the Soil at Hanwa after Addition of EDTA

***** Pb (soil) = 7.69 x 10, Zn (leaves) = 9.05 x 10

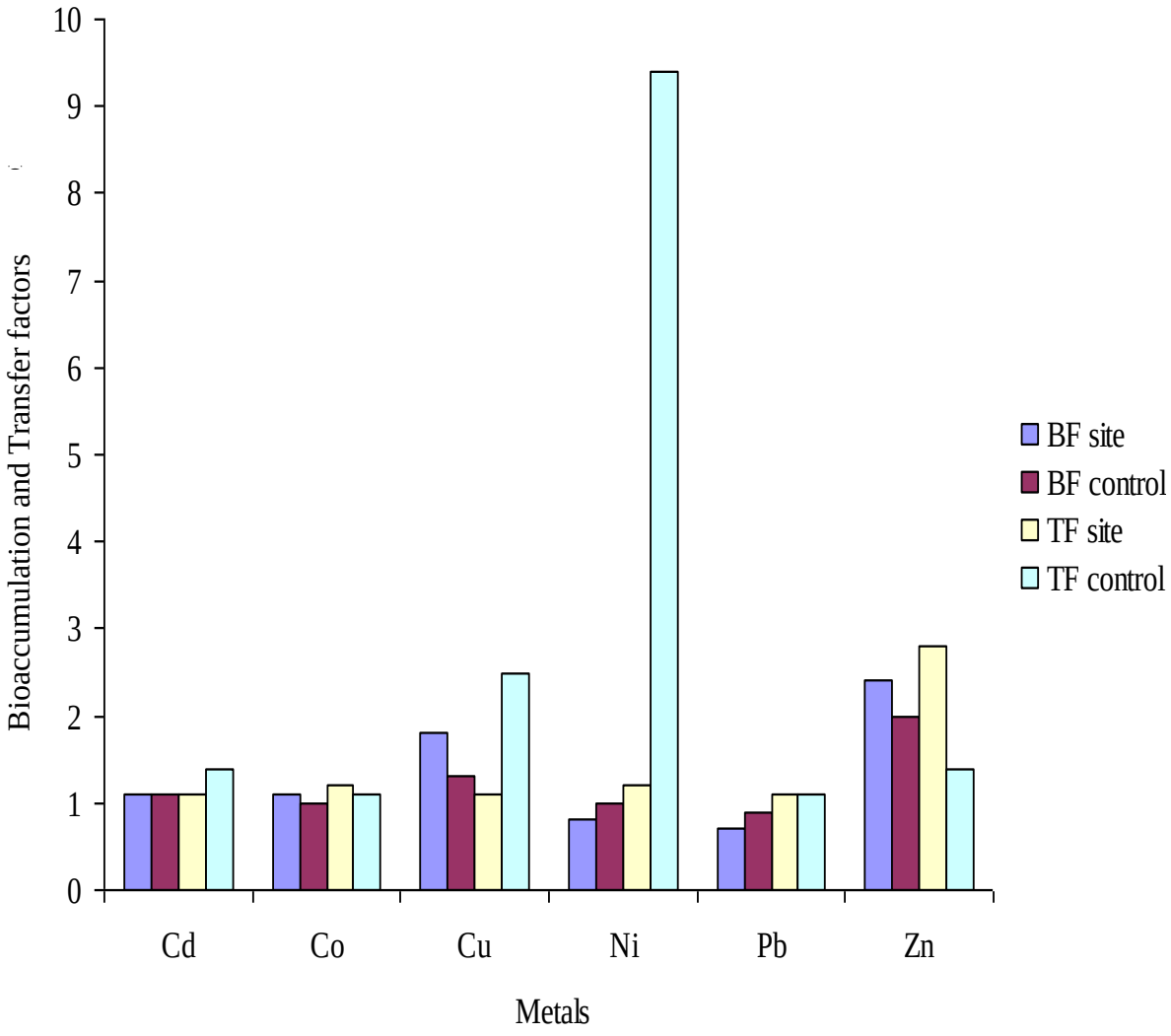


Figure 4.94: Bioaccumulation and Transfer Factors of Metals for *Vetivera zizanioide* Plant at Hanwa after Addition of EDTA

BF = Bioaccumulation factor; TF = Translocation factor

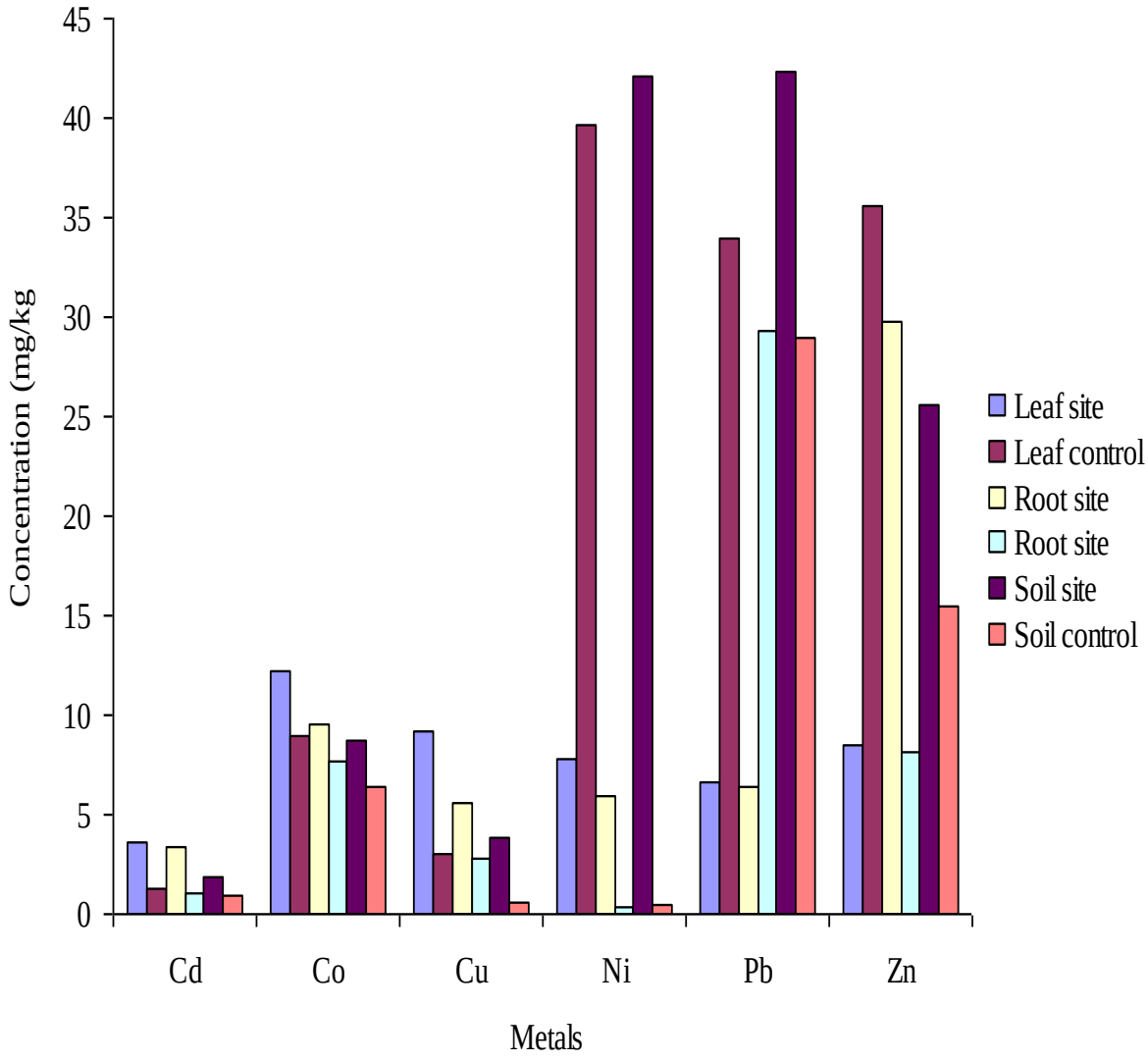


Figure 4.95: Concentrations of Metals in Different Parts of *Cymbopogon citratus* Plant and the Soil at Hanwa after Addition of EDTA

* Ni (leaves) = 7.82 x 10, Ni (roots) = 5.98 x 10, Pb (leaves) = 6.57 x 10, Pb (roots) = 6.42 x 10, Zn (leaves) = 8.44 x 10

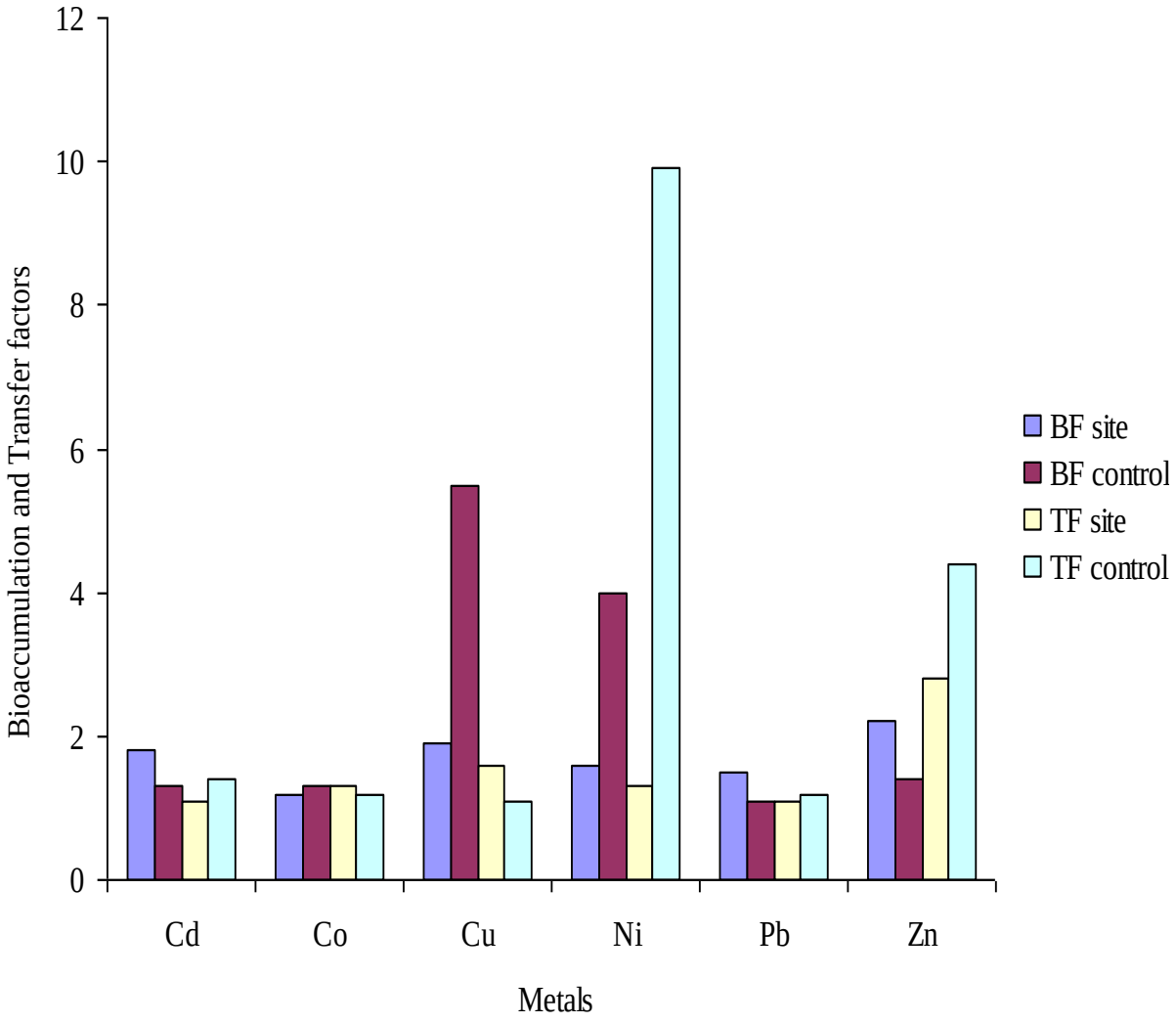


Figure 4.96: Bioaccumulation and Transfer Factors of Metals for *Cymbopogon citratus* Plant at Hanwa after Addition of EDTA

BF = Bioaccumulation factor; TF = Translocation factor.

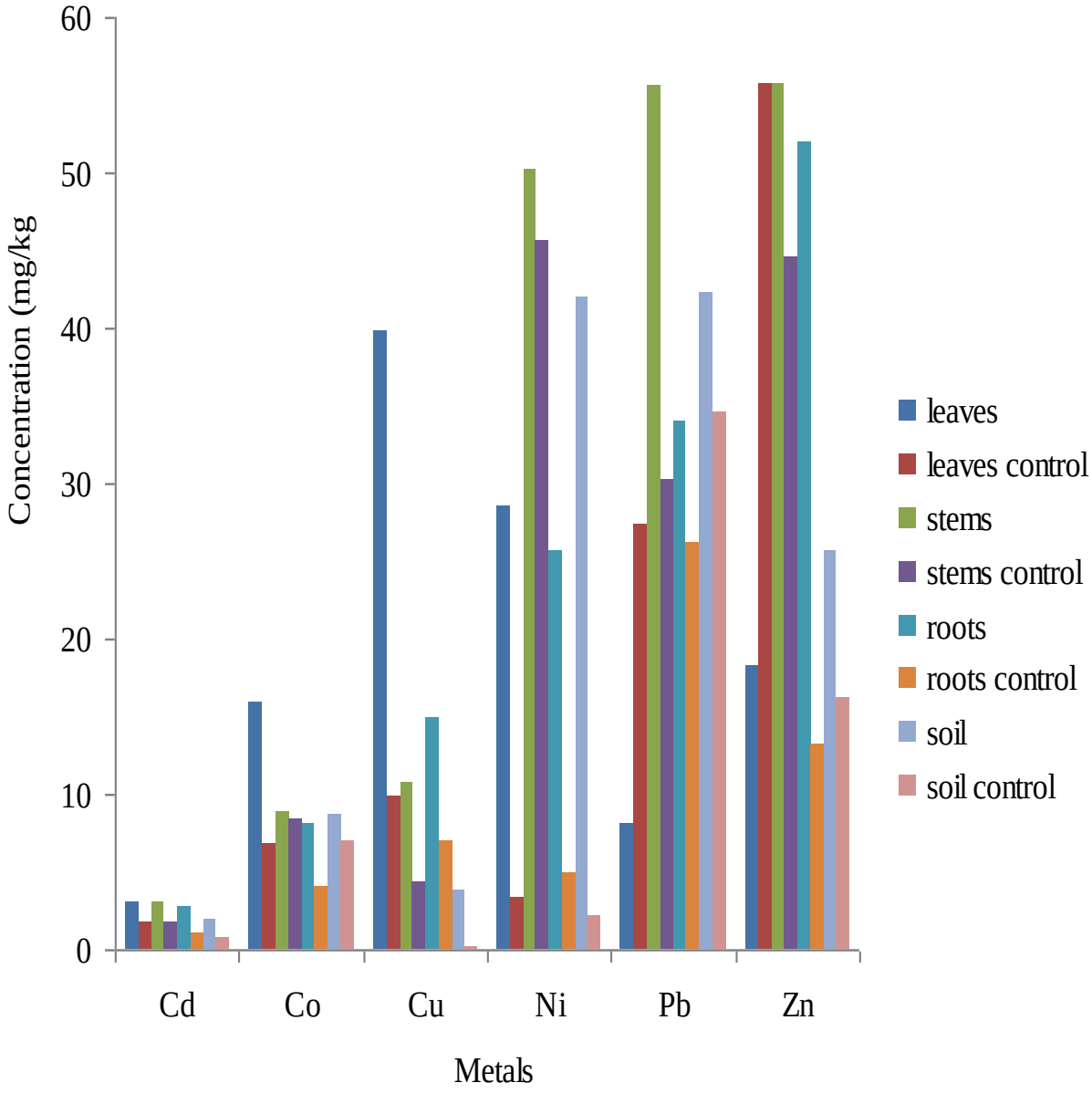


Figure 4.97: Concentrations of Metals in Different Parts of *Helianthus annus* Plant at Hanwa after Addition of EDTA

* Ni (leaves) = 28.5 x 10, Pb (leaves) = 8.16 x 10, Zn (leaves) = 18.22 x 10

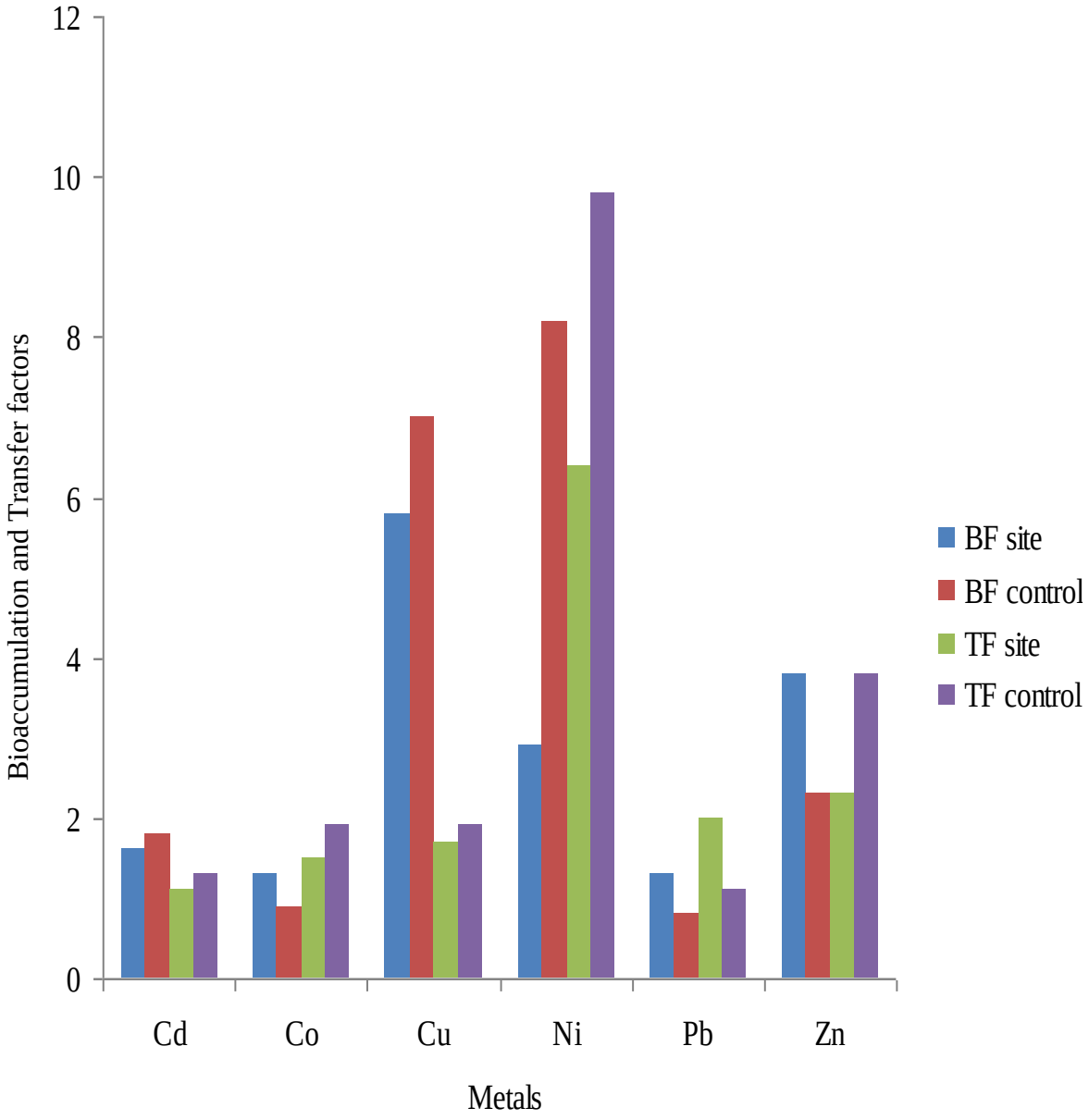


Figure 4.98: Bioaccumulation and Transfer Factors of Metals for *Helianthus annus* Plant at Hanwa after Addition of EDTA

BF = Bioaccumulation factor; TF = Translocation factor.

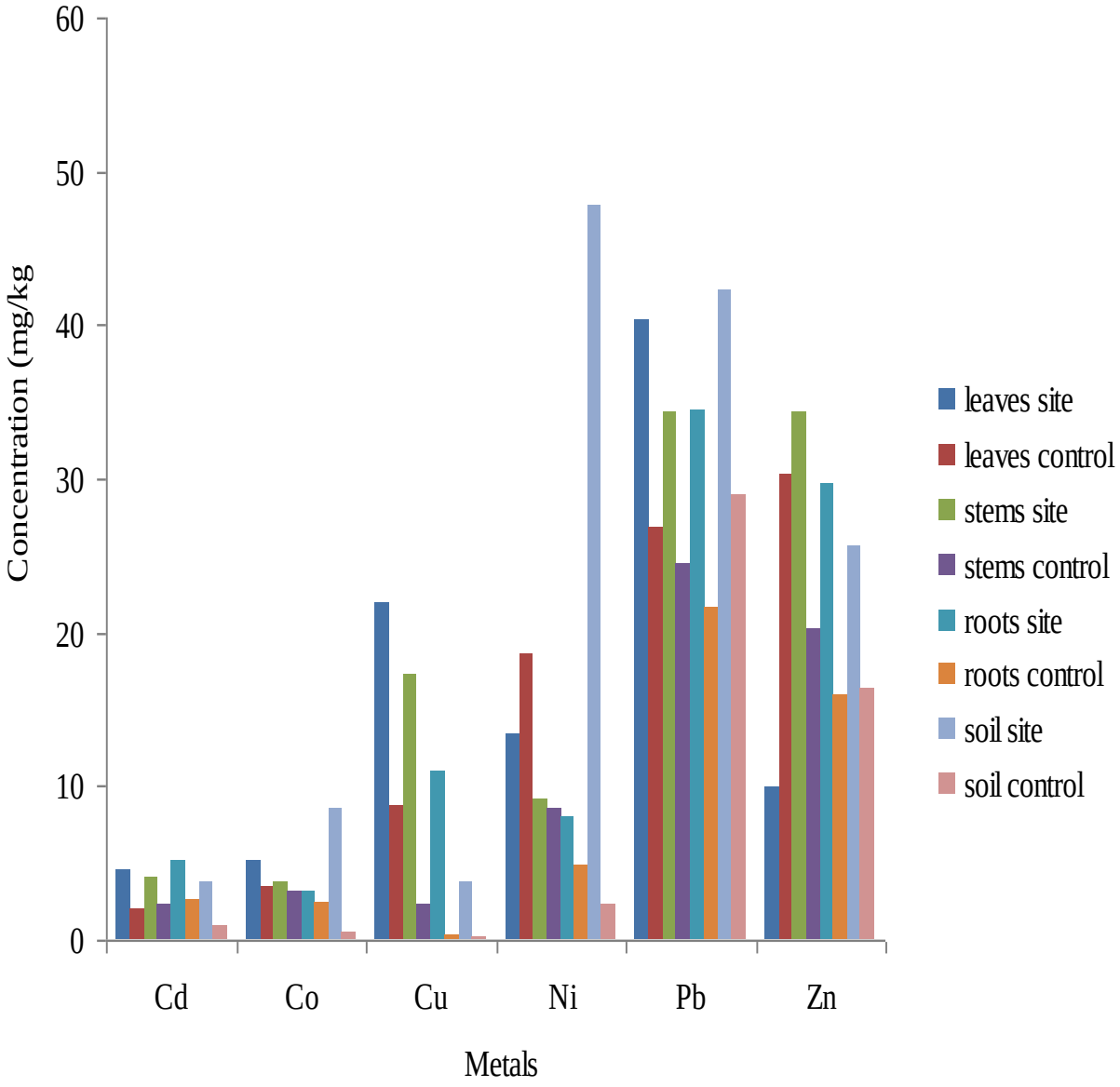


Figure 4.99: Concentrations of Metals in Different Parts of *Ipomoea asarifolia* Plant at Hanwa after Addition of EDTA

*Ni (leaves) = 13.3 x 10, Ni (stems) = 9.22 x 10, Ni (roots) 7.91 x 10, Zn (leaves) = 9.93 x 10

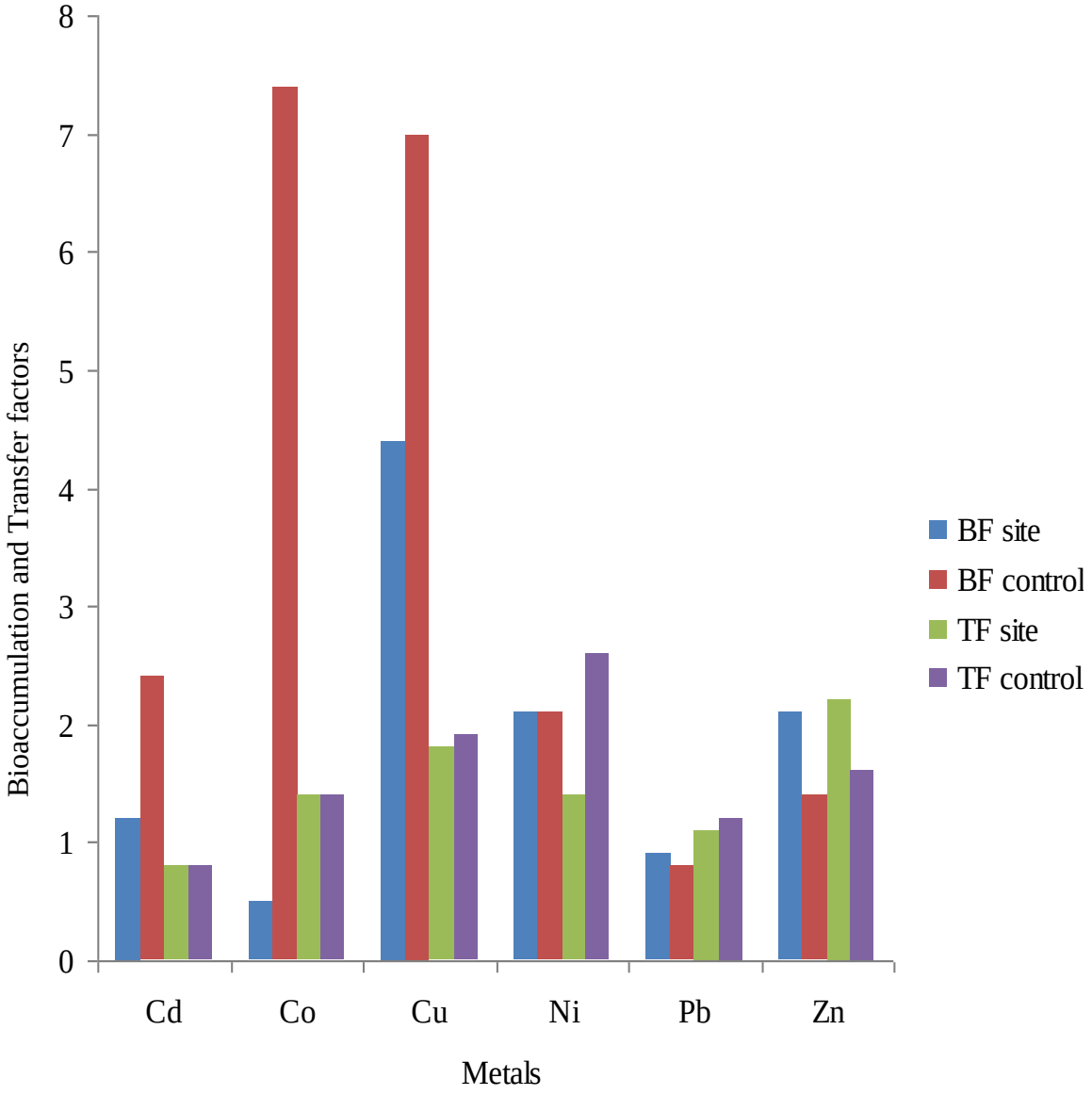


Figure 4.100: Bioaccumulation and Transfer Factors of Metals for *Ipomoea asarifolia* Plant at Hanwa after Addition of EDTA

BF = Bioaccumulation factor; TF = Translocation factor.

