

**KWAME NKRUMAH UNIVERSITY OF SCIENCE AND
TECHNOLOGY, KUMASI**

**DEPARTMENT OF ENVIRONMENTAL SCIENCE
COLLEGE OF SCIENCE**

**HEAVY METAL ACCUMULATION IN WASTEWATER IRRIGATED SOIL AND
LETTUCE (*Lactuca sativa*) AT DZORWULU AND AIRPORT RESIDENTIAL AREA IN
ACCRA**

BY:

DIVINE ADDO

MAY, 2014

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LETTUCE (*Lactuca sativa*) AT DZORWULU AND AIRPORT RESIDENTIAL AREA IN
ACCRA**

By:

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**A Thesis submitted to the Department of Environmental Science, Kwame Nkrumah
University of Science and Technology, in partial fulfillment of the requirements for the
award of the degree
of**

MASTER OF SCIENCE (ENVIRONMENTAL SCIENCE)

MAY, 2014

DECLARATION

The report presented in this thesis is the result of the research carried out by the Author.

This thesis has not been submitted in whatever form to any other institution, organization or body for the award of any degree. All inclusions from the work of others have been duly acknowledged.

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DEDICATION

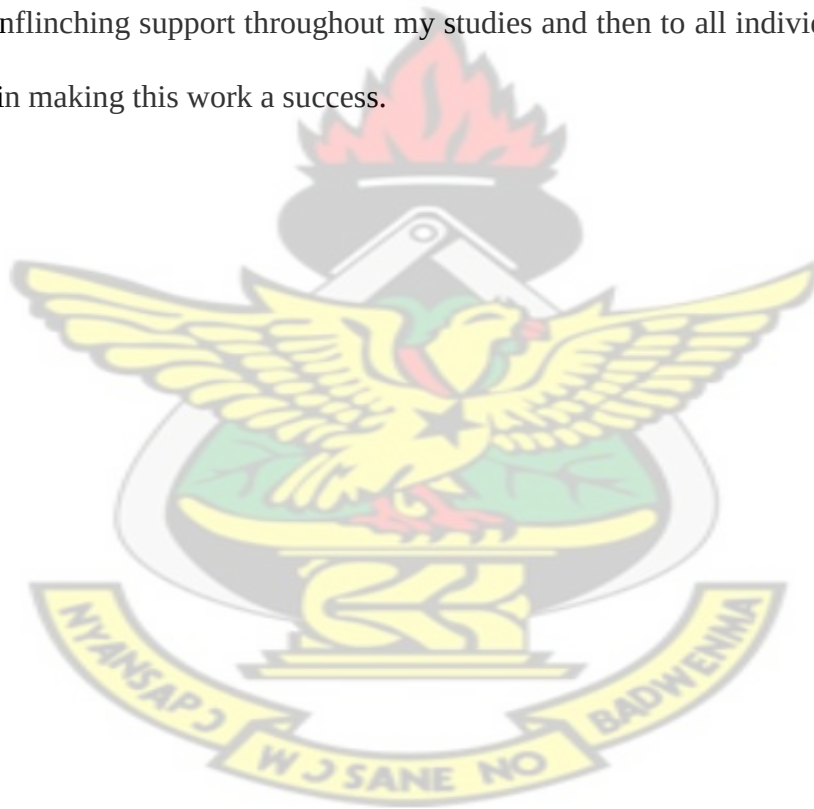
I dedicate this work to my wife Josephine Sarpong and to my parents

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I am most grateful to the Almighty God for his strength and protection throughout my entire study. I am also indebted to my supervisor, Mr Osei Akoto for his immense assistance and directions throughout this study. Many special thanks also go to Mr Frank Owusu Ansah, Biometrician of CRIG for his patience, and sacrifice in making this work a reality. I am also grateful to the Technical staff of soil science division of CRIG for their support. My appreciation also goes to my parents Justice Addo and Lucy Akubia as well as my sister Regina Mawuena Addo for their unflinching support throughout my studies and then to all individuals who helped in diverse ways in making this work a success.



ABSTRACT

Heavy metal contamination of agricultural soils due to human activities is a major concern globally. In this work, heavy metals accumulation in wastewater irrigated soil and lettuce at Dzorwulu and Airport residential area in Accra were investigated. Ten (10) soil samples were taken from each site. Soil properties such as pH, electrical conductivity (EC), organic carbon, cation exchange capacity (CEC) and heavy metals content were determined using standard procedures. Lettuce samples from the farms were analysed for heavy metals. The soils were found to be sandy clay loam and sandy loamy in texture and moderately to slightly alkaline. The organic carbon contents were found to be relatively low (0.90 ± 0.06 and 1.18 ± 0.02) for Dzorwulu and Airport residential area respectively. The mean CEC ranged between 1.58 ± 0.03 and 1.75 ± 0.04 for Airport residential area and Dzorwulu samples respectively. The soil EC result indicated low salt accumulations at both sites. The sequence of heavy metal levels in the soil samples from Airport residential area was in the order $Zn > Pb > Cu > Ni > Cd > Cr$ whilst that of Dzorwulu was in the order $Zn > Pb > Cu > Ni > Cr > Cd$. The Enrichment Factor results for soil samples from Dzorwulu showed minimal enrichment for Zn, Cu and Cr while Pb, Ni and Cd showed no enrichment. However, Pb, Cu and Zn were significantly enriched in the soils from Airport residential area. Geo-accumulation index (Igeo) values showed that soil from the Airport sites were not contaminated with Cr (-0.585), Ni (-0.327) and Cd (-0.524) but slightly contaminated with Cu and Zn. There was moderate contamination from Pb (Igeo 1.100). The Igeo values for Dzorwulu samples showed moderate contamination from Cd, but not from Ni. Results of degree of translocation of these metals by the plants from both sites showed a translocation factor (TF) > 1 for Zn in lettuce samples from Dzorwulu. Heavy metals concentration in the lettuce samples were above the FAO/WHO recommended levels. Overall,

the soils from both sides can be described as ranging from unpolluted to moderately polluted. The concentrations of metals in the lettuce indicate the abilities of the lettuce to uptake and accumulate metals from the soil on which it was grown. The levels of these heavy metals might place the consumers of this crop grown on such soils at a health risk with time.

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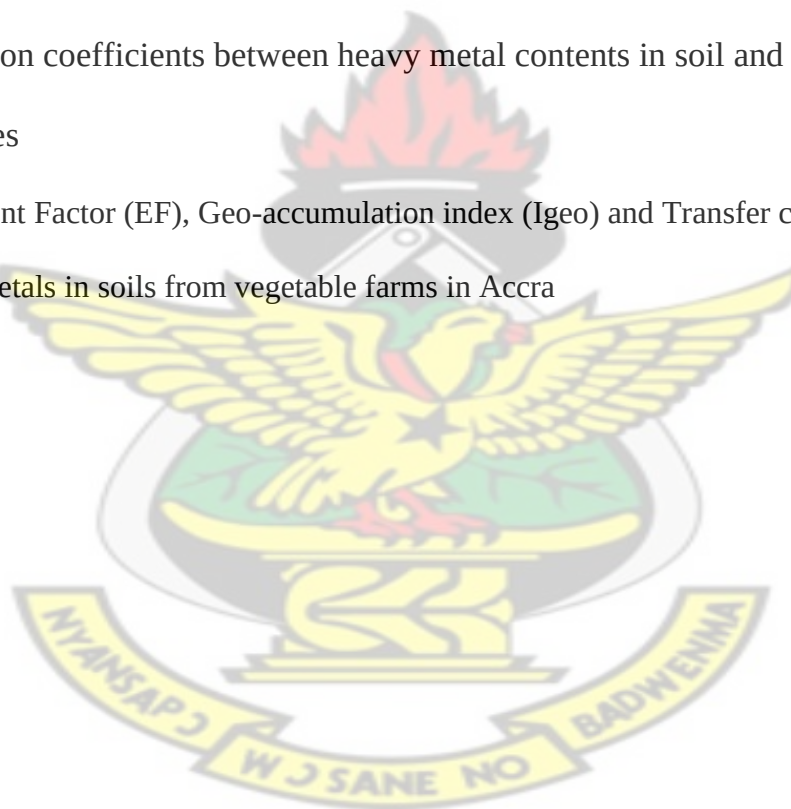
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CHAPTER ONE

1.0 Introduction

The use of urban wastewater for irrigation has been going on for a long time now and the major driving forces of this practice include water scarcity, easy availability and wastewater as a source of plant nutrients (Carr, 2003). In many semi-arid and arid regions of the world, fresh surface water is usually only available in sufficient quantities during the rainy season. Water for irrigation is required for the long dry season. Groundwater may be expensive to access because of low water tables that translate into the high costs associated with drilling wells and pumping the water (Cofie *et al.*, 2004).

Irrigation with urban wastewater in and around cities in many developing countries is a wide spread reality (Bradford *et al.*, 2003) and the city of Accra in Ghana is not an exception. An average of 280 million m³ of wastewater is generated daily in the country and wastewater irrigated urban farming takes place in open spaces close to water sources. The practice of open space urban farming is intensive, all-year round and market-oriented.

Vegetables constitute essential components of diet for the provision of protein, vitamins, iron, calcium and other nutrients, which are usually in short supply (Thompson and Kelly, 1990). Vegetables also act as buffering agents for acidic substances obtained during the digestion process. A mixture of municipal and domestic wastewater is used for vegetable production in some parts of Accra. These water sources contain heavy metals which in certain concentrations can be toxic to consumers of produce cultivated using this wastewater. Living organisms require trace amounts of some heavy metals including copper, iron, manganese and zinc as are micronutrients which are necessary for proper physiological development. In appropriate

amounts, they are essential for plants, but their excessive quantities may cause some disturbances in development of plants and result in their depressed quality. Studies have shown that continuous use of wastewater containing heavy metals for crop production tends to accumulate these heavy metals in the soil and it becomes bioavailable to crops with time (Toze, 2004).

Vegetables, especially leafy crops grown in heavy metals contaminated soils, accumulate higher amounts of metals than those grown in uncontaminated soils because of the fact that they absorb these metals through their leaves (Al Jassir *et al.*, 2005).

Research shows that wastewater carries appreciable amount of heavy metals (Pescod, 1992). Household effluents, drainage water, business effluents, atmospheric deposition and traffic related emissions transported with storm water carry a number of pollutants that enrich the urban wastewater with heavy metals (Oliveira *et al.*, 2007).

The use of wastewater for irrigating agricultural lands in Ghana is on the increase particularly in peri-urban areas of Accra, Kumasi and Tamale (Agodzo *et al.*, 2002). From a general survey among open-space farmers carried out in 2002, it was found that about 84% of nearly 800 farmers farming in and close to Accra and almost all 700 farmers in Tamale used wastewater for irrigation, at least during the dry seasons (Agodzo *et al.*, 2002).

1.1 Statement of problem

Wastewater plays complementary role in vegetable cultivation; however, irrigation with untreated wastewater can represent a major threat to public health, food safety, and

environmental quality. Wastewater irrigation of vegetables and fodder may serve as the transmission route for heavy metals in the human food chain (Delgado *et al.*, 1999).

Intake of heavy metal-contaminated vegetables may pose a risk to the human health. This is because heavy metals have the ability to accumulate in living organisms and can be toxic at elevated levels. It has been reported that prolonged consumption of unsafe concentrations of heavy metals through foodstuffs may lead to the chronic accumulation of the metals in the kidney and liver of humans causing disruption of numerous biochemical processes, leading to cardiovascular, nervous, kidney and bone diseases (Trichopoulos, 1997; Jarup, 2003).

Continuous use of wastewater for irrigation also leads to an increase in heavy metal content of the soil which leads to increase in plant uptake and contamination of ground water as a result of leaching of heavy metals (Delgado *et al.*, 1999). Metals are persistent pollutants that can be biomagnified in the food chains becoming increasingly dangerous to human and wildlife. Assessing pollutants in different components of the ecosystem has become an important task in preventing risk to natural life and public health.

Heavy metal concentration in the soils is a major concern because of their toxicity and threat to human life and the environment. There is a growing concern about the possibility of soil contamination resulting in uptake by plants and the introduction of the elements in vital food chains affecting food safety. Thus, knowledge of buildup of metals in the soils of cultivated areas is important to recognize potential ecological problems.

Though heavy metal contamination of soil resulting from wastewater irrigation is a cause for serious concern due to the potential health impacts of consuming contaminated produce, little

work has been done to explore the impact this practice has on the concentration of heavy metal in soil and vegetable crops in Ghana.

1.2 Main Objectives

The overall objective of this work was to determine the levels of heavy metals in soils and lettuce irrigated with wastewater.

1.2.1 Specific objectives

- To determine the total concentrations of heavy metals (Cd, Cu, Zn, Pb, Ni and Cr) in soils irrigated with wastewater,
- To determine the levels of accumulation of heavy metals in lettuce grown on wastewater irrigated soil,
- To assess the translocation factor of heavy metals from soil to plant.

