

**DETERMINATION OF LEVELS OF SELECTED HEAVY METALS IN SOIL
AND VEGETABLES GROWN AT THE MARKET
DUMPSITE IN ELDORET, KENYA.**

**BY
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**A Thesis Submitted in Partial Fulfillment of the Requirements for the Award of
Master of Science Degree in Analytical Chemistry of Moi University.**

MOI UNIVERSITY

2016

DECLARATION

Declaration by the Candidate

I hereby declare that this thesis is my own work and has not been presented for a degree in any other University. No part of this thesis may be reproduced without the permission of the author or Moi University.

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DEDICATION

This work is dedicated to my parents; Mr. Lazarus Kerich and Mrs. Catherine Kerich and the entire family for their tireless support not forgetting my dear wife Risper Kerich.

ABSTRACT

Dumpsites in urban centres are often used for agricultural purposes due to their nutrient-rich soils without regard to the risks of toxic heavy metal. In a similar quest Eldoret market dumpsite is becoming an ideal site for growing vegetables. Consequently, heavy metals accumulate in the vegetables then pass to human beings through consumption causing numerous adverse effects. This research was conducted to determine levels of lead (Pb), cadmium (Cd), copper (Cu), zinc (Zn), iron (Fe) and nickel (Ni) in the soil, then kales (*Brassica oleracea*) and spinach (*Spinacea oleracea*) grown in Eldoret market dumpsite. Sampling was done between the month of November 2014 to August 2015 to cover for the dry and wet seasons. The collected vegetable samples were oven-dried at 60°C, ground and digested using mixture of Li_2SO_4 , Se, H_2SO_4 and H_2O_2 while soil samples were oven-dried at 80°C, crushed and digested with same mixture as the vegetable samples. The levels of heavy metal in the samples were analyzed using Atomic Absorption Spectroscopy (AA). Calibration graphs were generated using standard solution of concentration ranging from 5 ppm to 20 ppm that gave values of R^2 ranging from 0.9962 to 0.9995. All data were analyzed using SPSS and significance considered at $p < 0.05$. Significance of variation in heavy metals concentrations for soil and in the vegetables during dry and wet season was statistically analyzed using unpaired t-test. The results showed that the soils had the following mean concentrations of heavy metals for the dry (D) and wet (W) seasons: Pb 1.74 mg/Kg (D) and 1.53 (W) mg/Kg, Cd 1.07 mg/Kg for both dry and wet seasons, Cu 51.75 mg/Kg (D) and 50.33 mg/Kg (W), Zn 72.68 mg/Kg (D) and 61.94 mg/Kg (W), Fe 552.51mg/Kg (D) and 554.56 mg/Kg (W) and Ni 52.56 mg/Kg (D) and 54.55 mg/Kg (W). In kales, mean concentration of heavy metals for both seasons were: Pb 1.435 mg/Kg; Cd 0.11 mg/Kg; Cu 41.24 mg/Kg; Fe 454.44 mg/Kg; Zn 33.67 mg/Kg and Ni 40.08 mg/Kg. In spinach the concentrations obtained for dry and wet seasons were: Pb 0.936 mg/Kg; Cd 0.89 mg/Kg; Cu 42.17 mg/Kg; Fe 441.05 mg/Kg; Zn 33.80 mg/Kg and Ni 38.19 mg/Kg respectively. The Levels of the heavy metals in vegetables were above the WHO/FAO acceptable limits except for Zn and Ni. The t-test results gave values of $p < 0.05$ implying that there was significant differences between the concentration of the heavy metals in the vegetables and in the soils. Based on the findings, it was therefore concluded that the vegetables grown in the Eldoret market dumpsite are not safe for human consumption due to the high levels of lead, cadmium, iron and copper which are likely to pose health complications to consumers. In order to safeguard people from these toxic vegetables, farming activities in the Eldoret market dumpsite should be prohibited.

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LIST OF ACRONYMS AND ABBREVIATIONS

AAS	Atomic absorption spectroscopy
APHA	American Public Health Association
ATSDR	Agency for Toxic Substances and Disease Registry
BEH	Bureau of Environmental Health
EC	European Commission
EPA	Environmental Protection Agency
FAO	Food and Agricultural Organization
FDA	Food and Drug Administration
FEPA	Federal Environmental Protection Agency
HPA	Health Protection Agency
IARC	International Agricultural Research Centers
IOSHIC	International Occupational Safety and Health Information Centre
IPCS	International Programme on Chemical safety
IWMI	International Water Management Institute
MDH	Minnesota Department of Health
MPN	Most probable number
SACN	Scientific Advisory Committee on Nutrition
SD	Standard deviation
SPCR	Soil Pollution Control Regulation
UNDP	United Nation Development Programme
UNSGAB	United Nation Secretary General's Advisory Board
USDHHS	United States Department of Health and Human Services
USEPA	United States Environmental Protection Agency
UV	Ultra Violet
WHO	World Health Organization

WSIS Water Stewardship Information Series

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CHAPTER ONE

INTRODUCTION

1.1 Background Information

There is a rise in urban agricultural practices in developing countries due to the high rate of urbanization that comes with associated challenges, especially the increased demand for food and employment. Urban agriculture is known to provide a complementary strategy to reduce urban poverty, food insecurity, enhance urban environmental management and ensure productive use of urban wastes. To a large extent, urban agriculture complements rural agriculture as it provides products that rural agriculture cannot supply easily like the perishable products. In Kenya, urban agriculture is a common practice as it acts as a source of income and food that would have otherwise been scarce (Githongo, 2010).

Although urban agriculture has many benefits, precaution should be taken to ensure the safety of the produce. Rapid and relatively unorganized urban expansion, industrial developments coupled with inadequate waste management causes significant alterations in the physical environment and increases accumulation of urban waste. Indeed, one of the most pressing concerns of urbanization in the developing world, especially in Africa; Kenya included, has been the problem of solid, liquid and toxic waste management. Such waste may be toxic or radioactive (UNDP, 2006; Kimani, 2007; Bekteshi *et al.*, 2015). These cities reveal aspects of waste-management problem such as heaps of uncontrolled garbage, roadsides littered with refuse; streams blocked by rubbish, inappropriately disposed toxic waste and disposal sites that constitute a health hazard to residential areas.

Waste generation in urban areas has increased with the ever rising population and the search of better livelihoods in towns and cities. This has also led to increased pressure on the urban infrastructure especially to the county councils which are responsible for

managing the cities (Grimm *et al.*, 2008). Availability of land for farming has also been affected negatively since fertile lands in the urban settlements are being used for building and other industrial activities. As a result, urban residents especially the low income earners make use of free land spaces 'no man's land' to grow food crops. Most often, the free land spaces include waste disposal sites, rail and road sides, close to market places, besides polluted water bodies, mechanic workshops and industrial areas among others.

The direct use of dumpsites for cultivating vegetables and the on-farm use of compost sourced from the dumpsites is a common practice in urban centers in developing countries. This practice is potentially harmful to the health and well-being of adjacent population. Studies conducted earlier on vegetables grown in a dumpsite have shown that dumpsites increase heavy metal concentration in food crops to levels that are harmful for human health (Kimani, 2007; Shemdoe, 2010; Ebong *et al.*, 2008).

Farming in urban areas in developing countries is also characterized by the use of wastewater which is regarded as a resource of global importance. The use of wastewater helps to circumvent the problem of water scarcity and nutrient deficiency in agricultural farms. However, occurrence of uncontrolled urban sewage farming like the use of untreated or partially treated wastewater is a common site in African cities. This practice exposes consumers of such produce to poisoning from heavy metals and other contaminants (Ebong *et al.*, 2008).

In Kenya, solid waste management has remained a challenge for the last decades. Most cities/estates in the country are littered with garbage which when eventually collected finds its way into open dumps. The use of open dumps for county solid waste in Kenya makes environmental pollution highly probable. These wastes attract birds, rats, flies and other animals to the dump. Animals feeding at the dump may transmit diseases to human living in the vicinity (Eddy *et al.*, 2006; Oyelola *et al.*, 2009).

This study was conducted in Eldoret Market dumpsite near Sosiani River, Uasin Gishu County, Kenya. Near the Eldoret Market dumpsite is a populated area that is occupied by low income population living in an overcrowded area with experiencing compromised sanitation and inadequate source of water for domestic use. County sewage and River Sosiani passes near Eldoret market dumpsite. In an attempt to cater for basic needs, residents living near Eldoret dumpsites grow vegetables and grains in the Eldoret market dumpsite. Other farmers use manure from the Eldoret market dumpsite to enhance fertility of their small lands at homes. The dump site manure is readily and also perceived to be a rich source of nutrients like nitrogen and these enable farmers to avoid the high cost of artificial fertilizers. Crops grown using dumpsite manure and on the dumpsite were perceived by the present study to be exposed to fecal contamination because residents near Eldoret market dumpsite frequently have to rely on unsewered communal toilets or use open space during the call of nature. In addition, the available sewerage effluent find their way to the river and consequently to the vegetable farm. This study was done to assess the levels of heavy metal contaminants in soil and vegetables grown on the dumpsite and frequently consumed in the region. The figure 1.1 below provides photos of vegetables grown in the Eldoret market dumpsite.



Figure 1.1: Pictures (a)kales, (b)kales, (c)kales and (d)spinach are of vegetables grown

in the Eldoret market dumpsite

1.2 Problem Statement

The Eldoret market dumpsite has become an ideal site for farming activities because of limited land spaces yet the use of a dumpsite for farming activities is a great environmental hazard and a threat to public health. Due to the wetness of the dumpsite, leachates easily soak into the soil and underground water. The leachates can increase heavy metal concentration in the soil and underground water to levels that may have harmful effects on soil, crop and human health (Ebong *et al.*, 2008). Human health is at risk because food crops absorb the hazardous heavy metals from the soil and are finally transferred to man and animals through consumption of the crops. Therefore consumers of vegetables grown in the Eldoret market dumpsite are vulnerable to health risks associated with heavy metal contamination. Exposure to heavy metal toxicity leads to health problem such as brain damage, mental retardation, cerebral palsy, lung cancer, gastrointestinal abnormalities, dermatitis and death of the unborn foetus among other complications (USEPA, 2002; Rotich *et al.*, 2006; UNDP, 2006).

Farming in the dumping site provides farmers with renewable nutrients giving rise to healthy and eye catching vegetables (Kassan, 2010; McKenzie, 2005). However, the river Sosiani water can be regarded as a potential source of pollutants to food crops since the wastewater may not properly be treated. Improperly treated wastewater contains a significant amount of toxic metals such as arsenic, chromium, cadmium, copper, lead, nickel, zinc, cobalt, magnesium and iron which will accumulate in the soil and get transferred to food crops grown on these soils posing health threat to consumers of the food crops. Disease-causing pathogenic organisms (bacteria, virus, protozoa etc.) along with other parasitic helminthes which can give rise to health hazards on human beings, animals and plants are also found in untreated or partially treated water. The pathogens

are transmitted by direct contact to farmers and also to the general public through consumption of irrigated produce especially crops eaten raw (Blumenthal *et al.*, 2006).

Vegetable contamination in the Eldoret market dumpsite may not only affect farmers who have a direct contact with the vegetables but also the Eldoret residents at large. Through water runoffs, some wastes from the dumpsite ends up in Sosiani River extending environmental and health risks to communities living within the vicinity as well as those living downstream who could be using the water. Vegetable vendors are also responsible for extending the health risks to other regions since most of them buy vegetables at a wholesale price from the dumpsite then sell at a retail price in Eldoret market and other places within the region.

To create awareness to the public, it was obligatory to determine the levels of heavy metals on vegetables grown in the Eldoret market dumpsite.

1.3 Objectives of the Study

1.3.1 General Objective

The general objective of this study was to determine levels of selected heavy metal contaminants in soil and vegetables grown in the Eldoret market dumpsite.

1.3.2 Specific Objectives

The specific objectives of the study were to:

- i. To determine levels of lead, cadmium, copper, zinc, iron and nickel in kales and spinach grown in Eldoret market dumpsite then compare the levels with acceptable standards of World Health Organization (WHO).
- ii. To determine levels of lead, cadmium, copper, zinc, iron and nickel in soil at Eldoret market dumpsite then compare the levels with acceptable standards of World Health Organization (WHO).

- iii. To compare levels of the selected heavy metal contaminants in soil samples during dry and wet season.
- iv. To compare levels of the selected heavy metal contaminants in vegetable samples during dry and wet season.

1.4 Hypotheses

Based on literature reviewed, the following hypotheses were formulated and verified:

- i. There are no differences on the levels of Lead, Cadmium, Copper, Zinc and Iron in Kales and Spinach grown in Eldoret market dumpsite from the WHO levels.
- ii. There are no difference in levels of Lead, Cadmium, Copper, Zinc, Iron and Nickel in soils at Eldoret Market Dumpsite from WHO levels
- iii. There are no difference on the levels selected heavy metals contaminants on soils during and wet season.
- iv. There are no difference on the levels of selected heavy metals contaminants in vegetables during dry and wet season.

1.5 Justification

The World Health Organization (WHO) estimates that about a quarter of the diseases facing mankind today occur due to prolonged exposure to environmental pollution (Prüss-Üstün and Corvalán, 2006; Kimani, 2007). Eldoret town with its high population density generates large quantities of wastes daily. This has led to the formation of a mountain of garbage in the Eldoret market dumpsite which exposes residents to environmental pollution. The town does not have any environmentally friendly method of wastes disposal; wastes are being indiscriminately and improperly disposed the dumpsite. The dumpsite is not covered and therefore leachates find their way to the nearby farm soil. Since heavy metals persist in the environment for long, the levels of heavy metals in both soil and plants grown in the Eldoret market dumpsite may be considerably high.

Owing to serious health risks associated with heavy metal and pathogenic contaminants, it was of practical importance to determine the levels of selected heavy metal contaminants in vegetables grown in the Eldoret market dumpsite. Moreover, there is no published documents that particularly shown the level of heavy metals in crops grown near dumpsite in Eldoret market dumpsite, therefore this research intended to also fill the existing gap and inform the locals with full knowledge on suitability or otherwise of such food crops for human consumption and give a suggestion on the precautionary action that ought to be undertaken.

1.6 Scope of the Study

The study was limited to soil and two different vegetable species: spinach (*Spinacea oleracea*) and kales (*Brassica oleracea*) grown in the Eldoret market dumpsite. The two vegetable species represented the major species grown in the dumpsite and are commonly consumed in Eldoret. Vegetables grown on contaminated soil of a dumpsite and irrigated using water from dumpsite are known to contain various contaminants. However, due to limited time and financial constraints, the analysis was based on a few heavy metal contaminants (lead, cadmium, copper, zinc, iron and nickel) in soil, kales and spinach.

CHAPTER TWO

LITERATURE REVIEW

2.1 Vegetables

Vegetables are part of special and culturally specific plants consumed raw, cooked, dried or in any suitable form for the promotion of good health; they are usually used in soups and sauces as an accompaniment for the main staples (Keller, 2003). Over the past years, consumption of fresh vegetables has greatly increased as consumers strive to eat healthy

diets; they perceive fresh vegetables to be more nutritious than their processed counterparts. Vegetables constitute an important part of the human diet; they are considered as “protective supplementary food” since they contain large quantities of minerals, vitamins, carbohydrates, essential amino acid and dietary fibers, which are required for normal functioning of human metabolic processes (Kearney, 2010). They also act as a neutralizing agent for acidic substances formed during digestion (Arai, 2002; Hashmi *et al.*, 2007; Magaji, 2012). Report of WHO/FAO (2004) showed that vegetables help in the prevention and alleviation of several micronutrient deficiency diseases, especially in the less developed countries which are prone to hunger and malnutrition.

Although vegetables are considered as important part of human diet, precautions should be undertaken to ensure safety of the produce. As human activities increased especially with increase in modern technologies and application of organic fertilizers such as sewage sludge, manure and wastewater; contamination of the human food chain have become inevitable (Heaton and Jones, 2008; Hamilton *et al.*, 2006). Contaminants accumulate in the soil then get transferred to food chain causing serious health hazards to human beings and animals. Many people could be at risk of the adverse health effects from consuming common market vegetables cultivated in contaminated soil since the condition of the soil is often unknown or undocumented. The populations most affected by heavy metal toxicity are pregnant women or very young children (Vahter *et al.*, 2007). Neurological disorders, central nervous system destruction and cancers of various body organs are some of the reported effects of heavy metal poisoning.