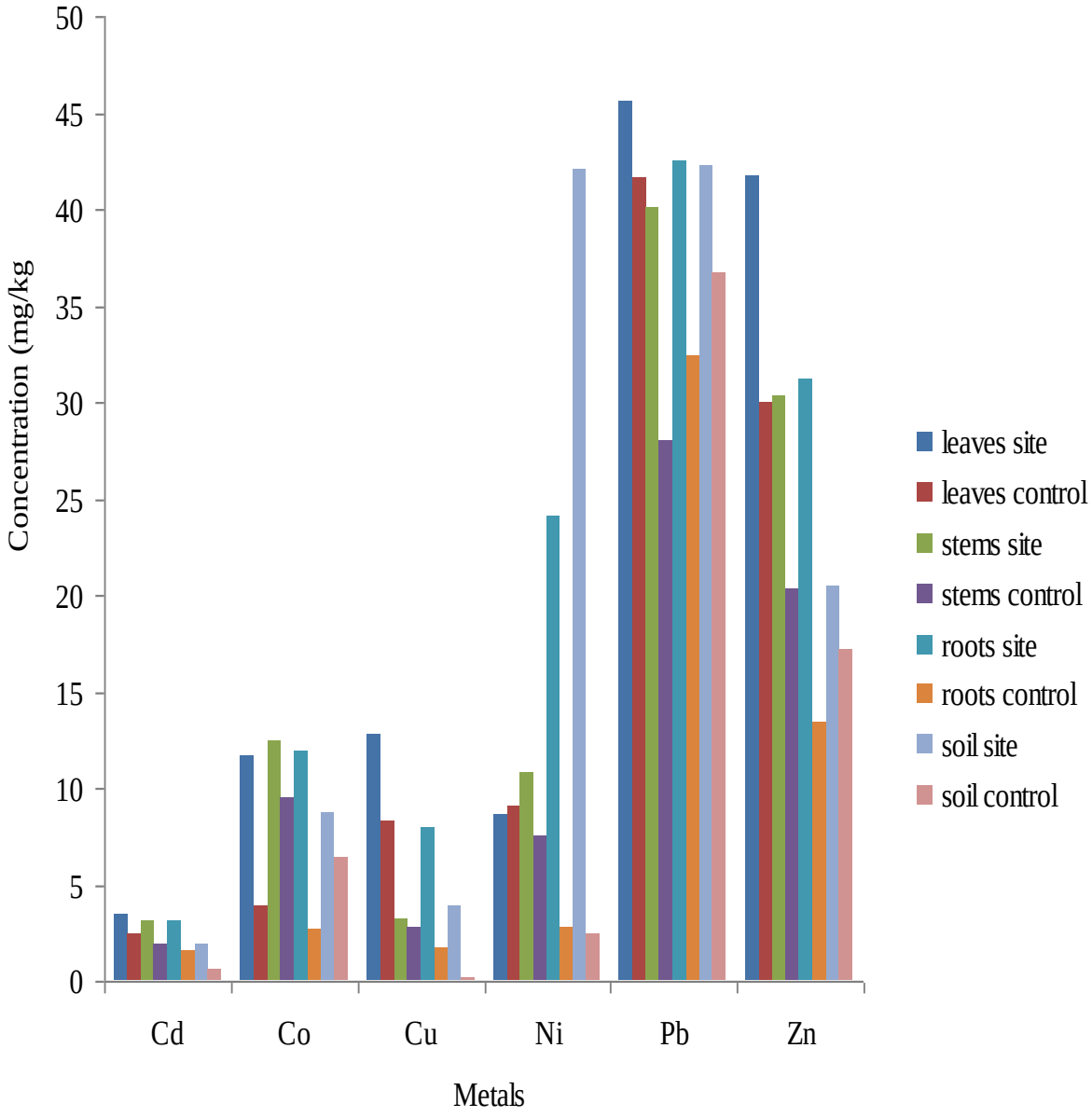


Figure 4.101: Concentrations of Metals in Different Parts of *Ricinus communis* Plant at Hanwa after Addition of EDTA

* Ni (leaves) = 8.56 x 10

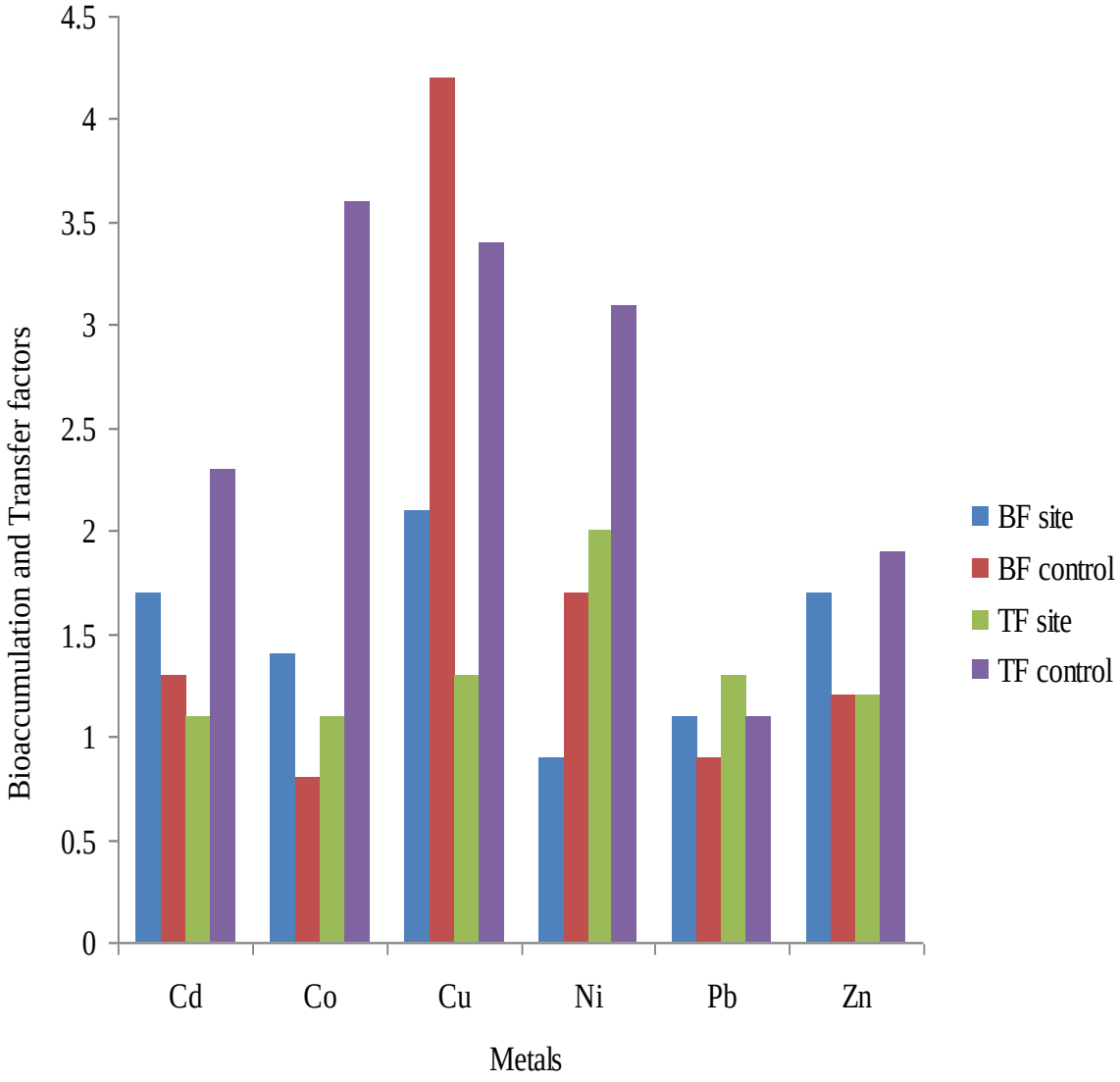
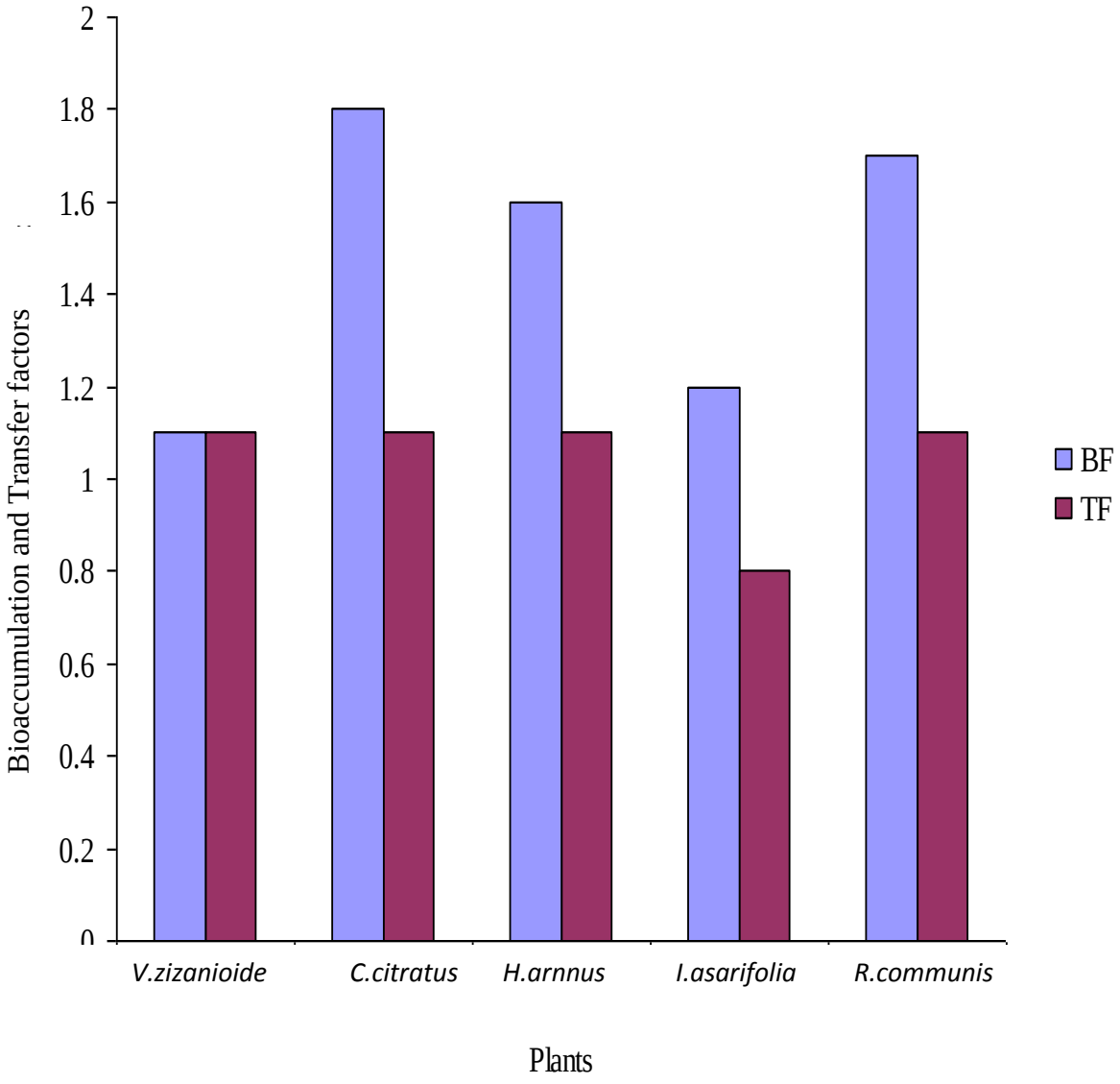


Figure 4.102: Bioaccumulation and Transfer Factors of Metals for *Ricinus communis* Plant at Hanwa after Addition of EDTA

BF = Bioaccumulation factor; TF = Translocation factor.



Figurer 4.103: Bioaccumulation and Transfer Factors for Cadmium in Different Plant Species at Hanwa Soil Treated with EDTA

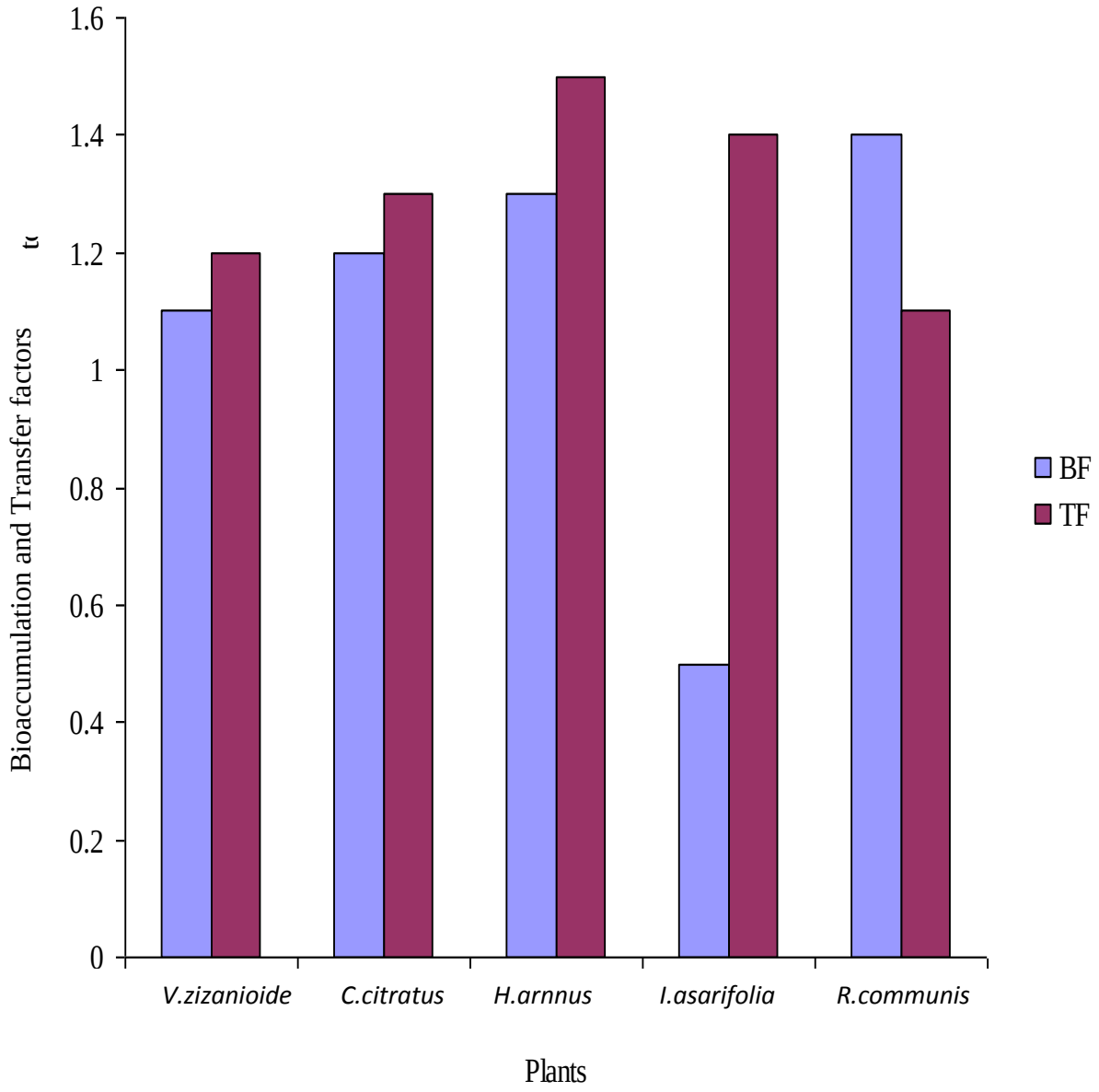


Figure 4.104: Bioaccumulation and Transfer Factors for Cobalt in Different Plant Species at Hanwa Soil Treated with EDTA

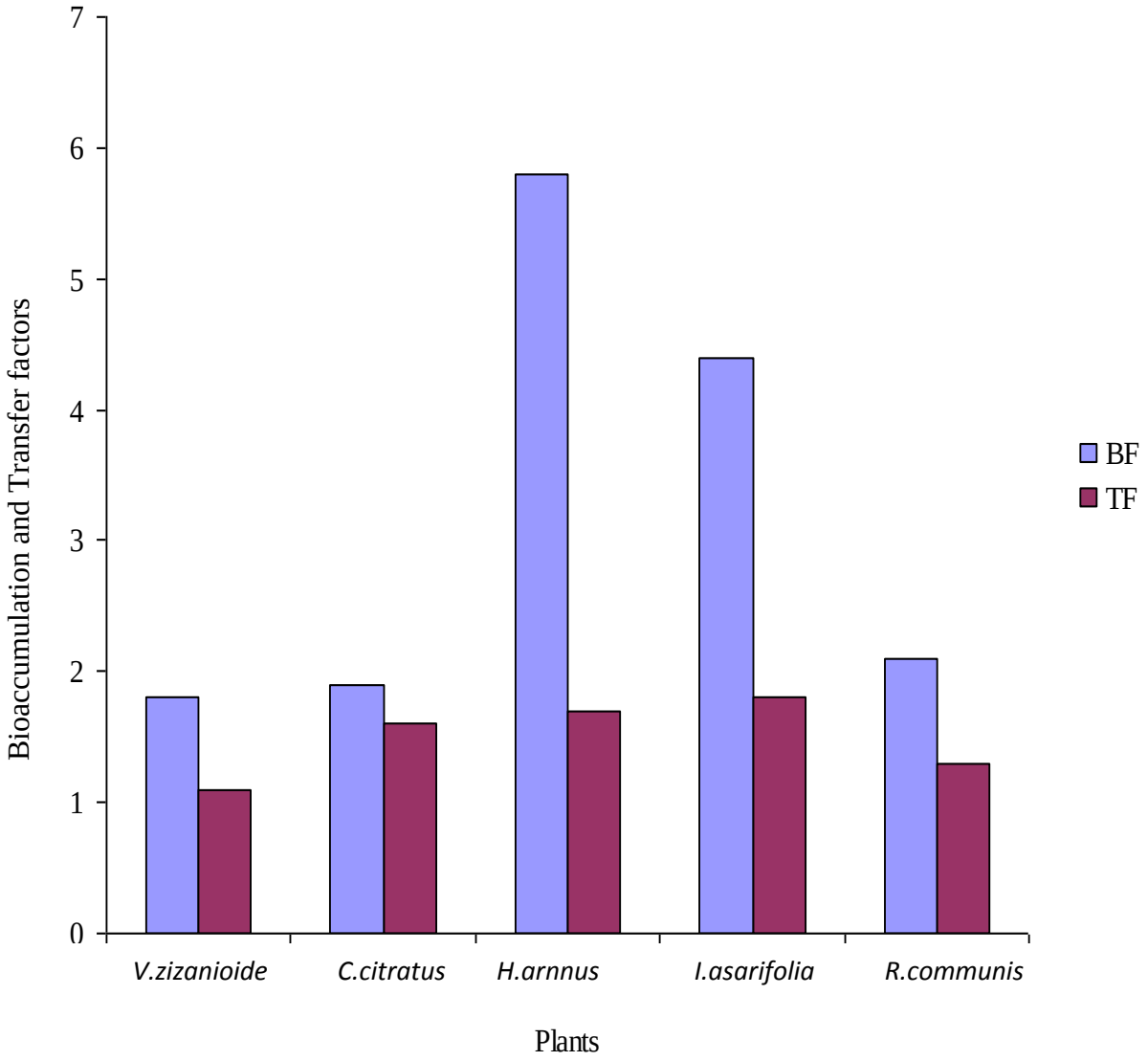


Figure 4.105: Bioaccumulation and Transfer Factors for Copper in Different Plant Species at Hanwa Soil Treated with EDTA

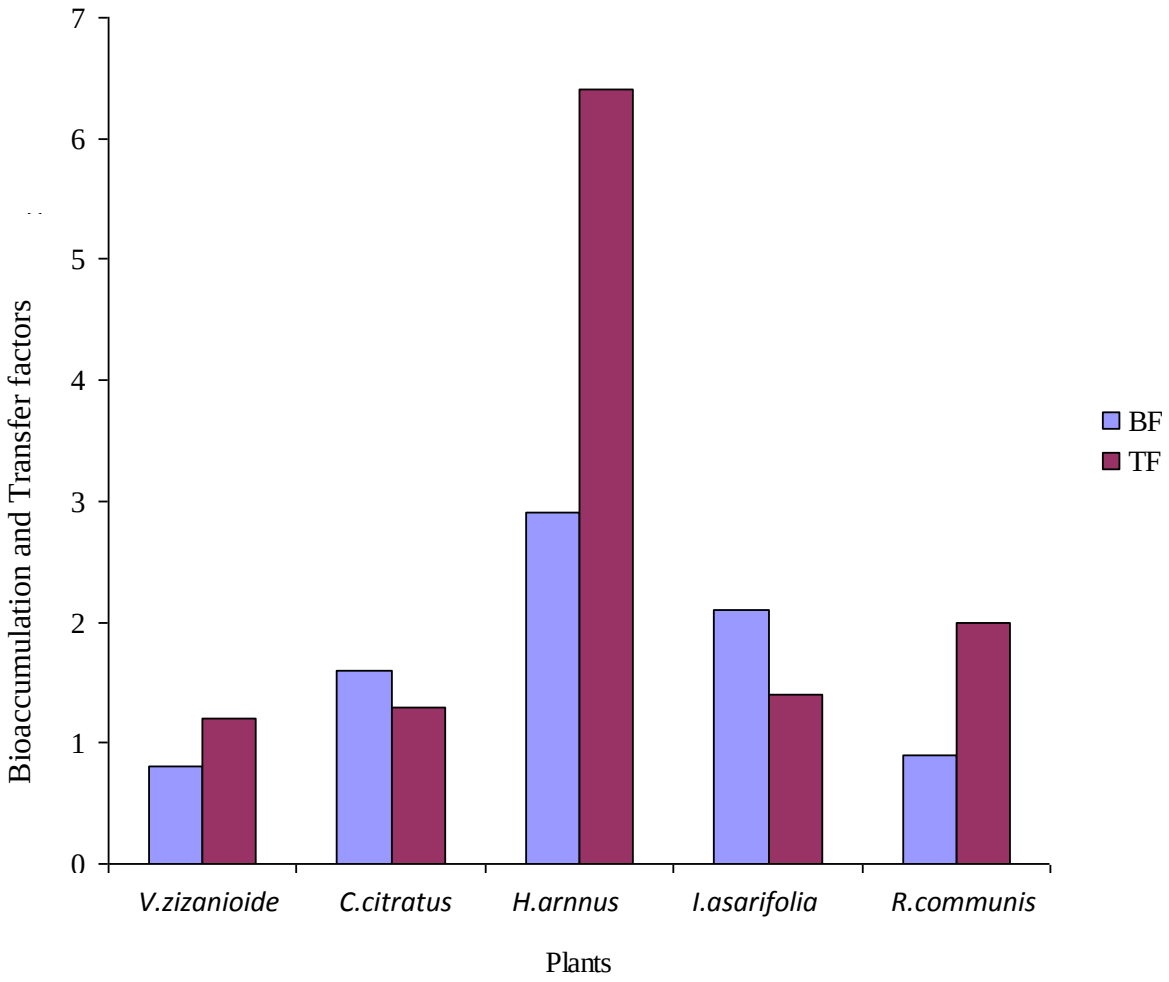


Figure 4.106: Bioaccumulation and Transfer Factors for Nickel in Different Plant Species at Hanwa Soil Treated with EDTA

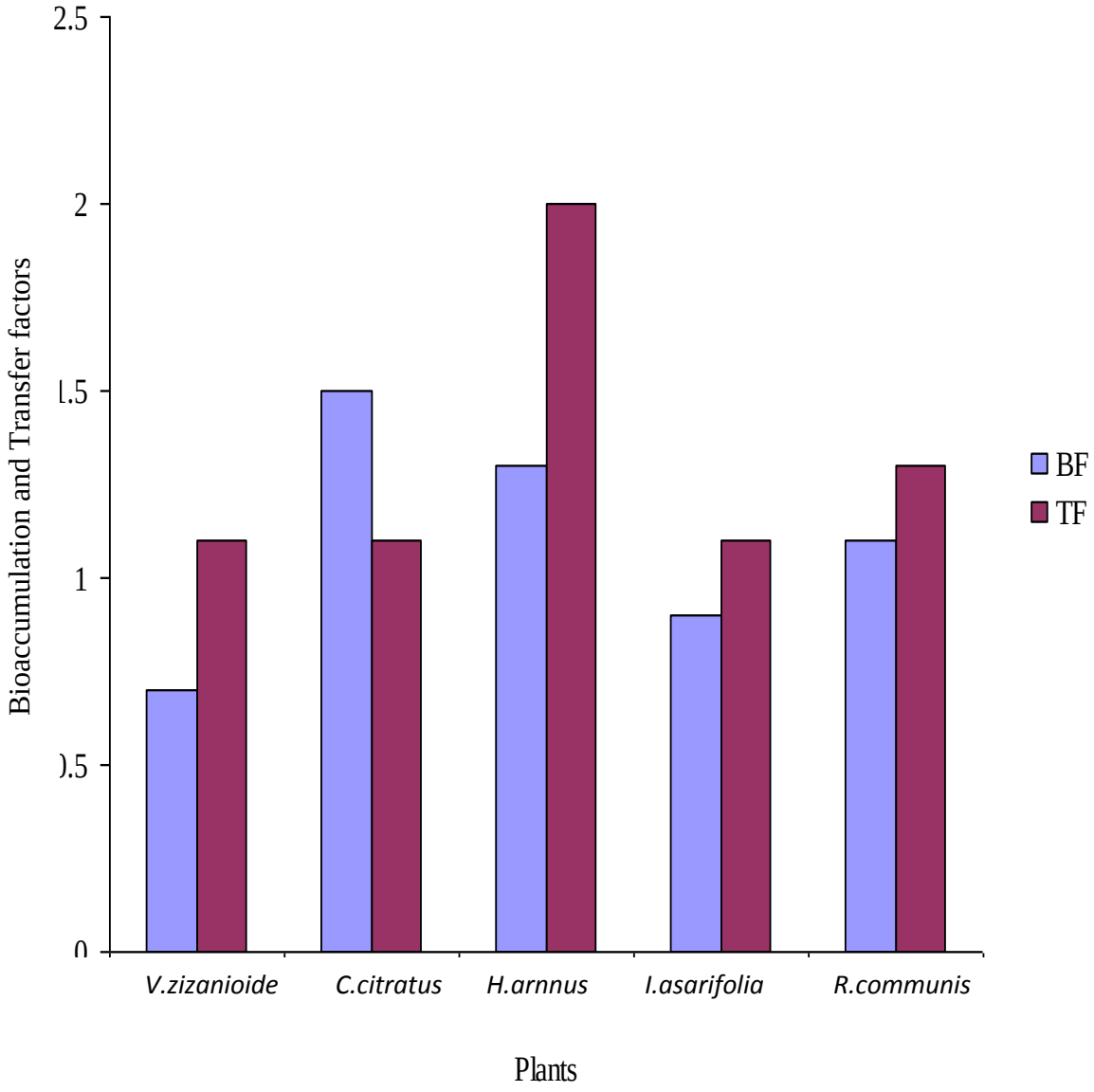


Figure 4.107: Bioaccumulation and Transfer Factors for Lead in Different Plant Species at Hanwa Soil Treated with EDTA

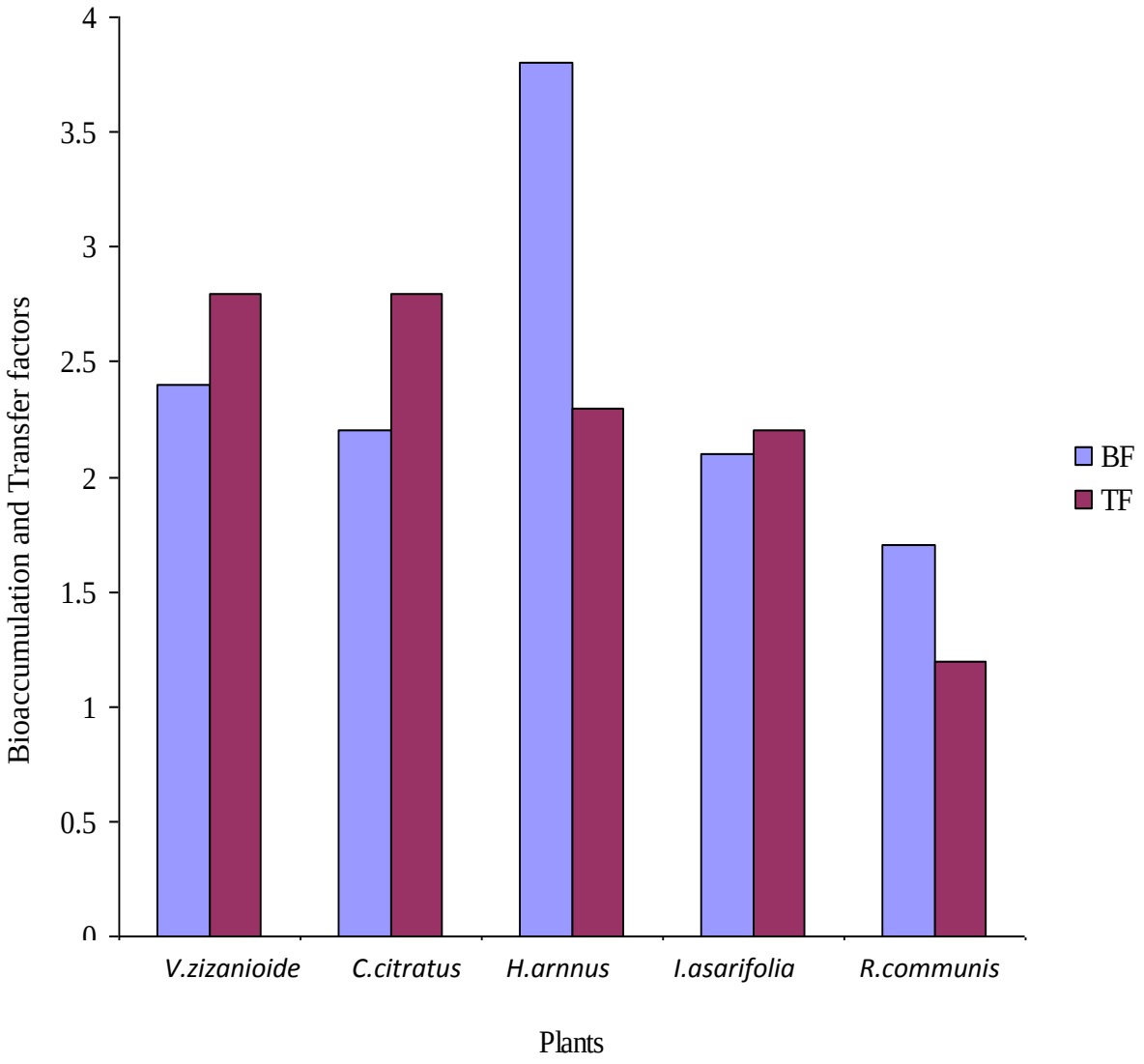


Figure 4.108: Bioaccumulation and Transfer Factors for Zinc in Different Plant Species at Hanwa Soil Treated with EDTA

(2.0) > *Ricinus communis* (1.3) > *Ipomoea asarifolia* (1.1) ≈ *Cymbopogon citratus* (1.1) ≈ *Vetivera zizanioide* (1.1). The BF and TF for Zn in different plant species followed the order of *Helianthus annus* (3.8) >*Vetivera zizanioide* (2.4) > *Cymbopogon citratus* (2.2) > *Ipomoea asarifolia* (2.1) > *Ricinus communis* (1.7) and *Cymbopogon citratus* (2.8) ≈ *Vetivera zizanioide* (2.8) > *Helianthus annus* (2.3) > *Ipomoea asarifolia* (2.2) > *Ricinus communis* (1.2) respectively.