1.3 Justification

Urban vegetable production plays a significant role in reducing poverty, providing a significant source of income to farmers, while meeting the nutritional needs of the society. However, irrigation is a source of concern as many farmers prefer to irrigate their farms with untreated wastewater due to all year-round availability and other advantages. However, wastewater irrigation is largely unregulated in low-income countries, and the costs and benefits are poorly understood. Public health concerns increase as in some instances; vegetables produced are

consumed in the raw state. Therefore knowledge of heavy metal concentrations in soil and vegetables irrigated with wastewater is important in assessing the threat it poses to human health and the environment.

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CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Importance of urban agriculture

Urban agriculture is defined as food and fuel grown within the daily rhythm of the city or town produced directly for the market and frequently processed and marketed by the farmers or their close associates. It includes aquaculture, livestock, orchards, vegetables and other crops (Smit and Nasr, 1992).

Urban agriculture plays an important role in ensuring constant supply of staple crops and animal products within the proximity of urban spaces, thus, ensuring adequate family nutrition. It is used as a food security strategy by poor urban households. Urban agriculture also provides employment opportunity for educationally disadvantaged and unemployed youths in cities (Dreschsel *et al.*, 2007). It supports livelihoods and generates considerable value in urban and peri-urban agriculture. It also provides income for families and acts as a source of livelihood even though there are environmental and health risks associated with its use (van Veenhuizen *et al.*, 2007).



Figure 2.1 Urban farming in Accra

2.2 Use of waste water for urban agriculture

The practice of wastewater use in urban agriculture has been there for more than a century but the practice is receiving renewed attention due to the increasing scarcity of freshwater resources in many arid and semi-arid regions and the demand for food in the urban and peri urban areas (Scott *et al.*, 2004).

The increase in population in the urban areas has increased the amount of wastewater discharged and this has provided the water used for growing food crops, thus increasing the food supply in these urban areas (Brown, 2003). Irrigation of crops with wastewater is estimated to be 20 million hectares in developing countries. Farmers have been using untreated wastewater for

centuries, but greater numbers now depend on it for their livelihoods. The practice of using wastewater in farming is preferred because it requires minimum capital to start (Dreschsel *et al.*, 2002).

Wastewater can be classified as raw or untreated wastewater, which is the liquid discharge from households, commercial premises and from municipal sewers. Treated or partially treated wastewater is the wastewater that has been treated by a natural or artificial purification process to improve its physical, chemical or bacteriological quality before it is discharged for use. Industrial effluent is water discharged from industrial processes containing high levels of heavy metals or other chemicals or organic constituents (Cornish *et al.*, 1999).

Household wastewater derives from a number of sources (toilet, kitchen sink, dishwashers, bath washer, and clothes washer, miscellaneous). Wastewater from the toilet is termed 'blackwater'. It has a high content of solids and contributes a significant amount of nutrients (nitrogen and phosphorus). Blackwater can be further separated into faecal materials and urine. Greywater consists of water from washing of clothes, from bathing and from the kitchen. The latter may have a high content of solids and grease, and depending on its intended reuse, treatment or disposal, can be combined with toilet wastes and form the blackwater. Both greywater and blackwater may contain human pathogens, though concentrations are generally higher in blackwater. (Van der Hoek, 2004)

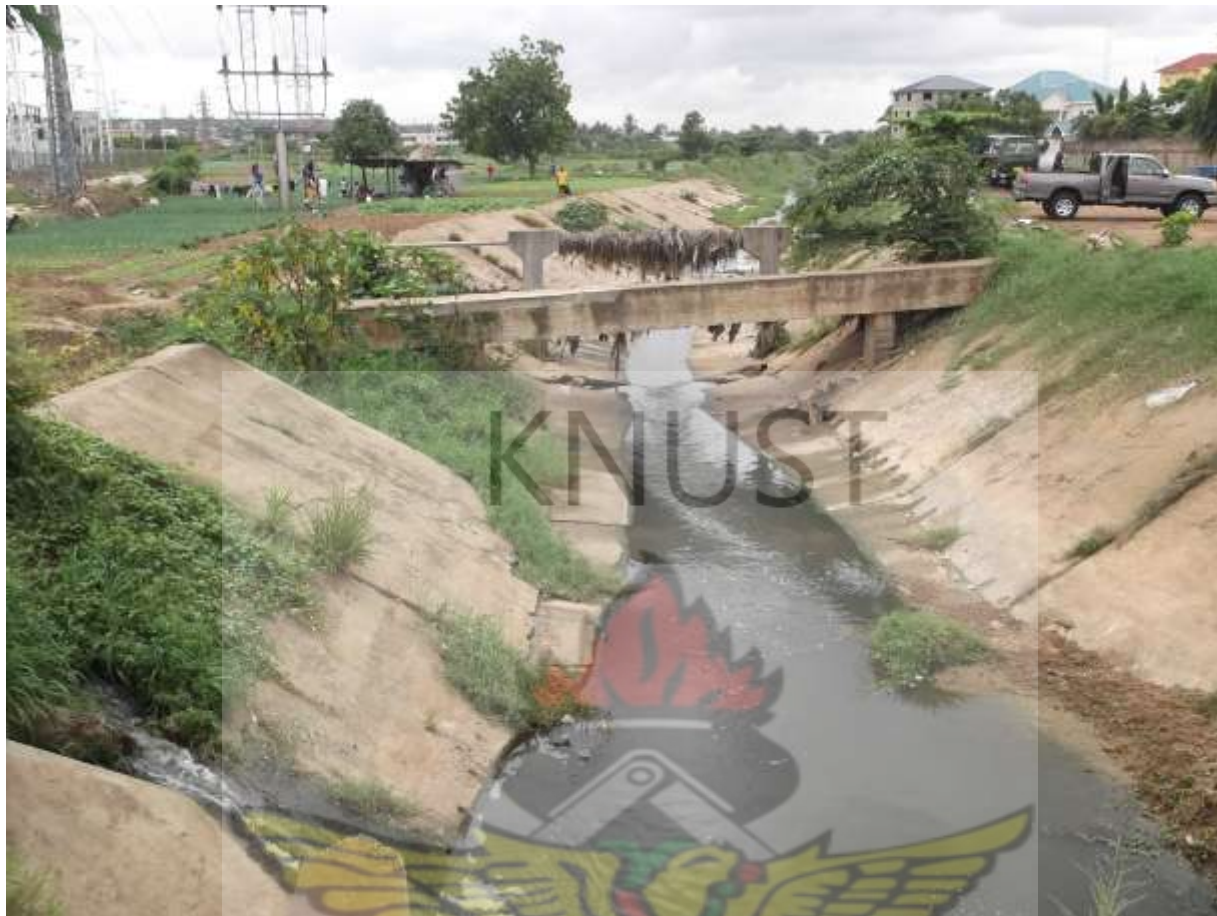


Figure 2.2 A polluted stream (Onyasia) used for irrigation at Dworwulu.

Wastewater irrigation plays a significant role in combating food shortages by supplying vegetables to meet the demand of the ever increasing population. Even though wastewater used for irrigation may well contain essential plant nutrients, it can also be a major source of heavy metal pollution for agricultural soils and its continuous use can have detrimental effects on the surrounding environment including people living around the irrigated gardens, the gardener and the eventual consumer (Ensink *et al.*, 2002; Van der Hoek *et al.*, 2002).



Figure 2.3 A polluted stream used for irrigation at Airport Residential area

2.3 Irrigation Method and Technologies Used

Obuobie *et al.* (2006) reported that watering cans, buckets, motorized pumps with hosepipe, surface irrigation methods are being used within urban Accra. The use of watering cans for irrigation was common in the two study sites visited (Figure 2.4).



Figure 2.4 Irrigation using watering cans

2.4 Risks associated with wastewater use

There are risks that are associated with wastewater use, and they include food grown using wastewater that may be contaminated with pathogenic organisms and disease vectors which are attracted by farming activities and are responsible for human diseases (Gombert, 1994). Heavy metals may also accumulate in soils and plants grown using wastewater. Hazardous materials from industrial waste and hospitals are also present in the wastewater and may also find themselves in the soils and plants when such wastewater is used to irrigate the crops. Wastewater has been linked to chronic health disorders such as diarrhea, cholera, typhoid and gastrointestinal diseases (Scott *et al.*, 2004). The use of wastewater for irrigation also leads to the risk of underground water pollution through leaching and sorption of heavy metals (Michel *et al.*,

2007). These health and environmental risks notwithstanding, wastewater is still being disposed of untreated into water ways (Lombi *et al.*, 2002).

2.5 Sources of heavy metals in contaminated soils

Soil is an essential natural resource for support of human life; but with time, its degradation has been constantly increasing due to the deposition of pollutants (Donahue *et al.*, 1983). The contamination of agricultural soils is often a direct or indirect consequence of anthropogenic activities (McLaughlin *et al.*, 1999).

The accumulation of heavy metals in agricultural soils is of increasing concern due to the food safety issues and potential health risks as well as its detrimental effects on soil ecosystems (McLaughlin *et al.*, 1999). Commercial and residential vegetable growing areas are often located in urban areas, and are subjected to anthropogenic contamination (Fernandez–Turiel *et al.*, 2001).

Heavy metals occur naturally in the soil environment from the pedogenetic processes of weathering of parent materials at levels that are regarded as *trace* ($<1000 \text{ mg kg}^{-1}$) and rarely toxic (Kabata-Pendias, 2001; Pierzynski *et al.*, 2000). Due to the disturbance of nature's slowly occurring geochemical cycle of metals by man, most soils of rural and urban environments may accumulate heavy metals above defined background values high enough to cause risks to human health, plants, animals, ecosystems, or other media (D'Amore *et al.*, 2005). The heavy metals essentially become contaminants in the soil environments because (i) their rates of generation via human activities are more rapid relative to natural ones, (ii) they become transferred from mines to random environmental locations where higher potentials of direct exposure occur, (iii) the

concentrations of the metals in discarded products are relatively high compared to those in the receiving environment, and (iv) the chemical form (species) in which a metal is found in the receiving environmental system may render it more bioavailable (D'Amore *et al.*, 2005).

Soils may become contaminated by the accumulation of heavy metals and metalloids through emissions from rapidly expanding industrial areas, mine tailings, leaded gasoline and paints, land application of fertilizers, animal manures, sewage sludge, pesticides, wastewater irrigation, coal combustion residues, spillage of petrochemicals, and atmospheric deposition (Khan *et al.*, 2008 ; Zhang *et al.*, 2010). 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). The major anthropogenic sources of heavy metals are discussed below.

2.5.1 Fertilizers: Historically, agriculture was the first major human influence on the soil (Scragg, 2006). To grow and complete the life cycle, plants must acquire not only macronutrients (N, P, K, S, Ca, and Mg), but also essential micronutrients. Some soils are deficient in heavy metals (such as Co, Cu, Fe, Mn, Mo, Ni, and Zn) that are essential for healthy plant growth (Lasat, 2000), and crops may be supplied with these as an addition to the soil or as a foliar spray. Large quantities of fertilizers are regularly added to soils in intensive farming systems to provide adequate nutrients for crop growth. The materials used to supply these nutrients contain trace amounts of heavy metals as impurities, which, after continued fertilizer, application may significantly increase their content in the soil (Jones and Jarvis, 1981). Metals, such as Cd and Pb, have no known physiological activity. Application of certain phosphatic fertilizers inadvertently adds Cd and other potentially toxic elements to the soil, including Hg, and Pb (Raven *et al.*, 1998).

2.5.2 Pesticides: Several common pesticides used fairly extensively in agriculture and horticulture in the past contained substantial concentrations of metals. For example, in the past decade, about 10% of the chemicals approved for use as insecticides and fungicides in UK were based on compounds which contain Cu, Hg, Mn, Pb, or Zn. Examples of such pesticides are copper-containing fungicidal sprays such as Bordeaux mixture (copper sulphate) and copper oxychloride (Jones and Jarvis, 1981). Lead arsenate was used in fruit orchards for many years to control some parasitic insects. Arsenic containing compounds were also used extensively to control cattle ticks and to control pests in banana in New Zealand and Australia, timbers have been preserved with formulations of Cu, Cr, and As and there are now many sites where soil concentrations of these elements greatly exceed background concentrations (McLaughlin *et al.*, 2007). Such contamination has the potential to cause problems, particularly if sites are redeveloped for other agricultural or nonagricultural purposes. Compared with fertilizers, the use of such materials has been more localized, being restricted to particular sites or crops (McLaughlin *et al.*, 2007).

2.5.3 Biosolids and Manures: The application of numerous biosolids (e.g., livestock manures, composts, and municipal sewage sludge) to land inadvertently leads to the accumulation of heavy metals in the soil (Basta *et al.*, 2005). Certain animal wastes such as poultry, cattle, and pig manures produced in agriculture are commonly applied to crops and pastures either as solids or slurries (Sumner, 2000). Although most manure are seen as valuable fertilizers, in the pig and poultry industry, the Cu and Zn added to diets as growth promoters and As contained in poultry health products may also have the potential to cause metal contamination of the soil (Chaney and Oliver, 1996). The manures produced from animals on such diets contain high concentrations of

As, Cu, and Zn and, if repeatedly applied to restricted areas of land, can cause considerable buildup of these metals in the soil in the long run.