Many researchers have revealed that some common vegetables are capable of accumulating high levels of metals from the soil. In a study carried out by Othman *et al.* (2001) on edible portions of five varieties of green vegetables: amaranths, Chinese cabbage, cowpea leaves, leafy cabbage and pumpkin leaves collected from several areas

in Dares Salaam, Africa; results showed that there was a direct positive correlation between Zn and Pb levels in soils with the levels in vegetables. Uptake and bioaccumulation of heavy metals by plants and vegetables depend on many factors such as species and nature of different vegetables (Lukšienė and Račaitė, 2008; Arora *et al.*, 2008; Richter *et al.*, 2015). Itanna *et al.* (2002) reported that leafy vegetables accumulate much higher contents of heavy metals as compare to other vegetables because leafy vegetables are most exposed to environmental pollution because of large surface area.

2.2 Waste water

Urban wastewater may be defined as a combination of liquid wastes from different sources such as domestic effluent consisting of black water i.e. toilet wastewater (excreta, urine and faecal sludge), grey water (kitchen and bathing wastewater), industrial effluents, agricultural effluents, hospital effluents and storm water (Raschid-Sally and Jayacody, 2008). As demand for fresh water intensifies, the use of county or industrial wastewater in agricultural sector is frequently seen as a common practice in many parts of the world. An estimated twenty million hectares in 50 countries worldwide are irrigated with raw or partially treated wastewater and this is likely to increase during the next few decades as water scarcity intensifies. Research results reported by Raschid-Sally and Jayacody (2008) indicate that, on a global level, around 200 million farmers use treated, partially treated and untreated wastewater to irrigate their crops. It is also estimated that 10 per cent of the world's population relies on food grown with contaminated wastewater (Corcoran *et al.*, 2010). The use of untreated and partially treated waste water for irrigation is particularly intense in arid/semi-arid regions and urban areas where unpolluted water is a scarce resource and wastewater enriched with nutrients is an important, drought-resistant resource for farmers (WHO, 2006; Wichelns & Qadir, 2015). Report of Raschid-Sally and Jayacody (2008) showed that the main

drivers of wastewater reuse in agriculture are: increasing urban water demand, increasing urban food demand, lack of alternative water sources, high nutrition value of wastewater and its consistency in supply. Farmers' ignorance on dangers associated with dumpsite manure and their need for plant nutrients has also contributed to the use of dumpsite manure.

Wastewater contains several plant macronutrients, principally nitrogen and phosphorus and in most cases, varying amounts of micronutrients such as boron, copper, iron, manganese, molybdenum and zinc (Coleman *et al.*, 2001). The nutrients results in increased crop yields without resorting to the use of artificial fertilizers and hence a reduction of the environmental impacts associated with the use and production of artificial fertilizers (WHO, 2006). A report by Murtaza *et al.* (2003) showed that leafy vegetables like cauliflower, cabbage, spinach etc. grow quite well in the presence of dumpsite. A review conducted by Hussein *et al.* (2001) also showed that wastewater is attractive and economically valuable for farmers because it contains important nutrients for crop growth. Similarly the use of wastewater benefit farmers through increased productivity, increased yields, faster growing cycles and additional water sources while decreasing their needs for artificial fertilizers. Richter *et al.*, (2015) and Stathatou *et al.*, (2015) stated that municipal wastewater besides being source of irrigation water, contain appreciable amounts of plant nutrients therefore there is potential for the nutrients present in recycled water to be used as fertilizer.

Besides the above mentioned advantages of wastewater that give rise to health and eye catching vegetables, application of dumpsite manure to farmlands carries a different set of risks to the environment and public health, especially where industrial wastes or household chemicals are part of the sewage flow. Negative effects are due to the presence of various substances including PCBs, pesticides, dioxins, heavy metals, asbestos,

petroleum products, pathogens and industrial solvents; many of them linked to soil contamination to soils and ailments ranging from cancer to reproductive abnormalities (Blumenthal *et al.*, 2002; Githongo, 2010).

Guideline values set by the World Health Organization (WHO) and United Nations Environment Program (UNEP) place restrictions on crops grown with wastewater and advise at least some sort of treatment of wastewater before its use (Blumenthal *et al.*, 2000). Excellent treatment options exist that can remove all harmful pathogens and bring heavy metal and nutrient loads within safe limits for use or disposal. However, majority of wastewater used in developing countries does not receive any conventional treatment before being directly applied to the agricultural land due to lack of funds. Planned and regulated use of wastewater remains, for many developing countries, an unobtainable goal in the near future (Wichelns & Qadir, 2015). A study conducted by Chepkole (2014) showed that domestic and industrial sewage in Eldoret is not properly treated because both the sewage treatment works cannot cope with total sewage discharge therefore the sewage wastewater can be regarded as a potential source of pollutants. In another study conducted by Githuku (2009), results indicated that the wastewater may not be suitable for irrigation as it poses a threat to the environment and health risks to farmers and consumers of the food crops. An investigation conducted by Gumbo (2010) in Malamulele, South Africa on the health implications of wastewater reuse in vegetable irrigation showed that there are potential health hazards associated with the practice since the levels of pollutants in wastewater exceeded the WHO guidelines.

Concern for public health has been the most important constraint in the use of wastewater in agriculture. Wastewater carries a wide spectrum of pathogenic organisms including bacteria, parasites and viruses which pose a risk to agricultural workers, crop handlers and consumers. When such water is used for irrigation, the soil becomes a reservoir of

enteric pathogens and has the potential to transmit various diseases of enteric origin (Kwashie, 2009). According to the report crops grown using dumpsite manure may be contaminated with pathogenic organisms and disease vectors which are responsible for human diseases like helminthiasis, cholera, typhoid, shigellosis, gastric ulcers caused by *Helicobacter pylori*, giardiasis and amoebiasis. Report of IWMI, (2006) showed that the use of wastewater for vegetable farming is a major source of diarrheal disease; the top cause of death among children in the developing world. In areas where human excreta is used as a fertilizer for crops, a high prevalence and intensity of *Ascaris* infection has often been reported for example, In China (Bethony *et al.*, 2006). Hookworm infection is also highly prevalent in wetter climates where excreta are used for example in Vietnam and Southern China. There was evidence of the transmission of cholera, typhoid and shigellosis when vegetables were irrigated with untreated wastewater in Santiago, Chile (Melloul *et al.*, 2002). Cross-sectional studies of symptomatic diarrheal disease indicated that there was a two-fold or greater risk of diarrheal disease associated with medium or high frequencies of consumption of uncooked onions irrigated with water consisting of wastewater. Consumption of raw vegetables coming from an area where untreated wastewater was used for irrigation in Santiago was related to an increase in seroprevalence to *Helicobacter pylori* (Allende & Monaghan, 2015). The problem of microbial contamination becomes more serious with the vegetables, because many of them are being consumed raw (Blumenthal *et al.*, 2002). However, the extent of contamination decreases if the vegetable's edible plant parts are above the ground, while it increases if they are near the ground.

Regarding chemical compounds in wastewater, the major health concern is due to metals (Chang *et al.*, 2002). Untreated wastewater irrigation plays a pivotal role in significantly increasing heavy metals in soil and crops. Wastewater increases individual metal in soil

by 2% to 80% and in crops by 14% to 90% (Sarabjeet and Dinesh, 2007). Sewage waste has been implicated as a potential source of heavy metals such as copper, cadmium, zinc, lead, nickel and iron in the edible and non-edible parts of vegetables. Wastewater irrigation leads to accumulation of heavy metals in the soil which often leads to degradation of soil and contamination of food chain mainly through the vegetable grown on such soils and lastly exposing human beings and animals to this contamination concluded that the use of wastewater for irrigation increased the contamination of Cd, Pb, and Ni in the edible portion of vegetables, potentially causing health risk in the long term. Similar findings have been documented from a study conducted in Harare, Zimbabwe, where farmers use wastewater for irrigating leafy vegetables (Mapanda *et al.*, 2005).

Studies conducted by Kisku *et al.*, (2000) in Kalipur, Bangladesh, on the uptake of Cu, Pb, Ni and Cd by *Brassica oleracea* from fields irrigated with industrial effluent indicated widespread contamination of heavy metals despite showing a healthy and gigantic external morphology. In another study on assessment of impact of heavy metal contamination on vegetables irrigated with polluted untreated effluent water from the sewage in Vinayakiya Nallah region of Jodhpur district, the results indicated that concentration of each metal exceeded the natural limits and the limits of FAO in all vegetable samples.

2.3 Dumpsite

Dumpsite is a land disposal site at which solid wastes are disposed off in a manner that does not protect the environment, (Kurian *et al.*, 2003). Open waste dumping constitutes serious problems since most of such disposal sites are not scientifically selected nor well planned or properly managed. They are also uncovered and unlined therefore allow leachates; a liquid formed by decomposing waste, to soak into the soil and underground water.

Open dumps are a source of various environmental and health hazards. The decomposition of organic materials produces methane, which may cause explosions and produce leachates, which pollute surface and ground water (Oyelola *et al.*, 2009). Additionally dumpsites constitute health hazard even to passers-by and those living near the dumps. This is due to the obnoxious smell oozing from the activities of micro-organisms on the organic waste. Uncontrolled burning of solid waste constitutes serious environmental pollution, adversely affecting solid waste workers and pickers.

Dumpsite managers in some cities have also been known to deliberately set periodic fires at the dumps in order to reduce the volume of the wastes, creating room for more wastes and thus extend the life of the dumps. Human may also cause intentional fires since metals are easier to spot and recover among ashes after the fires than among piles of mixed waste (USEPA, 2002; UNDP, 2006).

The global rise in human population has had a negative impact on availability of land for farming, especially in the urban and urban settlements. As a result, dumpsites have become an ideal site for farming activities. Research has shown that plants grown in these sites perform better compared to the surrounding areas because municipal wastes increase nitrogen, pH, cation exchange capacity, percentage base saturation, organic matter and soil nutrients for plant growth; decayed and composted wastes enhance soil fertility(Ogunyemi *et al.*, 2003).

However, a considerable proportions of plastic, paper, metals and batteries which are known to be sources of metals which may be hazardous to man and the environment are also present in a dumpsite (Pasquini and Alexander, 2004; Woodbury, 2005). Recent studies have revealed that wastes dumpsites can transfer significant levels of these toxic and persistent metals into the soil. The metals are eventually taken up by plants parts and

get transferred into the food chain therefore assessment of dumpsite soils for levels of hazardous metals is imperative for healthy crop production. Plants grown in some dumpsites of Nigeria were found to contain higher levels of heavy metals.

In Ghana, an experiment carried out on three waste dumpsites in Kumasi, where vegetable cultivation was practiced, found the levels of the two most toxic heavy metals i.e. cadmium and lead to be far higher in the vegetables than the WHO/FAO recommended values (Odai *et al.*, 2008). In another study conducted by Kimani (2007) in Dandora waste dumpsite in Nairobi showed high levels of heavy metals, in particular Pb, Hg, Cd, Cu and Cr in the soil samples obtained on the site. A medical examination of the children and adolescents living and schooling near the dumpsite indicated a high incidence of diseases that are associated with high exposure levels to these metal pollutants (Kimani, 2007).

A study conducted by Magaji (2012) within a dumpsite located at Mpape in Abuja to investigate the uptake of heavy metals by plants, the findings showed that the concentrations of heavy metals in some selected vegetables and tuber crop cultivated around Mpape dumpsite were higher than those from the control site and they were also above the Federal Environmental Protection Agency (FEPA) acceptable limit except iron and zinc in spinach that was within the limit. Hunachew and Sandip (2011) conducted a study with an aim to determine the levels of various heavy metals present in the soil and leachate of the Addis Ababa solid waste dumpsite and its potential ecological and public health risk. The results indicated that the concentration of heavy metals: zinc, chromium, nickel, cobalt and lead in the soil samples of the dumpsite and nearby open land were found higher than the internationally acceptable limit for the soil. No difference was observed in concentrations of trace elements between soil of the dumpsite and the nearby grazing land.

Mean concentration of As and Cr in the soil samples and leachates of Mtoni dumpsite bordering the Indian Ocean, were above the established contaminant limits of Tanzania standard soil quality (Shemdoe, 2010). Results on assessment of concentration of heavy metals (Fe, Zn, Pb, Cu and Cr) in and around Uwelu scrap car dumpsite in Benin City; southern Nigeria revealed that all the metals recorded their highest concentration. The level of Fe and Pb were above the FEPA minimum acceptable limit.

2.4 Heavy Metal Contaminants

Heavy metals are a group of elements with density greater than 4.5 g/cm^3 and tend to release electrons in chemical reactions to form simple cations. In solid and liquid states, they are characterized by good heat and electrical conductivity, high melting and boiling points and they were glossy and opaque nature. The metals classified as heavy metals include: copper, cobalt, chromium, cadmium, iron, zinc, lead, tin, mercury, manganese, nickel, molybdenum, vanadium and tungsten (Szyzewski *et al.*, 2009).

Although trace quantities of certain heavy metals such as iron, nickel, cobalt, copper, manganese, chromium and zinc are essential micronutrients for higher animals and plant growth; excessive concentration of the heavy metals in food and feed plants are of great concern. The presence of heavy metals at abnormal levels is of great concern because they have cumulative behavior, non-biodegradable nature, long biological half-lives and lack good mechanism for elimination from the body (Jarup, 2003; Babel and Dacera, 2006; Dashwood, 2014; McBride *et al.*, 2014; Wang *et al.*, 2015). The heavy metal ions form complexes with proteins, in which carboxylic acid ($-\text{COOH}$), amine ($-\text{NH}_2$), and thiol ($-\text{SH}$) groups are involved. These modified biological molecules lose their ability to function properly and result in the malfunction or death of the cells. When metals bind to these groups, they inactivate important enzyme systems, or affect protein structure, which is linked to the catalytic properties of enzymes. This type of toxin may also cause the

formation of radicals; dangerous chemicals that cause the oxidation of biological molecules (Neal and Guilarte, 2012).

Metals like mercury, lead, cadmium, aluminum, antimony, bismuth, barium and uranium are toxic and therefore non-essential for higher animals. Presence of such heavy metals in the atmosphere, soil and water even in traces can cause serious health problems to man and animals particularly in elevated concentrations.

The circulation and migration of metals in the natural environment are mainly related to such processes as rock decay, volcano eruptions, evaporation of oceans, forest fires and soil formation processes. Anthropogenic contamination of the environment by heavy metals include different branches of industry; the power industry, transport, municipal waste management, waste dumping sites, fertilizers and waste used to fertilize soil(He, 2004). The heavy metals from these sources are dispersed in the environment leading to contamination of soil, water and air (He, 2004; Ho, 2009; Jamalia *et al.*, 2009; Szycczewski *et al.*, 2009; Muhammad, 2009).

Human beings can be exposed to these metals through different paths such as air, water and food (Qiao-qiao *et al.*, 2007; Kim *et al.*, 2008; Hu *et al.*, 2010). Dietary intake is the main route of exposure for most people, although inhalation can play an important role in very contaminated sites. Information about heavy metal concentrations in food products and their dietary intake is very important for assessing their risk to human health.

Cultivation of crops for human or livestock consumption on contaminated soil can potentially lead to the uptake and accumulation of trace metals in the edible plant parts with a resulting risk to human and animal health (Ho, 2009). Heavy metals may disturb the normal functions of central nervous system, liver, lungs, heart, kidney and brain, produce hypertension, abdominal pain, skin eruptions, intestinal ulcer and different types

of cancer. Furthermore, consumption of heavy metal-contaminated food can seriously deplete some essential nutrients in the body causing a decrease in immunological defenses, intrauterine growth retardation, impaired psycho-social behavior and disabilities associated with malnutrition (Arora *et al.*, 2008).

Numerous studies link the presence of heavy metals such as Pb and Cd to incidence of cognitive impairments especially in children. Liu *et al.* (2005) reported that soil and vegetables polluted with Pb and Cd in Copsa Mica and Baia Mare, Romania, significantly contributed to decreased human life expectancy within the affected areas, reducing average age at death by 9–10 years. Turkdogan *et al.* (2002) suggested that the high prevalence of upper gastrointestinal cancer rates in the Van region of Turkey was related to the high concentration of heavy metals in the soil, fruit and vegetables. Sharma & Agrawal (2005) revealed carcinogenic effects of several heavy metals such as cadmium, iron, lead, mercury, zinc and nickel.

2.4.1 Lead

Lead is a naturally occurring soft, bluish-grey metal whose density is 11.342 g/cm^3 . It is the commonest of the heavy metals accounting for 13 mg/kg of the earth's crust. The melting point and boiling point of lead are $327.46 \text{ }^\circ\text{C}$ and $1749 \text{ }^\circ\text{C}$ respectively. Several isotopes of lead exist in nature in the following order of abundance: ^{208}Pb , ^{206}Pb , ^{207}Pb and ^{204}Pb (Hoefs, 2013).

2.4.1.1 Sources of Lead Exposure

The main source of lead is from old lead piping in the water distribution system. It can also be found in: batteries, solder, ammunition, pigments, paint, ceramic glaze, hair dyes, fishing equipment, leaded gasoline from vehicle exhausts, mining, plumbing and coal burning. Cigarette smoke and pesticide residues are other sources (Lawrence, 2011).