4.19 Metal Concentrations in the Non- EDTA Treated Soils after Harvest

The mean concentrations of metals (mg/kg) in the soils at the three study areas and control after harvesting of plants without EDTA application to the soils are presented in Figure 4.109 and Appendix XLIX. The results indicated that the concentrations of the studied metals at the test sites were still higher than in the control site. At Dakace, Cd - 3.80±0.02 mg/kg, Co - 8.25±0.04 mg/kg, Cu - 3.62±0.03 mg/kg, Ni - 5.95±0.08 mg/kg, Pb - 60.27±0.02 mg/kg, Zn - 40.3±0.04 mg/kg. At Gaskiya, Cd - 3.80±0.01 mg/kg, Co - 8.35±0.04 mg/kg, Cu - 4.00±0.04 mg/kg, Ni - 25.72±0.04 mg/kg, Pb - 59.80±0.01 mg/kg, Zn - 23.95±0.02 mg/kg. At Hanwa, Cd - 3.80±0.03 mg/kg, Co - 8.60±0.04 mg/kg, Cu - 4.01±0.05 mg/kg, Ni - 38.10±0.06 mg/kg, Pb - 63.53±0.06 mg/kg, Zn - 21.17±0.03 mg/kg. At control, Cd - 1.00±0.02 mg/kg, Co - 3.10±0.04 mg/kg, Cu - 1.37±0.02 mg/kg, Ni - 4.00±0.06 mg/kg, Pb - 16.90±0.03 mg/kg, Zn - 12.06±0.02 mg/kg.

4.20 Metal Concentrations in the EDTA Treated Soils after Harvest

The mean concentrations of metals (mg/kg) in the soils at the three study areas and control after harvesting of plants with EDTA application to the soils are presented in Figure 4.110 and Appendix L. The results indicated that the concentrations of the studied metals at the

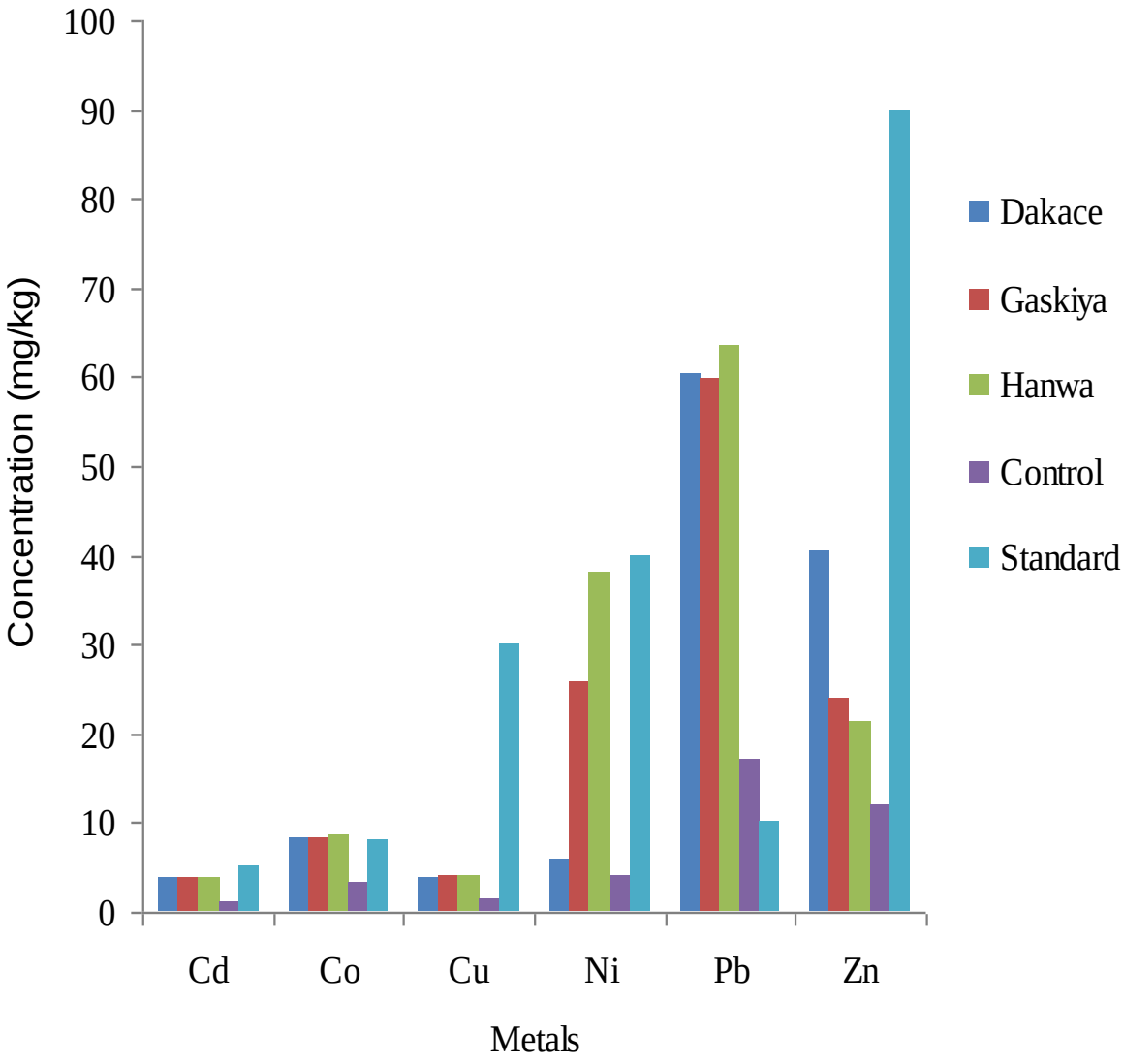


Figure 4.109: Mean Concentration of Metals at the Three Study Areas and Control after Harvest without EDTA

test sites were still higher than in the control site. At Dakace, Cd - 2.38±0.03 mg/kg, Co - 8.20±0.04 mg/kg, Cu - 1.92±0.03 mg/kg, Ni - 5.20±0.01 mg/kg, Pb - 42.75±0.08 mg/kg, Zn - 35.84±0.05 mg/kg. At Gaskiya, Cd - 2.66±0.02 mg/kg, Co - 8.00±0.04 mg/kg, Cu - 2.10±0.01 mg/kg, Ni - 8.10±0.04 mg/kg, Pb - 54.70±0.01 mg/kg, Zn - 20.25±0.02 mg/kg. At Hanwa, Cd - 2.42±0.03 mg/kg, Co - 8.50±0.03 mg/kg, Cu - 3.80±0.04 mg/kg, Ni - 29.42±0.03 mg/kg, Pb - 44.50±0.05 mg/kg, Zn - 20.49±0.01 mg/kg. At control, Cd - 0.70±0.02 mg/kg, Co - 2.10±0.01 mg/kg, Cu - 1.09±0.02 mg/kg, Ni - 2.40±0.01 mg/kg, Pb - 14.00±0.04 mg/kg, Zn - 11.06±0.01 mg/kg.

4.21 Percentage Metal Removal after Natural and EDTA-assisted Phytoextraction

The mean concentration of metals (mg/kg) in the soils before the planting was done, after the plants were harvested before and after the application of the EDTA on the soils at the three study areas and the control site, and the percentage removal of metals are presented in Figures 4.111, 4.112, Appendices LI and LII respectively. At Dakace site, the percentages of metals removed without EDTA application (natural) were: Cd- 52.5%, Co – 0.6%, Cu – 44.3%, Ni – 88.4%, Pb – 13% and Zn – 28%; with EDTA application: Cd – 70.3%, Co – 1.2%, Cu – 70.5%, Ni – 89.9%, Pb – 38.3% and Zn – 36%; At Gaskiya site without EDTA application(natural): Cd – 45.7%, Co – 15.7%, Cu – 24.5%, Ni – 69.7%, Pb – 21.2% and Zn – 17.1%; with EDTA application: Cd -62%, Co – 19.2%, Cu – 60.4%, Ni – 90.5%, Pb – 27.9% and Zn – 29.1%; At Hanwa site without EDTA application (natural): Cd – 36.7%, Co – 1.2%, Cu – 28.4%, Ni – 20.5%, Pb – 17.4% and Zn – 17.2%; with EDTA application: Cd – 59.7%, Co – 2.3%, Cu – 32.1%, Ni – 35.6%, Pb – 42.1% and Zn – 19.9%; At control site without EDTA application (natural): Cd – 46.5%, Co – 57.9%, Cu –

45%, Ni – 38.5%, Pb – 7.3% and Zn – 49.6%; with EDTA application: Cd – 62.6%, Co – 71.5%, Cu – 56.2%, Ni – 63.1%, Pb – 23.2% and Zn – 53.8%.

The order of the percentage removal of the metals at the test sites and the control are given as follows: at Dakace site, for natural phytoextraction- Ni > Cd > Cu > Zn > Pb > Co; for EDTA- assisted phytoextraction- Ni > Cu > Cd > Pb > Zn > Co; at Gaskiya site, for natural phytoextraction- Ni > Cd > Cu > Pb > Zn > Co; for EDTA- assisted phytoextraction- Ni > Cd > Cu > Zn > Pb > Co; at Hanwa**,** for natural phytoextraction- Cd > Cu > Ni > Pb > Zn > Co; for EDTA- assisted phytoextraction- Cd > Pb > Ni > Cu > Zn > Co and at Control site, for natural phytoextraction- Co > Zn > Cd > Cu > Ni > Pb; for EDTA- assisted phytoextraction- Co > Cd > Ni > Cu > Zn > Pb.

4.22 Pollution Indexes for Metals after Natural and EDTA-assisted Phytoextraction

The Nemero pollution indexes for the studied metals at the three study areas and the control site after the natural and EDTA-assisted phytoextraction processes are presented in Figures 4.113 and 4.114, and Appendices LIII and LIV respectively. The pollution levels of Cd, Cu, Ni and Zn were below 1, but Co and Pb were either equal or greater than 1. Co at the control site is less than 1 and Pb level still remain very high.

The grade standard of the Nemero Pollution Index of the soils at Dakace, Gaskiya, Hanwa and the control sites after both the natural and the EDTA-assisted phytoextraction processes are presented in Tables 4.4 and 4.5 respectively. The soils at Dakace and Gaskiya contain Zn, Cu, Ni at levels considered to be clean, Hanwa has clean levels of Zn and Cu, while the control soil has clean levels of Cd, Co,Cu, Ni and Zn. The levels of Cd at the three test sites, Co at Dakace site and Ni at Hanwa site were at warning stage. Co level

at Dakace and Gaskiya sites, Ni at Hanwa site and Pb at the control site were at slight pollution stages. The soils at the test sites still contained very high level of Pb. After the EDTA-assisted phytoextraction process, the level of Pb in the soil at the three test sites was still very high, but at the control site it was at the slight stage. Co at the three test sites was at warning stage, but at control site it was at clean stage. Zn, Cu, Ni and Cd were at clean stage in all the study areas and the control.

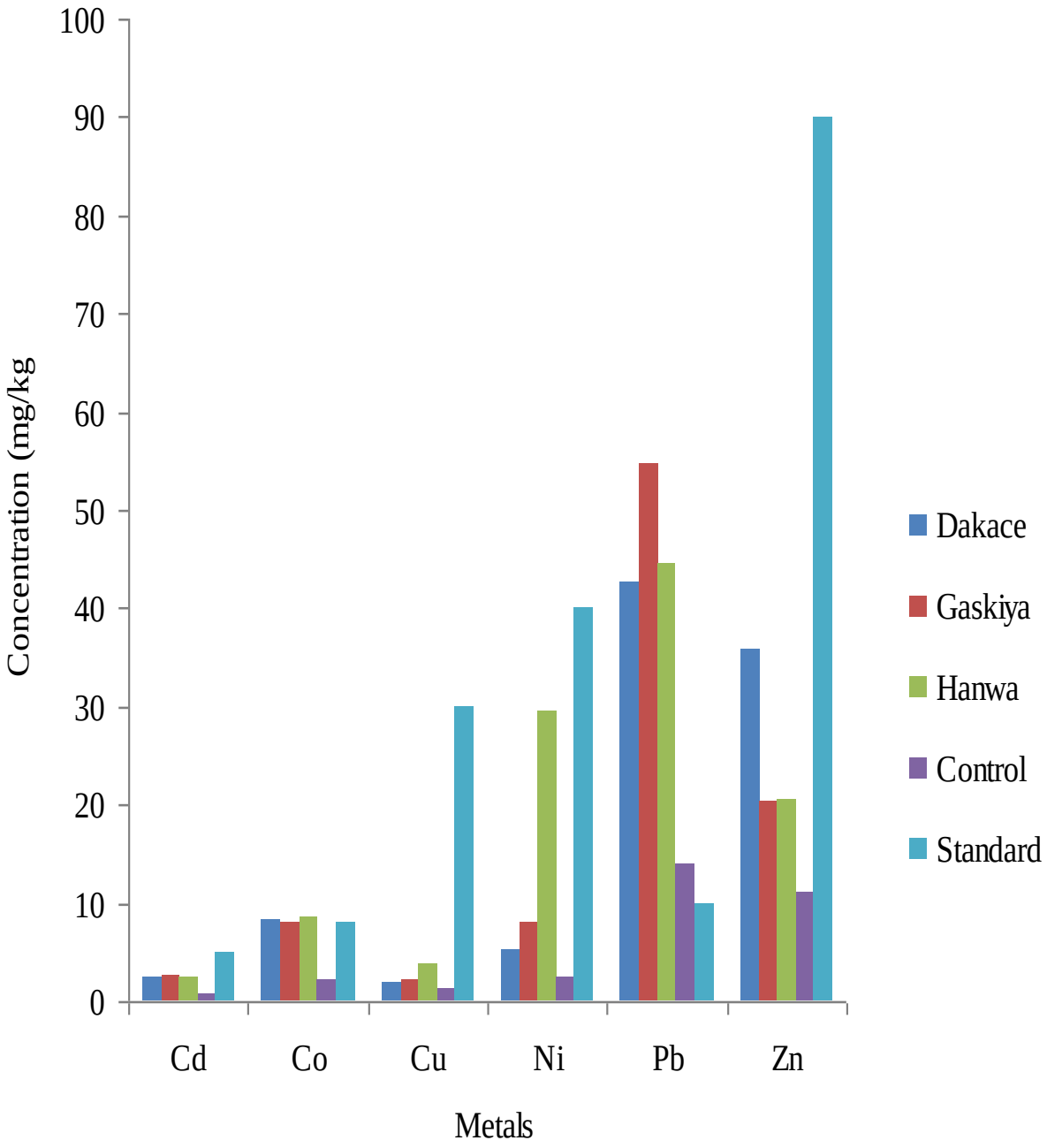


Figure 4.110: Mean Concentrations of Metals at the Three Study Areas and Control after Harvest with EDTA

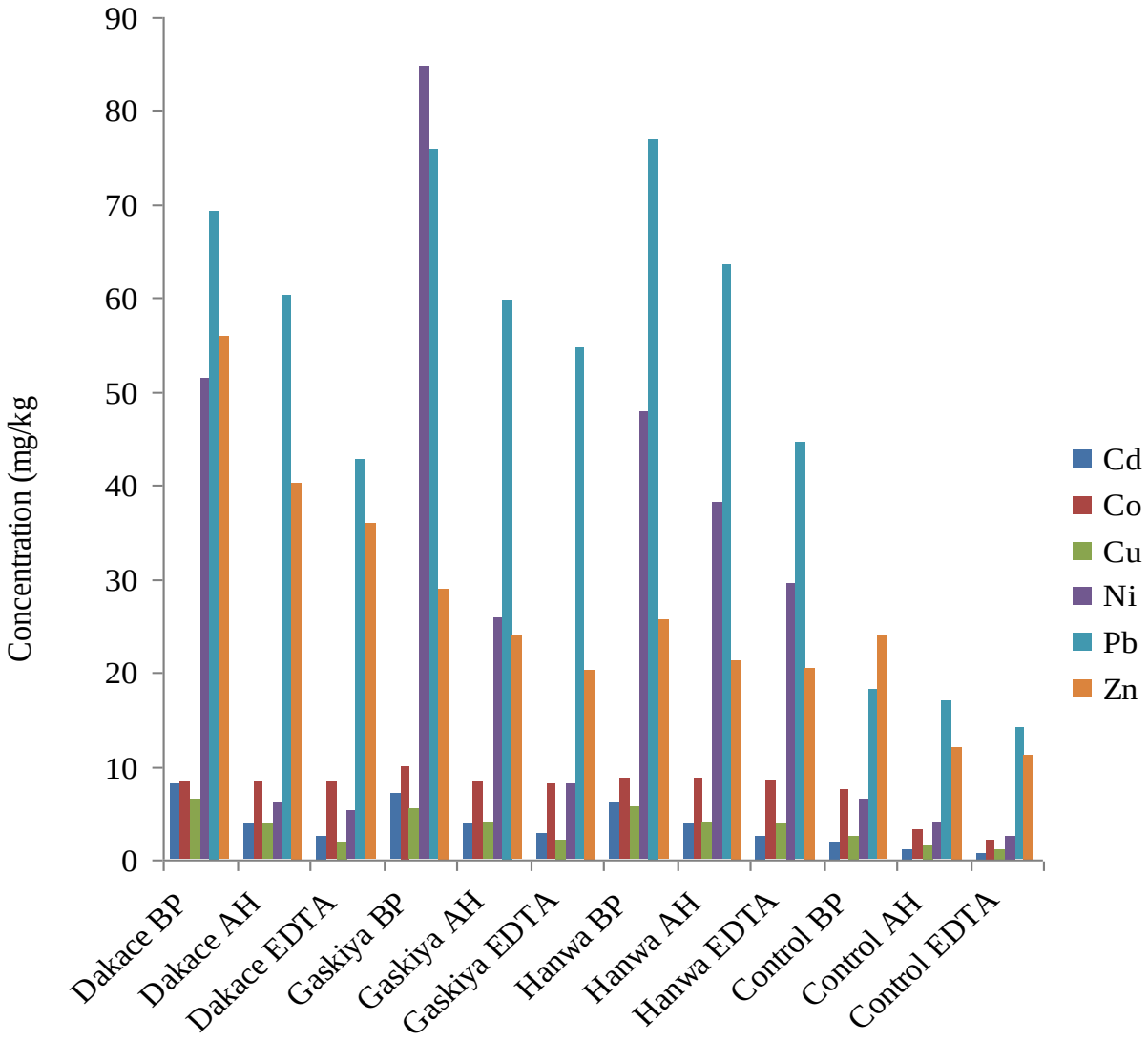


Figure 4.111: Mean Concentrations of Metals in Soils at the Test and Control Sites before Planting and after Harvest with and without Application of EDTA

BP = Before planting; AH = After harvest with no EDTA applied

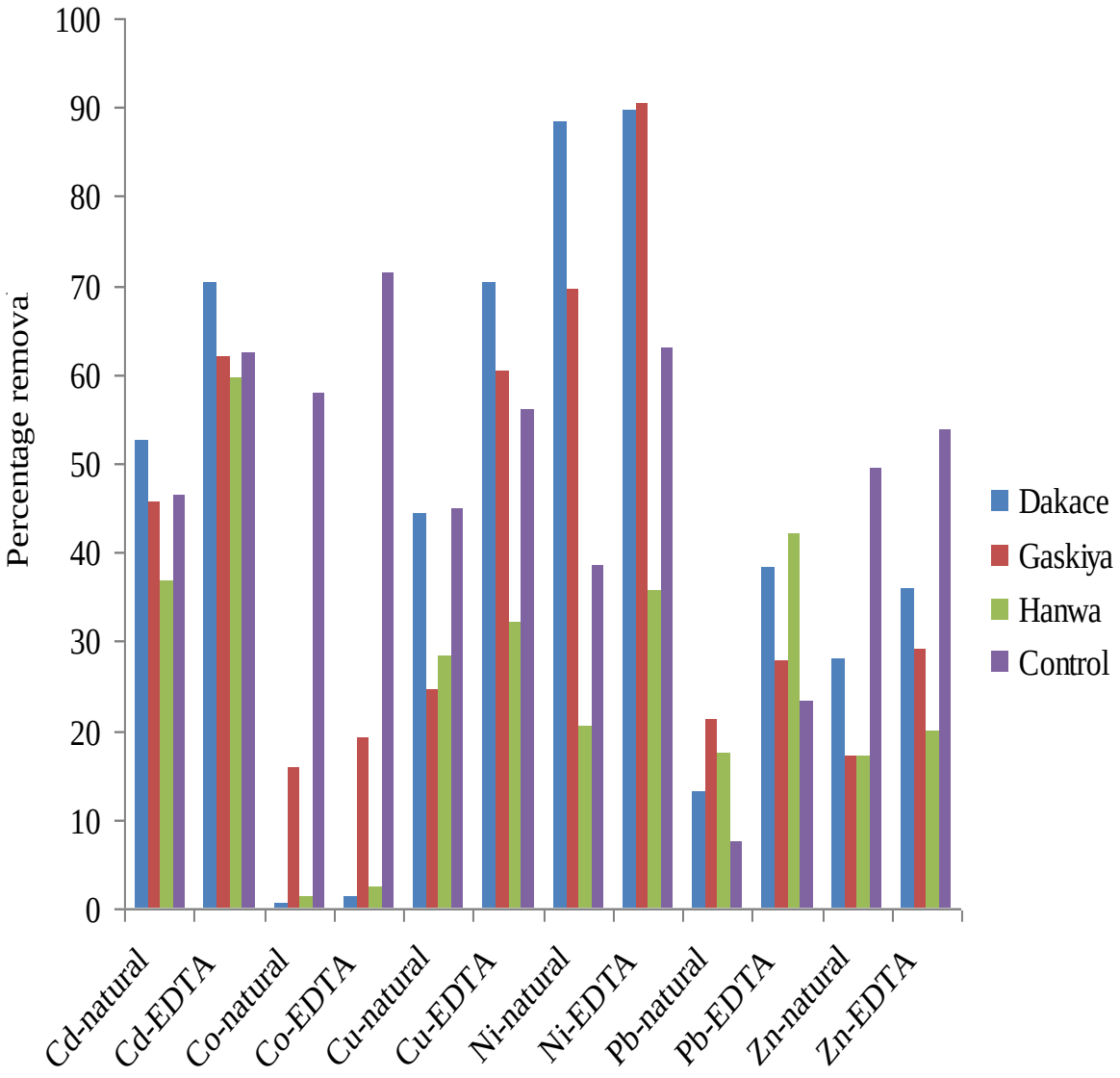


Figure 4.112: Percentages Removal of Metal at the Three Study Areas and Control with and wthout Application of EDTA

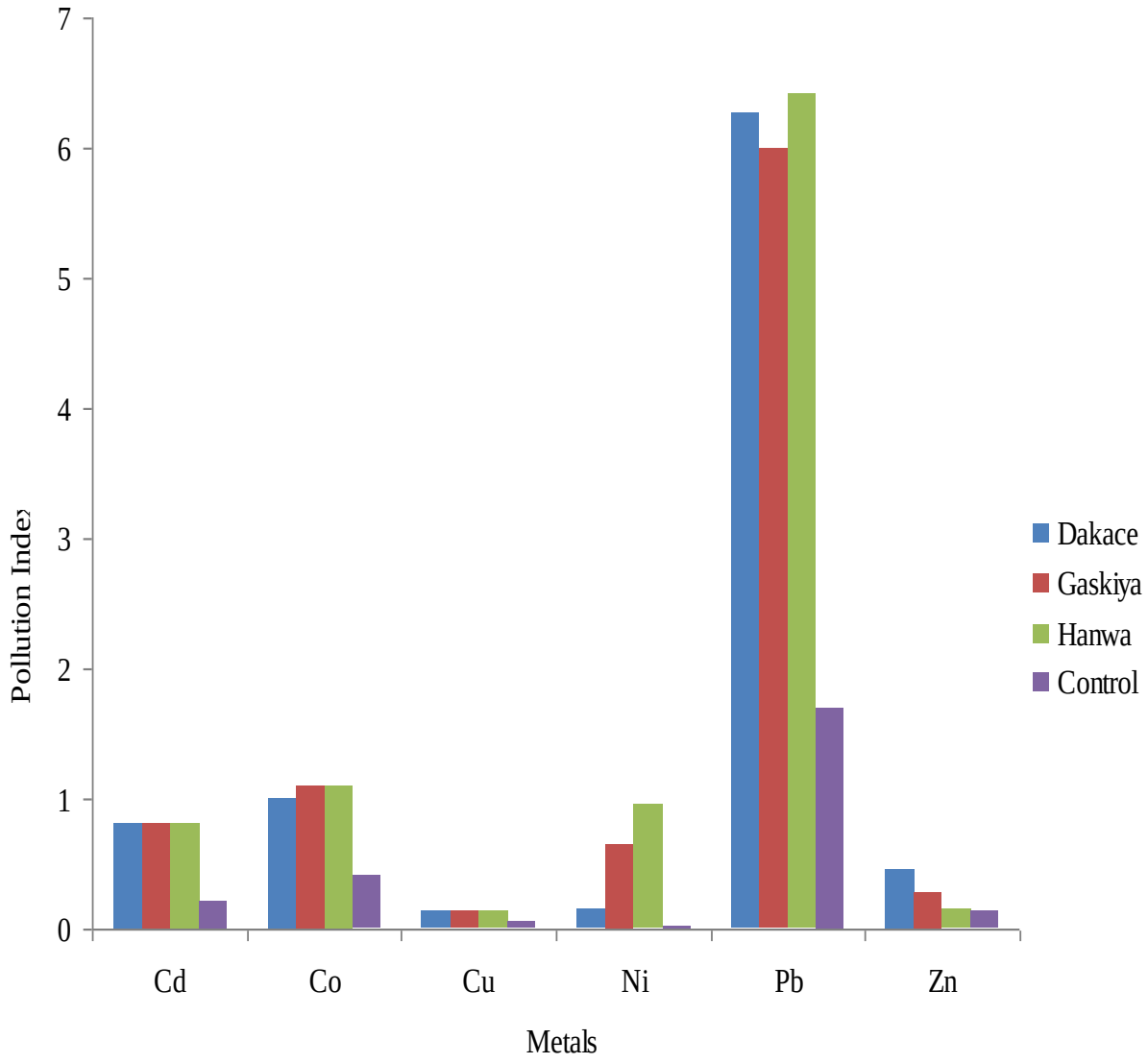


Figure 4.113: Nemero Pollution Index for Soils at the Three Study Areas and the Control Site after Natural Phytoextraction