Biosolids (sewage sludge) are primarily organic solid products, produced by wastewater treatment processes that can be beneficially recycled (USEPA, 1994). The potential of biosolids for contaminating soils with heavy metals has caused great concern about their application in agricultural practices (Canet *et al.*, 1998). Heavy metals most commonly found in biosolids are Pb, Ni, Cd, Cr, Cu, and Zn, and the metal concentrations are governed by the nature and the intensity of the industrial activity, as well as the type of process employed during the biosolids treatment (Mattigod and Page, 1983).

2.5.4 Wastewater: The application of municipal and industrial wastewater and related effluents to land dates back 400 years and now is a common practice in many parts of the world (Reed *et al.*, 1995). Worldwide, it is estimated that 20 million hectares of arable land are irrigated with waste water. In several Asian and African cities, studies suggest that agriculture based on wastewater irrigation accounts for 50 percent of the vegetable supply to urban areas (Bjuhr, 2007). Farmers generally are not bothered about environmental benefits or hazards and are primarily interested in maximizing their yields and profits. Although the metal concentrations in wastewater effluents are usually relatively low, long-term irrigation of land with such can eventually result in heavy metal accumulation in the soil (Reed *et al.*, 1995).

2.5.5 Mining and Industrial Wastes: Mining coupled with industries has passed on to many countries, the legacy of wide distribution of metal contaminants in soil. During mining, tailings are directly discharged into natural depressions, including onsite wetlands resulting in elevated

concentrations of heavy metals (DeVolder *et al.*, 2003). Extensive Pb and Zn ore mining and smelting have resulted in contamination of soil that poses risk to human and ecological health. Many reclamation methods used for these sites are lengthy and expensive and may not restore soil productivity. Soil heavy metal environmental risk to humans is related to bioavailability. Assimilation pathways of heavy metals include the ingestion of plant material grown in (food chain), or the direct ingestion of, contaminated soil (Basta and Gradwohl, 1998).

Other materials are generated by a variety of industries such as textile, tanning, petrochemicals from accidental oil spills or utilization of petroleum-based products, pesticides, and pharmaceutical facilities and are highly variable in composition (Sumner, 2000).

2.5.6 Air-Borne Sources: Airborne sources of metals include stack or duct emissions of air, gas, or vapor streams, and fugitive emissions such as dust from storage areas or waste piles (Smith *et al.*, 1995). Metals from airborne sources are generally released as particulates contained in the gas stream. Some metals such as As, Cd, and Pb can also volatilize during high-temperature processing. These metals will convert to oxides and condense as fine particulates unless a reducing atmosphere is maintained. Stack emissions can be distributed over a wide area by natural air currents until dry or wet precipitation mechanisms remove them from the gas stream. Fugitive emissions (pollutants released into air from leaks in equipment, pipe lines, seals, valves, etc., and not from the usual sources such chimneys, stacks, and vents.) are often distributed over a much smaller area because emissions are made near the ground. In general, contaminant concentrations are lower in fugitive emissions compared to stack emissions (Smith *et al.*, 1995).

The type and concentration of metals emitted from both types of sources will depend on site-specific conditions. All solid particles in smoke from fires and in other emissions from factory chimneys are eventually deposited on land or sea. Very high concentration of Cd, Pb, and Zn has been found in plants and soils adjacent to smelting works. Another major source of soil contamination is the aerial emission of Pb from the combustion of petrol containing tetraethyl lead; this contributes substantially to the content of Pb in soils in urban areas and in those adjacent to major roads. Zn and Cd may also be added to soils adjacent to roads, the sources being tyres, and lubricant oils (USEPA, 1996).

2.6 Factors affecting metal availability in soil

Plants cannot usually access the total pool of a metal present in the growth substrate. Instead, that fraction of the metal which plants can absorb is known as the available or bioavailable fraction (Norvell, 1991). Metals present in a soil can be divided into a number of fractions including; the soluble metal in the soil solution, metal-precipitates, metal sorbed to clays, hydrous oxides and organic matter, and metals within the matrix of soil minerals. These different fractions are all in dynamic equilibrium with each other (Norvell, 1991).

The fate and transport of a heavy metal in soil depends significantly on the chemical form and speciation of the metal. Once in the soil, heavy metals are adsorbed by initial fast reactions (minutes, hours), followed by slow adsorption reactions (days, years) and are, therefore, redistributed into different chemical forms with varying bioavailability, mobility, and toxicity (Shiowatana *et al.*, 2001; Buekers, 2007). Heavy metal distribution is believed to be controlled by reactions of heavy metals in soils such as (i) mineral precipitation and dissolution, (ii) ion

exchange, adsorption, and desorption, (iii) aqueous complexation, (iv) biological immobilization and mobilization, and (v) plant uptake (Levy *et al.*, 1992).

Organic matter is another soil component influencing the availability of heavy metals in soils through its binding effect on soil components (Naidu *et al.*, 2003) and presence of weak functional groups that dissociate under alkaline condition (Fine *et al.*, 2005). Metal ions can be complexed by organic matter altering their availability to plants. The COO⁻ groups in both solid and dissolved organic matter form stable complexes with metals. Hence, as the amount of organic matter present in soil increases the opportunity for forming stable metal-organic matter complexes increases. In general, plants are unable to absorb the large metal-complexes and so the bioavailability of metals decreases (Stevenson, 1976).

Soil pH is a key factor affecting heavy metal availability and mobility. A decrease in soil pH increases the mobility of heavy metals as a result of proton competition with these metals and decrease in negative binding sites (Horckmans *et al.*, 2007). Under alkaline conditions, functional groups present in soil organic matter dissociate, thereby increasing the bio-availability of heavy metals that are bound to organic matter (Fine *et al.*, 2005). Competition for metal cations by organic complexing ligands and soil surfaces at high pH also improves heavy metal movement and bio-availability in soils (Tack *et al.*, 2006).

2.7 Bioavailability and uptake of heavy metals by plants

Metal bioavailability refers to the fraction of heavy metal in soil that is accessible to the food chain and to the plant (Misra *et al.*, 2009). Plants are known to accumulate heavy metals in their edible portion as a result of cropping contaminated fields. Such accumulation is greatly

influenced by the concentration of the pollutant, chemical species of the pollutant in the soil, soil physicochemical properties as well as the plant's growth characteristics (Dudka and Chlopecka, 1990). Bioaccumulation takes place when substances are taken in the food chain from food and water. These substances accumulate because they cannot be broken down and used up by the organism or they are taken in faster than they are used up by organisms. Bioaccumulation is not hazardous when the substance accumulated is not harmful, but when compounds and heavy metals that are harmful to human health accumulate like Hg then bioaccumulation becomes dangerous (Brookes and Grath 1984).

When Cd, Zn, Pb, Hg, As, Cu, Cr, Ni and Mg accumulate in the soil over long times, they reduce food quality and quantity. A high heavy metals load in the soil reduces the functioning of soil biota resulting in reduced microbial activity (Kandeler *et al.*, 1996). Heavy metals have specific bioaccumulation characteristic and accumulate differently in the ecosystem. The metal being accumulated is the determining factor of where it bioaccumulates in an ecosystem.

Uptake of metals is considered to involve complexation, ion exchange, adsorption, inorganic micro precipitation, oxidation and reduction processes. Metal ions are adsorbed first to the surface of cells by the interactions between the metal ions and functional groups such as carboxyl, phosphate, hydroxyl, amino, sulphur, sulphide, and thiol which is present in the cell. (Wang and Chen 2006). Soil characteristics, which include pH and organic matter content affect the heavy metals adsorption in soil by plants (Jones, 1991) and therefore the heavy metals content in soil is not an indicator for heavy metals in plants because accumulation is plants and heavy metals specific.

Heavy metals accumulation varies from one plant to another, one heavy metal to another and the plant parts. (Linden *et al.*, 1994). Repeated application of poor quality irrigation water can strongly influence speciation of heavy metals that are of anthropogenic origin, reduce the soils sorption capacity for heavy metals and hence the metals eventually leached into soil solution making it more available for plant utilization (Sridhara *et al.*, 2008). Plant uptake of mobile ions present in the soil solution is largely determined by the total quantity of the ions in the soil solution, but in the case of strongly adsorbed ions, absorption seems to depend more upon the amount and surface area of roots. Roots excrete products like high molecular weight organic acids which form complexes and chelate with metal ions, thereby modifying heavy metal movement and fixation in soils (Wang *et al.*, 2009).

2.8 Health risk associated with heavy metal pollution

Soil is an essential natural resource for support of human life but its degradation has been constantly increasing due to deposition of pollutants. While soil serves as sinks for numerous waste products of natural and anthropogenic origins, they also are media for plant to grow and at the same time transmitters of pollutants to surface water and plants. Human health may be negatively affected by the consumption of crops grown on soils contaminated with heavy metals (Zeheng *et al.*, 2007).

Chronic low-level intakes of heavy metals have damaging effects on human beings and other animals since there is no good mechanism for their elimination (Bahemuka and Mubufu, 1999). Metals such as Pb, Hg, Cd and Cu are cumulative poisons. These metals cause environmental hazards and are reported to be exceptionally toxic. Vegetables take up heavy metals by absorbing them from contaminated soils as well as from deposits on parts of the vegetables exposed to the

air from polluted environments (Zurera *et al.*, 1989). The non-biodegradable nature of heavy metals and their long biological half-life make them a crucial environmental issue (Cui *et al.*, 2005).

Prolong consumption of unsafe concentrations of heavy metals through foodstuffs may lead to the chronic accumulation of heavy metals in the kidney and liver of humans causing disruption of numerous biochemical processes, leading to cardiovascular, nervous, kidney and bone diseases. Heavy metals have been reported to produce mutagenic, teragenic, neurotoxic and carcinogenic effects even at very low concentrations (Das, 1990).

2.9 Heavy metal accumulation in Vegetables

Vegetables constitute an important part of the human diet since they contain carbohydrates, proteins, vitamins, minerals and fibers which are essential for human health. They also act as neutralizing agents for acidic substances formed during digestion (Thompson and Kelly, 1990).

As human activities increases, especially with the application of modern technologies, pollution and contamination of the human food chain with heavy metals has become inevitable. Human exposure to heavy metals has risen in the last 50 years as a result of an exponential increase in the use of heavy metals in industrial processes and products.

Heavy metal contamination in vegetables cannot be underestimated as these food stuffs are important component of human diet. Heavy metal contamination of food is one of the most important aspect of food quality assurance (Marshall, 2004; Radwan and Salama, 2006; Wang *et al.*, 2005; Khan *et al.*, 2008). International and national regulations on food quality have lowered

the maximum permissible levels of toxic metals in food items due to an increased awareness of the risk these metals pose to food chain contamination (Radwan and Salama, 2006).

Leafy vegetables have greater potential of accumulating heavy metals in their edible parts than grain or fruit crops. Studies on the uptake of heavy metals by plants have shown that heavy metals can be transported passively from roots to shoots through the xylem vessels (Kirkham, 1977; Krijger *et al.*, 1999). In addition, plant organs such as fruit and seed that have low transpiration rates do not accumulate heavy metals because the storage organs are largely phloem-loaded and heavy metals are generally poorly mobile in the phloem. Zheljazkov and Neilsen (1996) found that the concentrations of heavy metals in vegetables per unit dry matter generally follow the order: leaves > fresh fruits > seeds.

2.10 Sources of heavy metal pollution in vegetables

Rapid industrialization and urbanization have contributed to the elevated levels of heavy metals in the urban environment of developing countries (Wongg *et al.*, 2003). Heavy metals are non biodegradable and persistent environmental contaminants which may be deposited on the surfaces and then adsorbed into tissues of the vegetables (Khairiah *et al.*, 2004). Heavy metals at concentrations exceeding the physiological demand of the plant could administer toxic effect in them and also could enter the food chain, get biomagnified and pose potential threat to human health (Sugiyama, 1994).

According to Dougherty and Hall (1995), the long term use of wastewater in agricultural land will result in the contamination of soils by heavy metals. Though most heavy metals are needed in trace amounts by growing plants, their excess can result in plant intoxication. But the presence of high heavy metal concentrations in plant tissues brings about poisoning problems in human

beings and other animals feeding on specific plant tissues (Alloway 1995). The occurrence of heavy metals in wastewater is of interest because they are often present at significant levels and if discharged into surface waters can have severe effects on the environment and public health.

It has been established that heavy metals in soils are associated with various chemical forms that relate to their solubility which directly bear on their mobility and biological availability. Heavy metals in soluble forms have high relation to their uptake by plants (Xian, 1989). In many developing countries it is a common practice to grow vegetables along banks of rivers passing through urban centers. Waters of such rivers have often been reported to be polluted with heavy metals (Mashauri and Mayo, 1990; Kashem and Singh, 1999; Othman, 2001).

