UNIVERSITY OF NAIROBI

COLLEGE OF BIOLOGICAL AND PHYSICAL SCIENCES

SCHOOL OF PHYSICAL SCIENCES

DEPARTMENT OF CHEMISTRY

INVESTIGATION OF HEAVY METALS IN COWPEAS, KALES AND SWEET POTATOES GROWN IN BUNGOMA AND KAKAMEGA COUNTIES, WESTERN KENYA.

By
Anthony Masika Pembere

A thesis submitted in partial fulfillment for the award of Master of Science in Environmental Chemistry of the University of Nairobi

DEDICATION

This thesis is dedicated to all those who have enabled me acquire knowledge.

DECLARATION

This thesis is my work and has not been presented for the award of a degree in any university.

Anthony Masika Pembere

Department of Chemistry

University of Nairobi

P.O Box 30197, Nairobi, Kenya

Supervisors:

Dr. Fredrick D.O. Oduor

Department of Chemistry

University of Nairobi

P.O Box 30197, Nairobi, Kenya

Dr. David K. Kariuki

Department of Chemistry

University of Nairobi

P.O Box 30197, Nairobi, Kenya

Prof. Isaac O. Jumba

Department of Chemistry

University of Nairobi

P.O Box 30197, Nairobi, Kenya

ACKNOWLEDGEMENTS

Many people helped, supported, and encouraged me during the completion of this project. The help and support given to me in many different ways was very important in enabling me to devote all my time to writing this thesis.

I wish to sincerely thank Dr. Fredrick D.O. Oduor, Dr. David K. Kariuki and Prof. Isaac O. Jumba for consistent academic guidance and support, without which the completion of this work would have been impossible.

Many colleagues assisted in numerous ways. My particular thanks go to Mr. John Munyao, Mr. Joel Bargul, Mr. Daniel Mijele and lecturers of the University of Nairobi, Department of Chemistry.

I am grateful to all my friends and family members who along the way have greatly assisted me.

ABSTRACT

This study investigates the level of heavy metals in selected food crops grown in Bungoma and Kakamega counties, Western Kenya. Copper (Cu), Lead (Pb), Cadmium (Cd), Chromium (Cr) and Zinc (Zn) were determined in cowpeas, kales, sweet potatoes and the soils which they grew on during the months of November 2010 (wet season) and February 2011 (dry season). A total of 25 sites were investigated. An Atomic Absorption Spectrophotometer was used for analysis of the samples after wet digestion and preparation of appropriate calibration standards. Lead in eleven percent of soil samples exceeded the range for unpolluted soils of 0.1 to 20 ppm. All cowpeas and kales samples had lead levels exceeding the recommended limit of 0.3 ppm while 95% of sweet potatoes samples exceeded the safe limit. Copper in soil samples was within the recommended limit of 100 ppm. Sweet potatoes and kales had copper concentrations within the recommended limit of 10 ppm, while 40 % of the cowpeas samples exceeded the safe limit. Zinc in soils, cowpeas, kales and sweet potatoes was within the range of background values for unpolluted environment. Chromium and cadmium were not detected in cowpeas, sweet potatoes and kales. There was positive correlation ($p>5$) between the wet and dry seasons, indicating insignificant seasonal variations in heavy metal concentrations.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

KEBS – Kenya Bureau of Standards

WHO – World Health Organization

NEMA –National Environment Management Authority

RNA-Ribonucleic Acid

DNA- Deoxyribonucleic Acid

ND- Not Detected

ppm- parts per million

DM- Dry Matter

SD- Standard Deviation

M- Mean

GOK- Government of Kenya

UNEP- United Nations Environment Programme

AAS- Atomic Absorption Spectroscopy

CHAPTER 1

INTRODUCTION

Bungoma County, located in the western region of Kenya, slopes from the foot of Mt. Elgon from the North where the altitude is over 2000 meters above sea level falling to the lower lying South and South West of altitude 1200 meters. The county has a population of 1,630,934 and an area of 2,069 km² (GOK, 2009). It is evenly distributed with an average population density of 482 persons per square kilometer. There is higher population density in the main urban centers and major factories. These include Webuye town, Nzoia Sugar Company, Bungoma town and Kimilili urban centres. Webuye town is located on co-ordinates 0^0 37'0''north, 34^0 46' 0''east (Central Intelligence Agency, 2012), along the busy Mombasa-Malaba highway and it is home to Pan African Paper Mills and Pan African Chemicals. Nzoia Sugar Company is located 20 kilometers from Webuye town centre. It deals with cultivation and milling of sugarcane and serves over 47,000 farmers in the larger Bungoma and Kakamega counties. It produces sugar and supports cane production through the provision of extension services to farmers with an extensive company nucleus estate covering 3600 hectares and an out grower zone spanning more than 23,500 hectares of cane (Omwoma *et al*., 2010).