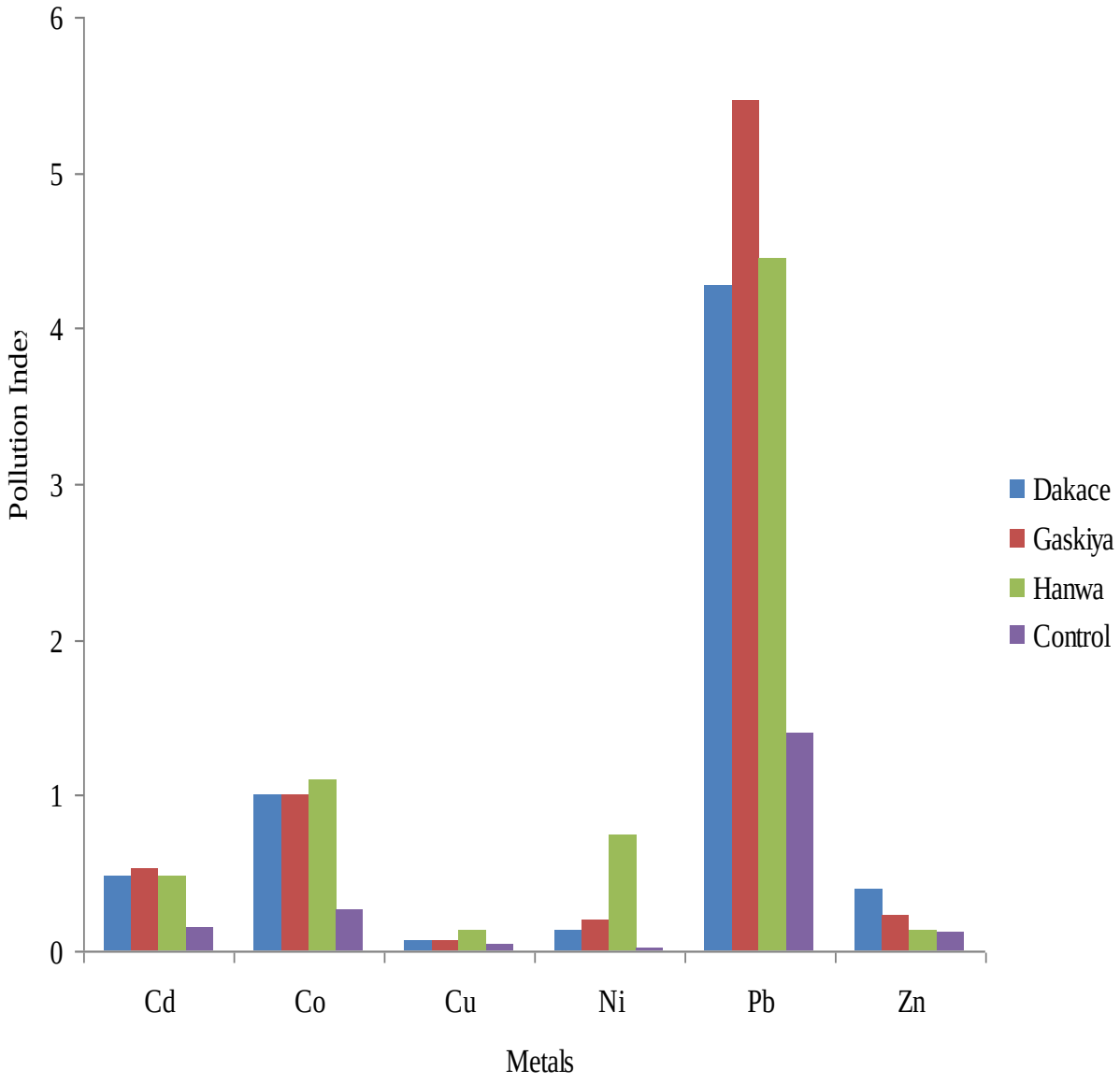


Figure 4.114: Nemero Pollution Index for Soils at the Three Study Areas and the Control Site after EDTA-Assisted Phytoextraction

Table 4.4: The Grade Standard of the Nemero Pollution Index Method after Harvest without EDTA

	I P≤ 0.7 Clean	II 0.7□ P ≤ 1 warning	III 1 □ P ≤ 2 slight	IV 2 □ P ≤ 3 heavy	V P > 3 very heavy
Dakace	Zn, Cu, Ni	Cd, Co		-	Pb
Gaskiya	Zn, Cu, Ni	Cd	Co	-	Pb
Hanwa	Zn, Cu	Cd, Ni	Co		Pb
Control	Cd, Co,Cu, Ni, Zn	-	Pb	-	-

Table 4.5: The Grade Standard of the Nemero Pollution Index Method after Application of EDTA

	I P≤ 0.7 Clean	II 0.7□ P ≤ 1 warning	III 1 □ P ≤ 2 slight	IV 2 □ P ≤ 3 heavy	V P > 3 very heavy
Dakace	Zn, Cu, Ni, Cd	Co	-	-	Pb
Gaskiya	Zn, Cu, Ni, Cd	Co	-	-	Pb
Hanwa	Zn, Cu, Cd, Ni	Co	-		Pb
Control	Cd, Co,Cu, Ni, Zn	-	Pb	-	-

CHAPTER FIVE

5.0 DISCUSSION

5.1 Physicochemical Parameters of the Soils.

The pH values obtained for the test soils ranged from 6.78 to 6.86, that is, slightly acidic, and slightly alkaline (7.50) for control soil. The pH of farmlands ranges from 4.5 to 8.4. The pH of soil affects the bioavailability of metals in the soil solution. Bioavailability of metals in soils decrease above pH 5.5 – 6 (Prasad, 2003). This might have affected the bioavailability of Cd, Co and Pb as indicated Figure 4.7. The present study showed that the soils were sandy loam which agreed with report of Ojanuga (1980) that the soils of Kaduna – Zaria area are sandy clay loam to sandy clay with sandy loam mainly on topsoil. When moisture content reached more than 4%, it could only cause the erosion of sandy loam soil to reduce by a small degree (Chen *et al*., 1996).

The percentage organic matter (% OM) ranged from 4.02 (at Hanwa) – 5.10 (at Gaskiya) but still higher than the values found in soils of the Nigerian savannah which range from 0.8 to 2.9% (Jones 1973; Jones and Wild 1975). The OM component of soil has negatively charged sites on the surfaces which adsorbed and hold positively charged ions (cations) by electrostatic force. This electrical charge is critical to the supply of cations to the plants. Cation exchange capacity (CEC) ranged from 9.8 to 15.6 cmol/kg^{-1}, normal CEC ranges in soils would be from < 3 cmol/kg, for sandy soils low in OM, to > 25 cmol/kg for soils high in certain types of clay or organic matter (OM). The CEC represents the ability of the soils to absorb or release cations and, consequently, is an important parameter in sites contaminated by heavy metals. Organic matter and clay minerals are responsible for the CEC (Ashraf *et al*., 2011).When pH decreases (acidic) more H^+ ions are attached to the colloids and push the other cations from colloids into the soil solution. Soil

OM will cause a greater CEC at near-neutral pH than under acidic conditions (Donald, 2000). Chloride contents ranged from 235.06 mg/kg to 265.91mg/kg. Elevated chloride contents decrease adsorption of metals on sediments due to chloride complexation which results in greater solubility and mobility of the metals (David and Joel, 1998).

The values for CEC, phosphates, nitrates and sulphates for the test sites were higher than those of the control. In solution, metals can exist either as free ions or as various complexes associated with organic or inorganic (e.g., anions such as PO_4^{2-} ,SO_4^{-2}, NO_3^-, or Cl^-) ligands which are soluble complexes at high pH (David and Joel, 1998).

5.2 Metal Levels in Soils before Planting

The mean concentrations of the studied metals in the soils at the three study areas (test soils) were higher than the control. Using one-way ANOVA, there was a significant difference ($P < 0.05$) between the metal levels at the test sites and the control. This implies that the dumping of scrap-metals on these soils has contributed significantly to the heavy metals contamination of the soils and can be a health risk since crops are planted on nearby farmlands. The concentrations of Cd, Co, Ni and Pb were higher than the standard regulatory limits as reported by Akpoveta *et al*., 2010. The Pearson correlations matrix of the physico-chemical parameters and the metals at three study areas indicated that Cd had negative correlation with all the soil physicochemical parameters except with PO_4^{3-} where it was positive; Co showed negative correlation with OM and PO_4^{3-} but positive correlation with pH, CEC, Cl^-, NO_3^- and SO_4^{2-} ; Cu had negative correlation with OM and SO_4^{2-} but had a positive correlation with pH, CEC, Cl^-, NO_3^- and PO_4^{3-} ; Ni showed negative correlation with PO_4^{3-} but showed a positive correlation with other soil parameters; for Pb there was a negative correlation between the metal and pH and PO_4^{3-} ; and for Zn, it showed

a negative correlation with CEC, Cl^-, NO_3^- and SO_4^{2-} but a positive correlation with pH, OM and PO_4^{3-}. The negative correlation means that as one variable (metal) increases in value, the second variable (physicochemical parameter) decreases in value; while the positive correlation means that as the metal value increases, the value for the physicochemical parameter also increases. Those values that are closer to 1 (either positively or negatively) means that the changes in the metal values are strongly correlated with changes in the physicochemical parameters (Nick, 2013).

Single Contamination Index (CI) was employed to evaluate the real quantitative information of key pollution multiples which is one of the current methods used in evaluation of the degree of heavy metal pollution in soil. The single contamination index for the triplicate data and the mean were evaluated. The single method cannot express accurately the comprehensive impact caused by each kind of heavy metals. The Nemero Pollution Index method takes not only the extreme value but also the environmental quality index based on weighted multi-factors. The method can reflect the degree of soil pollution caused by various heavy metals pollutants (Hong-gui *et al*., 2012).

The grade standard for the Nemero pollution index indicated that the three study areas (Dakace, Gaskiya and Hanwa) with Cu and Zn level $P \leq 0.7$ do not pose any environmental risk despite the anthropogenic activities in those areas. But it was observed that the soils at Dakace and Hanwa are slightly polluted ($1 \square P \leq 2$) with Cd, Co and Ni; soils at Gaskiya are slightly polluted with Cd and Co. The soils at all the three study areas were heavily polluted with Pb (and Ni at Gaskiya), $P \square 3$. Therefore, phytoextraction technique could be a very promising method for the heavy metals remediation. It is best suited for the remediation of diffusely polluted areas, where pollutants occur only at

relatively low concentration and superficially. This can be an effective remediation method at a variety of sites and on numerous contaminants (Luo *et al*., 2005).

5.3 Metals Bioavailability

The results of this study indicated that the unavailable Cd was mostly bound to the residual fraction (F6), Co was bound to organic matter (F5) and residual (F6) fractions, Cu was mostly bound to oxides (F4) and organic matter (F5) fractions, Ni was found in oxides (F4) fractions, Pb was mostly found bound to oxides (F4) and organic matter (F5) fractions, while Zn was bound to organic matter (F5) and Residual (F6) fractions. The distribution patterns varied among the six studied metals, and were similar for a certain metal among most of sample sites. For Cd in most of the samples, residual fractions (F6) accounted for more than 30% of their total concentrations; whereas about 20% of Pb presented in organic fraction (F5). A good proportion of Cu was found in the organic fraction (F5). The higher stability constant of copper complexes with organic matter leads to high organic fraction. Only under oxidizing conditions, can copper be leached into the environment (Venkateswaran *et al*., 2007).

Li and Thornton (2001) reported a significant association of Pb with the soil carbonate, while Kabata-Pendias and Pendias (1992) stated that there is a strong association of Pb with organic matter. Kabala and Singh (2001) and Ashraf *et al*. (2012) found that Zn was mostly concentrated in the residual fraction for agricultural calcareous soil. Different distribution patterns have been investigated by other authors, depending on the soil and contamination types (Kos *et al*., 2003). Tessier *et al*. (1979) reported that exchangeable Cd, Co, Cu, Ni, Pb, Zn and Fe are generally found to represent a minor fraction of the total

metal concentration of the solid. The results obtained for Fe and Mn oxides bound Fraction (F4) and organic matter bound Fraction (F5) indicated that these phases have a scavenging action for heavy metals that is far out of proportion to their own concentration. Only metals associated with water soluble (F1), exchangeable (F2) and carbonate (F3) fractions are readily available for plant uptake (Lasat, 2000). To assess the availability of heavy metals, only the soil labile fraction is taken into account because this fraction is often called, by extension, the bioavailable fraction (Gray *et al*., 2004). However, the bioavailable fraction can differ from one metal to another and from one receptor to another. The availability of metals for plants and micro-organisms in soil depends on the composition of the different compartments of soil such as carbonates, oxides, organic matter and silica. The sequential extraction has been used to highlight the relationship existing between these compartments, and also to assess the bioavailability and the potential threat of heavy metals to the environment. The disposition of cadmium and lead in F1, F2 and F3 fractions constitutes serious environmental problems because of their high mobility (Yang *et al*., 2013). The distribution of a given metal between various fractions does not necessarily reflect the relative scavenging action of discrete soil phases, but rather should be considered as operationally defined by the method of extraction (Tessier *et al*., 1979).

The bioavailability of the metals at the three different study areas is in the order: Dakace :- Cu > Zn > Ni > Pb > Cd > Co ; Gaskiya :- Cu > Zn > Ni > Co > Pb > Cd and Hanwa :- Cu > Ni > Zn > Pb > Cd >Co. Prasad (2003) reported that the most readily bioavailable metals include Ni, Zn, Cd and Cu. While more moderately bioavailable metals are Co, Mn and Fe. The metals that are generally considered to be not very bioavailable include Pb, Cr and U. Lead (Pb) is notorious for its lack of soil mobility, primarily due to

metal precipitation as insoluble phosphates, carbonates and hydroxides which have low solubilities in natural water. Bioavailability of metals in soils decrease above pH 5.5 – 6. The result of this study indicated that the bioavailabilities of the studied metals at the test sites (Dakace, Gaskiya and Hanwa) were higher than those at the control site except that of Co. Heavy metals in the soil from anthropogenic sources tend to be more mobile, hence bioavailable than pedogenic or lithogenic ones (Kuo *et al*., 1983; Kaasalainen and Yli-Halla, 2003; Kumar *et al*., 2011). Metal-bearing solids at contaminated sites can originate from a wide variety of anthropogenic sources in the form of metal mine tailings, disposal of high metal wastes in improperly protected landfills, leaded gasoline and lead-based paints, land application of fertilizing animal manures, biosolids (sewage sludge), compost, pesticides, coal combustion residues, petrochemicals and atmospheric deposition (Raymond and Felix, 2011). It is projected that the anthropogenic emission into the atmosphere, for several heavy metals, is one-to-three orders of magnitude higher than natural fluxes (Sposito and Page, 1984).

The low bioavailability of Cd, Co and Pb metals may be related to weak acidic soil property of the Dakace, Gaskiya and Hanwa. Previous studies have reported that when pH reached 7.5, Cd will be hardly dissolvable. At higher pH (6.5 or higher), water soluble Cd would enter the soil, existing mainly in state combining with clay mineral and oxide as well as residual fraction (Dai, 2006). In addition, Cd ion adsorption will be greatly enhanced at higher pH than at lower pH due to hydrolysis (Ali and Dzombak, 1996; Fijalkowski *et al*., 2012). It is also widely accepted that water soluble fractions of other metals, such as Pb, were rather low in alkaline soil (Wu, 2011).

5.4 Bioaccumulation and Transfer Factors

Bioavailability also referred to as the proportion of total metals that are available for incorporation into biota. Plant species as well as relative abundance and availability of necessary elements also control metal uptake rates. Phytoextraction is the uptake/absorption and translocation of contaminants by plant roots into the above ground portions of the plants (shoots) that can be harvested and burned gaining energy and recycling the metal from the ash (Tangahu, 2013). For phytoextraction to become a viable technology, plants with high tolerance and accumulation rates for several metals are required because polluted soils often contain high levels of several trace metal contaminants.

Bioaccumulation factor (BF), defined as the ratio of chemical concentration in a plant to its concentration in the soil, is used to measure the effectiveness of a plant in concentrating pollutant into the plant, while transfer factor (TF), the quotient of contaminant concentration in shoots to roots, which is used to measure the effectiveness of a plant in transferring a chemical from roots to shoots (Sun *et al*., 2011) .

The bioaccumulation and transfer factors were determined for each species at the three study areas to ascertain their phytoremediation potentials.

5.4.1 *Vetivera zizanioide* plant

This study shows that, generally the metal levels are higher in the leaves than in the roots and their concentrations were higher than the control. This indicated that the studied metals were absorbed from the soil by the plant roots and then translocated to the upper plant tissues. Using one-way ANOVA Duncan grouping, the concentrations Cd, Co, Cu, Ni, Pb and Zn in the soil and the tissues of *Vetivera zizanioide* at Dakace, Gaskiya and

Hanwa when compared to the control values showed significant difference ($P < 0.05$). But only Cd at Dakace showed no significant difference ($P > 0.05$). This result is in agreement with the report given by Aremu *et al*., (2013); Gunwal *et al*., (2014); Zhuang *et al*. (2007). The study showed that the bioaccumulation factors (BF) for Pb and Co in the plant harvested from Dakace and Gaskiya, and Co and Cu from Hanwa study areas were less than 1. But the transfer factors (TF) for all the metals studied at the three study areas were greater than 1.

At Dakace study area: The BF of the elements were of the order Cu > Ni > Zn ≈Cd > Pb > Co, while the TF was Zn > Cu > Ni > Cd ≈ Co ≈ Pb; At Gaskiya study area: The BF of the elements were in the order Zn > Cd ≈ Cu ≈ Ni > Co > Pb, while the TF followed the order Co > Zn > Cd ≈ Cu > Ni ≈ Pb; At Hanwa study area: The BF and TF of the elements were of the order Zn > Pb≈ Cd > Co ≈ Cu >Ni and Zn > Cd > Co ≈ Ni ≈ Cu ≈ Pb respectively. The degree of accumulation of each metal by the plant varied depending on their concentration and bioavailability.

Vetivera zizanioide plant has achieved a good phytoextraction process, whereby it has effectively removed from soil the heavy metal contaminants and transferred them from the roots of the plant into their aerial parts (Luo *et al*., 2005; Evangelou *et al*., 2007). They are plants that achieve a shoot- to- root (TF) metal concentration ratio greater than one. This study has shown that *Vetivera zizanioide* plant is a good bioaccumulator and hyperaccumulator for Cd, Cu, Ni and Zn because both their BF and TF are greater than 1. It is a poor accumulator of Pb because Pb is notorious for its lack of soil mobility, primarily due to metal precipitation as insoluble phosphates, which have low solubilities in natural water. But at Hanwa soil the plant showed bioaccumulating and hyperaccumulating ability

due to low phosphate content. Therefore, the plant has the potential to decontaminate metal-polluted soils . Highly tolerant to soil high in acidity, alkalinity, salinity, sodicity (Truong and Baker, 1998), *Vetiver's* ability to purify heavy metals from pig farms is ranked as: Zn > Cu > Pb (Liao *et al.*, 2003).

5.4.2 *Cymbopogon citratus* (Lemon grass) plant

This current study indicated that *Cymbopogon citratus* showed a steady increase in the absorption of the metals which agreed with the report by Dawle *et al*. (2014). Using one-way ANOVA Duncan grouping, the concentrations Cd, Co, Cu, Ni, Pb and Zn in the soil and the tissues of *Cymbopogon citratus* at Dakace, Gaskiya and Hanwa showed significant difference ($P < 0.05$) from those of the control. The BF and TF values of the elements studied at Dakace were of the order Ni > Cd > Pb > Zn > Co ≈ Cu and Zn > Cu > Cd ≈ Co > Ni > Pb respectively. The BF and TF values of the elements studied at Gaskiya were of the order Zn > Cu > Cd > Ni > Co >Pb and Ni > Cd > Pb > Co ≈ Cu ≈ Zn, while at Hanwa study area the BF and TF values were of the order Zn > Cu > Ni > Cd > Co > Pb and Zn > Cu > Cd > Ni ≈ Co > Pb. The BF and TF values for all the metals studied at the three study areas were greater than 1(except the BF for Pb and Co). This indicated that *Cymbopogon citratus* (Lemon grass) plant is a hyperaccumulator plant for all metals studied though the degree of accumulation varies from metal to metal.

Majid *et al.* (2013) reported that *Cymbopogon citratus* (Lemon grass) plant showed high efficiency for remediation of Pb, Ni, and Cd heavy metals. The high concentrations of Ni and Pb found in the shoots of tthis plant were reported to be higher than 0.1 % dry weight and 0.01 % for Cd which are considered as a standard for defining Ni, Pb, or Cd

hyperaccumulator plants in a natural environment (Chaney *et al*. 1997), and it is likely be a hyperaccumulator plant. This along with earlier reports on Pb accumulation in scented plants indicates the efficacy of different species of this genus for decontamination of multiple metal-polluted sites in phytoremediation industry. This study has shown that *Cymbopogon citratus* (Lemon grass) plant is a good bioaccumulator and hyperaccumulator for Cd, Ni and Zn because both their BF and TF are greater than 1.

5.4.3 *Helianthus annus* (Sunflower) plant

Generally there is an increase in the metal concentrations from the root to the stem and to the leaves of *Helianthus annus* **(**sunflower) plant, except for Ni where it is highest in stem at Dakace and Gaskiya study areas but highest in leaves at Hanwa study area. The metal levels for the test samples were higher than the control. The statistical analysis using One-way ANOVA Duncan grouping, showed that there is strong significant difference ($P < 0.05$) in the concentrations of the studied metals in the soil and the plant tissues. The BF for Cd, Co, Cu and Zn (Ni inclusive at Hanwa) were greater than 1. The study showed that metals were absorbed by the roots then translocated to the shoot, hence TF for all the studied metals were found to be greater than 1. The BF and TF followed the order:

Dakace - Cu > Cd ≈ Co > Zn > Ni > Pb and Ni > Cu > Pb > Co ≈ Zn > Cd respectively;

Gaskiya- Cu > Zn > Cd > Co > Ni > Pb and Zn > Cu > Pb > Ni > Co > Cd respectively;

Hanwa- Cu > Zn > Ni > Cd > Co > Pb and Ni >Zn > Pb >Cu > Co > Cd respectively.

Helianthus annus plant has a good phytoextraction potential for the removal of heavy metals from a contaminated soil (Solhi *et al*., 2005; Johnson *et al*., 2010). *Helianthus*

annus is a proven laboratory and field example for the emerging environmental and pollution studies. It is the most promising terrestrial candidate for metal and radionuclide removal from water (Prasad, 2007). This study has shown that *Helianthus annus* **(**sunflower) plant also has good phytoextraction potentials and has high hyperaccumulation for the studied metals because their TF are greater than 1.

5.4.4 *Ipomoea asarifolia* plant

The results showed that at the Dakace study area, the roots had the highest metal levels except for Ni where it is highest in the leaves. Only Cu had its BF greater than 1 and the TF for Co, Cu, Ni and Zn were greater than 1. Both Gaskiya and Hanwa study areas showed highest Cu, Pb and Zn concentrations in the leaves, Cd and Co in the roots while Ni in the stems of the *Ipomoea asarifolia* plant. The TF for the metals were greater than 1 at Gaskiya study site, while at the Hanwa site the TF for Cu, Ni, Pb and Zn were greater than 1, while those of Cd (0.6) and Co (0.9) a were less than 1. The BF and TF followed the order:

At Dakace, BF – Cu > Cd > Zn > Pb > Co > Ni; TF – Ni > Cu > Co ≈ Zn > Pb > Cd

At Gaskiya, BF – Cu > Zn > Cd > Ni > Co > Pb; TF – Ni > Cd ≈ Cu > Zn > Co > Pb

At Hanwa, BF – Ni > Cd ≈ Cu ≈ Zn > Co ≈ Pb; TF – Ni > Cu > Zn > Pb > Co > Cd

It was observed that *Ipomoea asarifolia* plant has less phytoremediation potential compared to other plants studied. It has been reported that only a longer growth period produces higher biomass that can enhance metal hyperaccumulation by the plant (Zaman *et al*., 2007).

5.4.5 *Ricinus communis* (Castor Oil) plant

The results of the concentrations (mg/kg) of metals in different parts of *Ricinus communis* at the three study areas and the control with their respective bioaccumulation and traslocation factors. indicated that there is a variation in the metal levels in the leaves, stems and roots of the plant. The statistical analysis using One-way ANOVA Duncan grouping, showed that there is a significant difference ($P < 0.05$) in the concentrations of the studied metals in the soil from the plant tissues at the three study areas. The BF for Cd, Co, Cu and Ni were greater than 1 while those of Pb and Zn were less than 1. All the metals (except Zn at Hanwa) have their TF greater than 1.

The BF and TF were of the order: Dakace-Ni > Cu > Co > Cd > Zn > Pb and Ni > Cu > Zn ≈ Cd ≈ Pb > Co respectively;

Gaskiya- Cu > Ni > Co > Zn > Cd > Pb and Ni > Zn > Cu > Co > Cd ≈ Pb > Co respectively;

Hanwa- Cu > Zn > Co > Cd > Ni > Pb and Ni > Pb ≈ Cd ≈ Co ≈ Cu > Zn respectively.

The studies indicated that the plant has the potential to accumulate the toxic trace elements from soil and this agreed with report given by Nathiyazhagan and Natarajan (2013). This plant has been identified as a trace metals accumulator in contaminated environments (Chaudhry *et al*., 1998; Solange, 2006; Huang *et al*., 2011). Therefore, *Ricinus communis* plant has a good phytoremediation potential.

Generally, Pb and Co were found to be among the least bioaccumulated metals studied. This is because Pb contamination in the environment exists as an insoluble form. It

is one of the metals that is generally considered to be not very bioavailable. Lead (Pb) is notorious for its lack of soil mobility, primarily due to metal precipitation as insoluble phosphates, carbonates and hydrated lead oxides which have low solubilities in natural water (Prasad, 2003). Co was reported to be moderately bioavailable (Abdel-Sabour and Al-Salama, 2007). Influx from solutions containing Co^{2+} was reported to be inhibited by Cd^{2+}, Cu^{2+} and Zn^{2+}, but Mn^{2+} and Ni^{2+} had no significant effect (Liu *et al*., 1998). Lower mobility of Co^{2+} in plants restricts its transport to the upper shoots from roots and its high levels can suppress the uptake of Cd by roots (Syamasri *et al*., 1994). Cd normally occurs in low concentration in the soils (Wagner, 1993). High level of Zn often accompany anomalous amounts of Cd in the environment. At the lowest concentration of Cd, high concentration of Zn suppresses Cd uptake, but at high concentration of Cd, high amount of Zn will increase Cd uptake (Hansford, 1972). Violina *et al*. (2008) reported that with the presence of of Zn and Cd in the soil, the content of Pb in the plants might increase or diminish. The competition or synergism between heavy metals and/or with other ions present in the soil system has a very significant effect on metal mobility in the root zone. Such synergism is found for Pb and Zn. According to Kabata-Pendias (2000), the Pb-Zn antagonism adversely affects the translocation of each element from roots to tops.