Lead is considered as the most significant heavy metal affecting vegetable crops (Kachenko and Singh, 2006).

2.4.1.2 Effects of Lead on Human Health

Lead is a non-essential metal to human body; it is a toxic heavy metal. According to Llobet *et al.*, (2003), lead is toxic even at low concentration. The recommended standard of lead in leafy vegetables is 0.3 mg/Kg (WHO/FAO, 2001). Lead is a potential human carcinogen. Lead poisoning is associated with etiology of a number of diseases such as inhibition of the synthesis of hemoglobin, dysfunctions in the kidneys, joints and reproductive systems and cardiovascular system as well as acute and chronic damages to the central nervous system and peripheral nervous system. Lead is also known to induce renal tumors, reduce cognitive development and increase blood pressure. Epidemiological studies show that exposure to lead during the early stages of children's development is linked to a drop in intelligence quotient and that for each 10 µg/dl of blood lead, intelligence quotient is reduced by at least 1-3 points (Canfield *et al.*, 2003; Chen *et al.*, 2005; Morgan, 2013). Other effects of lead include: abdominal pain, adrenal insufficiency, anemia, arthritis, arteriosclerosis, attention deficit, back problems, blindness, constipation, convulsions, deafness, depression, diabetes, dyslexia, epilepsy, fatigue, gout, impaired glycogen storage, hallucinations, hyperactivity, impotency, infertility, inflammation, learning disabilities, diminished libido, migraine headaches, multiple sclerosis, psychosis, thyroid imbalances and tooth decay (Lawrence, 2011).

2.4.2 Cadmium

Cadmium is a lustrous, silver-white, ductile and very malleable metal. Its surface has a bluish tinge and the metal is soft enough to be cut with a knife. Its density is 8.7 g/cm³ at 20 °C while the melting and boiling point are 321 °C and 767 °C respectively (Campbell,

2006). It is soluble in acids but not in alkalis. Cadmium is a metal with oxidation state of +2.

2.4.2.1 Sources of Cadmium Exposure

The main anthropogenic sources of cadmium include mining, smelting, burning coal or garbage containing cadmium, rechargeable batteries (nickel-cadmium batteries), pigments, solar cells, steel, metal plating and water pipes. Use of contaminated water for irrigation, fertilizers, municipal sewage sludge and compost can remarkably increase the cadmium uptake into plant tissues (Brevik and Burgess, 2013). Cigarette smoking is another source of cadmium exposure (WHO, 2000). For non-smoking population, food and water is the most important source of cadmium exposure (WHO, 2000). Cadmium just like lead is considered as the most significant heavy metal affecting vegetable crops.

2.4.2.2 Effects of Cadmium on Human Health

Cadmium is not essential to human body; there is no 'safe exposure' for the human body even at minute levels. The recommended standard of cadmium in leafy vegetables is 0.02 mg/Kg (WHO/FAO, 2001). Cadmium exposure to human beings may cause kidney damage, skeletal damage, irritation of the lungs and gastrointestinal tract, cancer of the lungs and prostate, abdominal pain and diarrhea.

The International Agency for Research on Cancer (IARC) has classified cadmium and cadmium compounds as carcinogenic to humans, meaning that there is sufficient evidence for their carcinogenicity in humans (Brevik and Burgess, 2013; Liao *et al.*, 2015). Excess patients of lung cancer were found among workers in a United States

cadmium recovery facility. In Japan, Itai-itai disease; a bone and kidney disorder was associated with chronic cadmium pollution of paddy water coming from the. Studies in children and pregnant women are still limited, but there is some evidence that elevated cadmium exposure during pregnancy may affect a child's motor skills and perception and that high cadmium levels in the urine of school children are associated with a weakened immune system (Schoeters *et al*, 2006).

2.4.3 Copper

It is a ductile, malleable, reddish-brown metallic element that is an excellent conductor of heat and electricity (HPA, 2010). Density of copper is 8.9 g/cm³ at 20 °C while the melting point and boiling point are 1083 °C and 2595 °C respectively.

2.4.3.1 Sources of Copper Exposure

Due to heat and electrical conductivity of copper as well as its resistance to corrosion, ductility and malleability, copper has many industrial applications and is widely used in electrical wiring, switches, electroplating, plumbing pipes, coins, metal alloys and fireworks (HPA, 2010). Copper is mostly found in: copper water pipes, pesticides, swimming pools, intra-uterine devices, dental amalgams, nutritional supplements especially prenatal vitamins, birth control, weak adrenal glands and occupational exposure. One may be exposed to copper by breathing air, eating food or drinking water containing copper as well as through skin contact with soil, water or other copper containing substances (Chen *et al.*, 2006).

2.4.3.2 Effects of Copper on Human Health

Copper is an essential element; small amounts are necessary in diets to ensure good health for living organisms including human beings (Prasad, 2013). However, if daily intake of 0.9 mg/day is exceeded, deficiency and toxic effects are observed (Singh and Garg, 2006; FDA, 2001). The recommended standard of copper in leafy vegetables is 40 mg/Kg (WHO/FAO, 2001). Main problem associated with copper is that if its concentration increases too sharply, the body's absorption of zinc will be impeded. Zinc deficiency contributes to infertility (Lawrence, 2011). Copper has also been associated with liver damage and kidney disease (MDH, 2006; Lawrence, 2011). Merck (2005) reported that copper is suspected to cause infant liver damages.

Acute symptoms of excess copper include salivation, epigastric pain, vomiting, diarrhea, stomach cramps, nausea, irritation of eyes and respiratory tract. Vomiting and diarrhea usually prevent more serious manifestations of copper toxicity that can include coma, shock, oliguria (diminished urine secretion), hemolytic anemia, acute renal (kidney) failure with tubular damage, hepatic necrosis (liver cell death), vascular collapse and death. Exposure to skin can cause inflammation, itching and burns (HPA, 2010).

2.4.4 Zinc

Zinc is a lustrous bluish-white metal. It is brittle and crystalline at ordinary temperatures, but it becomes ductile and malleable when heated between 110°C and 150°C. Its density is 7.11 g/cm³ at 20 °C. The melting and boiling point of zinc are 419.58 °C and 907 °C respectively.

2.4.4.1 Sources of Zinc Exposure

Zinc enters the air, water and soil as a result of both natural processes and human activities. Main sources of zinc to the environment are: mining, purification of zinc, lead and cadmium ores, steel production, coal burning and burning of wastes. Levels of zinc in soil increases mainly from disposal of domestic wastewater, zinc wastes from metal

manufacturing industries and coal ash from electrical utilities. Sludge and fertilizers also contribute to increased levels of zinc in the soil (ATSDR, 2005).

Other sources include: corrosion and leaching of plumbing, water-proofing products (zinc formate, zinc oxide), anti-pest products (zinc arsenate - in insecticides, zinc dithioamine as fungicide, rat poison, rabbit and deer repellents, zinc fluorosilicate as anti-moth agent), wood preservatives (as zinc arsenate), deodorants and cosmetics (as zinc chloride and zinc oxide), medicines and ointments (zinc chloride and oxide as astringent and antiseptic, zinc formate as antiseptic), paints and pigments (zinc oxide, zinc carbonate, zinc sulphide), printing inks and artists paints (zinc oxide and carbonate), colouring agent in various formulations (zinc oxide) and a UV absorbent agent in various formulations (Lawrence, 2011).

2.4.4.2 Effects of Zinc on Human Health

Zinc is an essential metal to human beings; it is extraordinarily useful in biological systems (Nriangu, 2007). However, beyond intake range of 8-11 mg/day deficiency and toxic effects are observed (FDA, 2001; Singh and Garg, 2006). The recommended standard of zinc in leafy vegetables is 99.40 mg/Kg (WHO/FAO, 2001). Toxicity of zinc in human beings is minimal; its major effect is interference with copper metabolism. Symptoms of an acute oral zinc dose may include: tachycardia, vascular shock, dyspeptic nausea, vomiting, diarrhea and damage of hepatic parenchyma. EPA currently classifies zinc and compounds as carcinogenic. Plum *et al.*, (2015) revealed carcinogenic effects of several heavy metals including zinc. The United States Food and Drug Administration have stated that zinc damages nerve receptors in the nose, which may cause anosmia. Reports of anosmia were also observed in the 1930s when zinc proportions were used in a failed attempt to prevent polio infections (Duncan-Lewis *et al.*, 2011).

2.4.5 Iron

Iron is a heavy, malleable, ductile, magnetic and silver-white metallic element that readily rusts in moist air. Its density is 7.8 g/cm^3 at $20 \text{ }^\circ\text{C}$ while the melting and boiling point are $1536 \text{ }^\circ\text{C}$ and 2861°C respectively. Iron is the fourth most abundant element in the Earth's crust and is mostly found as ions Fe^{2+} and Fe^{3+} . The most common ores of iron are hematite or ferric oxide (Fe_2O_3); magnetite or iron oxide (Fe_3O_4).

2.4.5.1 Sources of Iron Exposure

Iron is the most used of all the metals because of its low cost and high strength. Its applications go from food containers to family cars, from screw drivers to washing machines. The major sources of exposure to iron are: construction material, drinking water pipes, pigments in paints and in plastics. Other compounds are used as food colour and for treatment of iron deficiency in humans. Various iron salts are used as coagulants in water treatment (SACN, 2010).

2.4.5.2 Effects of Iron on Human Health

Iron is an essential metal to human body; it is vital to biological processes as in transport of oxygen in the body. However, intake beyond a range of 8-18 mg/day gives rise to deficiency and toxic effects (Singh and Garg, 2006; FDA, 2001).

Iron may cause conjunctivitis, choroiditis and retinitis if it contacts and remains in the tissues. The large amounts of ingested iron can cause excessive levels of iron in the blood which react with peroxides to produce free radicals, which are highly reactive and can damage DNA, proteins, lipids and other cellular components (Clifford, 2010). High doses of iron can also damage the intestinal mucosa and cause systemic shock and death. Iron

supplementation may favour infectious pathogens by providing them with a supply of iron for their growth and replication (SACN, 2010).

2.4.6 Nickel

Nickel is a lustrous white, hard and ductile metal whose density is 8.9 g/cm³ at 20 °C. Its melting point and boiling point are 1453 °C and 2913 °C. It occurs naturally in five isotopic forms: ⁵⁸Ni (67.8%), ⁶⁰Ni (26.2%), ⁶¹Ni (1.2%), ⁶²Ni (3.7%) and ⁶⁴Ni (1.2%) (Nestle, 2002). Nickel is one of the five ferromagnetic elements (Prasad, 2013). Nickel usually has two valence electrons but oxidation states of +1, +3 or +4 may also exist (WHO, 2005).

2.4.6.1 Sources of Nickel Exposure

Common uses of nickel include production of stainless steel and other corrosion-resistant metals containing nickel. Other products which contain nickel include rechargeable (Ni-Cd) batteries, coins, welding rods and wires, electronic or computer equipment and pigments for paints or ceramics. Nickel is also used in electroplating, electroforming and sintered metal coatings (WHO, 2005). The major sources of nickel contamination in the soil are metal plating industries, combustion of fossil fuels and nickel mining (Khodadoust *et al.*, 2004). It is also found in hydrogenated oils (margarine, commercial peanut butter) shellfish, air pollution, cigarette smoke (Lawrence, 2011).

2.4.6.2 Effects of Nickel on Human Health

The recommended standard of nickel in leafy vegetables is 67 mg/Kg (WHO/FAO, 2001). Many harmful effects of nickel are due to its interference with metabolism of essential metals such as Fe(II), Mn(II), Ca(II), Zn(II), Cu(II) or Mg (II) which can suppress or modify the toxic and carcinogenic effects of nickel. The toxic functions of

nickel probably result primarily from its ability to replace other metal ions in enzymes and proteins or to bind to cellular compounds containing O-, S-, and N-atoms, which are then inhibited (Cempel & Nickel, 2006). Exposure to nickel leads to cancer (oral and intestinal); its carcinogenicity have been reported by: the National Toxicology Program (NTP), the International Agency for Research on Cancer (IARC).

Nickel is a ubiquitous metal frequently responsible for allergic skin reactions and has been reported to be one of the most common causes of allergic contact dermatitis or asthma as reflected by positive dermal patch tests (Kitaura *et al.*, 2003; Cavani, 2005).

2.5 Analytical Techniques

Some analytical techniques used in the analysis of quality of food products are discussed below.

2.5.1 Atomic Absorption Spectroscopy (AAS)

It works on the principle that certain elements absorb certain wavelengths and this level of absorption is characteristic of each element. Also on principle that electrons in atoms can only exist in particular energy levels and when an electron moves to a higher energy level, electromagnetic radiation of a particular frequency is absorbed. Because of this, it's possible to measure the concentration of certain elements in a sample depending on how much of a specific wavelength is absorbed. AAS is a form of quantitative analysis as opposed to a qualitative analysis, as the element being tested must be known. This is because a wavelength must be emitted which is specific to the element being tested. This also allows for an individual element to be analyzed even if other elements are present in a sample. Popularity of AAS in quantitative analysis of elements is not surprising due to the high sensitivity and selectivity of the technique. Moreover, the technique is characterized by low detectability limit and high precision (Szyzewski *et al.*, 2009). In

AAS, the sample is atomized then a beam of electromagnetic radiation is passed through the vaporized sample. The wavelength at which absorption occurs is characteristic of the element and the degree of absorption is the function of concentration of atoms in the vapour; the greater the number of atoms in the sample, the more radiation is absorbed.

The atomic absorption spectrometer needs the following three components: a light source, a sample cell to produce gaseous atoms and a means of measuring the specific light absorbed. Hollow cathode lamp emits the atomic line spectrum of the element to be determined. The monochromator isolates the desired resonance line from the spectrum emitted by the hollow cathode lamp. A detector measures the intensity of the incident light and generates an electrical signal proportional to the intensity. The electrical signals are displayed on the read out as concentration of trace element that was being analyzed. The figure 2.1 below gives schematic representation of instrumentation of Atomic Absorption Spectroscopy.

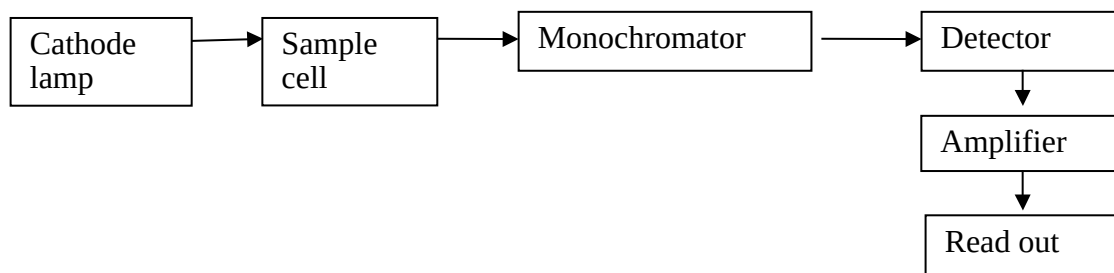


Figure 2.1: Schematic representation of instrumentation of atomic absorption spectroscopy

The first step in the AAS process is to determine the element to be tested in the sample and the suitable hollow cathode lamp must be placed in the spectrometer. Each element absorbs different wavelengths and so a separate lamp is needed for each element. The sample is then fed into the flame with the assistance of a nebulizer, which takes the test solution and vaporizes it thus converting it into atoms. The hollow cathode lamp emits

radiation and as the light passes through the flame, some of it is absorbed by the vaporized element. The light passes into a monochromator then to a detector. The light that reaches the detector is measured and compared to the intensity of the light that hit the detector when the sample was not present. The data processor then calculates the results obtained by the detector and the amount that was absorbed is displayed on the screen as concentration of trace element that was being analyzed. The Figure 2.2 gives a representation of absorption of radiations.

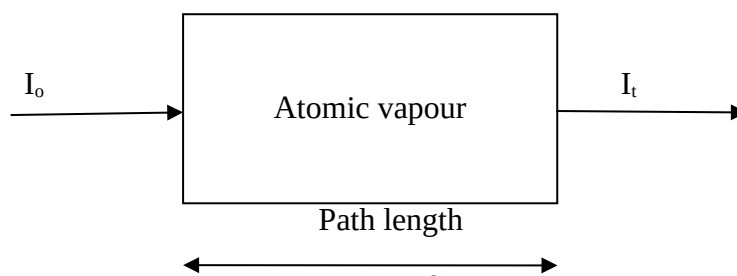


Figure 2.2: Schematic representation absorption of radiations in AAS

Where I_0 is the intensity of the radiations from the cathode lamp and I_t is the intensity of the radiations reaching the detector after some radiations have been absorbed by the atomic vapour.