2.11 Urban Wastewater Irrigation Farms in Accra

In Accra, irrigated vegetable production takes place on more than seven larger sites covering a total acre of about 298 ha. Some of the sites have been in use for more than 50 years. There are about 800-1000 vegetable farmers in Accra, of whom 60% produce exotic and 40% indigenous local or traditional vegetables. Some of the modern or exotic crops cultivated are lettuce, cabbage, spring onions, and cauliflower while the more traditional crops are tomatoes, okra, garden eggs (aubergine) and hot pepper (Obuobie *et al.*, 2005).

Plot sizes under cultivation in the city range between 0.01-0.02 ha per farmer, and max. 2.0 ha in peri-urban areas. The plot sizes of most of these sites have diminished over time because of land loss to estate development and widening of drains. This has led to reduced land reservations along the drains which used to be cultivated. Additional problems faced by farmers in relation to their farm size is tenure insecurity and low soil fertility (Obuobie *et al.*, 2005)

2.12 Heavy Metals

Heavy metal is a general term which applies to the group of metals and metalloids with an atomic density greater than 4 g/cm³ (Duffus, 2002). Heavy metals are often referred to as toxic elements because of the manifestation of their toxic effects in plants, animals and man. (Doelsch *et al.*, 2006). Heavy metals exist in different forms and are associated with a range of soil components which determine their bioavailability and reactivity (Tack *et al.*, 2006). They have variable oxidation states, exhibit paramagnetism and form coloured complex ions.

Although it is a loosely defined term, heavy metals are widely recognised and usually apply to the widespread contaminants of terrestrial and freshwater ecosystems. Unlike almost all organic pollutants, such as organochlorines, heavy metals are found naturally in soils and rocks with a subsequent range of natural background concentrations in soils, sediments, waters and organisms (Alloway, 1995). Anthropogenic releases can give rise to higher concentrations of these metals relative to the normal background values. The most important anthropogenic releases of heavy metals to the environment come from metalliferous mining and smelting, agricultural materials (pesticides and fertilizers), irrigation and application of sewage water and sludge, fossil fuel combustion (Alloway, 1995). Unlike many organic pollutants, which eventually degrade to carbon dioxide and water, heavy metals will tend to accumulate in the environment, especially in lake, estuarine or marine sediments and can be transported from one environment compartment to another (Duffus, 2002).

Whether the source of heavy metals is natural or anthropogenic, the concentrations in terrestrial and aquatic organisms are determined by the size of the source and adsorption and precipitation in soils and sediments. The extent of adsorption depends on the metal, the absorbent, the physico-chemical characteristics of the environment (e.g. pH, water hardness and redox

potential) and the concentrations of other metals and complex chemicals present in the soil water, river or lake. Heavy metals also accumulate in organisms as a result of direct uptake from the surroundings across the body wall, from respiration and from food (Duffus, 2002).

2.13 Characteristics of heavy metals used in the study

2.13.1 Lead

Lead is naturally found as a mineral combined with other elements, such as sulphur (i.e., PbS , PbSO_4), or oxygen (PbCO_3) (USDHHS, 1999). About half of Pb use goes for the manufacture of Pb storage batteries. Other uses include solders, bearings, cable covers, ammunition, plumbing, pigments, and caulking. Metals commonly alloyed with Pb are antimony (in storage batteries), Ca and tin Sn (in maintenance-free storage batteries), Ag (for solder and anodes), Sr and Sn (as anodes in electro-winning processes) (Manahan, 2003).

Inhalation and ingestion are the two routes of exposure and the effects from both are the same. Pb accumulates in the body organs, which may lead to poisoning or even death. The gastrointestinal tract, kidney and central nervous system are also affected by the presence of Pb (Muschack, 1990). Children exposed to lead are at risk for impaired development, lower IQ, shortened attention span, hyperactivity, and mental deterioration, with children under the age of six being at a more substantial risk. Adults usually experience decreased reaction time, loss of memory, nausea, insomnia, anorexia, and weakness of the joints when exposed to Pb (Muschack, 1990).

The most serious source of exposure to Pb in soil is through direct ingestion of contaminated soil or dust. In general, plants do not absorb or accumulate Pb however, in soils with high Pb content

it is possible for some Pb to be taken up by plants (Baldwin and Marshall, 1999). Studies have shown that lead does not readily accumulate in the fruiting parts of vegetable and fruit crops. Higher concentrations are more likely to be found in leafy vegetables (e.g., lettuce) and on the surface of root crops (e.g., carrots) (Rosen, 2002).

2. 13. 2 Chromium

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

Cr mobility depends on sorption characteristics of the soil, including clay content, iron oxide content, and the amount of organic matter present. Cr can be transported by surface runoff to surface waters in its soluble or precipitated form. Soluble and un-adsorbed Cr complexes can leach from soil into groundwater (Smith *et al.*, 1995). The leachability of Cr (VI) increases as soil pH increases. Most of Cr released into natural waters is particle associated, however, and is ultimately deposited into the sediment. Chromium is associated with allergic dermatitis in humans (Scragg, 2006).

Cr is an essential nutrient that helps the body use sugar, protein, and fat (Cervantes *et al.*, 2001). Breathing high levels of Cr can cause irritation to the nose, such as runny nose, nosebleeds, and ulcers and holes in the nasal septum. Ingesting large amounts of Cr can cause stomach upsets and ulcers, convulsions, kidney and liver damage, and even death (Gargas, *et al.*; 1994).

2. 13.3 Zinc

Zn occurs naturally in soil (about 70mg kg⁻¹ in crustal rocks) (Davies and Jones, 1988), but Zn concentrations are rising unnaturally, due to anthropogenic additions. Most Zn is added during industrial activities, such as mining, coal, and waste combustion and steel processing. Water is polluted with Zn, due to the presence of large quantities present in the wastewater of industrial plants. Plants often have a Zn uptake that their systems cannot handle, due to the accumulation of Zn in soils. Zn can interrupt the activity in soils, as it negatively influences the activity of microorganisms and earthworms, thus retarding the breakdown of organic matter (Greany, 2005).

Zn plays a role in immune function, protein synthesis, wound healing, DNA synthesis and cell division (Solomons, 1998). It also supports normal growth and development during pregnancy, childhood, and adolescence and is required for proper sense of taste and smell. A daily intake of zinc is required to maintain a steady state because the body has no specialized zinc storage system (Rink and Gabriel, 2000).

Zinc toxicity can occur in both acute and chronic forms. Acute adverse effects of high zinc intake include nausea, vomiting, loss of appetite, abdominal cramps, diarrhea, and headaches (Food and Nutrition Board, 2001). Intakes of 150–450 mg of zinc per day have been associated with such chronic effects as low copper status, altered iron function, reduced immune function, and reduced levels of high-density lipoproteins (Hooper *et al*; 1980). High intakes of zinc adversely affect some aspects of urinary physiology (Johnson *et al*; 2007).

2. 13.4 Cadmium

Cd is one of the most poisons heavy metal and is not known for any essential biological function in animals. In its compounds, Cd occurs as the divalent Cd^{2+} ion. Cadmium is directly below Zn in the periodic table and has a chemical similarity to that of Zn, an essential micronutrient for plants and animals. This may account in part for Cd's toxicity; because Zn being an essential element, its substitution by Cd may cause the malfunctioning of metabolic processes (Campbell, 2006).

The most significant use of Cd is in Ni and Cd batteries, as rechargeable or secondary power sources exhibiting high output, long life, low maintenance, and high tolerance to physical and electrical stress. Cd coatings provide good corrosion resistance coating to vessels and other vehicles. Other uses of cadmium are as pigments, stabilizers for polyvinyl chloride (PVC), in alloys and electronic compounds. Cadmium is also present as an impurity in several products, including phosphate fertilizers, detergents and refined petroleum products (Campbell, 2006). Cd is produced as an inevitable by-product of Zn and occasionally Pb refining. The application of agricultural inputs such as fertilizers, pesticides, and biosolids, the disposal of industrial wastes or the deposition of atmospheric contaminants increases the total concentration of Cd in soils, and the bioavailability of this Cd determines whether plant Cd uptake occurs to a significant degree (Weggler *et al.*, 2004). Cd is very bio-persistent but has few toxicological properties and, once absorbed by an organism, remains resident for many years.

Cd in the body is known to affect several enzymes. It is believed that the renal damage that results in proteinuria is the result of Cd adversely affecting enzymes responsible for reabsorption of proteins in kidney tubules (Manahan, 2003). The most spectacular and publicized occurrence

of Cd poisoning resulted from dietary intake of Cd by people in the Jintsu River Valley, near Fuchu, Japan was attributed to irrigated rice contaminated from an upstream mine producing Pb, Zn, and Cd. The victims were afflicted by *itai itai* disease. The symptoms are painful osteomalacia (bone disease) combined with kidney malfunction. The major threat to human health is chronic accumulation in the kidneys leading to kidney dysfunction. Food intake and tobacco smoking are the main routes by which Cd enters the body (Manahan, 2003).

2. 13.5 Copper

Cu is an essential micronutrient required in the growth of both plants and animals. In humans, it helps in the production of blood haemoglobin. In plants, Cu is especially important in seed production, disease resistance, and regulation of water (Davies and Jones, 1988). Cu is essential, but in high doses it can cause anaemia, liver and kidney damage, and stomach and intestinal irritation. Cu normally occurs in drinking water from Cu pipes, as well as from additives designed to control algal growth. While Cu's interaction with the environment is complex, research shows that most Cu introduced into the environment becomes, stable and results in a form which does not pose a risk to the environment. In fact, unlike some man-made materials, Cu is not magnified in the body or bioaccumulated in the food chain (Bjuhr, 2007). In the soil, Cu strongly complexes to the organic implying that only a small fraction of copper will be found in solution as ionic copper, Cu(II). The solubility of Cu is drastically increased at pH 5.5 (Martinez and Motto, 2000), which is rather close to the ideal farmland pH of 6.0–6.5 (Eriksson *et al.*, 1997).

2. 13.6 Nickel

Ni metal exists in the form of the nickelous ion, Ni (II) in low pH regions. In neutral to slightly alkaline solutions, it precipitates as nickelous hydroxide, $\text{Ni}(\text{OH})_2$, which is a stable compound. This complex readily dissolves in acid solutions forming Ni (III) and in very alkaline conditions; it forms nickelite ion, HNiO_2 , which is soluble in water (Pourbaix, 1974). In very oxidizing and alkaline conditions, nickel exists in form of the stable nickelo-nickelic oxide, (Ni_3O_4) , which is soluble in acid solutions. In acidic regions, however, these solids dissolve producing Ni^{2+} (Pourbaix, 1974).

Nickel occurs in the environment at low levels and is essential in small doses, but it can be dangerous when the maximum tolerable amounts are exceeded. At high concentrations, Ni can cause various kinds of cancer on different sites within the bodies of animals. The most common application of Ni is an ingredient of steel and other metal products. The major sources of nickel contamination in the soil are metal plating industries, combustion of fossil fuels, and nickel mining and electroplating (Khodadoust *et al.*, 2004). It is released into the air by power plants and trash incinerators and settles to the ground after undergoing precipitation reactions. It usually takes a long time for nickel to be removed from air. Nickel can also end up in surface water when it is a part of wastewater streams. The larger part of all Ni compounds that are released to the environment will adsorb to sediment or soil particles and become immobile as a result. In acidic soils, however, Ni becomes more mobile and often leaches down to the adjacent groundwater. Nickel is not known to accumulate in plants or animals and as a result Ni has not been found to bio-magnify up the food chain (Khodadoust *et al.*, 2004).

2.14 INDICES FOR SOIL POLLUTION ASSESSMENT

Among the commonly used methods in analyzing pollution intensity in the environments are the Enrichment Factor (EF) and Geoaccumulation Index (Igeo). Indices enable quality of the environment to be easily understood by non-specialist. They are also used to compare the pollution status of different areas of the environment (Tomlinson *et al.*, 1980).

2.14.1 Enrichment Factor

A common approach to estimate how much the soil is impacted (naturally and anthropogenically) with heavy metal is to calculate the Enrichment Factor (EF) for metal concentrations above un-contaminated background levels (Huu *et al.*, 2010). The EF method normalizes the measured heavy metal content with respect to a samples reference such as Fe, Al or Zn. The EF of a heavy metal in soil can be calculated with the following formula:

$$EF = \frac{C_n}{C_{ref}} \bigg/ \frac{B_n}{B_{ref}}$$

where: C_n - content of the examined element in the examined environment, C_{ref} - content of the examined element in the reference environment, B_n - content of the reference element in the examined environment, B_{ref} - content of the reference element in the reference environment. An element is regarded as a reference element if it is of low occurrence variability and is present in the environment in trace amounts. It is also possible to apply an element of geochemical nature whose substantial amounts occur in the environment but has no characteristic effects towards an examined element (Loska *et al.*, 1997).

Enrichment factor (EF) can be used to differentiate between the metals originating from anthropogenic activities and those from natural procedure and to assess the degree of anthropogenic influence. Six categories are recognised: < 1 background concentration, 1- 2 depletion to minimal enrichment, 2 – 5 moderate enrichment, 5 – 20 significant enrichment, 20 – 40 very high enrichment and > 40 extremely high enrichment (Sutherland, 2000).