The different plant species studied showed different phytoremediation potentials. *Vetivera zizanioide*, *Cymbopogon citratus* (Lemon grass) and *Helianthus annus* (Sunflower) plants showed better phytoextraction potentials for all the studied metals than *Ricinus communis* plant, though their BF and TF varied for each metal. *Ipomoea asarifolia* plant showed poor phytoextraction potential. *Vetivera zizanioide, Cymbopogon citratus* (Lemon grass) and *Helianthus annus* (Sunflower) plants have massive finely structured and

deep root systems compared to *Ricinus communis* and *Ipomoea asarifolia* plants. Plants extract most of their nutrients from top soil by roots penetrating the subsoil, and from upward migration of dissolved pollutants to the rooting zone above (Driel *et al*., 1995). It has been reported that the plants have high tolerance for a wide range of soil pH from 3.3 to 12.5 without soil amendment, and highly tolerant to growing medium high in acidity, alkalinity, salinity (Adams and Dafforn, 1997). The test results for the soil pH was from 6.78 – 6.86. Generally cationic metals are more soluble at lower pH levels, so increasing the pH to 6.5 or higher makes them less available to plants and therefore less likely to be incorporated in their tissues and ingested by humans. Raising pH has the opposite effect on anionic elements.

The phytoextraction potential of each plant species is determined by its BF and TF. The metals were extracted by each of the plant species and then translocated from the roots to the shoot, hence TF for all the metals found to be greater than 1. This factor illustrates the efficiency of the internal transport of metals from roots to shoots, and a value > 1 indicates that plant is a metal accumulator appropriate for phytoextraction (Gennaro *et al*., 2012). The TF values always lower than 1 suggest that plants grown on highly metal contaminated soils behaved as tolerant plants, thus excluding metal toxicity by accumulation in roots. Where the BF is greater than 1, the plant species is a good accumulator, and where the TF is greater than 1 the plant species is a hyperaccumulator of the metal (Baker and Brooks, 1989). Studies have shown *Vetivera zizanioide*, *Cymbopogon citratus* (Lemon grass) and *Helianthus annus* **(**sunflower) are hyperaccumulators (Evangelou *et al*., 2007; Aremu *et al*., 2013). Hyperaccumulators accumulate appreciable

quantities of metal in their tissue regardless of the concentration of metal in the soil, as long as the metal in question is present (Prasad and Freitas, 2003).

Paz-Ferreiro *et al*. (2014) reported that uptake of heavy metals is lower in field experiments than for the soils in the pot experiments. This is due to differences in soil moisture or microclimate and to the fact that field-grown plants can reach down to less polluted soil.

5.5 Effect of the Application of EDTA on the Concentrations of Metals in Different Fractions of the Soil

Generally, the results indicated that there were reductions in the concentrations of the metals in Fe and Mn oxides bound Fraction (F4), organic matter bound Fraction (F5) and Final residual Fraction (F6) when EDTA was added to the soils at the various study areas as compared to their concentrations before the addition of the EDTA. At Dakace study site the percentage reduction in Cd, Co, Cu, Ni, Pb and Zn from the Fe and Mn oxides bound Fraction (F4)- 7%, 57%, 100%, 65%, 50% and 59% respectively; organic matter bound Fraction (F5): 44%, 59%, 50%, 30%, 52% and 50% respectively; final residual Fraction (F6): 20%, 79%, 25%, 4%, 86% and 70% respectively. The results demonstrated that EDTA is an efficient soil amendment in enhancing Cu,Co, Cd, Ni, Pb, and Zn desorption from soil and in increasing their accumulation in plants.

At Gaskiya study area percentage reduction in Cd, Co, Cu, Ni, Pb and Zn from the Fe and Mn oxides bound Fraction (F4) – 12%, 53%, 44%, 53%, 52% and 69% respectively; organic matter bound Fraction (F5) – 9%, 52%, 91%, 14%, 51% and 96% respectively and final residual Fraction (F6) – 8%, 78%, 50%, 27%, 60% and 50% respectively. At Hanwa study area percentage reduction in Cd, Co, Cu, Ni, Pb and Zn from the Fe and Mn oxides

bound Fraction (F4) – 37%, 64%, 98%, 52%, 56%, 45% respectively; organic matter bound Fraction (F5) – 0%, 59%, 54%, 27%, 57%, 53% respectively and final residual Fraction (F6) – 7%, 76%, 75%, 27%, 55%, 75%. At the control site percentage reduction in Cd, Co, Cu, Ni, Pb and Zn from the Fe and Mn oxides bound Fraction (F4) – 2%, 5%, 76%, 6%, 5% and 56% respectively; organic matter bound Fraction (F5) – 10%, 12%, 37%, 43%, 5% and 62 respectively and final residual Fraction (F6) – 4%, 5%, 11%, 36%, 1% and 68% respectively.

The ability of EDTA for the desorption of heavy metals from different soil fractions is dependent on the strength of adsorption of the metal to a particular solid phase (Saifullah *et al*., 2009). Lo and Yang (1999) evaluated the effect of EDTA concentrations (0.01, 0.05, 0.10 M) on the extraction of Pb, Cu and Zn from four different fractions (carbonate, Fe/Mn oxides, organic matter, and clay mineral) of laboratory prepared metal-contaminated soils. These authors reported that in general, the removal of Cu and Zn from all the four fractions was similar at 0.01 and 0.05 M EDTA concentrations. However, extraction of Pb from the organic matter and carbonate fraction was dependent on the EDTA concentration. However, it was only 50% of the total Pb observed in these fractions. This research shows that efficiency of EDTA for Cd removal from all the four fractions was lower than the other studied metals except at Dakace site were it was higher than the removal of Ni in the organic(F5) and the final residual(F6) fractions. Efficiency of EDTA for extracting Pb from all the three fractions was higher than 50%. The efficiency of EDTA for Cu removal from all the three fractions was very high with the least value 44% and highest 100% were removed. These observations corroborate the strong affinity of the metals towards complexation with EDTA as can be seen from their conditional stability constants (Co^{2+} =

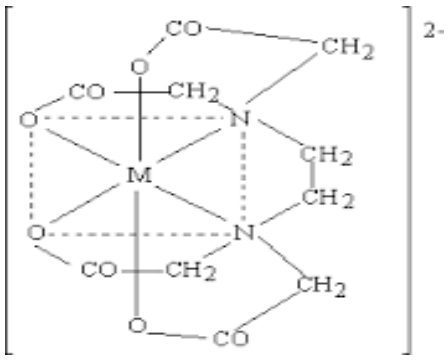
$2.0x10^{16}$; $Cd^{2+} = 2.9x10^{16}$; $Zn^{2+} = 3.2x10^{16}$; $Pb^{2+} = 1.1x10^{18}$; $Ni^{2+} = 4.2x10^{18}$; $Cu^{2+} = 6.3x10^{18}$). The divalent metals react with disodium salt of EDTA according to the following reaction:

$$Na_2Hy \rightleftharpoons 2Na^{+} + Hy^{2-}$$

$$M^{2+} + Hy^{2-} \rightleftharpoons My^{2-} + 2H^{+}$$

where Hy is the EDTA and M^{2+} is the divalent metal (Cd^{2+}, Co^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+} and Zn^{2+}).

The hypothesis is that complexing agent (EDTA) would be able to raise the concentration of the heavy metals in the soil solution. After its application the EDTA will be present as Metal-complexes. One EDTA molecule is able to bind and dissolve the metal ion in an 1:1 equimolar ratio (EAC, 2002). EDTA is a hexadentate ligand due to the most favourable combinations of the four carboxylic groups (for salt formation) and two amino nitrogen (for co-ordination) in its structure. The complexes formed are of chelate type, that is, the cations become bound in ring structure by the replacement of H^{+} ions from the –COOH groups and ring closing takes place by co-ordination of lone-pair of electrons on nitrogen atoms and the EDTA ion entirely wraps up a metal ion. The co-ordination is again six because of the six co-ordination bonds being formed by the central metal ion. The overall charge (2-) comes from the +2 on the original metal ion and the 4- on the $EDTA^{4-}$ ion.



5.6 Effect of EDTA on Phytoextraction of Metals

5.6.1 EDTA-assisted phytoextraction by *Vetivera zizanioide* plant

The application of EDTA to the soils at the three study areas increased the bioavailability of the metals, hence the increase in the metal levels in the different parts of the *Vetivera zizanioide* plant. The metal levels were higher in the leaves than in the roots. There were variations in the percentage increase for each of the metals studied so also their individual bioaccumulation and translocation factors when compared with their values before the addition of EDTA.

At Dakace study area, the increase in the metal levels in the entire plant were in the following multiples: Cd – 1.8, Co – 3.1, Cu – 2.9, Ni – 7.7, Pb – 1.1 and Zn – 1.3. There were improvements in the BF (except Cd and Ni) and TF (except Zn). Both the BF and TF were greater than 1, except the BF of Cd which was less than 1. At Gaskiya study area, the multiples were Cd – 1.5, Co – 1.7, Cu – 2.4, Ni – 5.2, Pb – 1.2 and Zn – 1.2. Both the BF and TF were greater than 1 except Ni which had a BF value less than 1. Co and Pb showed improvement in their BF while Cu, Ni and Pb also showed improvement in TF. At Hanwa study area, the increasing were by the following factors Cd – 1.9, Co – 1.7, Cu – 2.2, Ni –

3.4, Pb – 1.3 and Zn – 1.4. The plant showed improvement in the BF values for all the metals except Pb. The TF values for all the metals were greater than 1.

Wallace *et al.* (1974) reported that metal–EDTA complexes could increase solubility and phytoavailability of metals in soils. When EDTA is applied to soils, a large fraction of the total metals is dissolved and becomes available for phytoextraction without inducing a strong acidification of the growth medium. Chen *et al*. (2005) reported that *Vetivera zizanioide* had the capacity to tolerate high Pb concentrations in soils (Yahua *et al*., 2004). With the application of EDTA, the translocation ratio of Pb from vetiver roots to shoots was significantly increased. Moreover, EDTA has been shown to dissolve Pb adsorbed to soil particles (Means *et al*., 1978), increase Pb movement to roots via mass flow or diffusion, enhance metal uptake and trigger root to shoot translocation of heavy metals (Huang *et al*., 1997; Nascimento *et al*., 2006). Sangeeta and Subodh (2010) also reported that *Vetivera zizanioide* was the best plant species for phytoremediation (for both phtyostabilization and phytoextraction) of metal contaminated soils.

5.6.2 EDTA-assisted phytoextraction by *Cymbopogon citratus* (Lemon grass) plant

After the addition of EDTA to the soils at the three study areas, *Cymbopogon citratus* (Lemon grass) plant and soil showed an increase in the metal levels and the levels were higher in the leaves than in the roots. *Cymbopogon citratus* showed variations in the increase for each of the metals studied, so also their individual bioaccumulation and translocation factors when compared with their values before the addition of EDTA. At Dakace study area, the increase in the metal levels in the entire plant were in the following multiples: Cd – 2.0, Co – 2.1, Cu – 6.5, Ni – 10.1, Pb – 1.4 and Zn – 1.5. Increase in the

metal concentrations in the soil led to the improvement in the BF and TF values. At Gaskiya, the following incremental factors were observed Cd – 1.5, Co – 2.8, Cu – 3.3, Ni – 27.2, Pb – 1.5 and Zn – 1.6. The BF values for the studied metals (except Cd) and the TF values were all greater than 1. Co, Cu, Ni and Pb showed improvement in their BF values, while Co, Cu, Ni and Zn showed improvement in their TF values. At Hanwa, the incremental factors were: Cd – 1.4, Co – 1.8, Cu – 2.1, Ni – 8.0, Pb – 1.5 and Zn – 1.1. With the application of EDTA, Cd accumulations were found to be enhanced up to 458% and 400% above the soil Cd concentration in the root and shoot tissues respectively (Zaman *et al.* 2007).

The BF values for the studied metals and the TF values were all greater than 1. All the studied metals (except Zn) showed improvement in their BF values, while Ni and Zn showed improvement in their TF values. *Cymbopogon citratus* (Lemon grass) plant has been found to display a steady increase in the absorption of metals depending on the quantity of the metals present (Nisha *et al*., 2014)

5.6.3 EDTA-assisted phytoextraction by *Helianthus annus* (Sunflower) plant

The application of EDTA to the soil increased the bioavailabitlity of the studied metals in the soil, hence their greater extraction by *Helianthus annus* (Sunflower) plant. It was at Dakace study area that Cu and Zn were lower in the stems and roots compared to levels before the addition of EDTA. The metal levels were higher in the leaves than in the other parts of the plant, except for Ni at Gaskiya and Cd at Hanwa where their concentrations were highest in the stems. The increase in the metals levels in the entire plant were in the following multiples: At Dakace, Cd – 1.4, Co – 3.3, Cu – 0.7, Ni – 6.1, Pb

– 1.6 and Zn – 1.8. Only Cd did not show any improvement in the BF, while Co and Pb did not show improvement in their TF; at Gaskiya, the observed incremental factors were: Cd- 1.2, Co – 3.1, Cu – 1.7, Ni – 6.8, Pb –1.1 and Zn – 2.2. Only Ni and Pb had their BF less than 1 and all the studied metals had their TF greater than 1. The plant showed improvement in the BF of Cd and Co, and TF of Ni and Pb; and at Hanwa, the incremental factors were: Cd- 1.1, Co – 2.9, Cu – 2.2, Ni – 11.9, Pb – 1.3 and Zn – 1.8. All the studied metals had their BF and TF values greater than 1. The plant showed improvement in the BF values, and TF of Ni, Pb and Zn. Sunflower (*H. annus*) has been reported to be highly tolerant to heavy metals, showing a large intake of heavy metals into the roots, but poor translocation into the overground biomass (Jarmila *et al*., 2011). Sinegani & Khalilikhan (2010) mentioned sunflower (*Helianthus annus*) as a potential phytoextraction plant accumulating high concentrations of Cd from metal-contaminated soils and give the removal efficiency of Cd from the soil as 0.15%. Chelator induced detectable metal uptake enhancement occurs, particularly for energy plants sunflower (Yeh *et al.*, 2012). It was observed that for sunflower, chelate addition resulted in maximum removal of three non-essential heavy metals Cd, Ni, and Pb (Saifullah *et al*., 2009).

5.6.4 EDTA-assisted phytoextraction by *Ipomoea asarifolia* plant

Ipomoea asarifolia plant showed improvement in the extraction of the studied metals (except Pb) as a result of the application of EDTA to the soil. At Dakace study area, the concentrations of Co, Cu, Ni and Zn were highest in the leaves, Cd in the stems while Pb in the roots. The increases of the concentrations of the metals in the entire plant were in the following multiples: at Dakace, Cd – 2.5, Co – 2.0, Cu – 1.4, Ni – 4.8, Pb – 1.0, Zn – 1.2. There were an improvements in the BF for Co, Cu, Ni, Pb and Zn. The BF for the

studied metals were greater than 1 except for Co and Pb. The TF for the metals were also greater than 1 except that of Pb which was less than 1. At Gaskiya study area, Cu, Ni, Pb and Zn levels were highest in the leaves while Cd and Co were highest in the stems. The increases in the levels of the studied metals in the entire plant were by the following factors: Cd – 1.9, Co – 2.0, Cu – 1.3, Ni – 27.4, Pb – 1.1 and Zn – 2.8. There was an improvement in the BF for Co, Ni, Pb and Zn, and the TF for Co, Cu, Ni, Pb and Zn. The TF values for the studied metals were all greater than 1, so also the BF values (except for Co and Pb). At the Hanwa study area, the metal levels were highest in the leaves, while the concentrations of Co in the stems and roots of the plant were less. The levels of the studied metals in the entire plant increased by the following factors: Cd – 2.4, Co – 1.2, Cu – 2.7, Ni – 6.2, Pb – 1.1 and Zn – 2.5. There was an improvement in the BF for Cd, Cu, Pb and Zn, and the TF for Co, Cd, Ni and Zn. The TF values for the studied metals were all greater than 1 (except Cd), so also the BF values (except for Co and Pb).

5.6.5 EDTA-assisted phytoextraction by *Ricinus communis* (Castor Oil) plant

Ricinus communis (Castor Oil) plant showed improvement in the extraction of the studied metals as a result of the application of EDTA to the soil. At the Dakace study area, the metal levels increased considerable. The increases for the various metals studied in the plant were by the following factors: Cd – 1.5, Co – 2.2, Cu – 1.7, Ni – 9.9, Pb – 2.0 and Zn – 1.0. Cobalt, Cu, Pb and Zn showed improvement in their BF while the TF for Cd, Ni Pb and Zn also improved. At Gaskiya study area, the metal levels were highest in the leaves except Cd which was highest in the stems. The increases for the studied metals in the entire plant were by the following factors: Cd – 1.9, Co – 1.8, Cu – 1.5, Ni – 8.8, Pb – 2.1 and Zn – 1.4. There was an improvement in the BF values for Co, Cu, Pb and Zn, and in the TF

values for Cd, Cu, Ni and Pb. The TF values for all the studied metals were greater than 1, while the BF values for Co, Cu, Ni and Zn were greater than 1. At Hanwa, the metal levels were highest in the leaves. The increases for the studied metals in the entire plant were in the following multiples: Cd – 1.4, Co – 2.3, Cu – 1.5, Ni – 4.3, Pb – 1.9 and Zn – 0.9. There was an improvement in the BF values for all the studied metals, and in the TF values for Cu, Ni, Zn and Pb. The BF and TF values for all the studied metals were greater than 1.

Plant species vary in their response to take-up of heavy metals during EDTA-assisted phytoextraction. The efficiency of phytoextraction could be enhanced by the right combination of plant species and chelators. Huang *et al*., 1997 and Blaylock *et al*., 1997 were able to achieve rapid accumulation of Pb in plant shoots higher than 1% of shoot dry biomass with EDTA, the most commonly used chelating agent. Heavy metal concentrations in shoots and roots of plants significantly increased when EDTA addition levels were higher than 3 mmol/kg (Turan and Esringu, 2007). Maximum phytoextraction of metals were found with 5mmol/kg EDTA treatment (Sun *et al*., 2011). This study showed that the average accumulation of the studied metals in each plant species tested varied (Figures 4.50 – 4.55, 4.61 – 4.66 and 4.72 – 4.77).

Laboratory studies showed that EDTA is effective in removing heavy metals from contaminated soils, although extraction efficiency depends on many factors such as the bioavailability of heavy metals in soil, the strength of EDTA, electrolytes, pH and soil matrix (Turan and Esringu, 2007). Some plants can increase the capacity of their cell wall to bind metals. The cell walls contain some functional groups such as –COOH, -OH and –SH which enable the binding of divalent heavy metals ions thereby restricting metal uptake into the cell's cystoplasm (Mganga *et al*., 2011; Colzi *et al*., 2011; Pelloux *et al*., 2007).

Complexation of heavy metals by chelates could play an important role in controlling heavy metal solubility and concentration in soil, hence their phytoextraction. Large values of stability constants indicate stable complexes. Species in solution are generally in formation-dissociation equilibrium, and displacement reactions of any given metal by another are possible. The addition of a chelating agent to a solution of two or more metal ions leads to an order of metal ion complexation that is regulated by displacement of equilibrium constants (Chao *et al*., 1998). Under multiple metal-contaminated soil, the high concentrations of heavy metals may cause antagonistic or synergistic interaction among the different metals that could have enhanced or reduced the capacity of plants to uptake the individual metals (Sun *et al*., 2009). Application of EDTA in sufficiently large amount (EDTA:Metal stoichiometric ratio greater than 10) resulted in extraction of most metals. In contrast, Peters and Shem (1992) and Elliott and Brown (1989) reported that EDTA, at concentrations above the stoichiometrically required quantity, was not effective in the removal of metals from soil solution. This study showed no trend in the uptake of the studied metals by the tested plants.

High levels of soluble heavy metals resulting from application of EDTA may lead to contamination of ground water. The extent of metal leaching depends on the concentration of the EDTA applied, mode of application of the EDTA (split or single dose) and the time of the application of the EDTA. Therefore, the risk of leaching of metals from the soil could be minimized by increasing the biomass of the plant through the application of little quantity of fertilizer at the early stage of the plant growth, deep rooting system of the plant and the amount of EDTA applied (Barocsi *et al*., 2003).

5.7 Efficiency of the Phytoextraction

This study has shown that there was a decrease in the concentrations for all the studied metals in the soil after the plants were harvested from Dakace, Gaskiya, Hanwa and the control sites. At the Dakace and Hanwa study areas, it was observed that the decrease in Co concentration was not significant ($P > 0.05$) as compared to other studied metals. The percentages of the studied metals removed from the soils by the five plant species planted at the study areas and the control soil with the application of EDTA (EDTA-assisted phytoextraction) were higher than those by the plant species before the application of the EDTA (natural phytoextraction). Phytoextraction seems to have considerable potential for decontamination of soils contaminated with heavy metals.The goal of the phytoextraction process is to reduce heavy metal concentrations in contaminated soil to acceptable levels within a reasonable time frame.

The application of EDTA to soil containing heavy metals (Cu, Co, Cd, Ni, Pb and Zn), facilitated the heavy metal removal from the soil via plant uptake. Although there could be the possibility leaching, runoff, and erosion. The results of this study demonstrated that EDTA is an efficient soil amendment in enhancing Cu, Co, Cd, Ni, Pb, and Zn desorption from soil and in increasing their accumulation in plants. The data obtained in the experiment confirmed that all the plants were tolerant to heavy metals. It is generally noted in the literature that EDTA has taken a predominant place in increasing metal removal efficiency (Copper *et al*. 1999). Combining cropping or co-cropping system has enhanced the phytoextraction rates and the leaching risk caused by the application of the EDTA (Wei *et al*., 2011). Fuksova *et al*. (2009) reported that the remediation efficiency of the individual plant species in the co-cropping system did not differ from those obtained in

separate cropping mode. It improved the survival rate of the individual plant/crop and reduced the time period to accomplish the decontamination of a polluted soil. It also induced competition for phytoavailable nutrients and pollutants in the shared soil solution with stronger effect on the hyperaccumulator plant when grown on moderately contaminated soil (Jenna, 2012). Metal uptake by plant species is metal specific (Almas *et al*., 2012).

It has been reported that the phytoextracted metals can be recovered by incineration of the plant biomass to further concentrate the bio-ore. The bio-ores are reduced in the same way mineral ores are reduced; chemically or electrolytically (Chaney *et al*., 1999; Prasad, 2003). Thus, the re-introduction of the metal contaminants into the environment is minimized.

CHAPTER SIX

SUMMARY, CONCLUSION AND RECOMMENDATION

SUMMARY

A field trial to investigate the phytoextraction of cadmium (Cd), cobalt (Co), copper (Cu), nickel (Ni), lead (Pb) and zinc (Zn) by *Vetiveria zizanioide* (Jema), *Ipomoea asarifolia* (duman kada) *Helianthus annus* (sunflower), *Ricinus communis* L. (Castor oil plant) and *Cymbopogon citratus* (Lemon grass) planted on contaminated soils at Dakace, Gaskiya and Hanwa in Zaria Nigeria was carried out in the months of July to September,2013. The test and control sites were sandy loam in texture, slightly acidic for the test soils and slightly alkaline for the control soil. The %OM and CEC for the test soils were higher than the soils of the Nigerian savanna. The mean concentration of the studied metals in the soils at the three study areas (test soils) were higher than the control. The concentrations of Cd, Co, Ni and Pb were higher than the standard regulatory limits set by Joint FAO/WHO as reported by Akpoveta *et al*., 2010. The percentages of the studied metals removed from the EDTA treated soils and non EDTA treated soils by tested plants were: at Dakace site, without EDTA application (natural): Cd- 52.5%, Co – 0.6%, Cu – 44.3%, Ni – 88.4%, Pb – 13% and Zn – 28%; with EDTA application: Cd – 70.3%, Co – 1.2%, Cu – 70.5%, Ni – 89.9%, Pb – 38.3% and Zn – 36%. At Gaskiya site without EDTA application(natural): Cd – 45.7%, Co – 15.7%, Cu – 24.5%, Ni – 69.7%, Pb – 21.2% and Zn – 17.1%; with EDTA application: Cd -62%, Co – 19.2%, Cu – 60.4%, Ni – 90.5%, Pb – 27.9% and Zn – 29.1%. At Hanwa site without EDTA application (natural): Cd – 36.7%, Co – 1.2%, Cu – 28.4%, Ni – 20.5%, Pb – 17.4% and Zn – 17.2%; with EDTA application: Cd – 59.7%, Co – 2.3%,

Cu – 32.1%, Ni – 35.6%, Pb – 42.1% and Zn – 19.9%. The bioaccumulation and translocation factors determined for the studied metals by the tested plant species indicated that these plant species have the potentials for phytoremediation under field conditions even on soils not amended with EDTA.

CONCLUSION

The results of this research work showed that the concentrations of Cd, Co, Cu, Ni, Pb and Zn at Dakace, Gaskiya and Hanwa study sites were higher than the control site which implies that the dumping of scrap-metals on these soils has contributed significantly to the heavy metals contamination of the soils and can be of health risk since crops are planted on nearby farmlands. The plant species used in this work, *Vetiveria zizanioide* (Jema), *Ipomoea asarifolia* (duman kada) *Helianthus annus* (sunflower), *Ricinus communis* L. (Castor oil plant) and *Cymbopogon citratus* (Lemon grass) each showed a significantly higher absorption of Cd, Co Cu, Ni and Zn (except Pb which was low) when compared to their respective controls which led to the reduction in the levels of the metals studied in the study soils. It was also observed that treatment of the soils with EDTA enhanced the uptake of the studied metals in the plants by increasing the bioavailability of the metals in solutions. The bioaccumulation and translocation factors for the studied metals by the test plant species are indications that these species have the potentials for phytoremediation under field conditions even on soils not treated with EDTA. The order of the phytoextraction potentials for the plants were found to be in the following order: *Cymbopogon citratus* (Lemon grass) > *Vetiveria zizanioide s*(Jema) > *Helianthus annus* (sunflower) > *Ricinus communis* L. (Castor oil plant) > *Ipomoea asarifolia* (duman kada).

According to Baker and Brooks (1989), hyperaccumulators are metal specific and are adapted to precise climatic and soil conditions.

RECOMMENDATIONS

This technology is currently gaining considerable importance due to its potential for application to real world ecosystems. The following recommendations are hereby made:

(i) Other local plants could be investigated for better phytoremediation of these metals and other metals not studied in this research;

(ii) There use of other environmental friendly chelating agents could be studied on the phytoextraction of these metals;

(iii) Investigation can be carried out on how to recover these metals extracted to avoid reintroducing the metal contaminants into the environment, and

(iv) There is a need to develop new plants (genetically) that can increase phytoremediation potential so as to offer a viable remediation solution for polluted soils or farmlands.