2.5.2 Flame Photometer

A photoelectric flame photometer is a device used in chemical analysis to determine the concentration of certain metal ions, among them sodium, potassium, lithium, and calcium (Peitzman, 2010). Group 1 and Group 2 metals are quite sensitive to Flame Photometry due to their low excitation trait. In principle, flame photometry is a controlled flame test with the intensity of the flame colour quantified by photoelectric circuitry (Mendham, 2006). The intensity of the colour will depend on the energy that had been absorbed by the atoms that was sufficient to vaporize them. The sample is introduced to the flame at a

constant rate. Filters select which colours the photometer detects and exclude the influence of other ions. Before use, the device requires calibration with a series of standard solutions of the ion to be tested (Peitzman, 2010).

Flame photometry is crude but cheap compared to flame emission spectroscopy, where the emitted light is analyzed with a monochromator (Monteiro *et al.*, 2008). Its status is similar to that of the colorimeter (which uses filters) compared to the spectrophotometer (which uses a monochromator). It also has the range of metals that could be analyzed and the limits of detection are also considered.

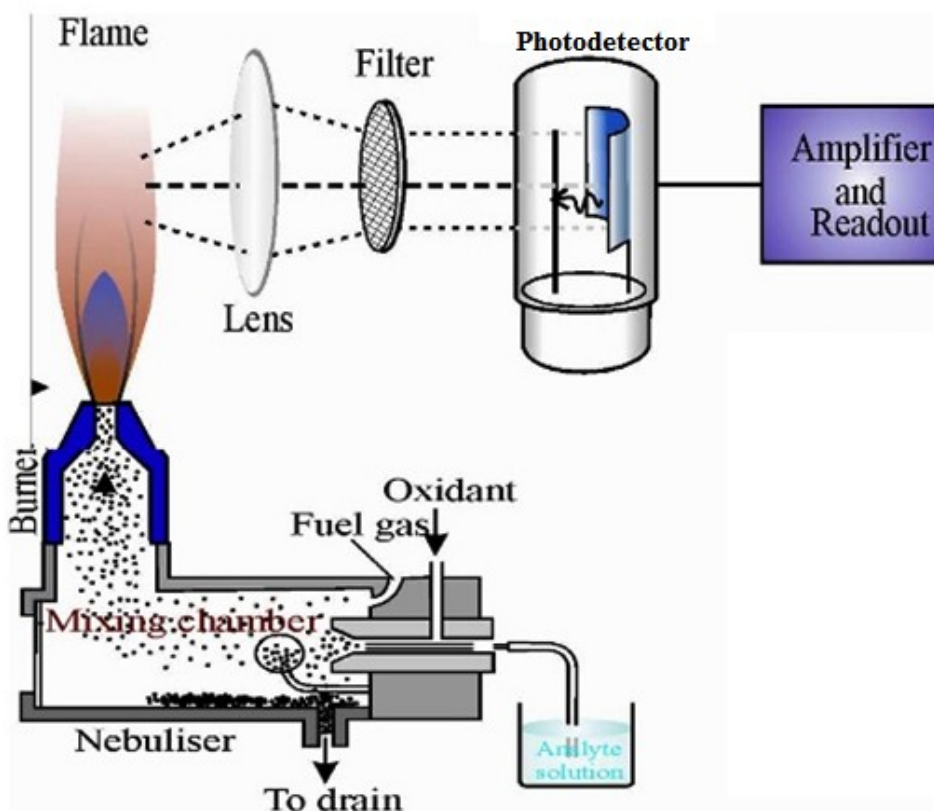


Figure 2.3: Schematic drawing of flame photometry (Source: Peitzman, 2010)

The major components of the instrument are sample delivery system, source, monochromator, detector and read out device.

CHAPTER THREE

MATERIALS AND METHODS

3.1 Sample Area and Sampling

The sample area was the Eldoret market dumpsite located at lower Eldoret town; approximately 400m away from the City Centre and occupies about 200m² of land. Its Geographic Positioning System (GPS) coordinates are 0°31'N 35°17'E. Vegetables are grown in this dumpsite. Surrounding the dumpsite is the Eldoret market and Uasin Gishu county houses. Sosiani River passes near the dumpsite. Dumping at the site was unrestricted; industrial, agricultural, domestic and medical wastes among others were deposited into the dumpsite. The dumpsite is open and thus animals have access to the dumpsite.

Sampling was done between the months of November 2014 to August 2015 to cater for both dry and wet seasons. Sampling was done six times (thrice in the dry season and thrice in the wet season). Soil and edible portions of spinach and kales were collected from the vegetable farms of the Eldoret market dumpsite near river Sosiani. Seven sites that were about 30-40 m apart were identified for sampling. Vegetable samples were collected randomly from seven identified sites into clean new polythene bags, labeled and transported to the laboratory. Soil samples were collected from three different points in each of the seven identified sites in a triangular pattern at a depth of between 0-15 cm; put into clean new polythene bags, labeled and transported to the laboratory. The 0-15 cm depth was considered to represent the plough layer and average root zone for nutrients uptake and heavy metal burden by plants (Eddy *et al.*, 2006; Odai *et al.*, 2008). The samples were transported to the laboratory after which they were kept in a fridge awaiting analysis. Figure 3.1 below shows location of the Eldoret market dumpsite.

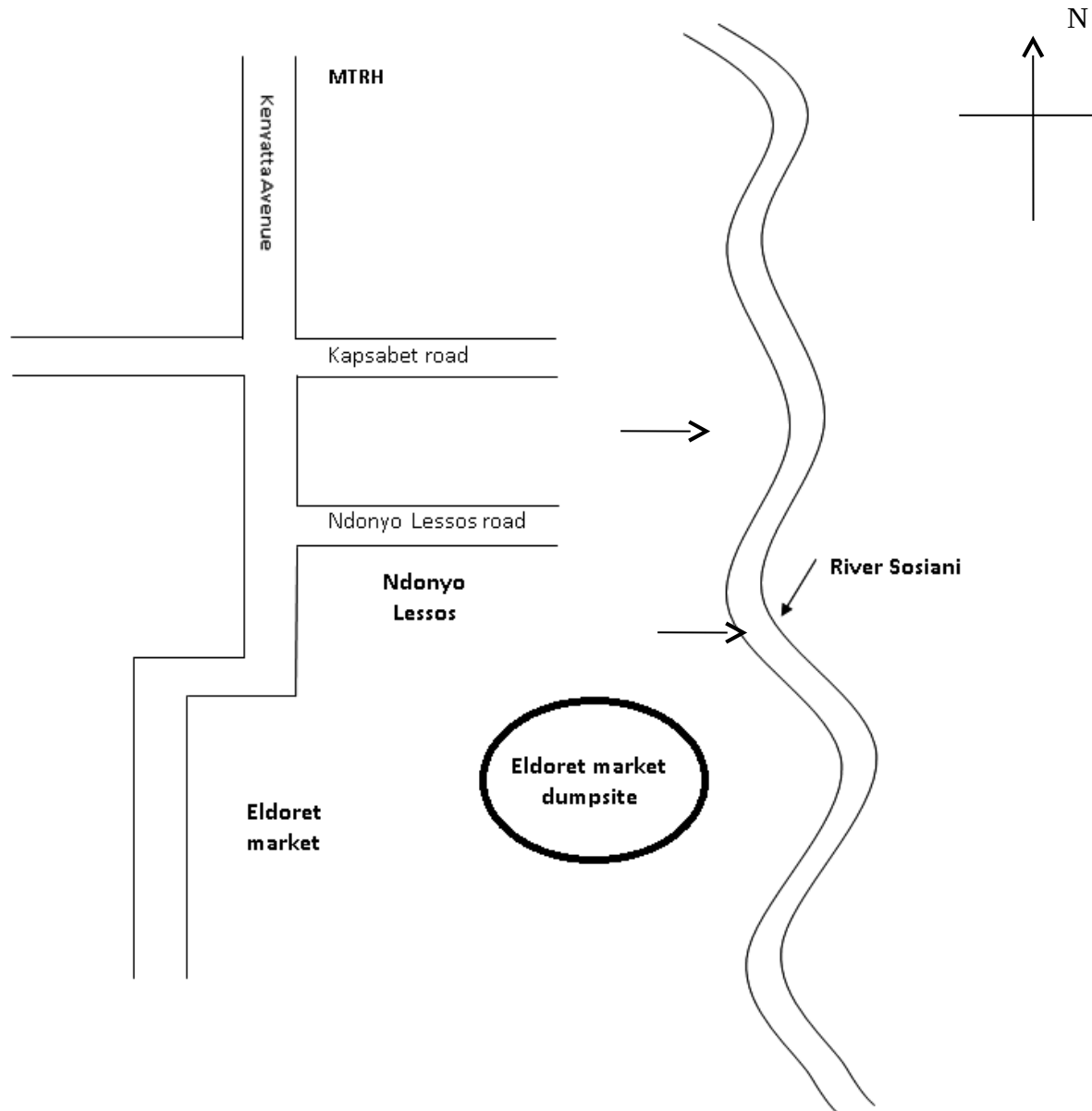


Figure 3.1: Map of Eldoret town showing location of the Eldoret market dumpsite

(GPS Coordinates: 0°31'N 35°17'E)

3.2 Analysis of Heavy Metal Contaminants

Analysis of the concentration of the heavy metals was done using Atomic Absorption Spectrometer (AAS) (Welz & Sperling, 2008). A standard mixture of hydrogen peroxide, lithium sulphate, sulphuric acid and selenium powder was used as a digestion mixture. The hydrogen peroxide oxidised organic matter while selenium powder acted as catalyst for the reaction and sulphuric acid completed the digestion at elevated temperatures. The mixture was prepared by accurately weighing 0.42g of selenium powder then added to 14 g of lithium sulphate. The 350 mL of 30% hydrogen peroxide was added to the mixture and mixed well after which 420 mL of concentrated sulphuric acid (18.4 Molar) was added slowly while cooling the mixture in an ice bath.

3.2.1 Preparation of Vegetable Samples

The vegetable samples were placed under running tap water to wash off soil particles and other debris then rinsed with distilled water. The samples were chopped then air-dried for 2 days after which they were dried in an oven at 60 °C for 24 hours. The dry samples were crushed in a mortar and the resulting powder digested by weighing 0.3 g of oven dried ground plant sample into a labeled digestion tube containing 4.4 mL of digestion mixture. The samples together with two reagent blanks were digested at 360 °C for 2 hours till the solution became colourless. The contents were allowed to cool after which about 25 mL of distilled water was added and mixed well until no more sediment dissolved then filtered. The mixture was made up to 50mL using distilled water, mixed well then allowed to settle so that a clear solution could be taken from top for analysis.

3.2.2Preparation of Soil Samples

Soil samples were oven dried for 72 hours at 80 °C after which the samples were crushed using a pestle and a mortar then sieved. The 0.3g of oven dried ground soil sample was

transferred into a labeled, dry digestion tube after which 4.4 mL of digestion mixture was added to each tube and to two reagent blanks. The samples together with the reagent blanks were digested at 360 °C for 2 hours till the solution became colorless. The contents were allowed to cool after which about 25 mL distilled water was added and mixed well until no more sediment dissolved then filtered. The mixture was made up to 50 mL using distilled water, mixed well then allowed to settle so that a clear solution could be taken from top for analysis.

3.3 Preparation of Stock and Working Solutions

3.3.1 Preparation of Stock and Working Solution of Lead

Stock solution of lead was prepared by dissolving 1.0g of lead in 20 mL of 1:1nitric acid : water ration then diluted to 1 L to give 1000 ppm of lead. A working solution of 100 ppm was prepared by pipetting 10mL from 1000 ppm stock solution into 100 mL volumetric flask then made to the mark using distilled water. Standard solutions of 5 ppm, 10 ppm and 15 ppm were prepared by pipetting 5 mL, 10 mL and 15 mL respectively of the working solution into 100 mL volumetric flask then made to the mark using distilled water. Using the standards, a calibration curve shown in Figure 3.2 below was produced and concentration of lead in each sample was determined directly using AAS. For all the metals under study, analysis was done in triplicates to ascertain the reproducibility of the results.

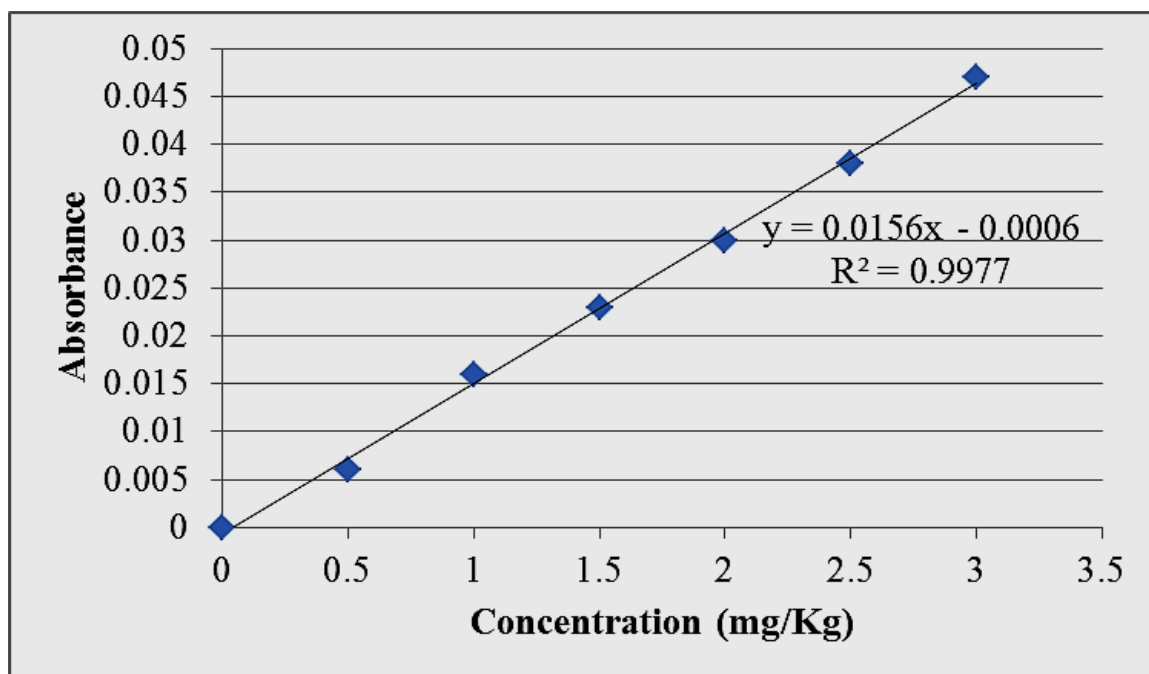


Figure 3.2: Calibration curve of lead

3.3.2 Preparation of Stock and Working Solution of Cadmium

Stock solution of cadmium was prepared by dissolving 1.0 g of cadmium in 10 mL of 1:1 nitric acid: water ratio then diluted to 1 L to give 1000 ppm of cadmium. A working solution of 100 ppm was prepared by pipetting 10 mL from 1000 ppm stock solution into 100 mL volumetric flask then made to the mark using distilled water. Standard solutions of 1 ppm, 2 ppm and 3 ppm were prepared by pipetting 1 mL, 2 mL and 3 mL respectively of the working solution into 100 mL volumetric flask then made to the mark using distilled water. Using the standards, a calibration curve shown in Figure 3.3 below was produced after which concentration of cadmium in each sample was determined directly using AAS.