Kakamega County boarders Bungoma to the North, Trans Nzoia to the North East, Uasin Gishu and Nandi counties to the East, Vihiga to the South, Siaya to the South West and Busia to the West.The county lies within altitude 1,250-2,000 m. It has a population of 1,660,651 and an area of 1,395 km² (GOK, 2009).Mumias town is located in this county and lies on coordinates 0^0 20' 11'' north, 34^0 29' 21'' East (Central Intelligence Agency, 2012). Mumias Sugar

Company, the largest sugar producer in Kenya lies in the vicinity of this town. The company occupies 4,295 hectares of land. Cultivation and milling sugarcane are the main activities undertaken by the company alongside power generation and wastewater treatment as supporting activities (ECMC, 2004). Mumias has a varying topography with a few hills and valleys dissected by a number of streams (GOK, 2002).

Both Webuye and Mumias areas have a tropical climate, and the heavily populated land around them is used mainly for growing sugarcane, maize, cassava, millet and food crops. The regions have a two-season rain regime, the long rains covering April to July while the short rains start in August to November. The average precipitation ranges from 1250 to 1800 mm (NRBMI, 2006).

"Heavy metals" is a general collective term, which applies to the group of metals and metalloids with atomic density greater than 4 g/cm^3, or 5 times or more, greater than water (Nriagu and Pacyna 1988; Garbarino *et al*., 1995, Hawkes, 1997). Heavy metals occur as natural constituents of the earth crust, and are persistent environmental contaminants since they cannot be degraded or destroyed. In rocks, they exist as their ores in different chemical forms, from which they are recovered as minerals, by mineral processing operations (Peplow, 1999; Lenntech, 2004). Heavy metals can be emitted into the environment by both natural and anthropogenic causes. Sources of anthropogenic contamination include the addition of manure, sewage sludge, fertilizers and pesticides to soils, municipal and industrial effluents, and vehicular emissions (Whatmuff, 2002; McBride, 2003; McLaughlin *et al*., 1999; UNEP / GPA, 2004).

Heavy metals enter the body system through food, air, and water and some bio-accumulate over a period of time (Lenntech, 2004; UNEP/GPA, 2004). The uptake of heavy metals by plants is an avenue of their entry into the human and animal food chain (Sharma *et al*., 2006; Kachenko and Singh, 2004). Plants can accumulate heavy metals, in or on their tissues due to their great ability to adapt to variable chemical properties of the environment. Thus plants are intermediate reservoirs through which heavy metals from soils, and partly from waters and air, move to man and animals. Heavy metals such asiron, cobalt, copper, manganese, molybdenum, and zinc are required by living organisms in various concentrations hence are beneficial. Excessive levels can be harmful to the health of the organism while other heavy metals such as mercury, plutonium, and lead, have no beneficial function in organisms, and their accumulation over time in the bodies of animals can cause serious health effects. Certain elements that are normally toxic, for certain organisms or under certain conditions, are also beneficial. Examples include vanadium, tungsten, and cadmium (Duffus, 2002). This has been illustrated by Lane and Morel (2000) who provided evidence of a biological role for Cd in the marine diatom *Thalassiosira weissflogii* under conditions of low zinc, typical of the marine environment.

This study was carried out around Webuye and Mumias in Bungoma and Kakamega counties respectively. Mumias and Nzoia sugar companies serve farmers in the larger Bungoma and Kakamega counties with extensive company nucleus estates and out grower zones. Cultivation of sugarcane involve application of phosphate fertilizers at the initial stage of planting and top dressing with nitrogen fertilizers at the stage of two to nine months of growth. Farmers also grow other crops (maize, beans, cassava, millet, sweet potatoes and vegetables) beside

sugarcane that involve fertilizer, manure and pesticides application. Various authors have reported on fertilizers, pesticides and manure as possible sources of Pb, Cd, Zn, Cr and Cu in the environment. According to Pendias and Pendias (2001) nitrogenous fertilizers contain lead in the range of 2 to 27 ppm, copper (1-15 ppm), zinc (1-42 ppm), chromium (3.2-19 ppm) and cadmium (0.05-8.5 ppm) while phosphate fertilizers contain lead (7-225 ppm), chromium (66-245 ppm), zinc (50- 500), cadmium (0.1-170 ppm), copper (1-300 ppm). Manure contain lead (6.6-15 ppm), copper (2-60 ppm), zinc (15-250 ppm), chromium (5.2-55 ppm), while pesticides contain lead (0-60 ppm), zinc (1.3-25 ppm) and copper (12-50 ppm). Since fertilizers, pesticides and manure have been applied in these areas for over three decades, they may elevate the level of Pb, Cd, Cu, Zn and Cr in soils and plants with serious implications on human and animal health.

Another possible source of Zn, Cu and Cd in these areas are industrial effluents from the sugar factories. Mumias and Nzoia sugar factories have been in these areas for over three decades. Industrial effluents from sugar industries have been reported as a possible source of Zn, Cu and Cd in the environment. Khan *et al*. (2003) while studying on the characterization and treatment of industrial effluents from sugar industries in Pakistan found mean Zn, Cu, and Cd levels to be 0.8 ppm, 1.6 ppm and 0.2 ppm respectively. Pan African Paper Mills at Webuye town is the largest paper factory in East Africa and has been in this region for over two decades. Its effluents may also be a possible source of Pb and Zn in the environment since Vema *et al.* (2005) studying on biosorption of Pb and Zn from pulp and paper industry by water hyacinth in India reported both Pb and Zn levels in paper industry effluents to be between 1.30 ppm and 1.39 ppm respectively.