2.14.2 Geoaccumulation Index

The geoaccumulation index (I_{geo}) has been widely employed in European trace metal studies. Originally used for bottom sediments, it has been successfully applied to the measurement of soil pollution (Yaqin *et al.*, 2008). The I_{geo} values enable the assessment of pollution by comparing current and pre-industrial concentrations, although it is not always easy to reach pre-industrial sediment layers (Yaqin *et al.*, 2008). Geoaccumulation Index is calculated using the formula;

$$I_{geo} = \log_2 \left(\frac{C_n}{1.5} \times B_n \right)$$

Where, C_n is the measured concentration of element n in the sediment and B_n is the geochemical background for the element n which is either directly measured in precivilization sediments of the area or taken from the literature. The factor 1.5 is introduced to include possible variations of the background values that are due to lithologic variations. Muller, (1981) proposed seven grades or classes of the geoaccumulation index. Class 0 (practically uncontaminated): $I_{geo} < 0$ Class 1 (uncontaminated to moderately contaminated): $0 < I_{geo} < 1$; Class 2 (moderately contaminated): $1 < I_{geo} < 2$; Class 3 (moderately to heavily contaminated): $2 < I_{geo} < 3$; Class 4 (heavily contaminated): $3 < I_{geo} < 4$; Class 5 (heavily to extremely contaminated): $4 < I_{geo} < 5$; Class 6 (extremely contaminated): $5 < I_{geo}$. Class 6 is an open class and comprises all values of the

index higher than Class 5. The elemental concentrations in Class 6 may be hundred fold greater than the geochemical background value.

2.14.3. Soil-Plant Transfer Coefficients

The transfer coefficient quantifies the relative differences in bioavailability of metals to plants and is a function of both soil and plant properties. Higher transfer coefficients reflect relatively poor retention in soils or greater efficiency of plants to absorb metals. Low coefficients reflect the strong sorption of metals to the soil colloids (Alloway and Ayres, 1997).



CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Study area

The study was carried out in Accra, the capital city of Ghana which lies within the coastal savannah zone. It covers an area of about 230 to 240 km² (Obuobie *et al.*, 2006). With an annual population growth rate of about 3.4 % in its current administrative boundary. Accra has an estimated population of 1.848 million (Ghana Statistical Service, 2010). Accra has an annual rainfall averaging 810 mm distributed over less than 80 days. The rainfall pattern of the city is bimodal with the major season falling between March and June, and a minor rainy season around October. Rain usually falls in intensive short storms and gives rise to local flooding where drainage channels are obstructed. Mean temperatures vary from 24 °C in August (the coolest) to 28 °C in March (the hottest) (Obuobie *et al.*, 2006). The vegetation of Accra consists of dense shrubs without grass in the west and grass with isolated patches of shrub and occasional trees in the east. Baobab and neem trees are also quite common in Accra (Obuobie *et al.*, 2006).

3.1.1 Description of sampling sites

Two main vegetable growing sites were selected in the Accra metropolis for the study namely; Dzorwulu, near the ECG substation and airport residential, behind CSIR in the Ayawaso-west sub-metro of Accra. The main source of irrigation water in the study site is urban drains. The contents of these drains vary from raw wastewater to diluted wastewater (mostly with runoffs). In Dzorwulu, a polluted stream (Onyasia) is used in combination with pipe-borne water, whiles at Airport residential area, a big drain that runs from the Airport through the Silver Star towers and other office buildings is used.

3.2 Sample collection and preparation

At each site, ten soil samples were randomly taken from the surface layer (0-15cm) of the irrigated soils with an earth chisel and a hand trowel throughout the farm. Uncultivated soil around the farms was also sampled to serve as control or reference sample. The samples were labeled, stored in a clean polythene bags and transported to the laboratory. The soils were air dried at room temperature for two weeks, mechanically ground using a wooden roller and sieved to obtain < 2 mm fraction. Soil samples were analyzed for the following parameters: pH, electrical conductivity (EC), organic carbon, cation exchange capacity (CEC), particle size analysis and heavy metals.

Ten lettuce samples were collected from the same sites where soils were collected, labeled and sent to the laboratory. The samples were washed in tap water and distilled water vigorously, dried in an air-circulating oven at 25°C, milled in a herbage mill, and repackaged in sealed plastic bags for analysis.

3.2.1 Soil analysis

The pH was measured using (1:2.5 soil water extract), electrical conductivity (EC) (1:5 soil water extract) and particle size analysis using hydrometer method (Bouycous, 1962). Organic carbon was determined by a modified Walkley and Black procedure as described by Nelson and Sommers (1982), cation exchange capacity (CEC) at pH 7 with ammonium acetate (Chapman, 1965).

3.2.2 PROCEDURES

Soil pH was determined using portable pH meter (Mettler Toledo SevenMulti) in a 1:2.5 soils - water suspension. A duplicate of 10.0 g of air-dried soil samples was weighed and 25 ml of distilled water was added to obtain a saturated suspension. The mixture was stirred and allowed to stand for 30 minutes after which a calibrated pH meter (calibrated with 7.00 and 4.00 buffers) was used to measure the pH of the soil samples.

Electrical conductivity (EC), of the soil samples was determined by measuring 10 g of the soil samples into 20 ml of distilled water and stirring for 30 minutes after which measurement were made with the conductivity meter (Mettler Toledo SevenMulti).

Percentage organic carbon in soils was determined by Walkley-Black method. 1.0 g of air-dried soil samples was weighed into 500 ml conical flasks and 10 ml of standard potassium dichromate was added to the samples in the flasks, followed by 20 ml of concentrated sulphuric acid. The mixture was shaken and allowed to stand for 30 minutes after which 200 ml of distilled water was added. This was followed by the addition of 10 ml of Orthophosphoric acid. 10 drops of diphenylamine indicator were added to the contents and were swirled to mix well. The samples were then titrated with standard ferrous ammonium sulphate until the solutions turned purple. Small drops of the ferrous ammonium sulphate were added to the solutions until the colour flashed to green. 0.5 ml of standard potassium dichromate was added to give an excess and then titrated drop by drop with the ferrous ammonium sulphate until the blue colour disappeared. Blank titrations were carried out in an identical way using the same reagents, but omitting the soil. The percentage organic carbon in the soil samples were then calculated using the formula below:

$$\% \text{ Organic Carbon} = \text{Dichromate used} - (\text{Factor} \times \text{Titre value of sample}) \times \text{Soil factor}$$

Where; Dichromate used = 10ml

$$\text{Factor} = \frac{\text{Dichromate used}}{\text{Mean Blank titre value}}$$

Cation exchange capacity (CEC) was determined at pH 7 with ammonium acetate (Chapman, 1965). In determining the Cation exchange capacity (CEC) content in the soil, the soil was leached with 1M NH_4OAc solution and the leachate discarded. The soil was washed with 95% ethanol to remove excess saturating solution, and the washings discarded. The adsorbed NH_4 was extracted by leaching the soil with 1M KCl solution and the extract transferred to a 250ml volumetric flask, diluted to volume with additional KCl solution. The concentration of $\text{NH}_4\text{-N}$ in the KCl extract was determined by distillation using kjeldahl distillator (Foss Tecator, Kjeltac 2100, Sweden).

The proportion of percent sand, silt and clay of the soil samples were calculated to determine soil textural class using hydrometer Method (Bouycous, 1962).

52.0 g of air-dried soil samples were weighed into 250 ml beakers and 20 ml of 20 % hydrogen peroxide (H_2O_2) were added to the samples in the beakers, and were left to stand until they got wet, after which they were dried on a hot plate and ground. This was followed by the addition of 100 ml of 5 % Calgon solution (Sodium hexametaphosphate) and mixed thoroughly, after which they were left to stand for 18 hours. The contents in the beakers were then washed into soil cup with distilled water, and were stirred with dispersing machine for 2 minutes. The cup was disconnected then the contents washed into 1 litre soil cylinders and were filled to the litre mark

with distilled water. The mouths of the cylinders were closed with rubber stoppers and turned completely upside down and back 20 times. 3 drops of Amyl alcohol ($C_5H_{11}OH$) were quickly added on top of the suspension to dissipate froth.

Hydrometer was gently placed in the soil suspensions and first reading taken within 40 seconds. The hydrometer was removed and washed with distilled water. After exactly 2 hours of continuous sedimentation, the second reading was taken with the hydrometer. The hydrometer was removed and washed with distilled water. The relative amounts of sand, silt and clay were then calculated using the formula below:

$$\% \text{ Sand} = 100 - 2 (X+2.88);$$

$$\% \text{ Clay} = 2 (Y+2.88);$$

$$\% \text{ Silt} = 100 - (A+B)$$

Where; X = First corrected hydrometer reading; Y = Second corrected hydrometer reading

A = % Sand

B = % Clay

Once the relative amounts of sand, silt and clay were known, the soils' textural classes were determined by using a soil textural triangle.

3.2.3 Determination of heavy metal in soil sample

In determining the heavy metal content in the soil samples, heavy metals were extracted using Diethylene-triamine-pentacetic acid (DTPA) solution buffered at pH 7.3. 5g of dried soil was mixed with 25 ml of DTPA extracting solution at pH 7.3 and kept on a rotary shaker at 120 rpm

for 2 hours. The mixture was then filtered through a Whatman No 1 filter paper and the filtrate collected and used for heavy metal analysis. The metal concentrations were determined by atomic absorption spectrophotometer using a VARIAN model AA 220 FS (Australia) Atomic Absorption Spectrophotometer (AAS). The AAS was calibrated with standard solutions of the respective metals and de-ionized water before it was used to measure the levels of heavy metals in the samples. Analyses were performed using hollow cathode lamps for Cu, Cr, Cd, Pb, Zn and Ni. All analyses were replicated and the data reported in mg/kg.

Table 1: Operating parameters for flame atomic absorption spectrophotometer

Metal	Wavelength (nm)	Slit width (nm)	Lamp current (mA)	Fuel
Cu	324.7	0.5	4	Acetylene
Cr	357.9	0.2	7	Acetylene
Cd	228.8	0.5	4	Acetylene
Pb	217.0	0.1	5	Acetylene
Zn	213.9	1.0	5	Acetylene
Ni.	232.0	0.2	4	Acetylene

3.2.4 Digestion of the lettuce samples for heavy metal analysis

In measuring heavy metal content in vegetable samples, samples were digested with aqua-regia (3:1, hydrochloric acid + nitric acid) by weighing 1 g of sample into digestion tubes. 30ml of HCl was added to the sample followed by 10ml of nitric acid in the digestion tubes and the mixture was heated in a digestion block inside a fume chamber at 150 °C for 2 hours. The digested samples were cooled and filtered through Whatman No. 1 filter paper and then the volumes were made up to 50 ml using volumetric flask. The filtrate was analysed on Atomic Absorption Spectrometer (Varian Spectra AA, 220FS) for Cd, Cu, Pb, Cr, Ni and Zn

3. 2.5 Determination of enrichment factor

To evaluate the magnitude of contamination in the environment, the enrichment factors (EF) were measured as the amount or ratio of the sample metal enrichment above the concentration present in the reference station or material. The following equation was used to calculate the EF values,

$$EF = \frac{\frac{C_n}{C_{ref}}}{\frac{B_n}{B_{ref}}}$$

where: C_n - content of the examined element in the examined environment, C_{ref} - content of the examined element in the reference environment, B_n - content of the reference element in the examined environment, B_{ref} - content of the reference element in the reference environment (Loska *et al.*, 1997). The Enrichment factors were calculated from the mean concentrations of the heavy metals in the sampling points in the study area. The control sampling point was considered to be the background value.

3.2.6 Index of Geoaccumulation (Igeo)

The geoaccumulation index (I_{geo}) values were calculated for different metals as introduced by Muller (1969) is as follows:

$$I_{geo} = \log_2 \left(\frac{C_n}{1.5} \times B_n \right)$$

Where C_n is the measured concentration of element n in the sediment sample and B_n is the geochemical background for the element n which is either directly measured in pre-civilization sediments of the area or taken from the literature (average shale value described by Turekian and

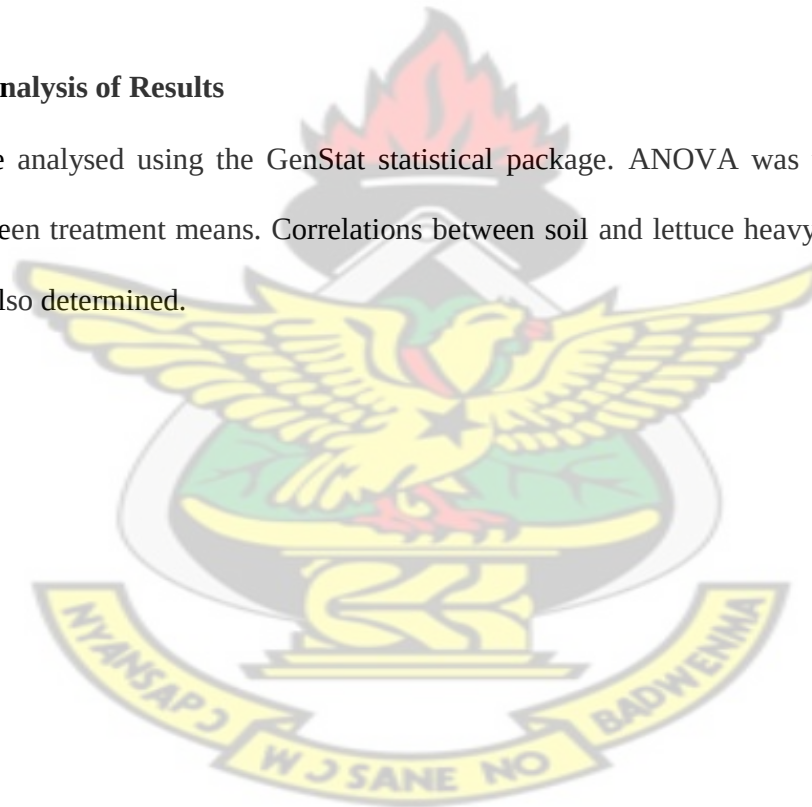
Wedepohl, 1961). The factor 1.5 is introduced to include possible variation of the background values that are due to lithogenic variations.