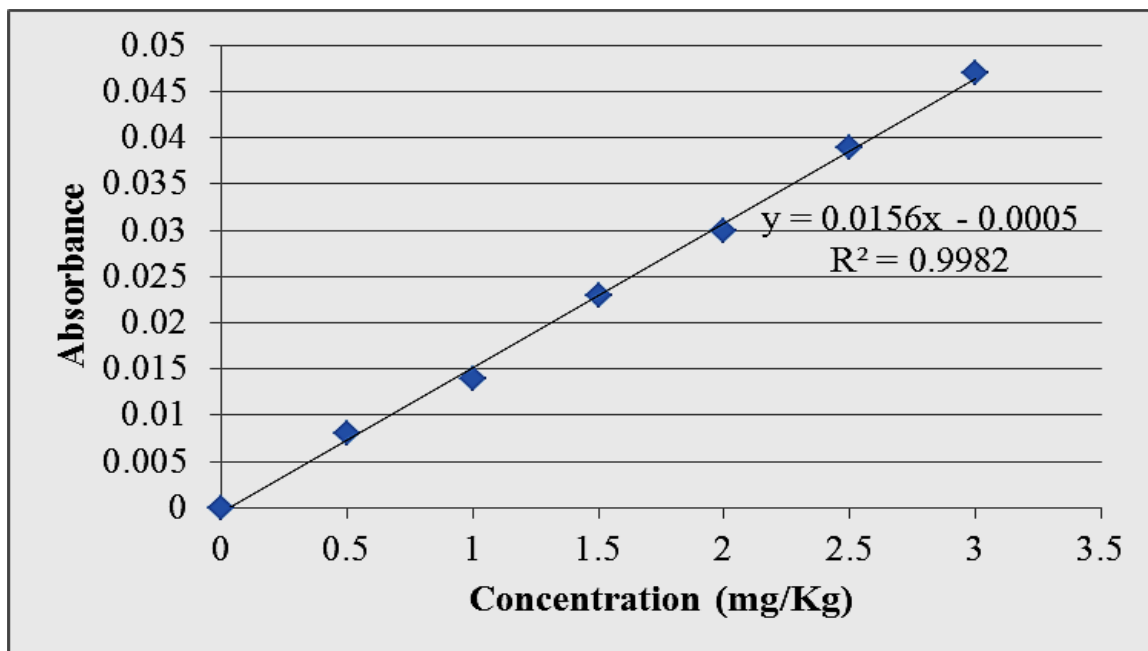


Figure 3.3: Calibration curve of cadmium

3.3.3 Preparation of Stock and Working Solution of Copper

Stock solution of copper was prepared by dissolving 1.0 g of copper in 10 mL of 1:1 nitric acid: water ratio then diluted to 1 L to give 1000 ppm of copper. A working solution of 100 ppm was prepared by pipetting 10 mL from 1000 ppm stock solution into 100 mL volumetric flask then made to the mark using distilled water. Standard solutions of 2 ppm, 5 ppm and 10 ppm were prepared by pipetting 2 mL, 5 mL and 10 mL respectively of the working solution into 100 mL volumetric flask then made to the mark using distilled water. Using the standards, a calibration curve shown in Figure 3.4 below was produced then concentration of copper in each sample was determined directly using AAS.

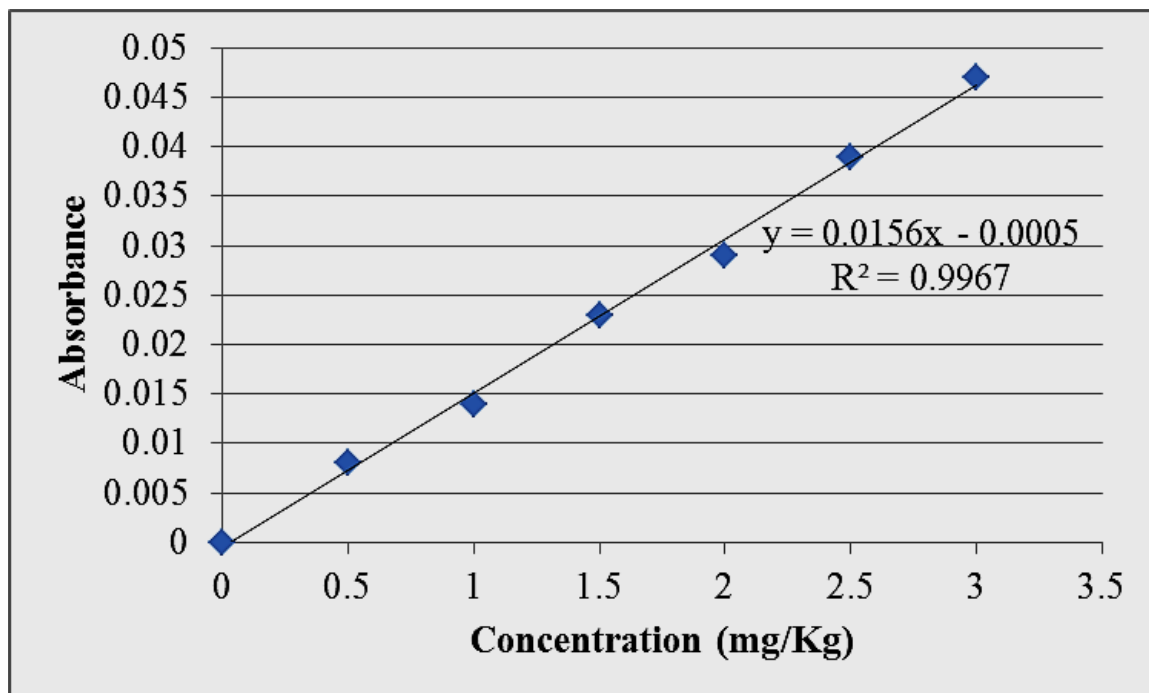


Figure 3.4: Calibration curve of copper

3.3.4 Preparation of Stock and Working Solution of Zinc

Stock solution of zinc was prepared by dissolving 1.0 g of zinc in 40 mL of 1:1 hydrochloric acid: water ratio then diluted to 1 L to give 1000 ppm of zinc. A working solution of 100 ppm was prepared by pipetting 10 mL from 1000 ppm stock solution into 100 mL volumetric flask then made to the mark using distilled water. Standard solutions of 0.5 ppm, 1.0 ppm and 1.5 ppm were prepared by pipetting 0.5 mL, 1.0 mL and 1.5 mL respectively of the working solution into 100 mL volumetric flask then made to the mark using distilled water. Using the standards, a calibration curve shown in Figure 3.5 below was produced and concentration of zinc in each sample was determined directly using AAS.

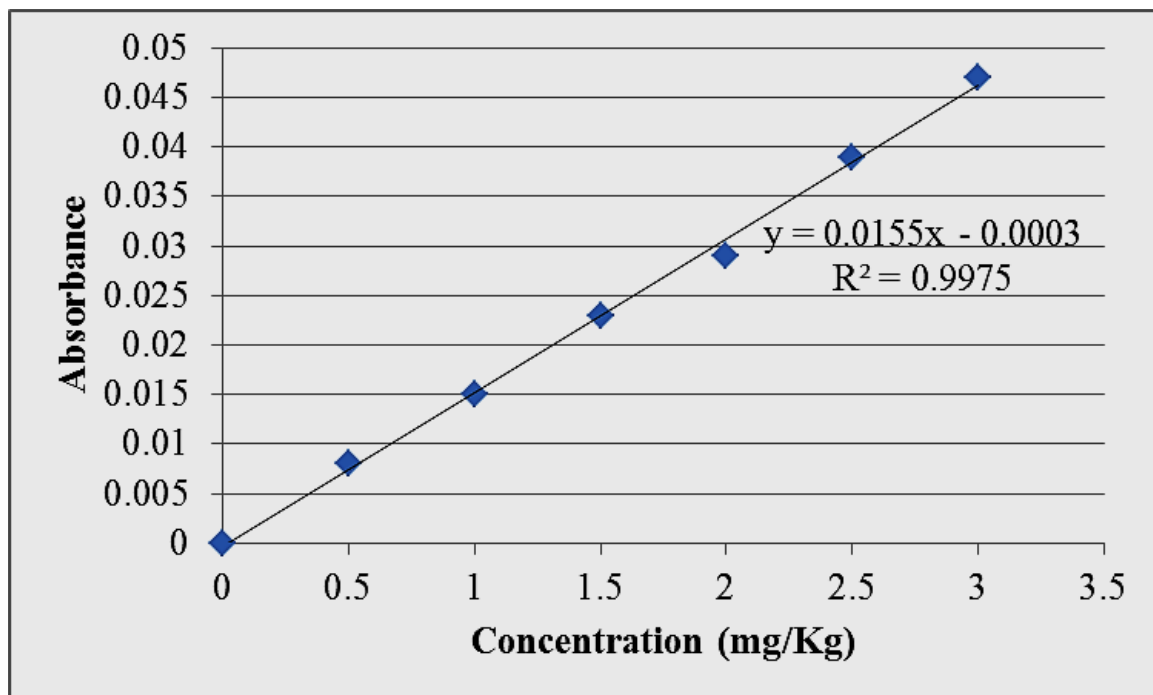


Figure 3.5: Calibration curve of zinc

3.3.5 Preparation of Stock and Working Solution of Iron

Stock solution of iron was prepared by dissolving 1.0 g of iron in 20 mL of 1:1hydrochloric acid: water ratio then diluted to 1 L to give 1000 ppm of iron. A working solution of 100 ppm was prepared by pipetting 10 mL from 1000 ppm stock solution into 100 mL volumetric flask then made to the mark using distilled water. Standard solutions of 5 ppm, 10 ppm and 15 ppm were prepared by pipetting 5 mL, 10 mL and 15 mL respectively of the working solution into 100 mL volumetric flask then made to the mark using distilled water. Using the standards, a calibration curve shown in Figure 3.6 below was produced and concentration of iron in each sample was determined directly using AAS.

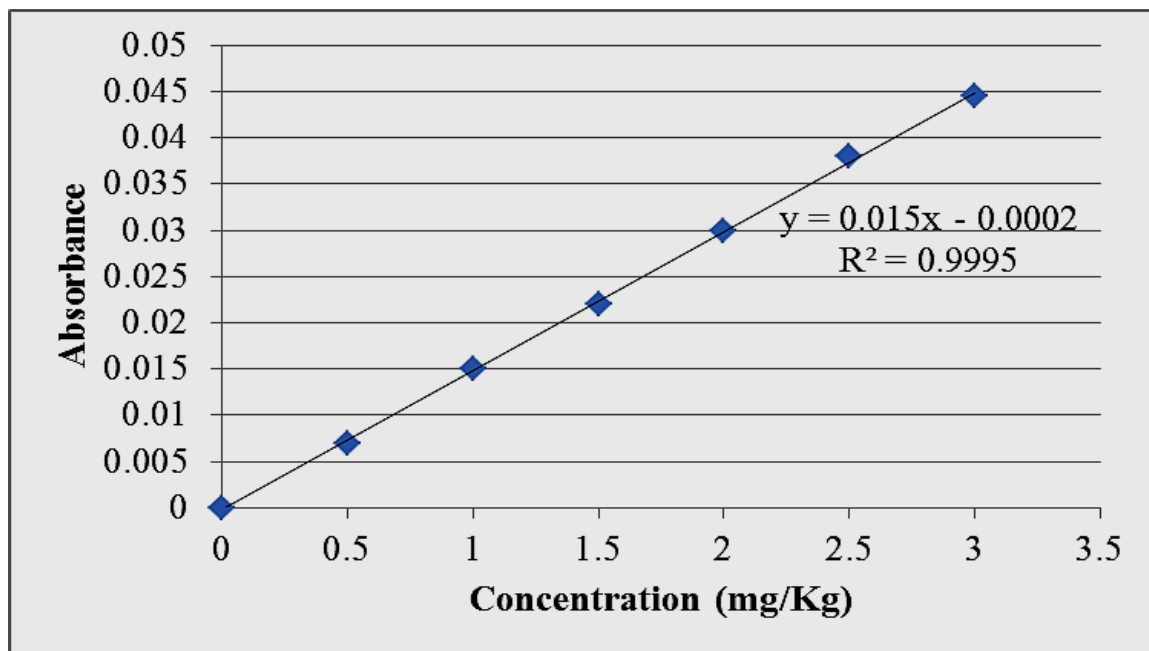


Figure 3.6: Calibration curve of iron

3.3.6 Preparation of Stock and Working Solution of Nickel

Stock solution of nickel was prepared by dissolving 1.0 g of nickel in 10 mL of 1:1 nitric acid then diluted to 1 L to give 1000 ppm of nickel. A working solution of 100 ppm was prepared by pipetting 10 mL from 1000 ppm stock solution into 100 mL volumetric flask then made to the mark using distilled water. Standard solutions of 5 ppm, 10 ppm and 15 ppm were prepared by pipetting 5 mL, 10 mL and 15 mL respectively of the working solution into 100 mL volumetric flask then made to the mark using distilled water. Using the standards, a calibration curve shown in Figure 3.7 below was produced and concentration of nickel in each sample was determined directly using AAS.

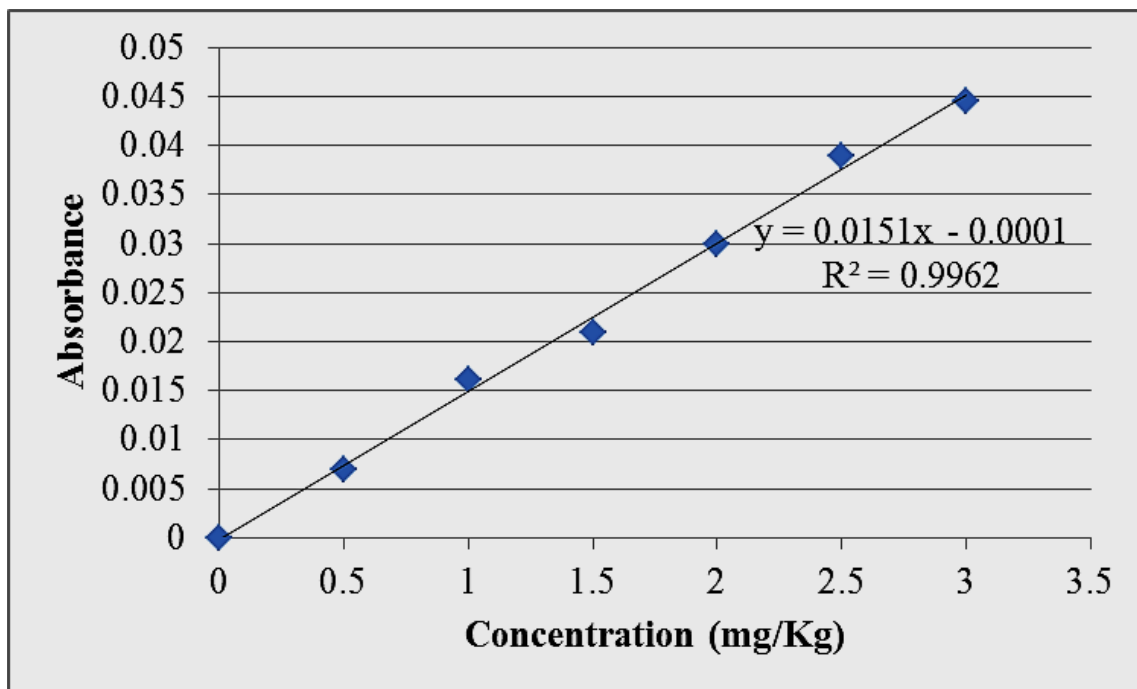


Figure 3.7: Calibration curve of nickel

3.4 Data Analysis and Presentation

Statistical analysis was done using SPSS version 20.0. Comparisons of mean concentration of heavy metals in soil and in grown vegetables were analyzed using t-test. Comparison of mean concentration of heavy metals in vegetables during dry and wet season was done using paired t-test. In all analysis, significance was considered at $P \leq 0.05$. Data was summarized and presented using tables and bar charts.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Introduction

Soil and vegetable samples from the Eldoret market dumpsite were analyzed to determine concentration of various heavy metals. The results obtained were compared with the acceptable standards of WHO/FAO (2001) and SPCR (2001) provided in [Appendix 1](#) and 2.

4.2 Mean Concentration of Heavy Metals in Soil

Mean concentration of heavy metals in soil was determined using AAS. Levels of heavy metals were compared with the acceptable limits of WHO/FAO (2001) and SPCR (2001). Comparison of levels of heavy metals in soil with the acceptable standards of SPCR (2001) is provided in Appendix I, while the comparison of mean concentration of the individual metal in soil during wet and dry seasons is provided in Table 4.1 below.

Table 4.1: Mean concentration of heavy metals in soil for dry and wet season

Heavy metals	No.	Minimum	Maximum	Mean	SPCR (2010)
Cadmium in soil during dry season	7	1.07	1.09	1.08±0.01	1.00
Cadmium in soil during wet season	7	1.05	1.08	1.07±0.03	1.00
Copper in soil during dry season	7	51.06	52.44	51.75±0.5	50.00
Copper in soil during wet season	7	50.03	50.22	50.13±0.4	50.00
Iron in soil during dry season	7	551.07	552.97	551.92±3.1	150.00
Iron in soil during wet season	7	554.43	554.53	554.48±3.3	150.00
Lead in soil during dry season	7	2.01	2.05	2.03±0.08	1.00
Lead in soil during wet season	7	1.91	1.97	1.94±0.06	1.00
Zinc in soil during dry season	7	72.63	72.83	72.73±1.3	100.00
Zinc in soil during wet season	7	61.35	61.45	61.40±1.2	100.00
Nickel in soil during dry season	7	52.54	52.58	52.56±0.7	50.00
Nickel in soil during wet season	7	54.55	54.77	54.66±0.8	50.00

The heavy metals analyzed in this study were available in soil with mean concentration ranging from 1.05 mg/Kg to 555.05 mg/Kg. Levels of all the heavy metals in soil were compared to the accepted limit set by WHO/FAO (2001) and SPCR (2010).