Cook and Morrow (1995), studying on anthropogenic sources of cadmium in Canada reported that fossil fuels contain cadmium in the range of 0.5 to 1.5 ppm. Vehicular emissions during agricultural land preparation, harvesting of sugarcane and wood transport for paper production may also be a source of Cd in these areas. The Mombasa-Uganda highway passes through Bungoma County and is also characterized by heavy traffic flow.

Cd and Pb may also emanate from municipal effluents from Webuye and Mumias urban centres. Jumba *et al.* (2006) linked animal health problems in Lake Nakuru National Park to cadmium and lead poisoning arising from the release of heavy metals after municipal waste and the subsequent uptake by the forages, thus highlighting the contribution of municipal effluents on Pb and Cd levels in the environment.

The study investigates the influence of these activities on copper (Cu), lead (Pb), cadmium (Cd), chromium (Cr) and zinc (Zn) composition and distribution in soils, cowpeas, kales and sweet potatoes grown and consumed in the two counties.

1.1 Problem Statement

Cowpeas, sweet potatoes and kales are staple foods in the western region of Kenya. Whereas Zn and Cu are essential elements, Pb, Cd and Cr are chronic elements. This study investigated the concentrations of these elements in the selected food crops and the soils on which they were grown, in order to ascetain if there were possible adverse health effects from consumption of the selected food crops. Furthermore, the same elements were determined in the soils to investigate if they were the source of the same in the food crops.

1.2.0 Objectives

1.2.1 Overall Objective

To determine the concentration of heavy metals in soils, kales, cowpeas and sweet potatoes in the industrial and agricultural areas of Webuye and Mumias.

1.2.2 Specific Objectives

1. To determine the concentration of lead (Pb), cadmium (Cd), zinc (Zn), copper (Cu) and chromium (Cr) in soils sampled around Webuye and Mumias during the wet (October/November) and dry (February/March) seasons.
2. To determine the concentration of lead (Pb), cadmium (Cd), zinc (Zn), copper (Cu) and chromium (Cr) in Kales, cowpeas, and Sweet potatoes sampled around Webuye and Mumias during the wet (October/November) and dry (February/March) seasons.

1.3 Justification

Limited studies have been carried out in the western Kenya sugar belt on the level of heavy metals in food crops, particularly on cowpeas, sweet potatoes and kales. Knowledge of the levels of Pb, Cd, Zn, Cr and Cu in the selected food crops and soils will be useful in determining their safety and suitability as stable foods and also ascertain if the soils were the main source of the elements.

CHAPTER 2

LITERATURE REVIEW

2.0 Heavy metals in Soils and Plants

Studies on heavy metals in soils and plants have been carried out by various authors in Kenya and across the world. In the Western region of Kenya, Omwoma *etal*. (2010) studied the impact of fertilizers on heavy metal loads in surface soils in Nzoia nucleus estate sugarcane farms. Analysis of heavy metals in top soil samples found elevated levels of heavy metals in the soils with mean concentrations (ppm) of 142.38, 59.12, 73.35, 116.27, 409.84 (dry season) and 144.22, 50.29, 72.14, 158.81, 368.83 (wet season) for Cr, Pb, Cu, Zn and Fe, respectively, compared with a control soil sample from an adjacent field where fertilizers were not applied having mean concentrations of 117.27, 61.87, 63.68, 123.49, 282.93 (dry season) 108.00, 50.68, 66.10, 114.23, 167.01 (wet season) respectively.

Inoti *etal*. (2011) also analyzed the heavy metal levels in tomato (*Lycopersicon esculentum L.*) and spinach (*Spinacia oleracea L.*) grown in Thika town, Kenya. The levels of Pb and Cd in spinach and tomatoes varied from 13.3-29.5 ppm, and 3.5-20.5 ppm respectively. Oyaro (2000) reported on heavy metals content in *Amaranthus Hybridus,Bidens Pilosa* and *Pennisetum* as environmetal pollution indicators in Nairobi City. The lead content in *amaranthus hybridus* ranged from 6.80- 422 ppm while *Bidens pilosa* had lead content in the range of 8.2–354 ppm. The city center and industrial areas had higher Pb levels than other areas. Samples from areas with heavy, slow moving vehicles such as round-abouts, corners, bus stops, pot-holed roads, valleys and uphills had higher Pb levels than other areas.

Kachenko and Singh (2004) investigated the source and magnitude of heavy metal contamination in soil and vegetable samples at 46 sites across four vegetable growing regions in New South Wales, Australia. The extent of metal contamination in soils sampled was greatest in regions located in the vicinity of smelters, such as in Boolaroo and Port Kembla. Soil metal concentrations decreased with depth at these two sites, suggesting contamination due to anthropogenic activities. The investigation highlighted the increased danger of growing vegetables in the vicinity of smelters.

In this chapter, subsections 2.1, 2.2, 2.3, 2.4 and 2.5 reviews the occurrence of copper, zinc, cadmium lead and chromium in soils and plants. The analytical method of choice in this study is discussed in subsection 2.6 while statistical analysis in subsection 2.7.