3.2.7 Soil-Plant Transfer Coefficients

The transfer coefficient was calculated by dividing the concentration of a metal in a vegetable crop by the total metal concentration in the soil using the expression C_p/C_s . Where C_p is the concentration of metals in plants and C_s is the concentration of the metals in corresponding soil.

3.3 Statistical Analysis of Results

The results were analysed using the GenStat statistical package. ANOVA was used to determine differences between treatment means. Correlations between soil and lettuce heavy metal contents at both sites were also determined.



4.0 RESULTS

The results of analysis of variance performed on the data are presented in tables 1-3.

Table 2: physico-chemical parameters in soils from vegetable farms in Accra

Sample site	pH	% Carbon (C)	CEC (Cmol _c kg ⁻¹ soil)	Conductivity $\mu\text{S cm}^{-1}$	Textural Class (USDA)
Airport	7.62 $\pm$ 0.05	1.18 $\pm$ 0.02	1.58 $\pm$ 0.03	0.25 $\pm$ 0.03	Sandy clay loam
Control	7.01 $\pm$ 0.01	1.09 $\pm$ 0.03	1.27 $\pm$ 0.04	0.21 $\pm$ 0.03	Sandy loam
LSD*	0.520	NS	NS	NS	
Dzorwulu	7.64 $\pm$ 0.01	0.90 $\pm$ 0.06	1.75 $\pm$ 0.04	0.40 $\pm$ 0.05	Sandy loam
Control	7.25 $\pm$ 0.26	0.77 $\pm$ 0.05	1.62 $\pm$ 0.03	0.37 $\pm$ 0.03	Sandy loam
LSD*	0.262	0.107	NS	NS	

n= 10

Table 3: Heavy metal concentration (mg kg⁻¹) in soils from vegetable farms in Accra

Sample site	Cu	Pb	Zn	Cr	Ni	Cd
Airport	4.78 $\pm$ 0.02	17.90 $\pm$ 0.01	21.73 $\pm$ 0.01	0.03 $\pm$ 0.00	0.80 $\pm$ 0.00	0.07 $\pm$ 0.01
Control	2.48 $\pm$ 0.01	5.56 $\pm$ 0.01	12.31 $\pm$ 0.01	0.03 $\pm$ 0.00	0.66 $\pm$ 0.00	0.06 $\pm$ 0.01
LSD *	NS	NS	7.553	NS	NS	NS
Dzorwulu	7.40 $\pm$ 0.01	24.02 $\pm$ 0.45	43.12 $\pm$ 0.63	0.06 $\pm$ 0.01	0.78 $\pm$ 0.08	0.05 $\pm$ 0.01
Control	3.71 $\pm$ 0.03	15.33 $\pm$ 0.83	20.86 $\pm$ 0.62	0.03 $\pm$ 0.01	0.71 $\pm$ 0.06	0.02 $\pm$ 0.01
LSD *	0.686	8.878	12.41	NS	NS	NS

Table 4: Heavy metal concentration (mg kg⁻¹) in lettuce from vegetable farms in Accra

Sample site	Cu	Pb	Zn	Cr	Ni	Cd
Airport	6.60 $\pm$ 0.27	25.65 $\pm$ 0.27	59.55 $\pm$ 0.10	0.70 $\pm$ 0.01	1.57 $\pm$ 0.21	0.07 $\pm$ 0.02
Dzorwulu	8.05 $\pm$ 0.03	34.37 $\pm$ 0.12	63.39 $\pm$ 0.10	0.52 $\pm$ 0.01	1.45 $\pm$ 0.06	0.05 $\pm$ 0.03
LSD *	NS	0.432	1.668	NS	0.107	NS

FAO/WHO STD 0.10 0.10 0.10 0.20 0.10 0.02

Values are means $\pm$ SD

*LSD: Least Significant Difference: NS values represent not significant

4.1 Physico-chemical Properties of the Soil

The basic physiochemical properties of the soil samples are summarized in Table 2. The texture class of the soil samples from airport residential area was sandy clay loam while its control sample was sandy loam. The texture class of soil samples from Dzorwulu however for both irrigated and control samples were sandy loam.

The soil pH of samples from airport residential area was significantly ($p < 0.05$) affected by the wastewater which has been used for irrigation. The result showed that pH values of irrigated soil samples were higher (7.62 ± 0.05) than those of the reference sample values (7.01 ± 0.01). The result also showed that pH values for soil samples from Dzorwulu were significantly ($p < 0.05$) affected by the wastewater. The pH value of the irrigated soil was 7.64 ± 0.01 while that of the control sample was 7.25 ± 0.26 (Table 2)

In the wastewater-irrigated soils obtained from airport residential area, the organic carbon content were not significantly ($p > 0.05$) different from the control soils. The values obtained for the irrigated sample was $1.18 \% \pm 0.02$ while, the control sample had a value of $1.09 \% \pm 0.03$. Organic carbon content from wastewater-irrigated soil samples from Dzorwulu were significantly ($p < 0.05$) higher when compared to that of the control samples. The mean organic carbon content of the irrigated sample was 0.90% , while that for the control was $0.77 \pm 0.05 \%$.

The mean CEC value obtained from wastewater-irrigated soil at Airport residential area was $1.58 \pm 0.03 \text{ Cmol}_c/\text{kg}$, slightly higher than that of the control sample ($1.27 \pm 0.04 \text{ Cmol}_c/\text{kg}$). The CEC value of irrigated sample from Dzorwulu was higher ($1.75 \text{ Cmol}_c/\text{kg}$) than its corresponding reference sample ($1.62 \pm 0.03 \text{ Cmol}_c/\text{kg}$). Comparing the two sampling site, Dzorwulu samples recorded higher CEC values than the samples of Airport residential area.

Electrical conductivity values for irrigated samples from Airport residential area were slightly higher ($0.25 \pm 0.03 \mu\text{S cm}^{-1}$) compared with values obtained from the control sample ($0.21 \pm 0.03 \mu\text{S cm}^{-1}$). The soil EC did not vary significantly ($p < 0.05$) at Dzorwulu sites as compared with the control. The mean EC values obtained for wastewater-irrigated irrigated soil sample at Dzorwulu was $0.40 \pm 0.05 \mu\text{S cm}^{-1}$ while $0.37 \pm 0.03 \mu\text{S cm}^{-1}$ was obtained for the control sample.

4.2 Heavy metals in soil

From Table 3, it was shown that heavy metal concentrations in samples from Airport residential area were higher than those of the control sample. Heavy metal concentration of wastewater irrigated samples ranged between $0.072 \pm 0.01 \text{ mg/kg}$ and $21.732 \pm 0.01 \text{ mg/kg}$. Zn recorded the highest concentration at Airport residential area ($21.73 \pm 0.01 \text{ mg kg}^{-1}$) followed by Pb (17.90 ± 0.01). Cr recorded the lowest mean concentration value (0.032 mg kg^{-1}) at Airport residential area. Cd, Cr, Cu, Ni and Pb concentrations in the irrigated soils from Airport residential area were not significantly different ($p > 0.05$) compared with the control soils.

Heavy metal concentrations in samples from Dzorwulu were also higher than those of the control sample values. Zn recorded the highest concentration at Dzorwulu ($43.12 \pm 0.63 \text{ mg kg}^{-1}$). Pb had the second highest concentration ($24.02 \pm 0.45 \text{ mg kg}^{-1}$) at Dzorwulu. The concentration of heavy metals ranged between $0.05 \pm 0.01 \text{ mg/kg}$ to $43.12 \pm 0.63 \text{ mg/kg}$. Cd recorded the lowest mean concentration value (0.02 mg kg^{-1}) at Dzorwulu. Cu, Pb and Zn concentrations obtained at Dzorwulu were significantly different ($p < 0.05$) from the control whilst Cr, Ni and Cd were not.

4.3 Heavy metals in lettuce

The mean of concentration of heavy metals found in edible portions of lettuce are presented in Table 4. From the results obtained, lettuce samples from Airport residential area had Zn recording the highest concentration of 59.55 ± 0.10 mg/kg, while Cd recorded the lowest value of 0.07 ± 0.02 mg/kg.

The result of lettuce samples analysed from Dzorwulu showed that Zn recorded the highest concentration (63.39 ± 0.10 mg/kg) followed by Pb which recorded a value of 34.37 ± 0.12 mg/kg. Cd recorded the lowest concentration 0.050 ± 0.03 mg/kg.

Comparing the heavy metal concentrations in lettuce grown on wastewater-irrigated soils at both sites, Zn and Pb recorded the highest concentration in the lettuce samples. The Cd concentrations in the lettuce grown on wastewater-irrigated soils at Dzorwulu and Airport residential area were not significantly different ($P > 0.05$). Similarly, the concentrations of Cr and Cu were not significantly different ($P > 0.05$) at both sites. However, there was significant difference ($P < 0.05$) between the concentration of Pb, Zn and Ni.

4.4 Element - Element Correlation Coefficients

The interrelationships between elements in soil and lettuce samples were determined using Pearson correlation coefficients. The coefficients were grouped according to the classification as shown in Table 5.

Table 5. Correlation coefficient classification

Classification Ranges of Coefficients	Classification
-0.75 to -1	Very strong negative correlation
-0.5 to -0.75	strong negative correlation
-0.25 to -0.5	weak negative correlation
0.1 to -0.25	Very weak negative correlation
0.1 to 0.25	Very weak positive correlation
0.25 to 0.5	weak positive correlation
0.5 to 0.75	strong positive correlation
0.75 to 1	Very strong positive correlation

Table 6. Correlation coefficients between heavy metal contents in soil and lettuce at both sites

Simple correlations Heavy metals	Correlation coefficient values
Cd	0.158
Cr	-0.310
Cu	0.929
Ni	-0.130
Pb	0.918
Zn	0.996

Simple statistical correlation was calculated for heavy metal concentration in soil and lettuce to identify the relationship that existed between the concentration of heavy metals in the soil and the lettuce. The correlation analysis showed a positive relationship between four out of the six heavy metals in the soil and lettuce samples analyzed. There was a positive correlation between the soil and lettuce for Zn ($r = 0.996$), Cu ($r = 0.929$), Pb ($r = 0.918$) and Cd ($r = 0.158$), at both sites.

Table 7: Enrichment Factor (EF), Geo-accumulation index (Igeo) and Transfer coefficient (TC) of heavy metals in soils from Dzorwulu and Airport residential area

Heavy metal	Sampling sites					
	AIRPORT			DZORWULU		
	EF	Igeo	TC	EF	Igeo	TC
Cu	1.921	0.357	1.380	1.095	0.408	1.087
Pb	3.214	1.100	1.432	0.862	0.063	1.430
Zn	1.764	0.235	2.740	1.137	0.462	1.470
Ni	1.195	-0.327	1.968	0.603	-0.452	1.854
Cd	1.043	-0.524	1.042	0.286	0.522	1.000
Cr	1.000	-0.585	0.045	1.000	0.276	7.608

4.5 Enrichment factor for soil samples

The results of the calculation of Enrichment Factor (EF) of heavy metal in soil are shown in Table 7. From the results, the mean EF calculation results indicated that samples from Dzorwulu had values for Zn (EF = 1.137), Cu (EF=1.095), Cr (EF = 1.00) in the category of minimal enrichment, while Pb (EF = 0.862), Ni (EF = 0.603), Cd (EF = 0.286) showed background

concentration. The heavy metal EF in soil samples from Dzorwulu follows the order $Zn > Cu > Cr > Pb > Ni > Cd$.

The EF of heavy metal in soils from Airport ranged from 1.000 to 3.214. Pb had the highest EF value of 3.214 indicating moderate enrichment compared to the other metals calculated, while Cr had the lowest EF value (1.000) indicating minimal enrichment. Cd (EF = 1.04), Ni (EF = 1.195), Zn (EF = 1.764) and Cu (EF = 1.921), were all in the category of minimal enrichment. The heavy metal EF in soil samples from Airport follows the order $Pb > Cu > Zn > Ni > Cd > Cr$.