The concentration of lead in soil in this study ranged from 1.91 to 2.05 mg/Kg for both seasons. The mean was 1.99 mg/kg. This concentration was above the safe limit of 1.00 mg/kg set by (SPCR, 2001). These findings are lower than those by Njagi (2013) who reported a range of 19.79 to 60.22 mg/Kg in vegetables and Premarathna *et al.* (2011) who reported a range of 15 to 311 mg/Kg. Similarly, McGrath *et al.* (2001) and Kimani (2007) reported lead values of 189 mg/Kg, 55 mg/Kg, 80 mg/Kg and 34.5 mg/Kg respectively.

Mean concentration of cadmium in soil ranged from 1.05 to 1.09 mg/Kg. Level of cadmium in soil was above the safe limit set by WHO/FAO (2001) and SPCR (2001). The level of cadmium in soil was significantly higher than its level in leafy vegetables (0.09 – 0.11 mg/kg).

Mean concentration of copper in soil ranged from 50.03 to 52.44mg/Kg. The mean concentration was 50.94 mg/kg which was slightly higher than the set limits of 50.00 mg/kg by WHO/FAO (2001). These findings are in line with those of Akubugwo *et al.*, (2012) who reported copper levels that were much higher than the set standards; 86.34 and 88.51 mg/Kg. Awokunmi *et al.*, (2010) reported even higher levels of copper from 95 to 6726 mg/Kg from soils collected from several dumpsites in Nigeria.

Mean concentration of zinc in soil ranged from 61.35to 72.83mg/Kg. These concentrations were well within the set limits of 100 mg/kg by WHO/FAO (2001). These concentrations were much lower compared with those reported by some studies done earlier evaluating the level of zinc in vegetables. Njagi (2013) reported a range of 128.11 mg/Kg to 289.27 mg/Kg. McGrath *et al.* (2001) and Kimani (2007) reported values of 200 mg/Kg and 133 mg/Kg respectively. Awokunmi *et al.* (2010) reported much higher zinc levels in soil ranging between 350-3052 mg/Kg.

The mean concentration of iron in soil ranged from 551.87 to 554.53mg/Kg. This level was higher than the set standards of 150 mg/kg by WHO/FAO (2001). These concentrations are above the range reported by Akubugwo *et al.*, (2012) and Njagi (2013) of between 73.62 mg/Kg to 226.39 mg/Kg and between 22.01 mg/Kg to 525.50 mg/Kg respectively. Other studies have reported higher values than those in the current study. Tsafe *et al.*, (2012) reported a value of 695.25 mg/Kg in the soils studied while Awokunmi *et al.*, (2010) reported values between 1100 to 10,920 mg/Kg.

Soils in this study recorded concentrations of nickel ranging from 52.54 to 54.77mg/kg. These levels were slightly higher than the set limits by WHO/FAO (2001). Literature reports far much higher values of 450 mg/Kg, 98 mg/Kg, 100 mg/Kg and 1650 mg/Kg recorded by Njagi, (2013), McGrath *et al.*, (2001), Awokunmi *et al.*, (2010) and Adefemi and Awokunmi, (2009) respectively.

Figure 4.1 below shows a comparison of the concentrations of heavy metals in soils in both dry and wet seasons.

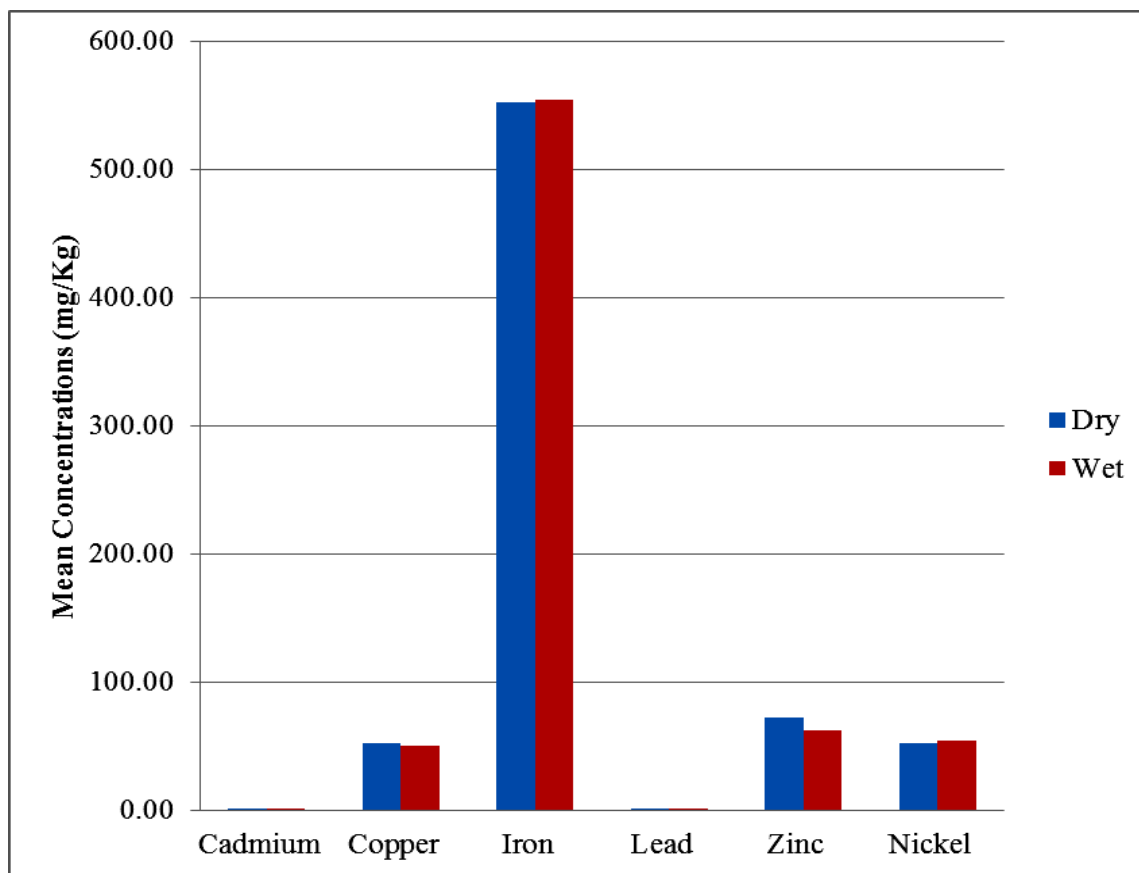


Figure 4.1: Levels of heavy metals in soil

4.3 Mean Concentration of Heavy Metals in Vegetables

Heavy metals in vegetables were analyzed using atomic absorption spectroscopy. The mean concentrations of heavy metals were compared with acceptable standards of WHO/FAO (2001). Levels of heavy metals in vegetables presented in this chapter are lead, cadmium, copper, zinc, iron and nickel.

4.3.1 Mean concentration of lead in kales and spinach

The mean concentrations of Pb in the two vegetable during dry and wet seasons for the six different sampling sites are shown below in Tables 4.2 and 4.3.

Table 4.2: Mean concentration of lead in kales and spinach from different sample sites

Sampling Site	Lead in kales (mg/Kg)		Lead in spinach (mg/Kg)	
	Dry season	Wet season	Dry season	Wet season
1	1.06±0.01	2.08±0.03	1.07±0.01	1.48±0.01
2	1.21±0.02	2.06±0.04	1.01±0.01	0.39±0.01
3	1.35±0.01	2.92±0.05	1.03±0.01	2.72±0.04
4	1.52±0.04	2.04±0.01	0.92±0.02	2.60±0.03
5	1.62±0.03	2.10±0.04	0.18±0.01	1.41±0.04
6	1.61±0.03	1.09±0.01	1.30±0.01	1.40±0.01
7	1.81±0.04	2.03±0.03	1.20±0.02	2.03±0.03

The mean concentrations of lead in kales ranged from 1.06 to 1.81 mg/Kg in the dry season and 1.09 to 2.92 mg/Kg for the wet season. The mean concentrations of lead in spinach ranged from 0.18 to 1.30 mg/Kg in the dry season and 0.39 to 2.72 mg/Kg for the wet season. Table 4.3 below shows the mean concentration of Lead in the spinach and the kales for the two seasons.

Table 4.3: Mean concentration of lead in kales and spinach (two seasons)

	No. of samples	Mean (mg/kg)	SD
Lead in Kales during dry season	7	1.46±0.02	0.261
Lead in Kales during wet season	7	1.42±0.04	0.528
Lead in spinach during dry season	7	0.96±0.03	0.367
Lead in spinach during wet season	7	0.91±0.03	0.805

Mean concentration of lead in kales and spinach for dry and wet season ranged from 0.96 mg/Kg to 1.46 mg/Kg. Mean concentration of lead was higher in kales compared to the concentrations in spinach.

Unpaired parametric independent t-test was used to determine and compare the statistical differences between the mean concentrations of Pb for two groups of samples (dry and wet season data for each vegetable). A probability level of $P < 0.05$ was considered statistically significant. The results are as shown in Table 4.4.

Table 4.4: t - test for the concentrations of lead in kales and spinach for both seasons

	T	Df	Sig. (2-tailed)	Mean Difference	95% Confidence Interval of the Difference	
					Upper	Lower
Lead in Kales during dry season	14.75	6	0.0001	0.84	1.69	1.21
Lead in Kales during wet season	10.26	6	0.0001	1.62	2.54	1.56
Lead in spinach during dry season	6.91	6	0.0005	0.62	1.29	0.62
Lead in spinach during wet season	5.65	6	0.0013	1.51	2.46	0.98

Key: T – t value, df – Degree of Freedom, Sig - Significance

Unpaired t-test indicated the difference in concentration of Pb in vegetables for the two seasons was statistically significant ($P < 0.05$).

Mean concentration of lead in leafy vegetables in this study ranged from 0.91 mg/kg to 1.46 mg/kg as shown in Table 4.3. The levels of lead in vegetables of the present study were significantly higher than the accepted limit of 0.30 mg/Kg set by WHO/FAO (2001). Therefore the vegetables are not safe for human consumption with respect to lead.

These concentrations were higher than those reported by Njagi (2013), Orisakwe *et al.* (2012), Naser *et al.* (2009) and Akubugwo *et al.* (2012). They reported values of between 0.39 ± 0.20 to 1.59 ± 0.03 mg/Kg, 0.35 to 1.89 mg/Kg, 0.49 to 1.97 m/Kg and 0.13 to 0.73

mg/Kg, respectively. However, the levels were lower than those reported by Muhammad *et al.* (2008) for lead metal levels in spinach, coriander, lettuce, radish, cabbage and cauliflower with values of 2.251, 2.652, 2.411, 2.035, 1.921 and 1.331 mg/Kg respectively.

The high lead concentrations recorded in vegetables may have been contributed by lead containing waste materials like batteries, discarded plumbing materials and solders which are commonly discarded in the dumpsite from the Eldoret town. Levels of lead in kales and spinach recorded high values during wet season compared to dry season. This is attributed to $Pb(CO_3)_2$ in the area which was highly soluble and thus the high uptake during wet season. Also availability of lead at high levels in vegetables during wet season may have been contributed significantly by water runoffs which carry wastes from different sources including garage effluent.

4.3.2 Mean concentration of cadmium in kales and spinach

The mean concentrations of Cd in the two vegetable during dry and wet seasons for the six different sampling sites are shown below in table 4.5 and 4.6.

Table 4.5: Mean concentration of cadmium in kales and spinach from different sample sites

Sample sites	Cadmium in kales (mg/Kg)		Cadmium in spinach (mg/Kg)	
	Dry season	Wet season	Dry season	Wet season
1	0.11±0.01	0.10±0.01	0.08±0.01	0.07±0.01
2	0.10±0.01	0.09±0.01	0.07±0.01	0.06±0.01
3	0.09±0.01	0.11±0.01	0.09±0.01	0.08±0.01
4	0.10±0.01	0.10±0.01	0.09±0.01	0.09±0.01
5	0.12±0.01	0.12±0.01	0.09±0.01	0.09±0.01
6	0.12±0.01	0.12±0.01	0.12±0.01	0.09±0.01
7	0.15±0.01	0.12±0.01	0.11±0.01	0.12±0.01

The mean concentrations of cadmium in kales ranged from 0.09 to 0.15mg/Kg in the dry season and 0.09 to 0.12 mg/Kg for the wet season. The mean concentrations of cadmium in spinach ranged from 0.07 to 0.12 mg/Kg in the dry season and 0.06 to 0.12 mg/Kg for the wet season. The mean concentration of cadmium was higher in kales followed by spinach. Table 4.6 below shows the mean concentration of cadmium in the spinach and the kales for the two seasons.

Table 4.6: Mean concentration of cadmium in kales and spinach from dry and wet seasons

	Number	Mean	Std.
	of samples	conc.	Deviation
Cadmium in Kales during dry season	7	0.11±0.02	0.02
Cadmium in Kales during wet season	7	0.11±0.01	0.01
Cadmium in spinach during dry season	7	0.09±0.02	0.02
Cadmium in spinach during wet season	7	0.09±0.03	0.02

Mean concentration of cadmium in kales and spinach for dry and wet season ranged from 0.09 mg/Kg to 0.11 mg/Kg.

Unpaired parametric independent t-test was used to determine and compare the statistical differences between the mean concentrations of Cd for two groups of samples (dry and wet season data for each vegetable). A probability level of $P < 0.05$ was considered statistically significant. The results are as shown in Table 4.7.

Table 4.7: t - test for the concentrations of cadmium in kales and spinach for both seasons

	T	Df	Sig. (2-tailed)	Mean Difference	95% Confidence Interval of the Difference	Upper	Lower
Cadmium in Kales during dry season	18.52	6	0.0001	0.081	0.12	0.09	
Cadmium in Kales during wet season	36.04	6	0.0001	0.08	0.11	0.10	

Cadmium in spinach during dry season	14.47	6	0.0001	0.064	0.10	0.07
Cadmium in spinach during wet season	11.975	6	0.0001	0.065	0.10	0.06

Key: T – t value, df – Degree of Freedom, Sig - Significance

Unpaired t-test indicated the difference in concentration of Cd in vegetables for the two seasons was statistically significant ($P < 0.05$).

The mean concentration of Cd in the vegetables were in the range 0.09 mg/Kg to 0.11mg/kg as shown in Table 4.6 which was significantly higher than the acceptable limit of 0.02 mg/Kg set by WHO/FAO (2001). This implies that the vegetables are not safe for human consumption as far as cadmium is concerned. The high concentration of cadmium in the vegetables may be due to the decay of abandoned electric batteries and other electronic components which are commonly disposed of in Eldoret (Jarup, 2003). It is also known that the application of agricultural inputs such as fertilizers, pesticides and biosolids as well as the disposal of industrial wastes or the deposition of atmospheric contaminants increases the total concentration of cadmium in soils and vegetables (Kabata-Pendias, 2010). Other studies carried out earlier are in agreement with the current study. A study of Odai *et al.* (2008) carried out on vegetables grown in a dumpsite in Kumasi showed that level of lead and cadmium in vegetables were higher than recommended values of WHO/FAO. A study of Ebong *et al.* (2008) on heavy metal contents of municipal and rural dumpsite soils and rate of accumulation by *Carica papaya* and *Talinum triangulare* in Uyo, Nigeria revealed that cadmium and lead in vegetables were 0.3 and 0.11 mg/kg which were above the recommended standards.

The level of cadmium in soil was significantly higher than its level in leafy vegetables. The mean concentration of cadmium was higher in kales than spinach. Cadmium recorded the lowest concentration in soil in all the locations compared to other metals in this study. This is in agreement with the report of Udosen *et al.* (2006) in Manihot Utilissima obtained from a municipal dumpsite, in Nigeria. This may be attributed to the low level of the metal in the earth's crust and as a non-essential element for plants.

4.3.3: Mean concentration of copper in kales and spinach

The mean concentrations of Cu in the two vegetable during dry and wet seasons for the six different sampling sites are shown below in Tables 4.8 and 4.9.

Table 4.8: Mean concentration of copper in kales and spinach from different sample sites

Sample sites	Copper in kales (mg/Kg)		Copper in spinach (mg/Kg)	
	Dry season	Wet season	Dry season	Wet season
1	44.13±1.63	40.12±1.18	42.08±1.69	40.07±1.18
2	41.12±1.21	40.08±1.16	43.08±1.52	41.08±1.21
3	42.09±1.51	40.08±1.11	45.11±2.01	42.12±1.92
4	43.08±1.52	40.08±1.02	44.11±1.93	40.11±1.18
5	43.08±1.51	40.07±1.28	43.11±1.61	40.10±1.19
6	40.09±1.18	41.09±1.61	44.10±1.82	41.10±1.31
7	41.08±1.19	41.08±1.92	44.11±1.84	40.09±1.32

The mean concentrations of copper in kales ranged from 40.09 to 44.13 mg/Kg in the dry season and 40.07 to 41.09 mg/Kg for the wet season. The mean concentrations of copper in spinach ranged from 42.08 to 44.11 mg/Kg in the dry season and 40.07 to 42.12 mg/Kg for the wet season. There was no significant difference in concentration of copper in the vegetables for both dry and wet seasons. Table 4.9 below shows the mean concentration of copper in the spinach and the kales for the two seasons.