2.1 Copper

2.1.1 Soil Composition

The copper content of a soil is the result of inputs of the metal from three different types of sources; the minerals in the soil parent material, anthropogenic inputs onto land, such as pesticides and manures, and deposition from the atmosphere. The soil parent material is generally the most important source of all micronutrients. Ultimately, all natural soil copper owes its origin to the primary minerals occurring in igneous rocks. Anthropogenic inputs directly to land are very diverse but can be conveniently divided into concentrated copper compounds (mostly residues from fungicides, or soil/crop treatments to rectify deficiency) used intentionally to act as a source of cupric ions, and other materials incidentally containing copper, such as livestock manures, sewage sludge and fertilizers (Pendias and Pendias, 2001; CDA, 1988; Kachenko and Singh, 2004).

Atmospheric inputs (both in rain and dry deposition) can vary considerably according to the proximity of industries emitting fumes containing copper and the types of particulate matter in windblown dust. These inputs are relatively small, except near to certain industrial sources, but are generally more uniform than other sources and affect larger areas (CDA, 1988; Breslin, 1999). Most copper deposited on soil from the atmosphere, agricultural use, solid waste and sludge disposal will be adsorbed with greater concentrations of copper measured in the upper 5–10 centimeters of soil in comparison to lower soil depths, except in sandy soils where the lability of bound copper is greater (Breslin, 1999).

2.1.2 Plant Composition

The essentiality of copper for normal healthy growth and reproduction in higher plants is largely due to its occurrence as a constituent of several proteins, mostly enzymes, which have varied butimportant metabolic functions. These copper-containing proteins have key roles in: respiration, photosynthesis, lignifications and phenol metabolism, protein synthesis and the regulation of auxins (CDA, 1988; Pendias and Pendias, 2001). Copper is translocated in the xylem and phloem vessels complexed with amino acids. It tends to accumulate in the root and is only sparingly translocated to the shoot. In the shoot it is bound in proteins and the copper in old leaves is not redistributed around the plant until senescence when the protein is hydrolysed (CDA, 1988). The appropriate content of copper in plants is essential both for health of the plant and for the nutrient supply to man and animals. The concentration of copper in plant tissues seems to be a function of its level in the nutrient solutions or in soils. The pattern of this relationship, however, differs among plant species and plant parts (Pendias and Pendias, 2001; ATSDR, 2004).

2.1.3 Occurrence of Copper in Animal Systems

Copper is an essential nutrient that is incorporated into a number of metalloenzymes involved in hemoglobin formation, drug/xenobiotic metabolism, carbohydrate metabolism, catecholamine biosynthesis, the cross-linking of collagen, elastin, and hair keratin, and the antioxidant defense mechanism (ATSDR, 2004). Copper-dependent enzymes, such as cytochrome c oxidase, superoxide dismutase, ferroxidases, monoamine oxidase, and dopamine β-monooxygenase, function to reduce activated oxygen species or molecular oxygen. Symptoms associated with copper deficiency in humans include normocytic, hypochromic anemia, leukopenia, and osteoporosis. Excess copper is stored in the liver and causes Wilson disease. The acceptable limit for human consumption of Copper is 10 ppm (Nair *et al*., 1997; ATSR, 2004).

2.2.0 Zinc

2.2.1 Soil Composition

Fertilizers, manure and municipal sludges applied to cropland soils are important source of trace metals, including zinc (Chang *et al*., 1987). On a worldwide basis, an estimated 1,193,000–3,294,000 metric tons of zinc per year are released to soil from anthropogenic sources (Nriagu and Pacyna, 1988). The four most important sources of zinc in soil were estimated to be smelter slugs and wastes, mine tailings, coal and bottom fly ash, and the discharge of commercial products such as fertilizers (Nriagu and Pacyna, 1988). Zinc undergoes reactions in sediment and soil involving precipitation/dissolution, complexation/dissociation, and adsorption/desorption. These reactions are controlled by the pH, redox potential, the concentration of zinc ions and other ions in the soil, the number and type of adsorption sites associated with the solid phase, and the organic ligands present that are capable of forming

complexes with zinc. In acidic sediments and soils, more zinc is available in ionic forms, and cation exchange processes influence its fate. Depending on the nature and concentrations of other mobile metals in sediments and soils, competition for the binding sites probably occurs. In the absence of suitable binding sites, zinc may be mobilized. In alkaline soils, the chemistry of zinc is dominated by interactions with organic ligands (Berry *et al*., 1999; Chang *et al*., 1987). Biological degradation of zinc complexes in soil is necessary for the normal operation of ecosystems to facilitate the recycling of zinc from litter, feaces, and dead organisms. In some environments, bacteria and fungi are able to oxidize zinc sulfide producing zinc sulfate, which will solubilize in the soil solution (WHO, 2001).