4.6 The Geo-Accumulation Index

The results for the individual elemental geo-accumulation (I_{geo}) values for each sampling site are presented in Table 7. The I_{geo} values for samples from Airport range from -0.327 to 1.100. The results obtained for Cr (-0.585), Ni (-0.327) and Cd (-0.524) fall within class 0 which represents practically uncontaminated. Both Cu and Zn are uncontaminated to moderately contaminated (I_{geo} = 0.357 and 0.235 respectively). Pb recorded the highest I_{geo} value of 1.100 representing moderate contamination. The mean values of I_{geo} for samples from Airport decrease in the order of $Pb > Cu > Zn > Cr > Cd > Ni$.

The I_{geo} values for Dzorwulu samples ranged from -0.452 to 0.522. From the results obtained, Cd had the highest I_{geo} value of 0.522 (moderately contaminated) while Ni had the least I_{geo} value of -0.452 (practically un-contaminated). The mean I_{geo} values of Dzorwulu samples decreased in the order $Cd > Zn > Cu > Pb > Cr > Ni$.

4.7 Soil-Plant Transfer Coefficients (TC)

The extent of metals accumulation in the vegetable (lettuce) sample at both sampling site are presented in Table 6. Results of TC obtained from lettuce samples at Dzorwulu ranged from 1.000 to 7.608. Cd recorded the lowest TC value (1.00), while Cr had the highest TC value (7.608). The order for average values of the translocation coefficient from soil to lettuce at Dzorwulu was $Cr > Ni > Pb > Zn > Cu > Cd$.

The TC values recorded from lettuce samples at Airport ranged from 0.045 to 2.740 with Zn recording the highest value of 2.740. The order for average values of the translocation factor from soil to lettuce at Airport was: $Zn > Ni > Pb > Cu > Cd > Cr$.

Comparing the values of TC obtained from both sites, lettuce samples from airport had higher transfer coefficient values than lettuce samples from Dzorwulu (Table 7). All the Heavy metals analysed from both sites with the exception of Cr (0.045) had TC values > 1 indicating high level of accumulation of metals in the plant (Alloway and Ayres, 1997).

5.0 DISCUSSION

5.1 Heavy metals in soil

The sequence of heavy metals concentration in cultivated soil samples from airport residential area were in the order of $Zn > Pb > Cu > Ni > Cd > Cr$ while that of Dzorwulu were in the order $Zn > Pb > Cu > Ni > Cr > Cd$. There were significant differences in the distribution of Zn and Pb at both sites. Zn recorded the highest mean concentration for both sites ($21.73 \pm 0.01 \text{ mg kg}^{-1}$) at Airport residential area and ($43.125 \pm 0.63 \text{ mg kg}^{-1}$) at Dzorwulu. The concentrations of heavy metals showed variations which may be ascribed to the variation in heavy metal sources and the quantity of heavy metals in irrigated water. Variations in the levels of heavy metal concentration in irrigated soils could also be attributed to variations in physico- chemical parameters such as pH, CEC, carbon, EC as well as the soil textural class. The alkaline nature of the soil could also account for the relatively low levels of the heavy metals since heavy metals are more mobile at $pH < 7$ (Smith, 1992). According to Smith and Giller (1992), heavy metal mobility decreases with increasing soil pH due to precipitation of hydroxides, carbonates or formation of insoluble organic complexes.

5.2 pH

The application of wastewater has led to changes in some soil physicochemical characteristics and heavy metal uptake by lettuce. The soil pH changes depending on pH of the wastewater used for irrigation, and the soil pH has a great influence on the mobility and bioavailability of heavy metals (Nigam et al., 2001). Heavy metals are generally more mobile at $pH < 7$ than $pH > 7$ and can move downward with water through the soil, and in some cases move to aquifers, surface streams, or lakes. The pH of the soils from both sites ranged from 7.62 ± 0.05 to 7.64 ± 0.01 , thus

the soil samples were slightly alkaline. This contributed to the relatively higher concentration of Pb, Zn and Cu in the soil and subsequently the lettuce.

5.3 Conductivity

Soil electrical conductivity is an indirect measurement that correlates very well with several soil physical and chemical properties such as particle size and soil texture (Wiatrak, 2009). Sands have low conductivity and clays have high conductivity. The soil electrical conductivity (EC) showed no significant difference ($p > 0.05$) at both sites as compared with the control. Boulding (1994) classified EC of soils as: non saline < 2 ; moderately saline 2-8; very saline 8-16; extremely saline >16 . Results of soil EC obtained from both sites had values < 2 (Table 2). The EC of the samples therefore can be classified as non-saline. The result obtained implied that soils from both sites have low salt accumulation or less soluble salts and will not affect plants. Plants absorb essential plant nutrients in the form of soluble salts, but excessive accumulation of soluble salts, called soil salinity, suppresses plant growth and result in death of plants (Maas, 1984).

5.4 Carbon

The mean percentage organic carbon of soil samples from both sites was found to be relatively low (0.90 ± 0.05 to 1.18 ± 0.01), this may be attributed to the textural class (sandy loam) of the soil. Clay soils are known to be high in carbon. Soil carbon improves the physical properties of soil. It increases the cation exchange capacity (CEC) and water-holding capacity of sandy soil and it contributes to the structural stability of clay soils by helping to bind particles into aggregates (Gao *et al.*, 1997)

Soil organic matter, of which carbon is a major part, holds a great proportion of nutrients, cations and trace elements that are of importance to plant growth. It prevents nutrient leaching and is integral to the organic acids that make minerals available to plants. It also buffers soil from strong changes in pH. It is widely accepted that the carbon content of soil is a major factor in its overall health (Okalebo *et al*, 1993).

Increase in soil organic carbon can lead to elevate the soil adsorption capacity by which accumulation of heavy metals could be enhanced. Gao *et al.*, (1997), suggested that metal adsorption at low metal loadings is related to soil organic matter content. Hence soil samples with low organic carbon content at both sites are characterized by low levels of heavy metals observed in the soil samples.

5.5 Cation Exchange capacity (CEC)

The CEC values obtained from wastewater irrigated soil samples at Airport was not significantly different (> 0.05) from the control samples. The mean value obtained for the wastewater irrigated sample was 1.58 ± 0.03 Cmol_c/kg while the control sample had a mean value of 1.27 ± 0.04 Cmol_c/kg. The result obtained from Dzorwulu also showed no significant difference between wastewater irrigated soil samples and that of the control samples. Samples from Dzorwulu had high CEC whiles samples from Airport had lower CEC values.

CEC is a measure of the quantity of cations that can be adsorbed and held by a soil. CEC is used as a measure of fertility, nutrient retention capacity, and the capacity to protect groundwater from cation contamination. CEC is dependent on the organic carbon and clay in soil. In general, the higher the organic carbon and clay content, the higher the CEC. The CEC gives the soil a

buffering capacity which may slow down the leaching of nutrient cations and positively charged pollutants because they affect both soluble and exchangeable metal levels (Yoo and James, 2002). The results obtained at both sites indicate that CEC and organic carbon recorded low values, indicating low metal retention capabilities and this could account for the low heavy metal concentration in the soil samples. The low values recorded at both sites could also be attributed to the low levels of organic carbon and the textural class of the soil (sandy loam).

5.6 Heavy metals in lettuce

Heavy metal accumulation by vegetables is a cause of serious concern due to the possible potential public health impacts (Bi *et al.*, 2006; Cui *et al.*, 2005). In this study, soil contamination with metals was due to wastewater irrigation. In general, the heavy metal concentrations in lettuce were higher than the FAO/WHO guideline values of 0.1-0.2 mg/kg Cr, 0.1 mg/kg Pb; 0.1 mg/kg Cu; 0.1 mg/kg Zn; 0.1 mg/kg Ni; 0.02 mg/kg Cd (Codex, 1995).

From the results obtained, Zn had the highest mean concentration range for lettuce samples from Dzorwulu ($63.39 \pm 0.10 \text{ mg kg}^{-1}$) followed by Pb ($34.37 \pm 0.12 \text{ mg kg}^{-1}$). Higher concentration of Zn was also recorded for lettuce samples at Airport ($59.55 \pm 0.10 \text{ mg kg}^{-1}$). Cu concentrations in the lettuce samples were also appreciable at both sites (6.60 ± 0.27 and $8.05 \pm 0.03 \text{ mg kg}^{-1}$ for Airport residential area and Dzorwulu respectively) with no significant difference between the values from both sites. Cd recorded the lowest mean concentration range for both sites ($0.05 \pm 0.03 \text{ mg kg}^{-1}$) for lettuce samples from Dzorwulu and $0.07 \pm 0.02 \text{ mg kg}^{-1}$ for samples from Airport residential area.

The sequence of heavy metals in the lettuce samples from both sites were in the order of $Zn > Pb > Cu > Ni > Cr > Cd$. Cr and Cd content were generally low in lettuce samples from both sites due to its low bioavailability. The positive correlation between the soil and lettuce contents of Zn, Cu, Pb and Cd at both sites (Table 6) is an indication that there was metal uptake by the lettuce sample from the soil on which they were cultivated. Metal uptake by plants can be affected by several factors including metal concentration in soils, soil pH, cation exchange capacity, organic matter content, type and variety of plant.

5.7 Soil Enrichment factor

Enrichment Factor (EF) of the heavy metals in soil samples from Dzorwulu showed that Zn, Cu and Cr had minimal enrichment while Pb, Ni and Cd had no enrichment. EF values between 0.5 and 1.5 indicate the metal is entirely from crust materials or natural processes, whereas EF values greater than 1.5 suggest that the sources are more likely to be anthropogenic (Zhang and Liu 2002). Normally, as the EF values increase, the contributions of the anthropogenic origins also increase. Therefore, the low values of EF (Pb 0.862, Ni 0.603 and Cd 0.286) showed that the slight heavy metal pollution of irrigated soils samples from Dzorwulu were not likely to originate from anthropogenic activities. These heavy metals probably originated from natural processes in the environment.

The results of the present study show that Pb, Cu and Zn were significantly enriched in the soils from Airport since EF values of these metals are greater than 1.5 (Table 7). The highest average EF was recorded for Pb with a value of 3.214. Copper has the second highest EF with an average value of 1.921. This suggests that Pb and Cu are from anthropogenic and the soils have been contaminated by these two metals in the recent years. The high EF value for Pb could also be

attributed to the source of water at the Airport Residential area. Wastewater from the Airport and offices around the airport city which includes new buildings under construction and runoffs from road side as well as other materials used for construction work can contribute to Pb and Cu pollution. The EFs of Cd and Ni for wastewater irrigated samples from Dzorwulu were less than 1 which suggests a natural source of these metals in the study area.

It is presumed that high EF values indicate an anthropogenic source of heavy metals, mainly from activities such as industrialization, urbanization, wastewater irrigation, fertilizers and pesticides used in agricultural activities, and others (Kwon *et al.*, 2001).

5.8 Geo-Accumulation Index

The index of geo-accumulation includes seven grades (0-6) ranging from unpolluted to very highly polluted. The result of the calculation of Geo-accumulation Index (Igeo) in soil samples from both sites is shown in Table 6. The negative values obtained at both sites according to contamination classification of Huu *et al.*, (2010) analysis of heavy metal concentrations in soil showed that the soil was not polluted by heavy metals (Cr, Ni and Cd). The Igeo index is not readily comparable with EF due to the nature of Igeo calculation which involves a logarithm function and a background multiplication factor of 1.5.

The Igeo index values for samples from Airport ranges from - 0.327 to 1.100. The results obtained shows that Cr (- 0.585), Ni (-0.327) and Cd (- 0.524) were not contaminated. Zn and Cu were however moderately contaminated (Igeo = 0.357 and 0.235 respectively). Pb recorded a high Igeo value of 1.100 representing moderate contamination. Pb is considered as a good

indicator for other toxic pollutants in urban storm water because it is relatively easy to monitor and its dangers are well documented (Muschack, 1990).

The Igeo values for Dzorwulu samples ranged from - 0.452 to 0.522. From the results obtained, Cd had the highest Igeo value of 0.522 (moderately contaminated) while Ni had the least Igeo value of -0.452 (practically uncontaminated). From the results of heavy metals analysed for both sites, the soil of the study area could therefore be classified as uncontaminated to moderately contaminated (based on the geo- accumulation index).

5.9 Soil-Plant Transfer Coefficients (TC)

The Results obtained from both sites showed a $TC > 1$ except TC value for Zn in Lettuce samples from Dzorwulu. Cr recorded the highest TC value for lettuce samples at Dzorwulu (7.608) while Zn recorded the highest TC value (2.740) for lettuce samples at Airport (Table 7). TC greater than 1 indicated high level of accumulation of metals in the plant. The result suggests that the heavy metals analyzed could be effectively translocated from the soil to the vegetable (lettuce). Higher transfer coefficients reflect relatively poor retention in soils or greater efficiency of plants to absorb metals. Low transfer coefficients reflect the strong sorption of metals to the soil colloids (Alloway and Ayres, 1997). This could be seen in the result in Tables 3 and 5 which showed low metal concentration in the irrigated soils but a relatively high heavy metal concentration in the lettuce grown on the soil.