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APPENDICES

Appendix I: Mean Concentration of Heavy Metals (mg/kg) in Soils at the Three Study Areas and the Control Site before Planting

	Cd	Co	Cu	Ni	Pb	Zn
Dakace	8.00±0.03	8.30±0.04	6.50±0.03	51.30±0.04	69.30±0.04	55.93±0.11
Gaskiya	7.00±0.02	9.90±0.05	5.30±0.03	84.93±0.07	75.90±0.04	28.90±0.12
Hanwa	6.00±0.02	8.70±0.05	5.60±0.05	47.90±0.06	76.90±0.05	25.58±0.06
Control	1.87±0.01	7.37±0.04	2.49±0.03	6.50±0.02	18.23±0.03	23.95±0.08
*Standard regulatory limits	5	8	30	40	10	90

***** Standard regulatory limits as reported by Akpoveta *et al*., 2010.

Appendix II: Single Contamination Index for Soils at Dakace, Gaskiya, Hanwa and Control

	Cd	Co	Cu	Ni	Pb	Zn
Dakace	1.6	1.04	0.18	1.28	6.95	0.62
Gaskiya	1.4	1.24	0.07	2.12	7.59	0.3
Hanwa	1.2	1.09	0.03	1.05	7.69	0.18
Control	0.37	0.92	0.08	0.05	1.82	0.27

Appendix III: The Nemero Pollution Index Method for Soils at Dakace, Gaskiya, Hanwa and Control

	Dakace	**Gaskiya**	**Hanwa**	**Control**
Cd	1.70	1.5	1.53	0.38
Co	1.07	1.4	1.23	1.01
Cu	0.22	0.18	0.19	0.08
Ni	1.54	3.35	1.12	0.06
Pb	7.11	7.66	7.84	1.96
Zn	0.67	0.32	0.21	0.20

Appendix IV: Metal Concentration (mg/kg) in Different Soil Fractions at Dakace

	Cd	Co	Cu	Ni	Pb	Zn
water soluble Fraction (F1)	0.80±0.02	6.50±0.02	0.40±0.02	22.80±0.08	26.00±0.03	51.20±0.03
Exchangeable Fraction (F2)	0.90±0.02	5.60±0.06	27.70±0.02	51.00±0.01	39.70±0.01	22.60±0.00
Carbonate bound Fraction (F3)	1.60±0.03	3.60±0.02	1.80±0.02	18.20±0.02	54.90±0.05	9.40±0.02
Fe and Mn oxides bound Fraction (F4)	1.50±0.02	7.20±0.08	1.30±0.00	19.00±0.04	51.20±0.04	10.66±0.04
Organic matter bound Fraction (F5)	0.90±0.02	6.00±0.07	1.40±0.01	15.90±0.01	55.60±0.05	2.04±0.02
Final Residual Fraction (F6)	2.50±0.02	11.80±0.01	0.20±0.02	12.10±0.09	43.20±0.04	18.68±0.03
Total metal recovery	8.2	40.7	32.8	139	270.6	114.58

Appendix V: Metal Concentration (mg/kg) in Different Soil Fractions at Gaskiya

	Cd	Co	Cu	Ni	Pb	Zn
water soluble Fraction (F1)	0.70±0.04	6.00±0.05	0.20±0.02	22.70±0.08	15.00±0.05	21.00±0.04
Exchangeable Fraction (F2)	0.90±0.02	4.90±0.09	5.70±0.02	24.40±0.04	44.10±0.03	19.32±0.03
Carbonate bound Fraction (F3)	1.20±0.03	6.30±0.02	1.80±0.02	18.10±0.07	48.30±0.03	9.60±0.03
Fe and Mn oxides bound Fraction (F4)	1.70±0.02	4.80±0.03	0.90±0.03	17.70±0.05	52.20±0.02	13.44±0.02
Organic matter bound Fraction (F5)	1.10±0.02	7.20±0.05	1.70±0.01	12.30±0.03	54.00±0.04	18.76±0.03
Final Residual Fraction (F6)	2.60±0.00	6.80±0.02	0.10±0.01	15.60±0.05	49.90±0.01	1.88±0.04
Total metal recovery	7.20	36.00	10.40	110.80	263.50	84.00

Appendix VI: Metal Concentration (mg/kg) in Different Soil Fractions at Hanwa

	Cd	Co	Cu	Ni	Pb	Zn
water soluble Fraction (F1)	0.80±0.04	6.50±0.06	0.20±0.02	23.10±0.02	31.60±0.01	35.08±0.06
Exchangeable Fraction (F2)	1.00±0.00	8.70±0.11	3.80±0.05	25.20±0.01	42.50±0.06	56.88±0.09
Carbonate bound Fraction (F3)	1.20±0.04	5.40±0.08	0.70±0.02	17.40±0.09	49.00±0.04	21.88±0.04
Fe and Mn oxides bound Fraction (F4)	1.90±0.01	7.70±0.03	2.00±0.01	18.60±0.09	51.60±0.04	18.80±0.02
Organic matter bound Fraction (F5)	0.80±0.01	7.10±0.05	2.60±0.01	12.40±0.07	57.30±0.04	1.46±0.03
Final Residual Fraction (F6)	2.70±0.05	8.30±0.09	0.40±0.02	16.60±0.02	50.00±0.01	10.88±0.05
Total metal recovery	8.4	43.7	9.7	113.3	282	144.98

Appendix VII: Metal Concentration (mg/kg) in Different Soil Fractions at the Control

	Cd	Co	Cu	Ni	Pb	Zn
water soluble Fraction (F1)	0.43±0.02	4.02±0.03	0.07±0.03	12.70±0.07	6.02±0.06	3.27±0.03
Exchangeable Fraction (F2)	0.52±0.02	3.21±0.05	0.57±0.03	13.90±0.06	17.00±0.03	2.46±0.02
Carbonate bound Fraction (F3)	0.67±0.03	2.87±0.04	0.20±0.03	9.80±0.05	25.95±0.02	4.02±0.03
Fe and Mn oxides bound Fraction (F4)	0.81±0.01	3.13±0.04	0.42±0.02	10.18±0.07	27.95±0.06	7.15±0.07
Organic matter bound Fraction (F5)	0.58±0.04	2.40±0.05	0.98±0.03	12.40±0.07	25.27±0.04	0.76±0.03
Final Residual Fraction (F6)	1.38±0.02	1.53±0.03	0.09±0.01	13.30±0.06	23.45±0.01	4.66±0.04
Total metal recovery	4.29	17.16	2.33	72.28	125.64	22.32

Appendix VIII: Percentage Bioavailable Metals Analysed in the Soils at Dakace, Gaskiya, Hanwa and the Control Sites

	Cd	Co	Cu	Ni	Pb	Zn
Dakace	40	39	91	66	42	73
Gaskiya	39	48	74	59	41	60
Hanwa	36	47	50	60	44	79
Control	38	36	59	50	39	44

Appendix IX : Concentration of Metals (mg/kg) in Different Parts of *Vetivera zizanioide* Plant and Soil, Bioaccumulation and Transfer Factors at Dakace

	Leaves	Roots	Soil	BF	TF
Cd site	2.10±0.01	1.90±0.03	1.80±0.01	1.1	1.1
control	(0.90±0.02)	(0.70±0.02)	(0.70±0.02	1.1	1.3
Co site	5.30.±0.07	5.20±0.03	8.40±0.04	0.6	1.1
control	(1.90±0.01)	(1.70±0.02)	(2.90±0.05)	0.6	1.1
Cu site	4.30±0.01	3.00±0.04	1.90±0.03	1.9	1.4
control	(2.50±0.02)	(1.00±0.01)	(1.40±0.01)	1.3	2.5
Ni site	9.50±0.02	8.10±0.02	4.90±0.08	1.8	1.2
control	(1.50±0.02)	(0.80±0.09)	(1.20±0.03)	1.0	1.9
Pb site	50.50±0.04	50.10±0.02	69.30±0.11	0.7	1.1
control	(33.30±0.05)	(32.70±0.07)	(36.70±0.02)	0.9	1.0
Zn site	85.90±0.04	20.52±0.06	55.93±0.05	1.1	4.2
control	(21.37±0.06)	(20.34±0.07)	(8.73±0.04)	1.1	2.4

Appendix X: Concentration of Metals (mg/kg) in Different Parts of *Cymbopogon citratus* (Lemon grass), Bioaccumulation and Transfer Factors at Dakace

	Leaves	Roots	Soil	BF	TF
Cd site	2.60±0.03	2.00±0.02	1.80±0.01	1.3	1.3
control	(1.00±0.03)	(0.80±0.08)	(0.80±0.02	1.1	1.3
Co site	6.40±0.04	5.00±0.02	8.40±0.04	0.7	1.8
control	(5.80±0.04)	(4.10±0.04)	(2.90±0.05)	1.7	1.8
Cu site	1.60±0.03	0.90±0.03	1.90±0.03	0.7	2.5
control	(0.90±0.03)	(0.50±0.00)	(0.10±0.02)	7	1.8
Ni site	7.70±0.03	6.20±0.10	4.90±0.08	1.4	1.2
control	(2.20±0.02)	(0.50±0.03)	(1.10±0.08)	1.2	4.4
Pb site	46.20±0.01	42.20±0.01	42.80±0.02	1.1	1.1
control	(32.80±0.04)	(30.90±0.07)	(34.70±0.02)	0.9	1.1
Zn site	51.41±0.06	22.54±0.02	41.33±0.04	0.9	2.3
control	(21.22±0.05)	(8.12±0.00)	(8.73±0.04)	1.6	2.6

Appendix XI: Concentration of Metals (mg/kg) in Different Parts of *Helianthus annus* (Sunflower) Plant, Bioaccumulation and Transfer Factors at Dakace

	Leave	Stem	Root	Soil	BF	TF
Cd site	3.30±0.05	2.40±0.01	2.10±0.02	1.80±0.01	1.4	1.4
control	(1.50±0.00)	(1.70±0.06)	(0.50±0.03)	(0.90±0.01	1.3	3.2
Co site	6.90±0.09	2.40±0.05	1.40±0.04	8.40±0.04	0.4	3.3
control	(3.10±0.01)	(0.80±0.04)	(1.00±0.03)	(2.90±0.05)	0.6	1.3
Cu site	28.20±0.02	21.80±0.02	13.10±0.05	6.50±0.03	3.2	1.9
control	(8.60±0.02)	4.20±0.02	(6.20±0.01)	(1.40±0.01)	4.5	1.0
Ni site	9.60±0.01	9.80±0.02	7.80±0.04	51.30±0.05	0.2	1.4
control	(8.40±0.05)	(4.50±0.04)	(4.10±0.07)	(10.20±0.03)	0.6	1.6
Pb site	40.50±0.02	36.00±0.01	38.20±0.02	69.30±0.11	0.6	1.0
control	(26.70±0.07)	(25.70±0.05)	(23.70±0.04)	(36.70±0.02)	0.7	1.1
Zn site	103.50±0.08	63.93±0.11	54.64±0.05	55.93±0.05	1.3	1.5
control	(46.40±0.11)	(20.01±0.05)	(26.19±0.09)	(8.73±0.04)	3.5	1.3

Appendix XII: Concentration of Metals (mg/kg) in Different Parts of *Ipomoea asarifolia* Plant, Bioaccumulation and Transfer Factors at Dakace

	Leave	Stem	Root	Soil	BF	TF
Cd site	1.50±0.03	1.50±0.00	1.80±0.05	1.80±0.01	0.9	0.8
control	(1.00±0.04)	(1.00±0.04)	(1.40±0.02)	(0.70±0.02	1.6	0.7
Co site	3.60±0.03	3.60±0.04	3.50±0.04	8.40±0.03	0.4	1.1
control	(3.00±0.03)	(1.60±0.02)	(0.40±0.02)	(2.90±0.05)	0.6	5.8
Cu site	14.90±0.03	10.00±0.03	9.10±0.01	6.50±0.03	1.7	1.4
control	(4.40±0.02)	(2.80±0.03)	(2.10±0.07)	(1.40±0.01)	2.2	1.7
Ni site	22.20±0.04	6.70±0.07	6.50±0.03	51.30±0.05	0.2	2.2
control	(2.20±0.05)	(0.90±0.08)	(0.50±0.04)	(1.10±0.08)	1.1	3.1
Pb site	31.10±0.07	40.00±0.04	41.00±0.03	69.30±0.11	0.5	0.9
control	(22.90±0.04)	(23.50±0.01)	(22.10±0.05)	(36.70±0.02)	0.6	1.0
Zn site	37.64±0.11	34.20±0.10	31.93±0.07	55.93±0.05	0.6	1.1
control	(8.78±0.00)	(12.30±0.04)	(7.76±0.02)	(8.73±0.04)	1.1	1.4

Appendix XIII: Concentration of Metals (mg/kg) in Different Parts of *Ricinus communis* (Castor Oil) Plant, Bioaccumulation and Transfer Factors at Dakace

	Leave	Stem	Root	Soil	BF	TF
Cd site	2.30±0.02	2.10±0.02	2.10±0.03	1.80±0.01	1.2	1.1
control	(1.40±0.05)	(1.40±0.04)	(1.10±0.05)	(0.70±0.02	1.9	1.3
Co site	6.20±0.03	6.10±0.02	4.10±0.02	8.40±0.03	0.7	1.5
control	ND	(3.50±0.08)	(2.50±0.01)	(3.00±0.03)	1.3	0.7
Cu site	8.40±0.03	6.80±0.02	2.90±0.04	6.50±0.03	0.9	2.6
control	(4.10±0.02)	(0.50±0.03)	(0.10±0.01)	(1.40±0.02)	2.7	1.9
Ni site	12.90±0.05	11.80±0.02	7.60±0.08	4.90±0.08	2.2	1.6
control	(1.40±0.01)	(0.60±0.02)	(1.20±0.05)	(0.50±0.04)	2.2	0.8
Pb site	25.70±0.06	19.90±0.02	22.00±0.04	69.30±0.11	0.3	1.1
control	(4.30±0.05)	(7.10±0.03)	(7.90±0.06)	(14.00±0.02)	0.5	0.7
Zn site	35.94±0.03	45.73±0.02	39.73±0.16	55.93±0.05	0.7	1.1
control	23.10±0.03)	(14.23±0.03)	(12.91±0.05)	(16.30±0.07)	1.0	1.4

Appendex XIV: Bioaccumulation and Transfer Factors for the Studied Metals in Different Plant Species at Dakace

		V.zizanioide	*C.citratus*	*H.annus*	*I.asarifolia*	*R.communis*
Cd	BF	1.1	1.3	1.4	0.9	1.2
	TF	1.1	1.3	1.4	0.8	1.0
Co	BF	0.6	0.7	0.6	0.4	0.7
	TF	1.1	1.3	3.3	1.1	0.7
Cu	BF	1.9	0.7	3.2	1.7	0.7
	TF	1.4	1.8	1.9	1.4	2.6
Ni	BF	1.8	1.4	0.2	0.2	2.2
	TF	1.2	1.2	1.4	2.2	1.6
Pb	BF	0.7	1.0	0.6	0.5	0.3
	TF	1.0	1.1	1.0	0.9	1.1
Zn	BF	1.0	0.9	1.3	0.6	0.7
	TF	4.2	2.3	1.5	1.1	1.1

Appendix XV: Concentration of Metals (mg/kg) in Different Parts of *Vetivera zizanioide* Plant and Soil, Bioaccumulation and Transfer Factors at Gaskiya

	Leaves	Roots	Soil	BF	TF
Cd site	3.00±0.01	2.00±0.02	1.90±0.01	1.3	1.5
control	(0.90±0.02)	(0.70±0.02)	(0.70±0.02)	1.1	1.3
Co site	8.60±0.01	3.40±0.00	8.10±0.04	0.7	2.5
control	(1.90±0.01)	(1.70±0.02)	(2.90±0.05)	0.6	1.1
Cu site	2.90±0.00	1.90±0.02	1.90±0.04	1.3	1.5
control	(2.50±0.02)	(1.00±0.01)	(1.40±0.01)	1.3	2.5
Ni site	9.80±0.06	8.80±0.03	7.00±0.04	1.3	1.1
control	(1.50±0.02)	(0.80±0.09)	(1.20±0.03)	1.0	1.9
Pb site	47.00±0.02	44.40±0.03	75.90±0.01	0.6	1.1
control	(33.30±0.05)	(32.70±0.07)	(36.70±0.02)	0.9	1.0
Zn site	48.50±0.13	30.80±0.17	28.91±0.06	1.4	1.6
control	(21.37±0.06)	(20.34±0.07)	(8.73±0.04)	1.1	2.4

Appendix XVI: Concentration of Metals (mg/kg) in Different Parts of *Cymbopogon citratus* (Lemon grass) Plant and Soil, Bioaccumulation and Transfer Factors at Gaskiya

	Leaves	Roots	Soil	BF	TF
Cd site	2.70±0.01	2.20±0.03	1.90±0.01	1.3	1.2
control	(1.00±0.03)	(0.80±0.08)	(0.80±0.02)	1.1	1.3
Co site	5.70±0.02	5.70±0.03	8.10±0.04	0.7	1.1
control	(5.00±0.04)	(4.10±0.00)	(2.90±0.05)	1.7	1.8
Cu site	3.10±0.00	2.90±0.03	1.90±0.04	1.6	1.1
control	(0.90±0.03)	(0.50±0.00)	(0.10±0.02)	7	1.8
Ni site	11.10±0.03	4.40±0.06	7.00±0.04	1.1	2.5
control	(2.20±0.02)	(0.50±0.03)	(1.10±0.08)	1.2	4.4
Pb site	43.40±0.01	41.50±0.01	51.70±0.01	0.8	1.0
control	(32.80±0.04)	(30.90±0.07)	(34.70±0.02)	0.9	1.1
Zn site	41.40±0.07	14.23±0.04	28.91±0.06	2.9	1.1
control	(21.22±0.05)	(8.12±0.00)	(8.73±0.04)	1.6	2.6

Appendix XVII: Concentration of Metals (mg/kg) in Different Parts of *Helianthus annus* (Sunflower) Plant and Soil, Bioaccumulation and Transfer Factors at Gaskiya

	Leaves	Stems	Roots	Soil	BF	TF
Cd site	2.40±0.02	2.30±0.02	2.10±0.04	3.80±0.01	0.6	1.1
control	(1.50±0.00)	(1.70±0.06)	(0.50±0.03)	(0.90±0.01)	1.3	3.2
Co site	7.40±0.03	1.20±0.03	1.00±0.02	8.10±0.04	0.4	4.3
control	(3.10±0.01)	(0.80±0.04)	(1.00±0.03)	(2.90±0.05)	0.6	1.3
Cu site	19.10±0.03	14.00±0.03	8.80±0.02	1.90±0.04	7.4	1.9
control	(8.60±0.02)	(4.20±0.02)	(6.20±0.02)	(0.10±0.01)	15	1.1
Ni site	11.70±0.07	10.40±0.07	10.50±0.05	17.00±0.04	0.6	1.1
control	(8.40±0.05)	(4.50±0.04)	(4.10±0.07)	(10.20±0.08)	0.6	1.6
Pb site	58.50±0.03	42.40±0.04	39.10±0.03	51.70±0.01	0.9	1.3
control	(26.70±0.07)	(25.70±0.05)	(23.70±0.04)	(36.70±0.02)	0.7	1.1
Zn site	95.00±0.13	51.26±0.09	29.52±0.04	25.15±0.02	2.3	2.5
control	(46.40±0.11)	(20.01±0.05)	(26.19±0.09)	(8.73±0.04)	3.5	1.3

Appendix XVIII: Concentration of Metals (mg/kg) in Different Parts of *Ipomoea asarifolia* Plant and Soil, Bioaccumulation and Transfer Factors at Gaskiya

	Leaves	Stems	Roots	Soil	BF	TF
Cd site	2.60±0.04	2.10±0.02	1.50±0.02	1.90±0.01	1.1	1.6
control	(1.00±0.04)	(1.00±0.04)	(1.40±0.03)	(0.70±0.02)	1.6	0.7
Co site	3.90±0.03	5.50±0.05	4.00±0.01	8.10±0.04	0.6	1.2
control	(3.00±0.03)	(1.60±0.02)	(0.40±0.02)	(2.90±0.05)	0.6	5.8
Cu site	13.20±0.04	10.70±0.01	7.70±0.08	1.90±0.04	5.5	1.6
control	(4.40±0.02)	(2.80±0.03)	(2.10±0.07)	(1.40±0.01)	2.2	2.8
Ni site	8.80±0.04	7.30±0.06	2.70±0.06	7.00±0.04	0.9	3.0
control	(2.20±0.05)	(0.90±0.08)	(0.50±0.04)	(1.10±0.08)	1.1	3.1
Pb site	37.90±0.2	36.50±0.04	34.10±0.03	75.90±0.05	0.5	1.1
control	(22.90±0.04)	(23.50±0.01)	(22.10±0.05)	(36.70±0.02)	0.6	1.0
Zn site	31.59±0.03	35.75±0.04	22.40±0.04	25.15±0.02	1.2	1.5
control	(8.78±0.00)	(12.30±0.04)	(7.76±0.02)	(8.73±0.04)	1.1	1.4

Appendix XIX: Concentration of Metals (mg/kg) in Different Parts of *Ricinus communis* (Castor Oil) Plant and Soil, Bioaccumulation and Transfer Factors at Gaskiya

	Leave	Stem	Root	Soil	BF	TF
Cd site	2.30±0.02	2.00±0.01	2.10±0.02	1.90±0.01	1.1	1.1
control	(1.40±0.05)	(1.40±0.04)	(1.10±0.05)	(0.70±0.02)	1.9	1.3
Co site	8.00±0.05	6.80±0.05	5.60±0.03	8.10±0.04	0.8	1.3
control	ND	(3.50±0.03)	(4.50±0.01)	(3.00±0.05)	1.3	0.7
Cu site	9.00±0.03	5.70±0.03	5.50±0.08	5.30±0.03	1.8	1.5
control	(4.10±0.02)	(0.50±0.03)	(0.10±0.01)	(1.40±0.02)	2.7	1.9
Ni site	12.40±0.05	12.80±0.06	7.80±0.03	7.00±0.04	1.6	1.6
control	(1.40±0.01)	(0.60±0.02)	(1.20±0.05)	(0.50±0.04)	2.2	0.8
Pb site	21.20±0.04	21.70±0.04	20.60±0.03	75.90±0.05	0.3	1.1
control	(4.30±0.05)	(7.10±0.03)	(7.90±0.06)	(14.00±0.02)	0.5	0.7
Zn site	32.00±0.05	31.60±0.02	36.40±0.11	28.91±0.06	1.2	1.9
control	(23.10±0.03)	(14.23±0.03)	(12.91±0.05)	(16.30±0.07)	1.0	1.4

Appendix XX: Bioaccumulation and Transfer Factors for the Studied Metals in Different Plant Species at Gaskiya

		V.zizanioide	*C.citratus*	*H.annus*	*I.asarifolia*	*R.communis*
Cd	BF	1.3	1.3	0.6	1.1	1.1
	TF	1.5	1.2	1.1	1.6	1.2
Co	BF	0.7	0.7	0.4	0.6	0.8
	TF	2.5	1.0	4.3	1.2	1.3
Cu	BF	1.3	1.6	7.4	5.5	1.8
	TF	1.5	1.1	1.9	1.6	1.5
Ni	BF	1.3	1.1	0.6	0.9	1.6
	TF	1.1	2.5	1.1	3.0	1.6
Pb	BF	0.6	0.8	0.9	0.5	0.3
	TF	1.1	1.0	1.3	1.1	1.3
Zn	BF	1.4	2.9	2.3	1.2	1.2
	TF	1.6	1.2	2.5	1.5	1.9

Appendix XXI: Concentration of Metals (mg/kg) in Different Parts of *Vetivera zizanioide* Plant and Soil, Bioaccumulation and Transfer Factors at Hanwa

	Leaves	Roots	Soil	BF	TF
Cd site	2.20±0.03	1.80±0.02	1.90±0.00	1.1	1.2
control	(0.90±0.02)	(0.70±0.02)	(0.70±0.01)	1.1	1.3
Co site	5.80±0.03	5.30±0.04	8.60±0.04	0.6	1.1
control	(1.90±0.01)	(1.70±0.02)	(2.90±0.05)	0.6	1.1
Cu site	3.30±0.05	2.90±0.01	5.60±0.03	0.6	1.1
control	(2.50±0.02)	(1.00±0.01)	(1.40±0.01)	1.3	2.5
Ni site	10.60±0.06	10.10±0.07	4.90±0.08	2.2	1.1
control	(1.50±0.02)	(0.80±0.09)	(1.20±0.03)	1.0	1.9
Pb site	46.30±0.04	42.80±0.05	42.30±0.06	1.1	1.1
control	(33.37±0.05)	(32.70±0.07)	(36.70±0.02)	0.9	1.0
Zn site	46.00±0.03	26.54±0.03	20.49±0.03	1.8	1.7
control	(21.37±0.06)	(20.34±0.07)	(8.73±0.04)	1.1	2.4

Appendix XXII: Concentration of Metals (mg/kg) in Different Parts of *Cymbopogon citratus* (Lemon grass) Plant and Soil, Bioaccumulation and Transfer Factors at Hanwa

	Leaves	Roots	Soil	BF	TF
Cd site	3.00±0.01	2.20±0.02	3.80±0.03	0.7	1.4
control	(1.00±0.03)	(0.80±0.08)	(0.80±0.02)	1.1	1.3
Co site	7.40±0.06	4.50±0.07	8.60±0.04	0.7	1.6
control	(5.80±0.04)	(4.10±0.04)	(2.90±0.05)	1.7	1.8
Cu site	4.80±0.00	2.30±0.11	5.60±0.03	0.6	2.8
control	(0.90±0.03)	(0.50±0.00)	(0.10±0.02)	7	1.8
Ni site	8.70±0.05	8.50±0.06	47.90±0.08	1.8	1.1
control	(2.20±0.02)	(0.50±0.03)	(1.10±0.03)	1.2	4.4
Pb site	45.70±0.03	43.60±0.01	76.90±0.06	0.6	1.1
control	(32.80±0.04)	(30.90±0.07)	(34.70±0.02)	0.9	1.1
Zn site	66.41±0.07	37.33±0.02	20.49±0.03	2.5	1.8
control	(21.22±0.05)	(8.12±0.00)	(8.73±0.04)	1.6	2.6

Appendix XXIII: Concentration of Metals (mg/kg) in Different Parts of *Helianthus annus* (Sunflower) Plant and Soil, Bioaccumulation and Transfer Factors at Hanwa

	Leaves	Stems	Roots	Soil	BF	TF
Cd site	2.70±0.02	2.80±0.03	2.50±0.03	3.80±0.03	0.7	1.1
control	(1.50±0.00)	(1.70±0.06)	(0.50±0.03)	(0.90±0.01)	1.3	3.2
Co site	5.80±0.05	3.90±0.01	2.20±0.06	8.60±0.04	0.5	2.2
control	(3.10±0.01)	(0.80±0.04)	(1.00±0.03)	(2.90±0.03)	0.6	1.3
Cu site	14.30±0.02	14.30±0.01	11.50±0.01	5.60±0.03	1.8	0.8
control	(8.60±0.02)	(4.20±0.02)	(6.20±0.01)	(1.40±0.01)	4.5	1.0
Ni site	11.10±0.03	11.40±0.10	7.90±0.02	47.90±0.08	0.2	1.4
control	(8.40±0.05)	(4.50±0.04)	(4.10±0.07)	(10.20±0.03)	0.6	1.6
Pb site	47.90±0.04	42.80±0.02	39.80±0.04	76.90±0.06	0.6	1.1
control	(26.70±0.07)	(25.70±0.05)	(23.70±0.04)	(36.70±0.02)	0.7	1.1
Zn site	65.81±0.09	43.03±0.02	50.40±0.07	20.49±0.03	2.6	1.1
control	(46.40±0.11)	(20.01±0.05)	(26.19±0.09)	(8.73±0.04)	3.5	1.3

Appendix XXIV: Concentration of Metals (mg/kg) in Different Parts of *Ipomoea asarifolia* Plant and Soil, Bioaccumulation and Transfer Factors at Hanwa

	Leaves	Stems	Roots	Soil	BF	TF
Cd site	1.50±0.02	1.60±0.03	2.50±0.01	1.90±0.00	1.1	0.6
control	(1.00±0.04)	(1.00±0.04)	(1.40±0.02)	(0.70±0.02)	1.6	0.7
Co site	4.20±0.11	3.90±0.11	4.40±0.01	8.70±0.03	0.5	0.9
control	(3.00±0.03)	(1.60±0.02)	(0.40±0.02)	(2.90±0.03)	0.6	5.8
Cu site	8.00±0.03	7.10±0.01	3.40±0.02	5.60±0.03	1.1	2.2
control	(4.40±0.02)	(2.80±0.03)	(2.10±0.07)	(1.40±0.01)	2.2	1.7
Ni site	79.10±0.03	92.20±0.05	35.30±0.14	42.10±0.04	1.6	2.4
control	(2.20±0.05)	(0.90±0.08)	(0.50±0.04)	(1.10±0.02)	1.1	3.1
Pb site	43.00±0.03	36.10±0.05	33.00±0.01	76.90±0.04	0.5	1.2
control	(22.90±0.04)	(23.50±0.01)	(22.10±0.05)	(36.70±0.02)	0.6	1.0
Zn site	27.63±0.01	24.69±0.03	13.79±0.03	20.49±0.03	1.1	1.9
control	(8.78±0.00)	(12.30±0.04)	(7.76±0.02)	(8.73±0.04)	1.1	1.4