2.2.2 Plant Composition

Zinc is acquired from the soil solution primarily as Zn^{2+}, but also potentially complexed with organic ligands, by roots which feed the shoots via the xylem. Transport from epidermal and cortical cells to the root xylem can occur via the cytoplasmic continuum of cells, linked by plasmodesmata, from which Zn is pumped into the stelar apoplast (Lasat & Kochian, 2000). This pathway is catalysed by plasma membrane and tonoplast transport activity. Zinc can also be delivered extracellularly to the stelar apoplast in regions where the casparian band is not fully formed. Zinc plays essential metabolic roles in the plant. It is a component of a variety of enzymes such as dehydrogenases, proteinases, peptidases and phosphohydrolases (Marschner, 1995;Lasat & Kochian, 2000). Severe Zn deficiency is characterized by root apex necrosis, whilst sublethal Zn deficiency induces spatially heterogeneous or interveinal chlorosis, the development of reddish-brown or bronze tints, and a range of auxin deficiency-like responses such as internode shortening, epinasty, inward curling of leaf lamina and reductions in leaf size

(Marschner, 1995; Chaney, 1993). In most crops, the typical leaf Zn concentration required for adequate growth approximates 15–20 mg kg^{-1} (Marschner, 1995). Zinc toxicity in crops is far less widespread than Zn deficiency. However, Zn toxicity occurs in soils contaminated by mining and smelting activities, in agricultural soils treated with sewage sludge, and in urban and peri-urban soils enriched by anthropogenic inputs of Zn, especially in low-pH soils (Chaney, 1993).

2.2.3 Zinc Functions in Animal Systems

Zinc is an essential nutrient for humans and animals that is necessary for the function of a large number of metalloenzymes, including alcohol dehydrogenase, alkaline phosphatase, carbonic anhydrase, leucine aminopeptidase, and superoxide dismutase. Zinc deficiency has been associated with dermatitis, anorexia, growth retardation, poor wound healing, hypogonadism with impaired reproductive capacity, impaired immune function, and depressed mental function (ATSDR, 2005; Mulhern *et al*., 1986). The recommended dietary allowance for zinc is 11 mg/day in men and 8 mg/day in women. Gastrointestinal symptoms reported in cases of excess zinc exposure include vomiting, abdominal cramps, and diarrhea, in several cases with blood (ATSDR, 2005). Animal studies suggest that exposure to very high levels of dietary zinc is associated with reduced fetal weight, alopecia, decreased hematocrit, and copper deficiency in offspring. Second generation mice exposed to zinc carbonate during gestation and lactation (260 mg/kg/day in the maternal diet), and then continued on that diet for 8 weeks, had reduced body weight, alopecia, and signs of copper deficiency for example lowered hematocrit and occasional achromotrichia (Mulhern *et al*., 1986).

2.3.0 Cadmium

2.3.1 Soil Composition

Cadmium in soils is derived from both natural and anthropogenic sources. Natural sources include underlying bedrock or transported parent material such as glacial till and alluvium. Anthropogenic input of cadmium to soils occurs by aerial deposition and sewage sludge, manure and phosphate fertilizer application. Cadmium is much less mobile in soils than in air and water. The major factors governing cadmium speciation, adsorption and distribution in soils are pH, soluble organic matter content, hydrous metal oxide content, clay content and type, presence of organic and inorganic ligands, and competition from other metal ions (OECD, 1994; Cook and Morrow, 1995).

The use of cadmium-containing fertilizers and sewage sludge is most often the primary reason for the increase in the cadmium content of soils over the last 20 to 30 years in Europe (Jensen and Bro-Rasmussen, 1992). Continuous application of fertilizer with a high rate of triple super-phosphate (1,175 kg P-ha-1·year^{-1}) for a period of 36 years resulted in a 14-fold increase in cadmium content of surface soils (Singh, 1994).

The average natural abundance of cadmium in the earth's crust has most often been reported from 0.1 to 0.5 ppm, but higher and lower values have also been cited depending on a large number of factors. Igneous and metamorphic rocks tend to show lower values, from 0.02 to 0.2 ppm whereas sedimentary rocks have much higher values, from 0.1 to 25 ppm. Fossil fuels contain 0.5 to 1.5 ppm cadmium, but phosphate fertilizers contain from 10 to 200 ppm cadmium (Cook and Morrow, 1995).

Cadmium in soils must be distinctly classified in three separate areas with regard to their relative effects on human health and the environment (Eggenberger and Waber, 1998). These

are agricultural soils, non-agricultural soils, and controlled landfills. Cadmium in controlled landfalls is virtually immobile, and is unlikely to have any effect on human health or the environment because it is so well contained. Cadmium in non-agricultural soils will generally not affect human health as it does not enter the food chain readily or may do so only indirectly by transfer from non-agricultural soils to agricultural soils via airborne or water transport. However, the amount thus transferred is considered to be relatively low and is not expected to be a significant proportion of the cadmium in non-agricultural soils. Cadmium in agricultural soils is likewise relatively immobile under normal conditions, but could become more mobile under certain conditions such as increased soil acidity and its cadmium level may be enhanced by the usage of phosphate fertilizers, manure or sewage sludge (Eggenberger and Waber, 1998; Cook and Morrow, 1995).