The translocation coefficient of heavy metals from soil to plant is an essential indicator that allows the assessment of mobility of heavy metals in plants and the danger of metal translocation to their edible parts. The concentrations of metals in the lettuce indicate the metal status and also

the abilities of plant species to uptake and accumulate metals from the substrate upon which they grow (Alloway, 1996). The average values for the concentration factor being smaller than 1 for all metals indicated high translocation from soil to plant.

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6.0 CONCLUSION AND RECOMMENDATIONS

6.1 CONCLUSION

An assessment of heavy metal contamination in wastewater irrigated soil was carried out in this study. Using a variety of indices (enrichment factor, geo-accumulation index, and Transfer coefficient) the level of anthropogenic impact was evaluated. The results obtained showed appreciable levels of heavy metal concentration in the soil and the lettuce samples from the study sites. The levels of contamination in soil and lettuce at both sites appeared to be as a result of anthropogenic activities. Generally, there was evidence of significant pollution with heavy metals (Cu, Zn, and Pb) in the soil. All the metals analysed on the lettuce showed levels which were above the FAO/WHO recommended levels. Heavy metals of public health concern like Pb and Cd showed varied results. While Pb concentration was high (25.65 ± 0.27 to 34.37 ± 0.12 mg/kg), Cd concentrations were relatively low (0.05 ± 0.03 to 0.07 ± 0.02 mg/kg) at both sites. The levels of these heavy metals might place the consumers of this crop and other crops grown on such soils at a health risk with time. The soils from both sites can be described as ranging from unpolluted to moderately polluted since all the samples collected showed a moderately high levels of contamination in at least one heavy metal (Cu, Zn, Pb, Cr, Ni and Cd).

The TCs for different heavy metals from soil to plant are a key component of human exposure to the metals via the food chain. Overall, the TC values for all the heavy metals analysed were found to be significant ($TC > 1$), while the translocation of Cr in lettuce samples from Airport is comparatively less (0.045).

There was a significant build-up of Heavy metals in the soils of the study area, which led to their contamination in lettuce in the study area.

6.2 Recommendations

Studies should be carried out at other locations within the metropolis and on other varieties of vegetables to determine the levels of contamination of these metals.

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APPENDIX A

Results of physicho-chemical parameters in soils from vegetable farm at Airport residential area

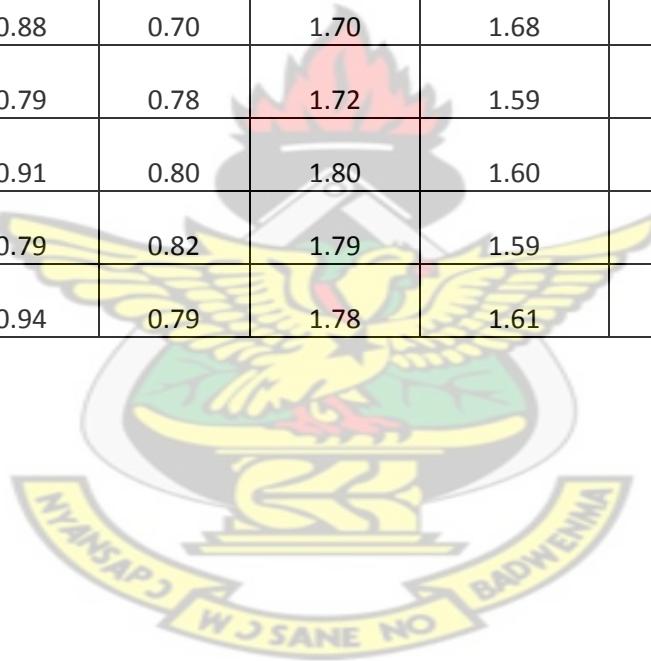
Sampling point	pH (Sample)	pH (control)	% C (Sample)	% C (control)	CEC (Sample) $\mu\text{S cm}^{-1}$	CEC (control) $\mu\text{S cm}^{-1}$	Conductivity (Sample) $\text{Cmol}_c \text{ kg}^{-1} \text{ soil}$	Conductivity (control) $\text{Cmol}_c \text{ kg}^{-1} \text{ soil}$
Point 1	7.60	7.02	1.19	1.03	1.55	1.32	0.26	0.25
Point 2	7.59	7.01	1.20	1.07	1.61	1.30	0.27	0.23
Point 3	7.57	6.99	1.21	1.08	1.59	1.20	0.29	0.23
Point 4	7.61	7.01	1.16	1.07	1.57	1.26	0.20	0.19
Point 5	7.57	7.00	1.18	1.10	1.61	1.27	0.22	0.17
Point 6	7.70	7.01	1.17	1.09	1.62	1.25	0.24	0.17
Point 7	7.57	7.00	1.15	1.12	1.51	1.29	0.25	0.19
Point 8	7.70	7.03	1.16	1.11	1.51	1.24	0.28	0.20
Point 9	7.59	7.01	1.17	1.10	1.56	1.26	0.28	0.24
Point 10	7.67	7.02	1.19	1.09	1.62	1.28	0.25	0.24

Results of physicho-chemical parameters in soils from vegetable farm at Dzorwulu

Sampling point	pH (Sample)	pH (control)	% C (Sample)	% C (control)	CEC (Sample) $\mu\text{S cm}^{-1}$	CEC (control) $\mu\text{S cm}^{-1}$	Conductivity (Sample) $\text{Cmol}_c \text{ kg}^{-1}$ soil	Conductivity (control) $\text{Cmol}_c \text{ kg}^{-1}$ soil
	7.65	7.50	0.94	0.84	1.72	1.68	0.42	0.32



Point 1								
Point 2	7.64	7.45	0.93	0.74	1.71	1.61	0.48	0.34
Point 3	7.62	7.70	0.92	0.76	1.79	1.60	0.42	0.36
Point 4	7.63	6.90	0.91	0.71	1.78	1.61	0.41	0.31
Point 5	7.66	6.91	0.94	0.72	1.70	1.59	0.39	0.39
Point 6	7.63	7.32	0.88	0.70	1.70	1.68	0.40	0.38
Point 7	7.64	7.20	0.79	0.78	1.72	1.59	0.41	0.40
Point 8	7.62	7.29	0.91	0.80	1.80	1.60	0.42	0.42
Point 9	7.63	6.98	0.79	0.82	1.79	1.59	0.36	0.36
Point 10	7.65	7.27	0.94	0.79	1.78	1.61	0.29	0.39



Concentration (mg/kg) of heavy metals in soil at Airport Residential area

Samplin g points	Cu (Sample)	Cu (control)	Pd (Sample)	Pd (control)	Zn (Sample)	Zn (control)	Cr (Sample)	Cr (control)	Ni (Sample)	Ni (control)	Cd (Sample)	Cd (control)
Point 1	4.780	2.489	17.908	5.564	21.730	12.317	0.031	0.034	0.799	0.668	0.070	0.060
Point 2	4.784	2.481	17.894	5.583	21.739	12.313	0.033	0.031	0.801	0.668	0.078	0.060
Point 3	4.783	2.487	17.906	5.567	21.730	12.310	0.034	0.032	0.804	0.669	0.074	0.056
Point 4	4.787	2.504	17.897	5.569	21.734	12.314	0.032	0.031	0.800	0.671	0.069	0.063
Point 5	4.721	2.489	17.910	5.563	21.730	12.291	0.032	0.031	0.800	0.669	0.053	0.067
Point 6	4.804	2.487	17.902	5.569	21.741	12.320	0.030	0.030	0.803	0.667	0.077	0.066
Point 7	4.788	2.488	17.899	5.567	21.709	12.319	0.031	0.033	0.790	0.668	0.073	0.053
Point 8	4.763	2.485	17.900	5.568	21.736	12.315	0.034	0.034	0.804	0.671	0.075	0.052
Point 9	4.788	2.492	17.901	5.566	21.739	12.312	0.032	0.031	0.802	0.667	0.075	0.064
Point 10	4.809	2.480	17.920	5.569	21.733	12.316	0.031	0.033	0.801	0.670	0.076	0.066

Concentration (mg/kg) of heavy metals in soil at Dzorwulu

Samplin g points	Cu (Sample)	Cu (control)	Pd (Sample)	Pd (control)	Zn (Sample)	Zn (control)	Cr (Sample)	Cr (control)	Ni (Sample)	Ni (control)	Cd (Sample)	Cd (control)
Point 1	7.402	3.682	24.009	13.948	43.231	20.802	0.059	0.027	0.798	0.821	0.020	0.049
Point 2	7.409	3.690	24.009	13.960	43.786	21.090	0.075	0.027	0.694	0.679	0.019	0.037
Point 3	7.402	3.681	23.988	14.948	42.109	20.706	0.072	0.039	0.734	0.653	0.020	0.031
Point 4	7.396	3.730	23.789	15.503	42.000	19.998	0.071	0.031	0.853	0.732	0.032	0.048
Point 5	7.401	3.721	24.146	15.439	42.978	20.670	0.071	0.034	0.802	0.698	0.021	0.067
Point 6	7.400	3.720	24.490	15.413	43.586	21.967	0.067	0.045	0.764	0.673	0.029	0.066
Point 7	7.391	3.740	24.678	15.938	43.267	20.875	0.059	0.039	0.648	0.791	0.030	0.061
Point 8	7.403	3.748	23.934	15.789	43.002	19.998	0.073	0.046	0.843	0.650	0.032	0.059
Point 9	7.389	3.739	24.201	15.939	43.706	20.932	0.069	0.048	0.754	0.670	0.031	0.048
Point 10	7.406	3.736	23.005	16.439	43.586	21.650	0.073	0.047	0.932	0.765	0.029	0.036

Concentration (mg/kg) of heavy metals in lettuce at Airport residential area

Sampling points	Cu	Pb	Zn	Cr	Ni	Cd
Point 1	6.793	25.001	59.455	0.698	1.098	0.060
Point 2	6.590	25.460	59.674	0.687	1.487	0.105
Point 3	6.978	25.560	59.396	0.699	1.753	0.094
Point 4	6.723	25.880	59.600	0.701	1.348	0.050
Point 5	6.596	25.528	59.585	0.705	1.689	0.045
Point 6	6.759	25.769	59.440	0.689	1.621	0.079
Point 7	6.603	25.850	59.635	0.710	1.723	0.059
Point 8	6.001	25.773	59.576	0.698	1.647	0.089
Point 9	6.658	25.870	59.656	0.706	1.684	0.066
Point 10	6.900	25.809	59.485	0.703	1.696	0.098

Concentration (mg/kg) of heavy metals in lettuce at Dzorwulu

Sampling points	Cu	Pb	Zn	Cr	Ni	Cd
Point 1	8.062	34.215	63.399	0.540	1.455	0.065
Point 2	8.050	34.389	63.450	0.525	1.485	0.089
Point 3	8.078	34.505	63.580	0.511	1.475	0.025
Point 4	8.027	34.459	63.350	0.537	1.385	0.023
Point 5	8.094	34.372	63.289	0.520	1.450	0.045
Point 6	8.068	34.259	63.198	0.524	1.530	0.075
Point 7	8.055	34.287	63.405	0.515	1.532	0.085
Point 8	8.035	34.378	63.390	0.545	1.390	0.020
Point 9	8.024	34.585	63.458	0.512	1.400	0.029
Point 10	8.015	34.296	63.425	0.520	1.395	0.045

APPENDIX B

Correlation of Metals in concentration in soil and lettuce.

Cd	1	-											
Cd1	2	0.158	-										
Cr	3	-0.7998	-0.3472	-									
Cr1	4	0.1942	0.9927	-0.3096									
Cu	5	-0.9456	-0.363	0.6693	-0.4221	-							
Cu1	6	-0.9099	-0.0189	0.4794	-0.0987	0.9291	-						
Ni	7	-0.2069	0.867	-0.2369	0.8068	0.0852	0.4443	-					
Ni1	8	0.9343	0.3332	-0.6206	0.3991	-0.9977	-0.9461	-0.1301	-				
Pb	9	-0.6094	-0.8619	0.5684	-0.8927	0.7842	0.522	-0.5212	-0.7653	-			
Pb1	10	-0.8517	-0.5901	0.6461	-0.6433	0.9655	0.8148	-0.1556	-0.9577	0.9179			
Zn	11	-0.86	-0.6183	0.715	-0.6598	0.9547	0.779	-0.2147	-0.9399	0.9273	0.9945	-	
Zn1	12	-0.9017	-0.5518	0.7455	-0.5931	0.9721	0.8166	-0.1474	-0.9576	0.8913	0.9898	0.9961	
		2	3	4	5	6	7	8	9	10	11	12	
	Cd	Cd1	Cr	Cr1	Cu	Cu1	Ni	Ni	Pb	Pb1	Zn	Zn1	