Appendix XXV: Concentration of Metals (mg/kg) in Different Parts of *Ricinus communis* (Castor Oil) Plant and Soil, Bioaccumulation and Transfer Factors at Hanwa

	Leaves	Stems	Roots	Soil	BF	TF
Cd site	2.30±0.03	2.20±0.01	2.20±0.04	3.80±0.03	0.6	1.1
control	(1.40±0.05)	(1.40±0.04)	(1.10±0.05)	(0.70±0.02)	1.9	1.3
Co site	5.50±0.05	5.10±0.03	5.10±0.03	8.60±0.04	0.6	1.2
control	ND	(3.50±0.08)	(4.50±0.01)	(3.00±0.03)	1.3	0.7
Cu site	6.70±0.01	5.40±0.03	4.50±0.02	5.60±0.03	1.2	1.3
control	(4.10±0.03)	(0.50±0.03)	(0.10±0.01)	(1.40±0.02)	2.7	1.9
Ni site	11.80±0.04	8.90±0.02	7.10±0.01	47.90±0.08	1.9	1.5
control	(1.40±0.01)	(0.60±0.02)	(1.20±0.05)	(0.50±0.03)	2.2	0.8
Pb site	25.30±0.04	21.50±0.03	20.60±0.01	76.90±0.04	0.3	1.1
control	(4.30±0.05)	(7.10±0.03)	(7.90±0.06)	(14.00±0.02)	0.5	0.7
Zn site	45.19±0.02	26.90±0.07	40.81±0.11	25.58±0.06	1.5	0.9
control	(23.10±0.03)	(14.23±0.03)	(12.91±0.08)	(16.30±0.07)	1.0	1.4

Appendix XXVI: Bioaccumulation and Transfer Factors for the Studied Metals in Different Plant Species at Hanwa

		V.zizanioide	*C.citratus*	*H.annus*	*I.asarifolia*	*R.communis*
Cd	BF	1.1	0.9	0.7	1.1	0.6
	TF	1.2	1.4	1.1	0.6	1.1
Co	BF	0.6	0.7	0.5	0.5	0.6
	TF	1.1	1.6	2.2	0.9	1.2
Cu	BF	0.6	0.6	1.8	1.1	1.2
	TF	1.1	2.8	0.8	2.2	1.3
Ni	BF	2.2	1.8	0.2	0.4	1.9
	TF	1.1	1.1	1.4	3.2	1.5
Pb	BF	1.1	1.1	0.6	0.5	0.3
	TF	1.1	1.1	1.1	1.2	1.1
Zn	BF	1.8	2.5	2.6	1.1	1.5
	TF	1.7	1.8	1.1	1.9	0.9

Appendix XXVII: Metal Concentration (mg/kg) in Different Soil Fractions with EDTA at Dakace

	Cd	Co	Cu	Ni	Pb	Zn
water soluble Fraction (F1)	0.80±0.05	4.05±0.04	0.10±0.04	6.10±0.07	20.00±0.01	10.30±0.07
Exchangeable Fraction (F2)	1.00±0.03	5.15±0.08	2.80±0.01	7.40±0.06	23.95±0.03	2.45±0.01
Carbonate bound Fraction (F3)	1.10±0.02	1.70±0.05	0.45±0.04	7.50±0.04	25.90±0.03	5.85±0.07
Fe and Mn oxides bound Fraction (F4)	1.40±0.02	3.10±0.04	ND	6.70±0.03	25.65±0.03	4.33±0.02
Organic matter bound Fraction (F5)	0.50±0.00	2.45±0.05	0.70±0.05	11.15±0.03	26.95±0.04	1.02±0.02
Final Residual Fraction (F6)	2.00±0.00	2.50±0.03	0.05±0.03	12.55±0.03	6.00±0.03	5.65±0.04
Total metal recovery	6.80	18.95	4.10	51.40	128.45	29.6

Appendix XXVIII: Metal Concentration (mg/kg) in Different Soil Fractions with EDTA at Gaskiya

	Cd	Co	Cu	Ni	Pb	Zn
water soluble Fraction (F1)	0.90±0.05	3.70±0.07	0.60±0.02	5.70±0.07	5.20±0.02	8.97±0.02
Exchangeable Fraction (F2)	1.10±0.03	4.50±0.03	0.75±0.04	6.65±0.11	24.50±0.01	4.80±0.03
Carbonate bound Fraction (F3)	1.20±0.02	2.35±0.03	0.25±0.01	8.90±0.09	22.65±0.01	1.74±0.03
Fe and Mn oxides bound Fraction (F4)	1.50±0.03	2.25±0.06	0.15±0.03	8.30±0.05	25.05±0.03	4.13±0.04
Organic matter bound Fraction (F5)	1.00±0.00	3.45±0.11	0.15±0.00	10.55±0.02	26.75±0.05	0.83±0.01
Final Residual Fraction (F6)	2.40±0.03	1.50±0.07	0.05±0.03	11.45±0.00	19.95±0.02	0.94±0.04
Total metal recovery	8.10	17.75	1.95	51.55	124.10	21.41

Appendix XXIX: Metal Concentration (mg/kg) in Different Soil Fractions with EDTA at Hanwa

	Cd	Co	Cu	Ni	Pb	Zn
water soluble Fraction (F1)	0.70±0.02	4.10±0.02	0.15±0.03	5.00±0.01	5.60±0.03	10.84±0.07
Exchangeable Fraction (F2)	1.00±0.05	4.40±0.03	1.70±0.02	8.00±0.07	18.70±0.03	12.21±0.01
Carbonate bound Fraction (F3)	1.20±0.01	2.50±0.03	0.15±0.02	8.55±0.07	23.55±0.05	6.68±0.07
Fe and Mn oxides bound Fraction (F4)	1.20±0.01	2.80±0.05	0.05±0.01	8.95±0.04	22.90±0.03	9.27±0.17
Organic matter bound Fraction (F5)	0.80±0.05	2.90±0.05	1.20±0.02	9.10±0.03	24.85±0.03	0.68±0.04
Final Residual Fraction (F6)	2.50±0.03	2.00±0.09	0.10±0.01	12.10±0.02	22.60±0.03	2.77±0.06
Total metal recovery	7.40	18.70	3.35	51.70	118.20	42.45

Appendix XXX: Metal Concentration (mg/kg) in Different Soil Fractions with EDTA at Control Site

	Cd	Co	Cu	Ni	Pb	Zn
water soluble Fraction (F1)	0.43±0.02	4.40±0.05	0.34±0.02	6.55±0.05	7.42±0.04	3.83±0.04
Exchangeable Fraction (F2)	0.52±0.02	3.27±0.05	0.57±0.03	8.00±0.05	23.32±0.03	9.13±0.03
Carbonate bound Fraction (F3)	0.62±0.03	2.80±0.03	0.17±0.03	9.22±0.04	24.90±0.02	3.94±0.03
Fe and Mn oxides bound Fraction (F4)	0.81±0.01	2.97±0.03	0.10±0.01	10.18±0.07	26.42±0.05	3.15±0.04
Organic matter bound Fraction (F5)	0.52±0.02	2.12±0.05	0.62±0.01	7.07±0.04	23.95±0.04	0.29±0.03
Final Residual Fraction (F6)	1.32±0.02	1.45±0.03	0.08±0.01	8.48±0.06	23.13±0.03	1.50±0.02
Total metal recovery	4.22	17.01	1.88	59.65	129.14	21.84

Appendix XXXI: Concentration of Metals (mg/kg) in Different Parts of *Vetivera zizanioide* Plant and Soil, Bioaccumulation and Transfer Factors at Dakace after Application of EDTA

	Leaves	Roots	Soil	BF	TF
Cd site	3.60±0.05	3.40±0.04	3.80±0.02	0.9	1.1
control	(1.10±0.02)	(0.80±0.03)	(0.90±0.01)	1.1	1.4
Co site	23.50±0.05	8.50±0.02	8.40±0.03	3.8	2.8
control	(6.60±0.01)	(6.10±0.07)	(6.40±0.03)	1.0	1.1
Cu site	13.90±0.10	7.30±0.01	6.50±0.03	3.3	1.9
control	(3.50±0.02)	(1.60±0.02)	(0.54±0.02)	1.3	2.5
Ni site	99.14±0.22	36.00±0.06	51.30±0.05	1.3	2.8
control	(4.70±0.04)	(0.50±0.08)	(2.70±0.04)	1.0	9.4
Pb site	50.20±0.06	45.50±0.05	42.80±0.02	1.1	1.1
control	(34.50±0.06)	(33.50±0.01)	(38.00±0.02)	0.9	1.1
Zn site	100.56±0.08	36.46±0.07	41.33±0.04	1.7	2.8
control	(35.80±0.05)	(25.27±0.01)	(15.40±0.11)	2.0	1.4

Appendix XXXII: Concentration of Metals (mg/kg) in Different Parts of *Cymbopogon citratus* (Lemon grass) Plant and Soil, Bioaccumulation and Transfer Factors at Dakace after Application of EDTA

	Leaves	Roots	Soil	BF	TF
Cd site	5.97±0.05	3.20±0.05	3.80±0.02	1.2	1.9
control	(1.30±0.02)	(1.10±0.04)	(0.90±0.02)	1.3	1.4
Co site	12.00±0.04	11.80±0.11	8.40±0.03	2.8	1.1
control	(9.00±0.01)	(7.70±0.11)	(6.40±0.03)	1.3	1.2
Cu site	11.67±0.04	4.60±0.04	6.50±0.03	1.3	2.5
control	(3.00±0.02)	(2.80±0.03)	(0.54±0.02)	5.5	1.1
Ni site	99.90±0.07	38.00±0.08	51.30±0.05	1.3	2.6
control	(39.60±0.13)	(0.40±0.05)	(0.50±0.04)	4.0	9.9
Pb site	63.90±0.02	58.60±0.04	69.30±0.11	0.9	1.1
control	(33.90±0.05)	(29.30±0.05)	(29.00±0.02)	1.1	1.2
Zn site	73.50±0.11	37.30±0.15	55.93±0.05	1.1	2
control	(35.54±0.05)	(8.16±0.02)	(15.46±0.04)	1.4	4.4

Appendix XXXIII: Concentration of Metals (mg/kg) in Different Parts of *Helianthus annus* (Sunflower) Plant and Soil, Bioaccumulation and Transfer Factors at Dakace after Application of EDTA

	Leaves	Stems	Roots	Soil	BF	TF
Cd site	5.10±0.01	2.80±0.03	2.60±0.01	3.80±0.02	0.9	1.5
control	(1.80±0.01)	1.80±0.04	(1.00±0.03)	(0.70±0.02)	1.8	1.3
Co site	13.10±0.09	13.10±0.02	9.00±0.04	8.40±0.03	1.4	1.5
control	(6.80±0.02)	(8.40±0.04)	(4.00±0.04)	(6.90±0.04)	0.9	1.9
Cu site	40.50±0.03	3.90±0.06	2.50±0.02	1.90±0.03	8.2	8.9
control	(9.80±0.04)	(4.40±0.03)	(6.90±0.03)	(0.10±0.02)	7	1.9
Ni site	23.80±0.12	96.30±0.04	14.70±0.04	4.90±0.08	9.2	4.1
control	(3.30±0.05	(45.70±0.06)	(5.00±0.02)	(2.20±0.06)	8.2	9.8
Pb site	63.90±0.06	39.60±0.00	35.40±0.06	42.80±0.02	1.1	1.5
control	(27.40±0.02)	(30.30±0.03)	(26.20±0.04)	(34.70±0.02)	0.8	1.1
Zn site	150.05±0.06	58.80±0.06	28.21±0.04	41.33±0.04	1.8	6.3
control	(55.82±0.12)	(44.70±0.11)	(13.20±0.03)	(16.30±0.07)	2.3	3.8

Appendix XXXIV: Concentration of Metals (mg/kg) in Different Parts of *Ipomoea asarifolia* Plant and Soil, Bioaccumulation and Transfer Factors at Dakace after Application of EDTA

	Leaves	Stems	Roots	Soil	BF	TF
Cd site	3.90±0.04	4.10±0.02	4.00±0.01	3.80±0.02	1.1	1.1
control	(1.90±0.11)	(2.20±0.06)	(2.50±0.03)	(0.90±0.01)	2.4	0.8
Co site	11.50±0.09	6.20±0.07	3.70±0.07	8.40±0.04	0.8	2.4
control	(3.40±0.04)	(3.10±0.01)	(2.40±0.05)	(0.40±0.01)	7.4	1.4
Cu site	17.80±0.02	15.80±0.01	11.90±0.01	1.90±0.03	8	1.5
control	(8.70±0.07)	(2.20±0.03)	(0.30±0.03)	(0.10±0.02)	7.0	1.9
Ni site	116.70±0.08	25.90±0.13	21.90±0.07	4.90±0.08	2.4	2.2
control	(18.60±0.06)	(8.60±0.05)	(4.80±0.02)	(2.20±0.06)	2.1	2.6
Pb site	31.90±0.03	35.50±0.05	36.90±0.04	42.80±0.02	0.8	0.9
control	(26.90±0.06)	(24.40±0.03)	(21.60±0.06)	(29.00±0.02)	0.8	1.2
Zn site	52.52±0.10	41.40±0.13	34.18±0.03	41.33±0.04	1.1	1.4
control	(30.30±0.04)	(20.20±0.07)	(15.90±0.04)	(16.30±0.07)	1.4	1.6

Appendix XXXV: Concentration of Metals (mg/kg) in Different Parts of *Ricinus communis* (Castor Oil) Plant and, Bioaccumulation and Transfer Factors at Dakace after Application of EDTA

	Leaves	Stems	Roots	Soil	BF	TF
Cd site	3.60±0.01	3.30±0.03	3.00±0.04	3.80±0.02	0.9	1.2
control	(2.40±0.01)	(1.90±0.02)	(1.50±0.01)	(0.70±0.02)	1.3	2.3
Co site	12.10±0.00	12.70±0.05	11.60±0.06	8.40±0.04	1.4	1.1
control	(3.90±0.04)	(9.40±0.07)	(2.60±0.05)	(6.40±0.03)	0.8	3.6
Cu site	12.10±0.06	10.90±0.01	6.80±0.02	1.90±0.03	5.2	1.7
control	(8.20±0.02)	(2.80±0.04)	(1.60±0.04)	(0.10±0.02)	4.2	3.4
Ni site	231.30±0.06	70.40±0.06	19.80±0.06	51.30±0.05	2.1	7.6
control	(9.00±0.08)	(7.50±0.04)	(2.70±0.06)	(2.40±0.06)	1.7	3.1
Pb site	43.70±0.02	47.30±0.03	44.20±0.04	42.80±0.02	1.1	1.1
control	(41.60±0.01)	(28.00±0.02)	(32.40±0.04)	(36.70±0.02)	0.9	1.1
Zn site	40.22±0.03	43.64±0.06	40.34±0.04	41.33±0.04	1.1	1.1
control	(29.98±0.06)	(20.29±0.05)	(13.43±0.00)	(17.16±0.04)	1.2	1.9

Appendix XXXVI: Bioaccumulation and Transfer Factors for the Studied Metals in Different Plant Species at Dakace Soil Treated with EDTA

		V.zizanioide	*C.citratus*	*H.annus*	*I.asarifolia*	*R.communis*
Cd	BF	0.9	1.2	0.9	1.1	0.9
	TF	1.1	1.9	1.5	1.1	1.2
Co	BF	3.8	2.8	1.4	0.8	0.7
	TF	2.8	1.1	1.5	2.4	0.8
Cu	BF	3.3	1.3	8.2	8.0	3.2
	TF	1.9	2.5	8.9	1.5	0.8
Ni	BF	1.3	1.3	9.2	2.4	2.2
	TF	2.8	2.4	4.1	2.2	1.6
Pb	BF	1.1	0.9	1.1	0.8	1.1
	TF	1.1	1.1	1.5	0.9	1.0
Zn	BF	1.7	1.1	1.8	1.1	1.2
	TF	2.8	2.0	6.3	1.4	1.0

Appendix XXXVII: Concentration of Metals (mg/kg) in Different Parts of *Vetivera zizanioide* Plant and Soil, Bioaccumulation and Transfer Factors at Gaskiya after Application of EDTA

		Leaves	Roots	Soil	BF	TF
Cd	site	3.80±0.04	3.60±0.00	3.80±0.01	1.1	1.1
	control	(1.10±0.02)	(0.80±0.03)	(0.90±0.01)	1.1	1.4
Co	site	12.20±0.03	7.70±0.01	9.90±0.03	1.1	1.6
	control	(6.60±0.01)	(6.10±0.07)	(6.40±0.03)	0.7	2.1
Cu	site	6.90±0.00	4.40±0.02	5.30±0.03	1.1	1.6
	control	(3.50±0.02)	(1.60±0.02)	(0.54±0.02)	1.3	2.5
Ni	site	54.10±0.12	43.30±0.06	84.90±0.06	0.6	1.2
	control	(4.70±0.04)	(0.50±0.08)	(2.70±0.02)	1.0	9.4
Pb	site	56.40±0.07	48.80±0.04	51.70±0.05	1.1	1.2
	control	(34.50±0.06)	(33.50±0.01)	(38.00±0.02)	0.9	1.1
Zn	site	66.96±0.08	29.29±0.03	25.15±0.06	1.4	1.6
	control	(35.80±0.05)	(25.27±0.01)	(15.40±0.11)	2	1.4

Appendix XXXVIII: Concentration of Metals (mg/kg) in Different Parts of *Cymbopogon citratus* (Lemon grass) Plant and Soil, Bioaccumulation and Transfer Factors at Gaskiya after Application of EDTA

		Leaves	Roots	Soil	BF	TF
Cd	site	3.70±0.06	3.40±0.02	3.80±0.01	0.9	1.2
	control	(1.30±0.03)	(1.10±0.01)	(0.90±0.01)	1.3	1.4
Co	site	21.10±0.06	11.10±0.03	9.90±0.03	1.6	1.9
	control	(9.00±0.01)	(7.70±0.11)	(6.40±0.03)	1.3	1.2
Cu	site	12.90±0.02	7.00±0.02	5.30±0.03	1.9	1.8
	control	(3.00±0.02)	(2.80±0.03)	(0.54±0.02)	5.5	1.1
Ni	site	324.70±0.10	99.20±0.58	84.90±0.06	2.5	3.3
	control	(39.60±0.13)	(0.40±0.05)	(0.50±0.04)	4.0	9.9
Pb	site	67.40±0.02	62.10±0.02	75.90±0.05	0.9	1.1
	control	(33.90±0.05)	(29.30±0.05)	(29.00±0.02)	1.1	1.2
Zn	site	46.60±0.02	38.80±0.06	25.15±0.02	1.3	3.3
	control	(35.54±0.05)	(8.16±0.02)	(15.46±0.04)	1.4	4.4

Appendix XXXIX: Concentration of Metals (mg/kg) in Different Parts of *Helianthus annus* (Sunflower) Plant and Soil, Bioaccumulation and Transfer Factors at Gaskiya after Application of EDTA

	Leave	Stem	Root	Soil	BF	TF
Cd site	2.90±0.03	2.70±0.03	2.70±0.04	1.90±0.01	1.5	1.1
control	(1.80±0.01)	(1.80±0.04)	(1.00±0.03)	(0.70±0.02)	1.8	1.3
Co site	13.20±0.06	9.10±0.02	7.80±0.09	9.90±0.03	1.1	1.4
control	(6.80±0.02)	(8.40±0.04)	(4.00±0.04)	(6.90±0.04)	0.9	1.9
Cu site	30.10±0.02	8.10±0.02	7.60±0.01	5.30±0.03	2.9	2.5
control	(9.80±0.04)	(4.40±0.03)	(6.90±0.03)	(0.10±0.02)	7.0	1.9
Ni site	64.30±0.08	107.20±0.04	51.66±0.11	84.90±0.06	0.9	1.7
control	(3.30±0.05)	(45.70±0.06)	(5.00±0.02)	(2.20±0.06)	8.2	9.8
Pb site	87.00±0.07	33.80±0.05)	25.50±0.03	75.90±0.05	0.6	2.4
control	(27.40±0.02)	(30.30±0.03)	(26.20±0.04)	(34.70±0.02)	0.8	1.1
Zn site	107.34±0.16	44.41±0.06	28.29±0.04	28.91±0.06	2.1	2.7
control	(55.82±0.12)	(44.70±0.11)	(13.20±0.03)	(16.30±0.07)	2.3	3.8

Appendix XL: Concentration of Metals (mg/kg) in Different Parts of *Ipomoea asarifolia* Plant and Soil, Bioaccumulation and Transfer Factors at Gaskiya after Application of EDTA

	Leave	Stem	Root	Soil	BF	TF
Cd site	3.90±0.01	4.10±0.01	4.00±0.02	3.80±0.01	1.1	1.3
control	(1.90±0.11)	(2.20±0.06)	(2.50±0.03)	(0.90±0.01)	2.4	0.8
Co site	7.10±0.01	14.50±0.08	4.70±0.02	9.90±0.03	0.9	2.3
control	(3.40±0.04)	(3.10±0.01)	(2.40±0.05)	(0.40±0.04)	7.4	1.4
Cu site	21.30±0.02	18.50±0.07	9.70±0.04	5.30±0.03	3.1	2.1
control	(8.70±0.07)	(2.20±0.03)	(0.30±0.03)	(0.10±0.02)	7.0	1.9
Ni site	391.90±0.06	95.90±0.14	30.40±0.02	84.90±0.06	2	8
control	(18.60±0.06)	(8.60±0.05)	(4.80±0.02)	(2.20±0.06)	2.1	2.6
Pb site	43.70±0.02	40.60±0.03	30.00±0.08	51.70±0.01	0.7	1.4
control	(26.90±0.06)	(24.40±0.05)	(21.60±0.06)	(29.00±0.02)	0.8	1.2
Zn site	117.77±0.00	88.10±0.06	44.71±0.06	28.91±0.06	2.9	2.3
control	(30.30±0.04)	(20.20±0.07)	(15.90±0.04)	(16.30±0.07)	1.4	1.6

Appendix XLI: Concentration of Metals (mg/kg) in Different Parts of *Ricinus communis* (Castor Oil) Plant and Soil, Bioaccumulation and Transfer Factors at Gaskiya after Application of EDTA

	Leaves	Stems	Roots	Soil	BF	TF
Cd site	3.30±0.03	3.70±0.02	2.90±0.03	3.80±0.01	0.9	1.2
control	(2.40±0.01)	(1.90±0.02)	(1.50±0.01)	(0.70±0.02)	1.3	2.3
Co site	14.90±0.02	12.20±0.01	11.70±0.05	9.90±0.03	1.3	3.2
control	(3.90±0.04)	(9.40±0.07)	(2.60±0.05)	(6.40±0.03)	0.8	3.6
Cu site	12.20±0.05	11.00±0.02	6.90±0.03	1.90±0.04	5.3	1.7
control	(8.20±0.09)	(2.80±0.04)	(1.60±0.04)	(0.10±0.02)	4.2	3.4
Ni site	276.00±0.12	64.40±0.09	14.90±0.10	84.90±0.06	1.4	11
control	(9.00±0.08)	(7.50±0.04)	(2.70±0.06)	(2.40±0.01)	1.7	3.2
Pb site	45.70±0.03	44.50±0.05	44.50±0.02	51.70±0.01	0.9	1.3
control	(41.60±0.01)	(28.00±0.02)	(32.40±0.04)	(36.70±0.02)	0.9	1.1
Zn site	52.98±0.05	46.00±0.02	43.39±0.03	25.15±0.02	1.9	1.1
control	(29.98±0.06)	(20.29±0.05)	(13.43±0.00)	(17.16±0.04)	1.2	1.9

Appendix XLII: Bioaccumulation and Transfer Factors for the Studied Metals in Different Plant Species at Gaskiya with EDTA

		V.zizanioide	*C.citratus*	*H.annus*	*I.asarifolia*	*R.communis*
Cd	BF	1.1	0.9	1.5	1.1	0.9
	TF	1.1	1.2	1.1	1.3	1.2
Co	BF	1.0	1.6	1.0	0.9	1.3
	TF	1.6	1.9	1.4	2.3	1.2
Cu	BF	1.1	1.9	2.9	3.1	5.3
	TF	1.6	1.8	2.5	2.1	1.7
Ni	BF	0.6	2.5	0.9	2.1	1.6
	TF	1.2	3.3	1.7	8.0	1.6
Pb	BF	0.7	0.9	0.6	0.7	0.9
	TF	1.2	1.1	2.4	1.4	1.3
Zn	BF	1.4	1.2	2.1	2.9	1.9
	TF	1.6	3.3	2.7	2.3	1.1

Appendix XLIII: Concentration of Metals (mg/kg) in Different Parts of *Vetivera zizanioide* Plant and Soil, Bioaccumulation and Transfer Factors at Hanwa after Application of EDTA

	Leaves	Roots	Soil	BF	TF
Cd site	3.80±0.01	3.70±0.06	3.80±0.03	1.1	1.1
control	(1.10±0.02)	(0.80±0.03)	(0.90±0.01)	1.1	1.4
Co site	10.30±0.01	8.50±0.02	8.70±0.03	1.1	1.2
control	(6.60±0.01)	(6.10±0.07)	(6.40±0.03)	1.0	1.1
Cu site	6.80±0.06	6.70±0.04	3.80±0.05	1.8	1.0
control	(3.50±0.02)	(1.60±0.02)	(0.54±0.02)	1.3	2.5
Ni site	39.00±0.04	32.10±0.09	42.10±0.04	0.8	1.2
control	(4.70±0.04)	(0.50±0.08)	(2.70±0.02)	1.0	9.4
Pb site	56.80±0.02	56.30±0.03	76.90±0.04	0.7	1.1
control	(34.50±0.06)	(33.50±0.01)	(38.00±0.02)	0.9	1.1
Zn site	90.50±0.25	32.70±0.13	25.58±0.06	2.4	2.8
control	(35.80±0.05)	(25.27±0.01)	(15.40±0.11)	2.0	1.4

Appendix XLIV: Concentration of Metals (mg/kg) in Different Parts of *Cymbopogon citratus* (Lemon grass) Plant and Soil, Bioaccumulation and Transfer Factors at Hanwa after Application of EDTA

	Leaves	Roots	Soil	BF	TF
Cd site	3.60±0.01	3.40±0.02	1.90±0.00	1.8	1.1
control	(1.30±0.03)	(1.10±0.01)	(0.90±0.01)	1.3	1.4
Co site	12.20±0.02	9.50±0.02	8.70±0.03)	1.2	1.3
control	(9.00±0.01)	(7.70±0.11)	(6.40±0.03)	1.3	1.2
Cu site	9.20±0.01	5.60±0.06	3.80±0.05	1.9	1.6
control	(3.00±0.02)	(2.80±0.03)	(0.54±0.02)	5.5	1.1
Ni site	78.20±0.11	59.80±0.02	42.10±0.04	1.6	1.3
control	(39.60±0.13)	(0.40±0.05)	(0.50±0.02)	4.0	9.9
Pb site	65.70±0.03	64.20±0.07	42.30±0.04	1.5	1.1
control	(33.90±0.05)	(29.30±0.05)	(29.00±0.02)	1.1	1.2
Zn site	84.40±0.11	29.80±0.07	25.58±0.06	2.2	2.8
control	(35.54±0.05)	(8.16±0.02)	(15.46±0.04)	1.4	4.4

Appendix XLV: Concentration of Metals (mg/kg) in Different Parts of *Helianthus annus* (Sunflower) Plant and Soil, Bioaccumulation and Transfer Factors at Hanwa after Application of EDTA