2.3.2 Plant Composition

Although Cd is considered to be a nonessential element for plants, it is effectively absorbed by both the root and leaf systems. Soil pH is the major soil factor controlling both total and relative uptake of Cd. Although an appreciable fraction of Cd is taken up passively by roots, Cd is also absorbed metabolically. The Cd content of plants is of the greatest concern as a Cd reservoir and as the pathway of Cd to man and animals, thus ,tolerance and adaptation of some plants species to higher Cd levels, although important from the environmental point of view, create a health risk (Pendias and Pendias, 2001; ATSDR, 2008). The cadmium contents of foodstuffs may vary widely with the agricultural practices utilized in the particular areas such as phosphate fertilizer, sewage sludge and manure application, the types of crops grown, and atmospheric cadmium deposition from natural or anthropogenic sources (Pendias and Pendias, 2001).

2.3.3 Dietary Composition

In man and animal nutrition, Cd is a cumulative poison. Acute dietary doses (10-30 mg/kg/day) of cadmium can cause severe gastrointestinal irritation, vomiting, diarrhea, and excessive salivation, and doses of 25 mg of Cd/kg body weight can cause death. Low-level chronic exposure to Cd can cause adverse health effects including gastrointestinal, hematological, musculoskeletal, renal, neurological, and reproductive effects (ATSDR, 2008;Cook and Morrow, 1995).

2.4.0 Lead

2.4.1 Soil Composition

Natural lead is a mixture of four stable isotopes, 208 Pb (51–53%), 206 Pb (23.5–27%), 207 Pb (20.5–23%), and 204 Pb (1.35–1.5%). Lead isotopes are the stable decay product of three naturally radioactive elements: 206 Pb from uranium, 207 Pb from actinium, and 208 Pb from thorium. Lead is not a particularly abundant element, but its ore deposits are readily accessible and widely distributed throughout the world. Its properties, such as corrosion resistance, density, and low melting point, make it a familiar metal in pipes, solder, weights, and storage batteries.

Lead exists in three oxidation states: Pb(0); Pb(II); and Pb(IV). In the environment, lead primarily exists as Pb(II). Pb(IV) is only formed under extremely oxidizing conditions and inorganic Pb(IV) compounds are not found under ordinary environmental conditions (King and Ramachandran, 1995; Sutherland and Milner, 1990).

Land is the ultimate repository for lead, and lead released to air and water ultimately is deposited in soil or sediment. For example, lead released to the air from leaded gasoline or in

stack gas from smelters and power plants will settle on soil, sediment, foliage, or other surfaces. The heaviest contamination occurs near the highway, in the case of leaded gasoline, or near the facility, in the case of a power plant or smelter. Nearly all forms of lead that are released to soil from anthropogenic sources, such as $PbSO_4$, $PbCO_3$, PbS, $Pb(OH)_2$, $PbCrO_4$, and PbClBr, are transformed by chemical and biotic processes to adsorbed forms in soil. The transformation process involves the formation of lead complexes with binding sites on clay minerals, humic acid and other organic matter, and hydrous iron oxides (Chaney *et al*., 1988; Chuan *et al*., 1996; Sauve *et al*., 1997).

2.4.2 Uptake, Transport and Localization in Plants

Pb is available to plants from soil and aerial sources. The extent to which Pb enters plants via the leaves depends on the ability of leaves to absorb Pb from aerial sources, which in turn depends on the specific leaf morphology (Godzik, 1993). However the bulk of the Pb taken up by plants remains in the roots (Kumar *et al*., 1995). Pb accumulates in the surface layers of soils and therefore it is difficult to reliably measure the portion of soil Pb directly available to plants. Its availability depends highly on soil conditions. Pb binds to organic material in the soil. Soil particle size and cation exchange capacity as well as plant factors such as root surface area, root exudates, mycorrhization and rate of transpiration affect the availability and uptake of Pb (Davies, 1995). The absorption of Pb in soil follows the Langmuir relation and increases with increasing pH between 3.0 to 8.5 (Lee *et al*., 1998). After being taken up by roots, the localization of Pb is greater in roots than in other parts of the plants. Pb binds strongly to the carboxyl groups of the carbohydrates galacturonic acid and glucuronic acid in the cell wall, which restricts its transportation via apoplast. In general dicots accumulate significantly higher