Table 4.9: Mean concentration of copper in kales and spinach from dry and wet seasons

	Number	of Mean	Std.
	samples		Deviation
Copper in Kales during dry season	7	42.10±1.21	1.41
Copper in Kales during wet season	7	40.37±1.10	0.48
Copper in spinach during dry season	7	43.67±1.31	0.98
Copper in spinach during wet season	7	40.67±0.99	0.79

Mean concentration of copper in kales and spinach for dry and wet season ranged from 40.37 mg/Kg to 43.67 mg/Kg.

Unpaired parametric independent t-test was used to determine and compare the statistical differences between the mean concentrations of Cu for two groups of samples (dry and wet season data for each vegetable). A probability level of $P < 0.05$ was considered statistically significant. The results are shown in Table 4.10 below.

Table 4.10: t - test for the concentrations of copper in kales and spinach for both seasons

	T	Df	Sig.(2-tailed)	95% Confidence Interval of the Difference	
				Lower	Upper
Copper in Kales during dry season	78.60	6	0.0001	43.41	40.79
Copper in Kales during wet season	219.35	6	0.0001	40.82	39.92
Copper in spinach during dry season	116.962	6	0.0001	44.59	42.76 3
Copper in spinach during wet season	135.52	6	0.0001	41.40	41.40

Key: T – t value, df – Degree of Freedom, Sig - Significance

Unpaired t-test indicated the difference in concentration of Cu in vegetables for the two seasons was statistically significant ($P < 0.05$).

Mean concentration of copper in leafy vegetables ranged from 40.37mg/Kg to 43.67 mg/Kg as shown in Table 4.9; these levels were higher the accepted level of 40.00mg/Kg (WHO/FAO, 2001). Njagi, (2013) reported levels ranging from the lowest value of 0.38 ± 0.19 mg/Kg to 1.72 ± 0.11 mg/Kg while Uwah *et al.* (2011) recorded copper values of between 0.81 mg/Kg and 1.75 mg/Kg in spinach and lettuce grown in Nigeria respectively. Akubugwo *et al.*, (2012) and Muhammad *et al.* (2008) reported low ranges of 1.20 to 3.42 mg/Kg and 0.25 mg/Kg to 0.92mg/Kg while Sharma *et al.*, (2006) reported copper concentration of (2.25-5.42mg/Kg) in vegetables grown in wastewater

areas of Varanasi, India. Mean concentration of copper in vegetables in this study was found to be much lesser than in its soil. The transfer of copper from the soils to the vegetables in this study was low. This could be explained by the fact that copper contents do not move in plants and remain stagnant in roots (Prasad, 2013).

4.3.4 Mean concentration of zinc in kales and spinach

The mean concentrations of Zn in the two vegetable during dry and wet seasons for the six different sampling sites are shown below in Tables 4.11 and 4.12.

Table 4.11: Mean concentration of zinc in kales and spinach for different sample sites

Sample sites	Zinc in kales (mg/Kg)		Zinc in spinach (mg/Kg)	
	Dry season	Wet season	Dry season	Wet season
1	35.44±0.91	30.32±0.82	34.21±1.81	30.34±0.93
2	36.57±1.00	30.28±0.92	35.48±1.61	31.54±0.99
3	34.81±0.99	32.27±1.09	36.12±1.67	29.26±0.82
4	38.29±1.60	31.28±1.08	40.00±1.73	33.47±0.95
5	37.89±1.54	34.23±1.24	35.06±1.49	32.30±1.01
6	33.19±1.43	30.21±0.95	34.16±1.39	30.69±0.98
7	37.26±1.61	29.27±0.75	38.96±1.69	31.63±0.97

The mean concentrations of zinc in kales ranged from 33.19 to 38.29 mg/Kg in the dry season and 29.27 to 34.23 mg/Kg for the wet season. The mean concentrations of zinc in spinach ranged from 34.16 to 38.96mg/Kg in the dry season and 29.26 to 33.47 mg/Kg for the wet season. The mean concentrations of zinc in all the vegetables were within the accepted level of 99.4 mg/Kg as per the requirements of WHO/FAO (2001). Table 4.12 below shows the mean concentration of zinc in the spinach and the kales for the two seasons.

Table 4.12: Mean concentration of zinc in kales and spinach for dry and wet season

	Number of samples	Mean	Std. Deviation
Zinc in kales during dry season	7	36.21±1.86	1.83

Zinc in kales during wet season	7	31.12±0.82	1.66
Zinc in spinach during dry season	7	36.28±1.91	2.31
Zinc in spinach during wet season	7	31.32±0.93	1.37

Mean concentration of zinc in kales and spinach for dry and wet season ranged from 31.12 mg/Kg to 36.28 mg/Kg.

Unpaired parametric independent t-test was used to determine and compare the statistical differences between the mean concentrations of Zn for two groups of samples (dry and wet season data for each vegetable). A probability level of $P < 0.05$ was considered statistically significant. The results are as shown in Table 4.13.

Table 4.13: t - test for the concentrations of Zinc in kales and spinach for both seasons

	T	Df	Sig.(2-tailed)	95% Confidence Interval of the Difference	
				Lower	Upper
Zinc in Kales during dry season	52.32	6	0.0001	37.90	34.51
Zinc in Kales during wet season	219.35	6	0.0001	40.82	39.92
Zinc in spinach during dry season	116.96	6	0.0001	44.59	42.76
Zinc in spinach during wet season	135.52	6	0.0001	41.40	41.40

Key: T – t value, df – Degree of Freedom, Sig - Significance

Unpaired t-test indicated the difference in concentration of Zn in vegetables for the two seasons was statistically significant ($P < 0.05$).

The mean concentration of zinc in leafy vegetables in this study ranged from 31.12mg/Kg to 36.28 mg/Kg as shown in Table 4.12. The concentrations of zinc metal in all the vegetables were lower than the accepted level of 90 mg/Kg as per WHO/FAO (2001) requirements. The results of this study were in far much higher than those reported by Njagi (2013) of 0.38 ± 0.19 mg/Kg to 2.43 ± 0.15 mg/Kg and Muhammad *et al.* (2008) who reported the amount of zinc in leafy vegetable samples as 0.461 (spinach), 0.705 (coriander), 0.743 (lettuce), 1.893 (radish), 0.777 (cabbage) and 0.678 (cauliflower) mg/Kg respectively. Akubugwo *et al.* (2012) also reported lower values of zinc than those reported in this study with values ranging from 1.06 ± 0.02 to 2.82 ± 0.01 mg/Kg in *Amaranthus hybridus* vegetables. Levels of zinc in spinach and kales were significantly higher during dry season than in wet season. This implies that zinc was soluble in the soil and hence easily washed away. The mean concentration of zinc was higher in spinach than in kales. The transfer factor of zinc was significant compared to that of copper; this is evidence that zinc was soluble in the soil and hence high accumulation in plant tissues.

4.3.5 Mean concentration of iron in kales and spinach

The mean concentrations of Fe in the two vegetable during dry and wet seasons for the six different sampling sites are shown below in Tables 4.14 and 4.15.

Table 4.14: Mean concentration of iron in kales and spinach from different sample sites

Sample sites	Iron in kales (mg/Kg)		Iron in spinach (mg/Kg)	
	Dry season	Wet season	Dry season	Wet season
1	426.27±3.63	467.70±6.95	433.55±4.63	449.35±5.62
2	428.82±4.69	466.25±6.84	432.4±4.53	459.35±6.00
3	430.37±4.52	471.75±6.93	433.13±4.72	438.25±4.63
4	432.22±5.03	499.35±7.01	429.24±4.03	435.45±4.11
5	431.99±4.12	477.3±6.99	430.56±4.11	438.65±4.93
6	443.73±5.53	470.35±6.52	431.69±4.13	445.1±5.02
7	442.84±5.19	473.15±6.39	427.68±3.63	490.25±7.01

The mean concentrations of iron in kales ranged from 426.27 to 443.73 mg/Kg in the dry season and 466.25 to 499.35 mg/Kg for the wet season. The mean concentrations of iron in spinach ranged from 427.68 to 433.55 mg/Kg in the dry season and 435.45 to 490.25 mg/Kg for the wet season. Mean concentration of iron in spinach and kales were significantly higher during wet season compared to dry season. Level of iron in kales and spinach during dry and wet season were higher than the accepted level of 425 mg/kg according to WHO/FAO (2001). Table 4.15 below shows the mean concentration of iron in the spinach and the kales for the two seasons.

Table 4.15: Mean concentration of iron in kales and spinach for dry and wet season

	Number of samples	Mean	Std. Deviation
Iron in kales during dry season	7	433.75±4.95	6.82
Iron in kales during wet season	7	475.12±6.11	11.28
Iron in spinach during dry season	7	431.18±4.99	2.14
Iron in spinach during wet season	7	450.91±6.01	19.17

Mean concentration of iron in leafy vegetables ranged from 431.18 mg/Kg to 475.12 mg/Kg as shown in Table 4.15 above. Unpaired parametric independent t-test was used to determine and compare the statistical differences between the mean concentrations of Fe for two groups of samples (dry and wet season data for each vegetable). A probability level of $P < 0.05$ was considered statistically significant. The results are as shown in Table 4.16.

Table 4.16: t - test for the concentrations of Iron in kales and spinach for both seasons

	T	Df	Sig.(2-tailed)	95% Interval Difference Upper	Confidence of the Lower
Iron in Kales during dry season	168.26	6	0.0001	440.06	427.44
Iron in Kales during wet season	111.44	6	0.0001	485.55	464.68
Iron in spinach during dry season	523.30	6	0.0001	433.19	429.16
Iron in spinach during wet season	62.23	6	0.0001	468.63	433.18

Key: T – t value, df – Degree of Freedom, Sig - Significance

Unpaired t-test indicated the difference in concentration of Fe in vegetables for the two seasons was statistically significant ($P < 0.05$).

Mean concentrations of iron in kales and spinach during dry and wet seasons in this study were higher than the accepted level of 425 mg/Kg (WHO/FAO, 2001). These values of Fe for this study were higher than those reported by Tsafe *et al.* (2012) with mean content of 54.05 mg/Kg and Uwah *et al.* (2011) who reported an iron content of 15.96 ± 0.18 mg/Kg in *Amaranthus caudatus* vegetables and values of 42.84 ± 0.27 mg/Kg in *Lactuca sativa* vegetables. Akubugwo *et al.* (2012) reported an even higher iron metal content of up to 147.41 ± 0.01 mg/Kg in the *Amaranthus hybridus* vegetables. Results reported by

Aweng *et al*, (2011) recorded an iron content of 0.65 - 2.76 mg/Kg in the vegetables which were lower than those of the current study. The results revealed that iron recorded the highest mean metal concentration in soil at all the locations compared to other metals. This is in agreement with the study of Amusan *et al*. (2005) on plants from some rural and municipal dumpsites within Ife, Nigeria. This could be attributed to the availability of the metal in the earth's crust, at dumpsites and its high utilization by plants. Although iron recorded the highest mean concentration in soil, its transfer factor was low compared to other metals. This implies that solubility of iron in the dumpsite soil was low depending on factors like pH. Mean concentration of iron in spinach and kales were significantly higher during wet season compared to dry season. The high level of iron in spinach and kales during wet season may have come as result of water run offs. Level of iron was higher in kales followed by spinach.

4.3.6 Mean concentration of nickel in kales and spinach

The mean concentrations of Ni in the two vegetable during dry and wet seasons for the six different sampling sites are shown below in Tables 4.17 and 4.18.

Table 4.17: Mean concentration of nickel in kales and spinach from different sample sites

Sample sites	Nickel in kales (mg/Kg)		Nickel in spinach (mg/Kg)	
	Dry season	Wet season	Dry season	Wet season
1	46.27±2.42	37.7±1.63	43.55±2.86	34.35±1.53
2	48.82±3.01	36.25±1.99	44.4±2.91	35.35±1.67
3	40.37±2.43	31.75±1.43	43.13±2.73	32.25±1.13
4	42.22±2.63	39.35±1.98	42.24±2.43	35.45±1.67
5	41.99±2.06	37.3±1.97	43.56±2.71	30.65±0.53
6	44.73±2.94	38.35±1.99	39.69±1.93	32.1±1.03
7	42.84±2.05	33.15±1.11	47.68±2.69	30.25±0.73

The mean concentrations of nickel in kales ranged from 40.37 to 48.82 mg/Kg in the dry season and 31.75 to 39.35 mg/Kg for the wet season. The mean concentrations of nickel

in spinach ranged from 39.69 to 47.68mg/Kg in the dry season and 30.25 to 35.45 mg/Kg for the wet season. Table 4.18 below shows the mean concentration of nickel in the spinach and the kales for the two seasons.

Table 4.18: Mean concentration of nickel in kales and spinach for dry and wet season

	Number of samples	Mean	Std. Deviation
Nickel in kales during dry season	7	43.89±2.11	2.90
Nickel in kales during wet season	7	36.26±1.19	2.80
Nickel in spinach during dry season	7	43.46±3.02	2.39
Nickel in spinach during wet season	7	32.91±1.92	2.15

Mean concentration of nickel in kales and spinach for dry and wet season ranged from 32.91 mg/Kg to 43.89 mg/Kg.

Unpaired parametric independent t-test was used to determine and compare the statistical differences between the mean concentrations of Ni for two groups of samples (dry and wet season data for each vegetable). A probability level of $P < 0.05$ was considered statistically significant. The results are as shown in Table 4.19.

Table 4.19: t - test for the concentrations of nickel in kales and spinach for both seasons

	T	D	Sig.	Mean	95% Confidence	
					Difference	Interval of the Difference
			(2-tailed)		Upper	Lower
Nickel in kales during dry season	40.00	6	0.0001		46.57	41.20
Nickel in kales during wet season	34.25	6	0.0001		38.85	33.67
Nickel in spinach during dry season	47.93	6	0.0001		45.68	41.24
Nickel in spinach during wet season	40.48	6	0.0001		34.90	30.92

Key: T – t value, df – Degree of Freedom, Sig - Significance

Unpaired t-test indicated the difference in concentration of Ni in vegetables for the two seasons was statistically significant ($P < 0.05$).

Mean concentration of nickel in kales and spinach were 32.91 mg/kg and 43.89mg/Kg respectively as shown in Table 4.18. These levels are within accepted level of 67mg/Kg set by WHO/FAO (2001). These findings agree with those of Premarathna *et al.*, (2011) who reported a mean concentration of nickel ranging from 2.3 to 37.80 mg/Kg in various leafy vegetables. Other studies have reported lower values of nickel in vegetables. Njagi (2013) reported a range of 13.02 ± 0.54 to 35.23 ± 1.04 mg/Kg. Okoronkwo *et al.* (2005)

reported values of between 22.59 mg/Kg and 24.47 mg/Kg in the vegetables. On the other hand, Naser *et al.* (2009) in Bangladesh reported lower levels of nickel than those of this study of 5.369 mg/Kg in the vegetables.

4.4 Transfer Factors of the Heavy Metals from Soil to Vegetables

Transfer factor of heavy metal is the ratio of the concentration of heavy metal in a plant to the concentration in soil. It signifies the amount of heavy metals in the soil that ended up in the vegetable crop (Chojnacka *et al.*, 2005). Transfer factor was calculated to understand the extent of risk and associated hazard due to ingestion of heavy metal consequent upon accumulation in edible portion of vegetables. The heavy metal transfer factor from soil to the vegetables was calculated as follows:

$$\text{Transfer Factor} = \frac{\text{Metal content in plant (mg/kg)}}{\text{Metal content in soil (mg/kg)}}$$

Table 4.20 below provides transfer factors of heavy metals from soil to vegetables for both dry and wet seasons.

Table 4.20: Transfer factors of the heavy metals from soil to vegetables for dry and wet seasons

Metal	Transfer factor (kales)	Transfer factor (spinach)
Cadmium (D)	0.11	0.09
Cadmium (W)	0.10	0.08
Copper (D)	0.80	0.83
Copper (W)	0.80	0.81
Iron (D)	0.79	0.78
Iron (W)	0.86	0.81
Lead (D)	0.84	0.55
Lead (W)	0.92	0.60
Zinc (D)	0.50	0.50
Zinc (W)	0.50	0.51
Nickel (D)	0.84	0.83
Nickel (W)	0.67	0.60

The letters in the parenthesis (D and W) stand for dry and wet season respectively. From the results provided in Table 4.20 above, the transfer factors for kales ranged from 0.10 (Cd) to 0.92 (Pb) while for spinach, the transfer factors ranged from 0.08 (Cd) to 0.83 (Fe) as shown in Table 4.20. Considering the two vegetables the order for soil to plant transfer factors was Ni>Cu>Fe>Pb>Zn>Cd for the dry season and Fe>Cu>Pb>Ni>Zn>Cd for the wet season. In general cadmium had lowest transfer factor in spinach and kales for both seasons while iron had the highest.