	Leaves	Stems	Roots	Soil	BF	TF
Cd site	3.00±0.03	3.10±0.04	2.80±0.01	1.90±0.00	1.6	1.1
control	(1.80±0.01)	(1.80±0.04)	(1.00±0.03)	(0.70±0.02)	1.8	1.3
Co site	16.00±0.09	8.90±0.05	8.10±0.03	8.70±0.03	1.3	1.5
control	(6.80±0.02)	(8.40±0.04)	(4.00±0.04)	(6.90±0.04)	0.9	1.9
Cu site	39.90±0.02	10.70±0.01	15.00±0.01	3.80±0.05	5.8	1.7
control	(9.80±0.04)	(4.40±0.03)	(6.90±0.03)	(0.1±0.02)	7.0	1.9
Ni site	285.00±0.13	50.30±0.04	25.70±0.04	42.10±0.04	2.9	6.4
control	(45.20±0.06)	(3.30±0.05)	(5.00±0.02)	(2.20±0.06)	8.2	9.8
Pb site	81.60±0.04	55.70±0.02	34.00±0.03	42.30±0.04	1.3	2
control	(27.40±0.02)	(30.30±0.03)	(26.20±0.04)	(34.70±0.02)	0.8	1.1
Zn site	182.24±0.01	62.80±0.27	51.99±0.06	25.58±0.06	3.8	2.3
control	(55.82±0.12)	(44.70±0.11)	(13.20±0.03)	(16.30±0.7)	2.3	3.8

Appendix XLVI: Concentration of Metals (mg/kg) in Different Parts of *Ipomoea asarifolia* Plant and Soil, Bioaccumulation and Transfer Factors at Hanwa after Application of EDTA

	Leaves	Stems	Roots	Soil	BF	TF
Cd site	4.50±0.11	4.00±0.02	5.10±0.02	3.80±0.03	1.2	0.8
control	(1.90±0.11)	(2.20±0.06)	(2.50±0.03)	(0.90±0.01)	2.4	0.8
Co site	5.10±0.09	3.80±0.02	3.20±0.03	8.60±0.04	0.5	1.4
control	(3.40±0.04)	(3.10±0.01)	(2.40±0.05)	(0.40±0.01)	7.4	1.4
Cu site	21.90±0.04	17.30±0.02	10.90±0.01	3.80±0.05	4.4	1.8
control	(8.70±0.07)	(2.20±0.03)	(0.30±0.03)	(0.1±0.02)	7.0	1.9
Ni site	133.10±0.03	6.80±0.05	7.80±0.07	47.90±0.08	1.1	9
control	(18.60±0.06)	(8.60±0.05)	(4.80±0.02)	(2.20±0.06)	2.1	2.6
Pb site	40.30±0.03	34.30±0.02	34.50±0.04	42.30±0.06	0.9	1.1
control	(26.90±0.06)	(24.40±0.05)	(21.60±0.06)	(29.00±0.02)	0.8	1.2
Zn site	99.31±0.10	34.36±0.04	29.76±0.02	25.58±0.06	2.1	2.2
control	(30.30±0.04)	(20.20±0.07)	(15.90±0.04)	(16.30±0.07)	1.4	1.6

Appendix XLVII: Concentration of Metals (mg/kg) in Different Parts of *Ricinus communis* (Castor Oil) Plant and Soil, Bioaccumulation and Transfer Factors at Hanwa after Application of EDTA

	Leaves	Stems	Roots	Soil	BF	TF
Cd site	3.40±0.01	3.10±0.02	3.10±0.01	1.90±0.00	1.7	1.1
control	(2.40±0.01)	(1.90±0.02)	(1.50±0.01)	(0.70±0.02)	1.3	2.3
Co site	11.60±0.03	12.40±0.02	11.90±0.01	8.70±0.03	1.4	1.1
control	(3.90±0.04)	(9.40±0.07)	(2.60±0.05)	(6.40±0.03)	0.8	3.6
Cu site	12.70±0.01	3.20±0.03	7.90±0.01	3.80±0.05	2.1	1.1
control	(8.20±0.02)	(2.80±0.04)	(1.60±0.04)	(0.1±0.02)	4.2	3.4
Ni site	85.60±0.02	10.80±0.06	24.10±0.07	42.10±0.04	0.9	2
control	(9.00±0.08)	(7.50±0.04)	(2.70±0.06)	(2.40±0.01)	1.7	3.1
Pb site	45.60±0.02	40.10±0.04	42.50±0.01	42.30±0.06	1.1	1.3
control	(41.60±0.01)	(28.00±0.02)	(32.40±0.04)	(36.70±0.02)	0.9	1.1
Zn site	41.73±0.06	30.28±0.02	31.19±0.04	20.49±0.03	1.7	1.2
control	(29.98±0.06)	(20.29±0.05)	(13.43±0.00)	(17.16±0.04)	1.2	1.9

Appendix XLVIII: Bioaccumulation and Transfer Factors for the Studied Metals in Different Plant Species at Hanwa with EDTA

		V.zizanioide	*C.citratus*	*H.annus*	*I.asarifolia*	*R.communis*
Cd	BF	1.1	1.8	1.6	1.2	1.7
	TF	1.1	1.1	1.1	0.8	1.1
Co	BF	1.1	1.2	1.3	0.5	1.4
	TF	1.2	1.3	1.5	1.4	1.1
Cu	BF	1.8	1.9	5.8	4.4	2.1
	TF	1.1	1.6	1.7	1.8	1.3
Ni	BF	0.8	1.6	2.9	2.1	0.9
	TF	1.2	1.3	6.4	1.4	2.0
Pb	BF	0.7	1.5	1.3	0.9	1.1
	TF	1.1	1.1	2.0	1.1	1.3
Zn	BF	2.4	2.2	3.8	2.1	1.7
	TF	2.8	2.8	2.3	2.2	1.2

Appendix XLIX: Mean Concentration of Metals (mg/kg) in the Soils at the Three Study Areas and Control after Harvesting of Plants without EDTA Appliction

	Cd	Co	Cu	Ni	Pb	Zn
Dakace	3.80±0.02	8.25±0.04	3.62±0.03	5.95±0.08	60.27±0.02	40.30±0.04
Gaskiya	3.80±0.01	8.35±0.04	4.00±0.04	25.72±0.04	59.80±0.01	23.95±0.02
Hanwa	3.80±0.03	8.60±0.04	4.01±0.05	38.10±0.06	63.53±0.06	21.17±0.03
Control	1.00±0.02	3.10±0.04	1.37±0.02	4.00±0.06	16.9±0.03	12.06±0.02

Appendix L: Mean Concentration of Metals (mg/kg) at the Three Study Areas and Control after Harvesting of Plants after EDTA Appliction

	Cd	Co	Cu	Ni	Pb	Zn
Dakace	2.38±0.03	8.20±0.04	1.92±0.03	5.20±0.01	42.75±0.08	35.84±0.05
Gaskiya	2.66±0.02	8.00±0.04	2.10±0.01	8.10±0.04	54.70±0.01	20.25±0.02
Hanwa	2.42±0.03	8.50±0.03	3.80±0.04	29.42±0.03	44.50±0.05	20.49±0.01
Control	0.70±0.02	2.10±0.01	1.09±0.02	2.40±0.01	14.00±0.04	11.06±0.01

Appendix LI: Mean Concentration of Metals (mg/kg) in Soils at the Test and Control Sites before Planting and after Harvest with and without Application of EDTA

	Cd	Co	Cu	Ni	Pb	Zn
Dakace BP	8.00±0.03	8.30±0.04	6.50±0.03	51.30±0.04	69.30±0.04	55.93±0.11
Dakace AH	3.80±0.02	8.25±0.04	3.62±0.03	5.95±0.08	60.27±0.02	40.30±0.04
Dakace EDTA	2.38±0.03	8.20±0.04	1.92±0.03	5.20±0.01	42.75±0.08	35.84±0.05
Gaskiya BP	7.00±0.02	9.90±0.05	5.30±0.03	84.93±0.07	75.90±0.04	28.90±0.12
Gaskiya AH	3.80±0.01	8.35±0.04	4.00±0.04	25.72±0.04	59.80±0.01	23.95±0.02
Gaskiya EDTA	2.66±0.02	8.00±0.04	2.10±0.01	8.10±0.04	54.70±0.01	20.25±0.02
Hanwa BP	6.00±0.02	8.70±0.05	5.60±0.05	47.90±0.06	76.90±0.05	25.58±0.06
Hanwa AH	3.80±0.03	8.60±0.04	4.01±0.05	38.1±0.06	63.53±0.06	21.17±0.03
Hanwa EDTA	2.42±0.03	8.5±0.03	3.80±0.04	29.42±0.03	44.50±0.05	20.49±0.01
Control BP	1.87±0.01	7.37±0.04	2.49±0.03	6.50±0.02	18.23±0.03	23.95±0.08
Control AH	1.00±0.02	3.10±0.04	1.37±0.02	4.00±0.06	16.90±0.03	12.06±0.02
Control EDTA	0.70±0.02	2.10±0.01	1.09±0.02	2.40±0.01	14.00±0.04	11.06±0.01

Appendix LII: Percentage Removal of Metal at the Three Study Areas and Control with and without Application of EDTA

	Dakace	Gaskiya	Hanwa	Control
Cd-natural	52.5	45.7	36.7	46.5
Cd-EDTA	70.3	62	59.7	62.6
Co-natural	0.6	15.7	1.2	57.9
Co-EDTA	1.2	19.2	2.3	71.5
Cu-natural	44.3	24.5	28.4	45
Cu-EDTA	70.5	60.4	32.1	56.2
Ni-natural	88.4	69.7	20.5	38.5
Ni-EDTA	89.9	90.5	35.6	63.1
Pb-natural	13	21.2	17.4	7.3
Pb-EDTA	38.3	27.9	42.1	23.2
Zn-natural	28	17.1	17.2	49.6
Zn-EDTA	36	29.1	19.9	53.8

Appendix LIII: The Nemero Pollution Index Method for Soils at Dakace, Gaskiya, Hanwa and Control after Harvest without EDTA

	Dakace	Gaskiya	Hanwa	Control
Cd	0.80	0.80	0.80	0.21
Co	1.0	1.1	1.1	0.40
Cu	0.13	0.13	0.13	0.05
Ni	0.15	0.64	0.95	0.01
Pb	6.28	6.0	6.42	1.7
Zn	0.45	0.27	0.14	0.13

Appendix LIV: The Nemero Pollution Index Method for Soils at Dakace, Gaskiya, Hanwa and Control after Application of EDTA

	Dakace	Gaskiya	Hanwa	Control
Cd	0.48	0.53	0.48	0.14
Co	1.00	1.00	1.10	0.26
Cu	0.06	0.07	0.13	0.04
Ni	0.13	0.20	0.74	0.01
Pb	4.28	5.47	4.45	1.40
Zn	0.4	0.23	0.13	0.12

Appendix LV: The Pearson Correlations Matrix of the Physico-chemical Parameters and the Metals at Three Study Areas

	pH	OM	CEC	Cl^-	PO_4^{3-}	NO_3^-	SO_4^{2-}	Cd	Co	Cu	Ni	Pb	Zn
pH	1												
OM	0.474	1											
CEC	0.572	0.820*	1										
Cl^-	0.635	0.644	0.927**	1									
PO_4^{3-}	0.049	0.275	-0.300	-0.465	1								
NO_3^-	0.393	0.330	0.805	0.821*	-0.767	1							
SO_4^{2-}	-0.049	0.342	0.633	0.698	-0.659	0.660	1						
Cd	-0.117	-0.553	-0.553	-0.556	0.141	-0.277	-0.785	1					
Co	0.150	-0.126	0.048	0.393	-0.356	0.082	0.434	-0.346	1				
Cu	0.710	-0.125	0.015	0.149	0.025	0.123	-0.519	0.578	0.092	1			
Ni	0.251	0.433	0.386	0.555	-0.035	0.074	0.605	-0.809	0.759	-0.251	1		
Pb	-0.018	0.028	0.475	0.514	-0.816*	0.740	0.817*	-0.570	0.156	-0.363	0.210	1	
Zn	0.231	0.011	-0.414	-0.532	0.873*	-0.679	-0.912*	0.492	-0.438	0.426	-0.347	-0.842*	1

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

**. Correlation is significant at the 0.01 level (2-tailed).

Appendix LVI : One-Way ANOVA for Metals at Dakace and the Control Sites

		Sum of Squares	df	Mean Square	F	Sig.
Cd	Between Groups	56.427	1	56.427	112.478	0.000
	Within Groups	2.007	4	0.502		
	Total	58.433	5			
Co	Between Groups	1.500	1	1.500	1.625	0.271
	Within Groups	3.693	4	0.923		
	Total	5.193	5			
Cu	Between Groups	12.995	1	12.995	2.400	0.046
	Within Groups	21.657	4	5.414		
	Total	34.652	5			
Ni	Between Groups	3257.340	1	3257.340	23.419	0.008
	Within Groups	556.360	4	139.090		
	Total	3813.700	5			
Pb	Between Groups	1925.683	1	1925.683	316.654	0.000
	Within Groups	24.325	4	6.081		
	Total	1950.009	5			
Zn	Between Groups	1534.720	1	1534.720	20.837	0.010
	Within Groups	294.614	4	73.653		
	Total	1829.334	5			

Appendix LVII: One-Way ANOVA for Metals at Gaskiya and the Control Sites

		Sum of Squares	df	Mean Square	F	Sig.
Cd	Between Groups	39.527	1	39.527	78.791	0.001
	Within Groups	2.007	4	0.502		
	Total	41.533	5			
Co	Between Groups	9.627	1	9.627	2.699	0.176
	Within Groups	14.267	4	3.567		
	Total	23.893	5			
Cu	Between Groups	11.016	1	11.016	3.301	0.014
	Within Groups	13.350	4	3.338		
	Total	24.367	5			
Ni	Between Groups	9704.282	1	9704.282	3.612	0.010
	Within Groups	10747.827	4	2686.957		
	Total	20452.108	5			
Pb	Between Groups	2700.457	1	2700.457	3064.001	0.000
	Within Groups	3.525	4	0.881		
	Total	2703.983	5			
Zn	Between Groups	16.534	1	16.534	0.582	0.048
	Within Groups	113.614	4	28.403		
	Total	130.148	5			

Appendix LVIII: One-Way ANOVA for Metals at Hanwa and the Control Sites

		Sum of Squares	df	Mean Square	F	Sig.
Cd	Between Groups	25.627	1	25.627	2.697	0.016
	Within Groups	38.007	4	9.502		
	Total	63.633	5			
Co	Between Groups	2.667	1	2.667	0.684	0.455
	Within Groups	15.587	4	3.897		
	Total	18.253	5			
Cu	Between Groups	14.539	1	14.539	4.233	0.011
	Within Groups	13.738	4	3.435		
	Total	28.278	5			
Ni	Between Groups	2825.340	1	2825.340	1565.285	0.000
	Within Groups	7.220	4	1.805		
	Total	2832.560	5			
Pb	Between Groups	2829.247	1	2829.247	274.382	0.000
	Within Groups	41.245	4	10.311		
	Total	2870.493	5			
Zn	Between Groups	87.707	1	87.707	2.819	0.017
	Within Groups	124.467	4	31.117		
	Total	212.175	5			

Appendix LIX: One- Way ANOVA for *V. zizanioide* Plant and Soil on Non-treated Soil

		Sum of Squares	df	Mean Square	F	Sig.
Cd	Between Groups	7.531	5	1.506	32.714	0.000
	Within Groups	0.276	6	0.046		
	Total	7.807	11			
Co	Between Groups	23.114	5	4.623	59.809	0.000
	Within Groups	0.464	6	0.077		
	Total	23.577	11			
Cu	Between Groups	3.413	5	0.683	3.183	0.096
	Within Groups	1.287	6	0.214		
	Total	4.700	11			
Ni	Between Groups	1616.255	5	323.251	1011.239	0.000
	Within Groups	1.918	6	0.320		
	Total	1618.172	11			
Pb	Between Groups	650.148	5	130.030	27.032	0.000
	Within Groups	28.861	6	4.810		
	Total	679.009	11			
Zn	Between Groups	991.609	5	198.322	2.185	0.184
	Within Groups	544.585	6	90.764		
	Total	1536.194	11			

Appendix LX: One -Way ANOVA for *C. citratus* Plant and Soil on Non-treated Soil

		Sum of Squares	df	Mean Square	F	Sig.
Cd	Between Groups	5.034	5	1.007	64.429	0.000
	Within Groups	.094	6	0.016		
	Total	5.127	11			
Co	Between Groups	20.059	5	4.012	243.749	0.000
	Within Groups	.099	6	0.016		
	Total	20.157	11			
Cu	Between Groups	7.604	5	1.521	2.057	0.203
	Within Groups	4.437	6	0.739		
	Total	12.041	11			
Ni	Between Groups	1766.209	5	353.242	1017.524	0.000
	Within Groups	2.083	6	0.347		
	Total	1768.292	11			
Pb	Between Groups	942.025	5	188.405	225.134	0.000
	Within Groups	5.021	6	0.837		
	Total	947.046	11			
Zn	Between Groups	1125.160	5	225.032	7.288	0.016
	Within Groups	185.257	6	30.876		
	Total	1310.417	11			

Appendix LXI: One- Way ANOVA for *H. annus* Plant and Soil on Non-treated Soil

		Sum of Squares	df	Mean Square	F	Sig.
Cd	Between Groups	4.578	5	0.916	33.671	0.000
	Within Groups	0.163	6	0.027		
	Total	4.741	11			
Co	Between Groups	68.792	5	13.758	171.568	0.000
	Within Groups	0.481	6	0.080		
	Total	69.273	11			
Cu	Between Groups	307.522	5	61.504	2.756	0.125
	Within Groups	133.893	6	22.315		
	Total	441.415	11			
Ni	Between Groups	1620.339	5	324.068	193.259	0.000
	Within Groups	10.061	6	1.677		
	Total	1630.400	11			
Pb	Between Groups	1542.883	5	308.577	6.325	0.022
	Within Groups	292.716	6	48.786		
	Total	1835.600	11			
Zn	Between Groups	3739.640	5	747.928	11.590	0.005
	Within Groups	387.195	6	64.532		
	Total	4126.835	11			

Appendix LXII: One -Way ANOVA for *I. asarifolia* Plant and Soil on Non-treated Soil

		Sum of Squares	df	Mean Square	F	Sig.
Cd	Between Groups	10.835	5	2.167	67.313	0.000
	Within Groups	0.193	6	0.032		
	Total	11.028	11			
Co	Between Groups	55.525	5	11.105	100.008	0.000
	Within Groups	0.666	6	.111		
	Total	56.191	11			
Cu	Between Groups	94.120	5	18.824	4.858	0.040
	Within Groups	23.247	6	3.874		
	Total	117.367	11			
Ni	Between Groups	2355.002	5	471.000	0.784	0.596
	Within Groups	3603.203	6	600.534		
	Total	5958.205	11			
Pb	Between Groups	1792.292	5	358.458	850.553	0.000
	Within Groups	2.529	6	.421		
	Total	1794.821	11			
Zn	Between Groups	470.256	5	94.051	4.666	0.044
	Within Groups	120.939	6	20.156		
	Total	591.195	11			

Appendix LXIII: One- Way ANOVA for *R. communis* Plant and Soil on Non-treated Soil

		Sum of Squares	df	Mean Square	F	Sig.
Cd	Between Groups	7.356	5	1.471	260.775	0.000
	Within Groups	.034	6	0.006		
	Total	7.390	11			
Co	Between Groups	19.988	5	3.998	10.993	0.006
	Within Groups	2.182	6	0.364		
	Total	22.170	11			
Cu	Between Groups	14.078	5	2.816	14.087	0.003
	Within Groups	1.199	6	0.200		
	Total	15.277	11			
Ni	Between Groups	1547.807	5	309.561	690.895	0.000
	Within Groups	2.688	6	0.448		
	Total	1550.496	11			
Pb	Between Groups	4638.910	5	927.782	1946.226	0.000
	Within Groups	2.860	6	0.477		
	Total	4641.771	11			
Zn	Between Groups	618.574	5	123.715	16.587	0.002
	Within Groups	44.752	6	7.459		
	Total	663.326	11			

Appendix LXIV: One- Way ANOVA for *V. zizanioide* Plant and Soil on EDTA Treated Soil

		Sum of Squares	df	Mean Square	F	Sig.
Cd	Between Groups	3.266	5	0.653	7.970	0.013
	Within Groups	0.492	6	0.082		
	Total	3.758	11			
Co	Between Groups	49.625	5	9.925	1.478	0.321
	Within Groups	40.285	6	6.714		
	Total	89.910	11			
Cu	Between Groups	84.838	5	16.968	5.009	0.037
	Within Groups	20.325	6	3.388		
	Total	105.164	11			
Ni	Between Groups	4893.120	5	978.624	7.554	0.014
	Within Groups	777.262	6	129.544		
	Total	5670.382	11			
Pb	Between Groups	263.879	5	52.776	5.460	0.031
	Within Groups	57.994	6	9.666		
	Total	321.872	11			
Zn	Between Groups	3849.474	5	769.895	14.327	0.003
	Within Groups	322.414	6	53.736		
	Total	4171.888	11			

Appendix LXV: One-Way ANOVA for *C. citratus* Plant and Soil on EDTA Treated Soil

		Sum of Squares	df	Mean Square	F	Sig.
Cd	Between Groups	5.187	5	1.037	3.951	0.026
	Within Groups	1.575	6	0.263		
	Total	6.762	11			
Co	Between Groups	72.282	5	14.456	3.738	0.007
	Within Groups	23.205	6	3.868		
	Total	95.487	11			
Cu	Between Groups	106.613	5	21.323	24.505	0.001
	Within Groups	5.221	6	0.870		
	Total	111.833	11			
Ni	Between Groups	38898.611	5	7779.722	2.283	0.172
	Within Groups	20441.974	6	3406.996		
	Total	59340.585	11			
Pb	Between Groups	988.211	5	197.642	84.365	0.000
	Within Groups	14.056	6	2.343		
	Total	1002.267	11			
Zn	Between Groups	1990.664	5	398.133	3.568	0.008
	Within Groups	669.504	6	111.584		
	Total	2660.168	11			

AppendixLXVI: One-Way ANOVA for *H. annus* Plant and Soil on EDTA Treated Soil

		Sum of Squares	df	Mean Square	F	Sig.
Cd	Between Groups	0.894	5	0.179	1.239	0.395
	Within Groups	0.866	6	0.144		
	Total	1.760	11			
Co	Between Groups	21.220	5	4.244	11.396	0.005
	Within Groups	2.234	6	0.372		
	Total	23.455	11			
Cu	Between Groups	683.086	5	136.617	19.813	0.001
	Within Groups	41.371	6	6.895		
	Total	724.457	11			
Ni	Between Groups	15022.018	5	3004.404	4.161	0.050
	Within Groups	4331.889	6	721.982		
	Total	19353.907	11			
Pb	Between Groups	234.227	5	46.845	2.894	0.114
	Within Groups	97.131	6	16.189		
	Total	331.358	11			
Zn	Between Groups	8661.687	5	1732.337	10.198	0.007
	Within Groups	1019.194	6	169.866		
	Total	9680.881	11			

Appendix LXVII: One-Way ANOVA for *I. asarifolia* Plant and Soil on EDTA Treated Soil

		Sum of Squares	df	Mean Square	F	Sig.
Cd	Between Groups	7.382	5	1.476	12.300	0.004
	Within Groups	0.720	6	0.120		
	Total	8.102	11			
Co	Between Groups	14.356	5	2.871	0.988	0.495
	Within Groups	17.436	6	2.906		
	Total	31.792	11			
Cu	Between Groups	545.413	5	109.083	306.908	0.001
	Within Groups	2.133	6	0.355		
	Total	547.546	11			
Ni	Between Groups	23771.317	5	4754.263	1.955	0.219
	Within Groups	14592.132	6	2432.022		
	Total	38363.449	11			
Pb	Between Groups	508.924	5	101.785	65.058	0.001
	Within Groups	9.387	6	1.565		
	Total	518.311	11			
Zn	Between Groups	4352.873	5	870.575	3.942	0.063
	Within Groups	1325.028	6	220.838		
	Total	5677.900	11			

Appendix LXVIII: One-Way ANOVA for *R. communis* Plant and Soil on EDTA Treated Soil

		Sum of Squares	df	Mean Square	F	Sig.
Cd	Between Groups	1.358	5	0.272	3.628	0.074
	Within Groups	0.449	6	0.075		
	Total	1.807	11			
Co	Between Groups	49.068	5	9.814	69.591	0.001
	Within Groups	0.846	6	0.141		
	Total	49.914	11			
Cu	Between Groups	136.047	5	27.209	38.254	0.001
	Within Groups	4.268	6	0.711		
	Total	140.315	11			
Ni	Between Groups	19020.176	5	3804.035	4.250	0.050
	Within Groups	5370.329	6	895.055		
	Total	24390.505	11			
Pb	Between Groups	189.500	5	37.900	36.838	0.001
	Within Groups	6.173	6	1.029		
	Total	195.673	11			
Zn	Between Groups	1157.066	5	231.413	18.781	0.001
	Within Groups	73.930	6	12.322		
	Total	1230.996	11			

Appendix LXIX: Publications

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2015; 3(1): 1-5
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Phytoextraction of heavy metals by *Vetivera zizanioide, Cymbopogon citratus and Helianthus annuls*

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Abstract: The research work under field conditions is to investigate the connection between the heavy metals concentration in soil and their bioaccumulation in *Vetivera zizanioide, Cymbopogon citratus* (Lemon grass) and *Helianthus annuls* (sunflower) collected from test site and a control area in Zaria-Nigeria. The collection was done by dividing the test and control sites each into four quadrants, five plants samples of each speciess and soil samples were collected from each quadrant in a diagonal basis. The concentrations of Cd, Co, Cu, Ni, Pb and Zn in different parts of each of the plant speciess collected from the test and control soils were determined using atomic absorption spectrophotometry. The test levels of the metals were higher ($P \leq 0.05$) than those at the control site and the limits recommended by Food and Agricultural Organisation/World Health Organisation (FAO/WHO). The heavy metal concentrations were higher in leaves ($P \leq 0.05$) than in roots of the plants tested. *Vetivera zizanioide* showed the bioaccumulation factor (BF) and translocation factor (TF) values for the studied metals greater than 1 (except Co and Pb that had their BF less than 1). *Cymbopogon citratus* showed BF values of Cd, Ni and Pb were greater than 1, but TF of all the metals studied were greater than 1. *Helianthus annus* plant had BF values for Cd, Cu and Zn greater than 1, but TF values for all the metals studied were greater than 1. This indicated that *Vetivera zizanioide, Cymbopogon citratus* and *Helianthus annuls* have good phytoextraction potentials for the removal of heavy metals from contaminated soils.
Keywords: *Vetivera Zizanioide, Cymbopogon Citratus, Helianthus Annuls,* Bioaccumulation Factor, Translocation Factor, Phytoextraction

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The effect of application of EDTA on the phytoextraction of heavy metals by *Vetivera zizanioide, Cymbopogon citratus* and *Helianthus annuls*

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Abstract: This study investigates the effect of the application of EDTA (ethylenediamine-tetraacetic acid) on the phytoextraction of Cd, Co, Cu, Ni, Pb, and Zn by *Vetivera zizanioide, Cymbopogon citratus* and *Helianthus annuls* harvested from test site (with EDTA) and a control area (without EDTA) in Zaria-Nigeria. The concentrations of Cd, Co, Cu, Ni, Pb, and Zn in different parts of each of the plant speciess collected from the test and control soils were determined using atomic absorption spectrophotometry. Application of 5 mmol/kg EDTA in soil did not affect plant growth but significantly increased Cd, Co, Cu, Ni, Pb, and Zn concentrations in shoots and roots of the plants. The concentrations of heavy metals measured in the tissues of plants collected from the test site were higher ($P \leq 0.05$) than in the control. The percentage increase in the metal concentration for each plant species were:- for *Vetivera zizanioide,* Cd – 75%, Co – 205%, Cu– 190%, Ni – 645%, Pb – 5% and Zn – 29%; for *Cymbopogon citratus,* Cd – 100%, Co – 109%, Cu – 551%, Ni – 907%, Pb – 39% and Zn – 50%; for *Helianthus annuls,* Cd – 21%, Co – 235%, Cu – 44%, Ni – 507%, Pb – 70% and Zn – 02%. The heavy metal concentrations were higher in leaves ($P \leq 0.05$) than in roots of the plants. The translocation factor (TF) for all the metals studied were greater than 1.The results of this study demonstrated that EDTA is an efficient soil amendment in enhancing desorption of Cd, Co, Cu, Ni, Pb, and Zn from soil and in increasing their accumulation in plants. As for plant speciess tested, the effectiveness in the uptake of the metals studied was *Helianthus annuls* < *Vetivera zizanioide* < *Cymbopogon citratus*.

Keywords: Vetivera *Zizanioide, Cymbopogon Citratus, Helianthus Annuls*, EDTA, Translocation Factor, Phytoextraction

Appendix LXX: Texture Triangle