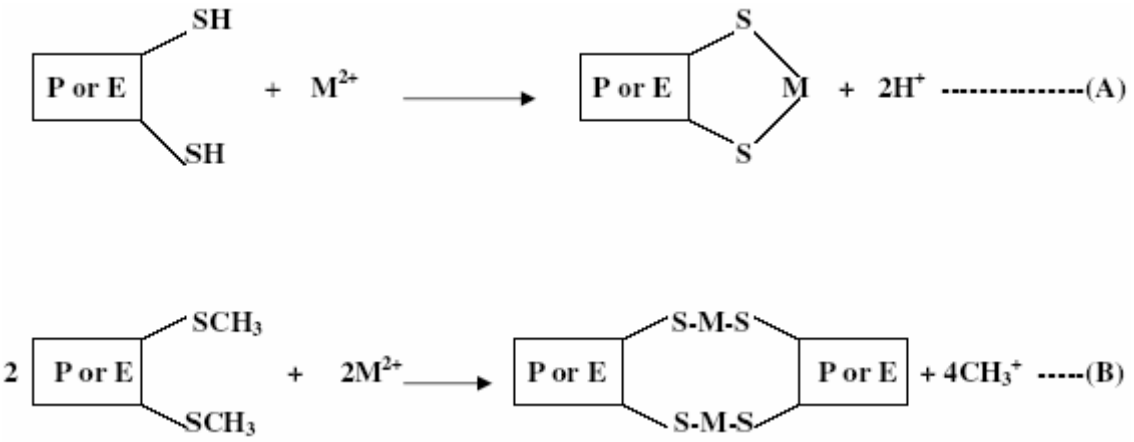
amounts of Pb in the roots than monocots (Huang *et al*, 1997). Pb transported from the soil to the root cells has to cross the root-cell plasma membrane. One possible transport pathway of Pb across the plasma membrane appears to be through plasma membrane cation channels, such as Ca-channels. The pattern of distribution of Pb in the roots considerably differs depending on whether the concentrations of Pb are lethal or non-lethal (Seregin *et al*., 2004). At lower concentrations, Pb ions predominantly flow in the apoplast, whereas at higher concentrations, the barrier function of plasmalemma is damaged and a greater amount of Pb enters into the cells. The content of Pb in various plant organs tends to decrease in the following order: roots>leaves>stem>inflorescence>seeds. However this order can vary with plant species (Antosiewicz, 1992). Leaves differ in their abilities to accumulate Pb depending on age. Maximum Pb content is found in senescing leaves and least in young leaves (Godzik, 1993).

2.4.3 Dietary Composition

The threshold intake limit for the human body set by WHO is 0.3 mg/kg, above this limit, it can result in lead poisoning, characterized by blindness, deafness, hypertension, impairment of kidney function and neurological disorder. Todd (1996) emphasized that most of the accumulated lead is sequestered in the bones and teeth. This causes brittle bones and weakness in the wrists and fingers. Lead that is stored in bones can re-enter the blood stream during periods of increased bone mineral recycling (i.e., pregnancy, lactation, menopause and advancing age). Mobilized lead can be redeposited in the soft tissues of the body and can cause musculoskeletal, renal, ocular, immunological, neurological, reproductive, and developmental effects. McDonald and Potter (1996) studied the possible effects of lead exposure on mortality

in a series of 454 children who were hospitalized for lead poisoning at Boston's Children Hospital between 1923 and 1966 and who were traced through 1991. Of the 454 patients eligible for the study, 88% had a history of paint pica or known lead exposure; 90% had radiologic evidence of skeletal changes consistent with lead poisoning; and 97% had characteristic gastrointestinal, hematologic, and/or neurologic symptoms.

Generally, the poisoning effects of heavy metals are due to their interference with the normal body biochemistry in the metabolic processes. When ingested, in the acid medium of the stomach, they are converted to their stable oxidation states (Zn^{2+}, Pb^{2+}, Cd^{2+}, As^{2+}, As^{3+}, Hg^{2+} and Ag^{+}) and combine with the body's biomolecules such as proteins and enzymes to form strong and stable chemical bonds. The equations below show their reactions during bond formation with the sulphydryl groups (-SH) of cysteine and sulphur atoms of methionine (-SCH_3) (Ogwuegbu and Muhanga, 2005).



Where: (A) = Intramolecular bonding; (B) = Intermolecular bonding; P = Protein; E = Enzyme; M = Metal

The hydrogen atoms or the metal groups in the above case are replaced by the poisoning metal and the enzyme is thus inhibited from functioning, whereas the protein–metal compound acts as a substrate and reacts with a metabolic enzyme. The most toxic forms of these metals in their ionic species are the most stable oxidation states, for example, Cd^{2+}, Pb^{2+}, Hg^{2+}, Ag^{+} and As^{3+}. In their most stable oxidation states, they form very stable biotoxic compounds with the body's bio-molecules, which become difficult to be dissociated, due to their bio-stabilities, during extraction from the body by medical detoxification therapy (Ogwuegbu and Muhanga, 2005).

2.5.0 Chromium

2.5.1 Soil Composition

Chromium is a common element of rocks, especially those of basic and ultramafic igneous origin, and soils derived from them are correspondingly enriched. Chromium (III) and (VI) have highly contrasting chemical properties. In unpolluted soils, the relatively insoluble and less mobile chromium (III) predominates in the form of hydroxides and oxides and adsorbed onto clay particles, soil organic matter, metal oxyhydroxides and other negatively charged surfaces. Sorption tends to increase with increasing soil pH. In contact with air, chromium (VI) is the most stable form in soil (McGrath, 1995); although only a small percentage of the chromium (III) in soils is normally present in an oxidisable form (Bartlett and James, 1988). Although dissolved oxygen in the soil solution can mediate conversion of chromium (III) to (VI), it is considered to be a much less significant mechanism than that found with manganese oxides.