4.5 Comparison of levels of heavy metals in soil, spinach and kales for the dry and wet seasons

4.5.1 Comparison of levels of lead in soil, spinach and kales for the dry and wet seasons

Figure 4.2 below shows that the levels of Pb for the two vegetables were higher in wet season than its corresponding levels in dry season. Compared to the concentrations of Pb in soil, the mean concentrations of Pb in the two vegetables were slightly lower. This was

attributed to the high transfer factor of Pb (0.72) which implies most of the lead in the soil was transferred to the vegetables. Noteworthy, the concentration of Pb in the dry season was higher than in wet season for both vegetables. This was attributed to the fact that during wet season, most the metals ions in the soil are washed away by surface runoff and thus the concentration of the metal ions in the soil drops significantly.

4.5.2 Comparison of Levels of Cadmium (Cd) in Soil, Spinach and Kales for the Dry and Wet Seasons

Figure 4.3 shows the mean concentration of Cd in soils, kales and spinach during dry and wet seasons. There was a statistically significant difference in levels of cadmium in soil, kales and spinach during dry and wet season. Levels of cadmium in the two vegetables were higher for the dry season than the corresponding wet season levels. This was attributed to the low transfer factor of Cd which was 0.094. However, the concentration of Cd in the soil in the two seasons was far much higher than the concentration of Cd in the vegetables.

4.5.3 Comparison of Levels of Copper (Cu) in Soil, Spinach and Kales for the Dry and Wet Season

Figure 4.4 below shows that the levels of copper in both vegetables were higher in dry season than the corresponding levels in wet season. There was a significant difference in concentration of copper in both vegetables for the dry and wet season. The transfer factor of copper to vegetables was fairly low compared to other metals with the transfer factors being less than 0.805. This explains why the concentration of Cu in the soil as much higher than the Cu in the vegetables.

4.5.4 Comparison of Levels of zinc (Zn) in Soil, Spinach and Kales for the Dry and Wet Season

Figure 4.5 below shows that the concentrations of zinc in the two vegetables were higher for the dry season than the corresponding levels in the wet season. The difference in concentrations for the two seasons was significantly significant at 0.05 levels. The transfer factor of zinc to vegetables was fairly low (0.501) and this explains why the difference in concentration of Zn in the soil and the vegetables was high. Noteworthy, the concentration of Zn in the dry season was higher than in wet season for both vegetables. This was attributed to the fact that during wet season, most the metals in the soil are washed away by surface run-off and thus the concentration of the metal ions in the soil drops significantly.

4.5.5 Comparison of Levels of iron (Fe) in Soil, Spinach and Kales for the Dry and Wet Season

Figure 4.6 below shows that the levels of iron in kales and spinach were more or less the same for the dry season than wet season. The difference was statistically significant at 0.05 level. The uptake of iron by the vegetables was very high as outlined by the high transfer factors (0.96 for dry season and 0.92 for wet season) provided in Table 4.20 above. However, transfer factors of iron in spinach and kales during dry season were fairly high.

4.5.6 Comparison of Levels of nickel (Ni) in Soil, Spinach and Kales for the Dry and Wet Season

Figure 4.7 below shows that the levels of nickel in kales and spinach were more or less the same for the dry season than wet season. The difference was positively insignificant at 0.05 level. This was attributed to the similar transfer factors of Ni for both seasons

(0.831 for dry season and 0.634 for wet season). Remarkably, the concentration of Ni in the dry season was higher than in wet season for both vegetables. This was attributed to the fact that during wet season, most the metal ions in the soil are washed away by surface run-off and thus the concentration of the metal ions in the soil drops significantly.

4.6 Summary of Findings

Results obtained in this study have shown that waste dumpsites contribute significant levels of toxic metals to soil and finally to crops. Soil to plant transfer is one of the paths of human exposure to metals through food chain. In order to assess the health risks associated with contamination by heavy metals, it was necessary to determine the transfer factor of metals from soil to edible portions of the vegetables. In this study, the soil to plant transfer factor for various metals in two common vegetables consumed by local residents were calculated and provided in [Table 4.20 above](#). The results indicates that uptake of heavy metals by vegetables does not increase linearly with increasing concentrations of metals in soils. This is in agreement with the findings of Liu *et al.*, (2005). The apparent advantage of this phenomenon is that although long term polluted water from river Sosiani and town wastes result into elevated levels of metals in soil, the same will not be proportionately transferred to the food chain. As far as the transfer factors are concern Fe had the highest transfer factor while Cd had the lowest mobility. The transfer factors also indicate that vegetables can accumulate heavy metals to high levels. Thus vegetables should not be grown in contaminated soil.

CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

This research work has revealed that plants grown on the Eldoret town dumpsite have accumulated toxic metals to levels that are harmful to animals and human health. Thus efforts should be intensified to discourage the practice of cultivating at dumpsite. The soil and vegetables grown in the Eldoret town dumpsite was contaminated with toxic heavy metals such as; Pb, Cd, Cu, Zn, Fe and Ni. Though zinc and nickel were within safe limits, levels of lead, copper, iron and cadmium in vegetables exceeded the standards of WHO/FAO (2001) by 0.89, 1.7, 22.74, and 0.08 which translates into by an approximate margin of 296.67%, 4.25%, 5.35% and 400% respectively. Therefore the vegetables were polluted and should not be consumed. The continuous dumping and decay of waste at the dumpsite may lead to the enrichment of the soil with other pollutants. Therefore the use of the Eldoret town dumpsite for growing vegetables should be discontinued with immediate effect.

5.2 Recommendations

In order to safeguard the health of the town's residents, intervention measures need to be undertaken. These measures include: the ministry of Health and that of Agriculture should come up with health education programmes for the general population on dangers of consumption of crops grown in and around the waste disposal sites and on the need to shift from raising vegetables at the dumpsite. This may be a useful idea for reducing health risks to the farmers themselves and to consumers of the vegetables that are produced in the area.

The government should put in place certain monitoring processes and empower NEMA together with other relevant institutions such as the county governments that deal with

solid waste disposal management at the county levels, to be able to assess solid waste disposal practices and impose penalties if good practices are not followed in disposal of solid waste. Modern wastes disposal facilities should be acquired by the authorities concerned and appropriate waste disposal sites chosen by experts to avoid exposure of pollutants to food crops and underground water through leachates from the wastes.

Separation and recycling of wastes should be encouraged to help reduce the heavy metal load at the dumpsite. Likewise, generation of waste should be reduced by using less waste generating means in various human activities. The less waste generating means may include use of more oral medication than injectable, using recyclable or reusable products wrappers or containers and discourage the use of non-biodegradable materials.

The county government should consider safe and protected dumpsites for the rapidly expanding Eldoret town and repair the broken pipes that expose vegetables to contamination.

A medical examination on children residing near the dumpsite should be undertaken and proper medication be administered if the children have high metal content.

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APPENDICES

Appendix I: Acceptable standards of heavy metals in leafy vegetables (mg/Kg)

Heavy metals	Cadmium	Lead	Copper	Zinc	Iron	Nickel
WHO/FAO (2001)	0.02	0.3	40	99.4	425	67
Luo <i>et al.</i> (2011)	0.05	0.2	10	20	NS	NS

KEY

NS- Not specified

Appendix II: Acceptable standards of heavy metals in soil (mg/Kg)

Heavy metals	Cadmium	Lead	Copper	Zinc	Iron	Nickel
WHO/FAO (2001)	NS	100	NS	600	NS	NS
SPCR (2001)	1	50	50	150	150	30
Netherlands	0.5	40	NS	NS	NS	15

KEY

NS- Not specified

Appendix III: Mean Concentrations of Heavy Metals in Soils (Dry and Wet Seasons)

Sampling Site	Dry season			Wet season		
	Sample 1	Sample 2	Sample 3	Sample 1	Sample 2	Sample 3
	1	2	3	1		

Cadmium	1.07	1.09	1.08	1.03	1.11	1.07
Copper	51.06	51.75	52.44	50.04	50.13	50.22
Iron	551.87	551.92	551.97	554.43	554.48	554.53
Lead	2.05	2.03	2.01	1.97	1.94	1.91
Zinc	72.83	72.73	72.63	61.35	61.40	61.45
Nickel	52.54	52.56	52.58	54.55	54.66	54.77

Appendix IV: Mean Concentration of lead in kales (Dry and Wet Seasons)

Sampling Site	Dry season			Wet season		
	Sample 1	Sample 2	Sample 3	Sample 1	Sample 2	Sample 3
1	1.08	1.04	1.06	2.06	2.10	2.08
2	1.22	1.21	1.22	2.08	2.04	2.06
3	1.35	1.35	1.34	2.91	2.93	2.92
4	1.49	1.53	1.51	2.04	2.04	2.03
5	1.65	1.59	1.62	2.09	2.11	2.10
6	1.61	1.61	1.60	1.09	1.11	1.10
7	1.82	1.78	1.80	2.03	2.03	2.02

Appendix V: Mean Concentration of Lead in spinach for Dry and Wet seasons(mg/Kg)

Sampling Site	Dry season			Wet season		
	Sample 1	Sample 2	Sample 3	Sample 1	Sample 2	Sample 3
1	1.04	1.10	1.07	1.46	1.50	1.48
2	1.00	1.02	1.01	0.42	0.36	0.39
3	1.03	1.03	1.02	2.74	2.70	2.72
4	0.95	0.89	0.93	2.60	2.60	2.61
5	0.19	0.17	0.18	1.42	1.40	1.41
6	1.30	1.30	1.31	1.40	1.40	1.39
7	1.23	1.19	1.21	2.00	2.06	2.03

Appendix VI: Mean Concentration of Cadmium in Kales for Dry and Wet Seasons (mg/Kg)

Sampling Site	Dry season			Wet season		
	Sample 1	Sample 2	Sample 3	Sample 1	Sample 2	Sample 3
1	0.14	1.08	1.11	0.10	0.10	0.10
2	0.09	1.11	0.60	0.09	0.10	0.09
3	0.10	1.10	0.09	0.13	0.08	0.11
4	0.15	0.05	0.10	0.10	0.10	0.09
5	0.12	0.12	0.11	0.15	0.07	0.11
6	0.14	1.10	0.12	0.12	0.12	0.13
7	0.14	1.16	0.15	0.11	0.13	0.12

Appendix VII: Mean Concentration of Cadmium in Spinach for Dry and Wet Seasons (mg/Kg)

Sampling Site	Dry season			Wet season		
	Sample 1	Sample 2	Sample 3	Sample 1	Sample 2	Sample 3
1	0.08	0.08	0.07	0.07	0.07	0.06
2	0.05	0.09	0.07	0.04	0.08	0.06
3	0.10	0.08	0.09	0.10	0.06	0.08
4	0.13	0.05	0.09	0.09	0.09	0.08
5	0.09	0.09	0.08	0.10	0.08	0.09
6	0.15	0.09	0.12	0.09	0.11	0.10
7	0.11	0.11	0.10	0.14	0.10	0.12

Appendix VIII: Mean Concentration of Copper in Kales for Dry and Wet Seasons (mg/Kg)

Sampling Site	Dry season			Wet season		
	Sample 1	Sample 2	Sample 3	Sample 1	Sample 2	Sample 3

1	44.10	44.16	44.13	40.11	40.15	40.13
2	41.15	41.11	41.14	40.07	40.11	40.09
3	42.12	42.08	42.10	40.12	40.06	40.09
4	43.07	43.11	43.09	40.06	40.10	40.08
5	43.07	43.11	43.09	40.11	40.06	40.07
6	40.08	40.12	40.10	41.07	41.11	41.09
7	41.11	41.07	41.09	41.04	41.13	41.10

**Appendix IX: Mean Concentration of Copper in Spinach for Dry and Wet Seasons
(mg/Kg)**

Sampling Site	Dry season			Wet season		
	Sample 1	Sample 2	Sample 3	Sample 1	Sample 2	Sample 3
1	42.06	42.10	42.08	40.09	40.05	40.07
2	43.06	43.10	43.08	41.05	41.11	41.08
3	45.10	45.14	45.12	42.14	42.10	42.12
4	44.10	44.14	44.13	40.09	40.13	40.11
5	43.10	43.14	43.12	40.11	40.11	40.10
6	44.08	44.12	44.10	41.08	41.12	41.10
7	44.09	44.13	44.11	40.13	40.07	40.10

**Appendix X: Mean Concentration of Zinc in Kales for Dry and Wet Seasons
(mg/Kg)**

Sampling Site	Dry season			Wet season		
	Sample 1	Sample 2	Sample 3	Sample 1	Sample 2	Sample 3
1	35.46	35.42	35.44	30.29	30.35	30.32
2	36.54	36.60	36.57	30.30	30.26	30.28
3	34.83	34.79	34.81	32.26	32.28	32.27
4	38.29	38.39	38.34	31.26	31.30	31.28
5	37.88	37.92	37.90	34.21	34.25	34.23
6	33.17	33.21	33.19	30.21	30.21	30.20
7	37.29	37.23	37.26	29.25	29.29	29.27

**Appendix XI: Mean Concentration of Zinc in Spinach for Dry and Wet Seasons
(mg/Kg)**

Sampling Site	Dry season			Wet season		
	Sample 1	Sample 2	Sample 3	Sample 1	Sample 2	Sample 3

Site	1	2		1		
1	34.19	34.23	34.21	30.32	30.36	30.34
2	35.51	35.45	35.48	31.52	31.56	31.54
3	36.10	36.14	36.12	29.24	29.28	29.26
4	39.97	40.03	40.01	33.45	33.49	33.48
5	35.08	35.04	35.06	32.28	32.32	32.30
6	34.16	34.16	34.17	30.67	30.71	30.69
7	38.94	38.98	38.96	31.61	31.65	31.63

Appendix XII: Mean Concentration of Iron in Kales for Dry and Wet Seasons (mg/Kg)

Sampling Site	Dry season			Wet season		
	Sample 1	Sample 2	Sample 3	Sample 1	Sample 2	Sample 3
1	426.25	426.29	426.27	467.68	467.72	467.70
2	428.80	428.84	428.82	466.23	466.27	466.25
3	430.35	430.39	430.37	471.73	471.77	471.75
4	432.20	432.24	432.22	499.33	499.37	499.35
5	431.97	432.01	431.99	477.28	477.32	477.30
6	443.71	443.75	443.73	470.33	470.37	470.35
7	442.82	442.86	442.84	473.13	473.17	473.14

Appendix XIII: Mean Concentration of Iron in Spinach for Dry and Wet Seasons (mg/Kg)

Sampling Site	Dry season			Wet season		
	Sample 1	Sample 2	Sample 3	Sample 1	Sample 2	Sample 3
1	433.52	433.58	433.54	449.32	449.38	449.34
2	432.43	432.47	432.45	459.38	459.32	459.34
3	433.10	433.16	433.13	438.22	438.28	438.24
4	429.28	429.20	429.24	435.42	435.48	435.44
5	430.53	430.59	430.56	438.62	438.68	438.64
6	431.72	431.66	431.69	445.14	445.06	445.10
7	427.63	427.73	427.68	490.21	490.29	490.25

Appendix XIV: Mean Concentration of Nickel in Kales for Dry and Wet Seasons (mg/Kg)

Dry season				Wet season		
Sampling Site	Sample 1	Sample 2	Sample 3	Sample 1	Sample 2	Sample 3

g Site	1			1		
1	46.24	46.30	46.27	37.67	37.73	37.70
2	48.79	48.85	48.82	36.22	36.28	36.24
3	40.34	40.40	40.37	31.72	31.78	31.75
4	42.19	42.25	40.22	39.32	39.38	39.35
5	41.96	42.02	41.99	37.27	37.33	37.30
6	44.70	44.76	44.73	38.32	38.38	38.34
7	42.81	42.87	42.84	33.12	33.18	33.14

**Appendix XV: Mean Concentration of Nickel in Spinach for Dry and Wet Seasons
(mg/Kg)**

g Site	Dry season			Wet season		
	Sample 1	Sample 2	Sample 3	Sample 1	Sample 2	Sample 3
1	43.52	43.58	43.56	34.32	34.38	34.34
2	44.37	44.43	44.40	35.32	35.38	35.35
3	43.10	43.16	43.14	32.22	32.28	32.24
4	42.21	42.27	42.24	35.42	35.48	35.46
5	43.53	43.59	43.56	30.62	30.68	30.64
6	39.66	39.72	39.69	32.07	32.13	32.10
7	47.65	47.71	47.68	30.22	30.28	30.24