The rate of oxidation increases as soil pH decreases, probably as a result of increasing solubility of chromium (III) under more acidic conditions. Elevated concentrations of chromium (VI) in soil are most likely to be from pollution. Chromium (VI) is often found as chromate, although it

is typically in pH-dependent equilibrium with other forms including dichromate, and it is considered more soluble and more mobile than chromium(III), (McGrath, 1995). Although not readily adsorbed to most mineral surfaces, chromium (VI) is absorbed by clay minerals that possess exposed inorganic hydroxyl groups, such as iron and aluminium oxides. Adsorption tends to increase with decreasing pH. Chromium (VI) is a powerful oxidising agent and will readily react with soil organic matter to form chromium (III) (Bartlett and James, 1988; McGrath, 1995). Soil pH and the presence of iron oxides, soil organic matter and low soil oxygen levels influence reduction. In assessing the risk to human health posed by chromium contaminated soils, the ratio of chromium (III) to the more toxic chromium (VI) should be taken into account. While chromium (VI) is the more stable form in aerobic soils, organic matter can reduce it to chromium (III) which may be precipitated and hence unavailable for re-oxidation. Ideally the Soil Guideline Value would apply only to the concentration of chromium (VI) in soil, but there are significant practical challenges to doing so. Many analytical procedures for determining chromium in soil employ procedures that allow interconversion of the two forms and therefore accurate analysis of environmental samples to determine the relative proportions of chromium (0), (III) and (VI) presents a considerable challenge (Trupheme *et al*, 2000; Vitale *et al*, 2000; Frenzel, 1998). The reactive nature of chromium (VI) means that sample collection, preservation and ultimately analysis are difficult to undertake without altering the original state of chromium in the soil.

2.5.2 Plant Composition

Concentrations of chromium in plant-available form are extremely low in most soils, and this is reflected in low concentrations of the element in plants. Anthropogenic sources of chromium

are believed to be responsible for elevated concentrations of this metal in plants. The toxicity of Cr in plants depends on its oxidation state. Symptoms of Cr toxicity appear as wilting of tops and root injury. Chlorotic bands on cereals, and brownish red leaves are typical features (McGrath, 1995; Pendias and Pendias, 2001).

2.5.3 Dietary Composition

The toxicity of chromium in humans depends upon its oxidation state. Hexavalent chromium is more toxic than the trivalent form. Chromium (III) is an essential element, and the UK Committee on Medical Aspects of Food Policy have recommended a dietary intake above 25 μg chromium (III) per day for adults and between 0.1 and 1 μg kg^{-1} per day for children and adolescents (DH, 1991). Chromium containing substances of various chemical compositions and chromium oxidation states have been shown to cause sensitisation, or to produce reactions (skin or respiratory effects) in already sensitised people. Chromium (IV) is toxic both to human and animal health. Reduced sperm count and plasma testosterone were observed in male New Zealand rabbits administered 3.6 mg chromium (VI)/kg/day as potassium dichromate for 10 weeks by gavage (Yousef *et al*., 2006). Sperm count was decreased by 18%, total sperm output was decreased by 25.9%, total number of mobile sperm was decreased by 34.3%, and number of dead sperm increased by 23.9%. In addition, relative weight of testes and epididymis were decreased by 22.2% and plasma testosterone was decreased by 20.8%. The respiratory tract in humans is a major target of inhalation exposure to chromium compounds. Chromate sensitive workers acutely exposed to chromium (VI) compounds may develop asthma and other signs of respiratory distress. Five individuals who had a history of contact dermatitis to chromium were exposed via a nebulizer to an aerosol containing 0.035 mg chromium (VI)/mL as potassium

dichromate. A 20% decrease in the forced expiratory volume of the lungs was observed and was accompanied by erythema of the face, nasopharyngeal pruritus, nasal blocking, coughing, and wheezing (Olaguibel and Basomba 1989). Oral exposure of animals to chromium (VI), but not chromium (III), compounds resulted in functional and histopathological changes to the immune system (Snyder and Valle 1991). Splenocytes prepared from rats given potassium chromate in drinking water at 16 mg chromium(VI)/ kg/day for 3 weeks showed an elevated proliferative response of T-and B-lymphocytes to the mitogens, concanavalin A and liposaccharide, compared with splenocytes from control rats.

2.6.0 Analytical Method Used for Determination of Heavy Metals

2.6.4 Atomic Absorption Spectrometry

Atomic absorption measures the amount of light at the resonant wavelength which is absorbed as it passes through a cloud of atoms. As the number of atoms in the light path increases, the amount of light absorbed increases in a predictable way. By measuring the amount of light absorbed, a quantitative determination of the amount of analyte element present can be made. The use of light sources and careful selection of wavelength allow the specific quantitative determination of individual elements in the presence of others (Welz and Sperling, 2007; Skoog *et al*., 2007). Beer- Lamberts law is applied. This law defines the logarithmic dependence between the transmission, (*T),* of light through a substance and the product of the absorption coefficient (α) of the substance of specific wavelength (*ℓ).* This can be expressed as a simple relationship;

$$A = \epsilon \ell c = \alpha \ell$$

where A is absorbance and c is the concentration of the absorbing species.

Thus, if the pathlength and the molar absorptivity are known and the absorbance is measured, the concentration of the substance can be deduced (Welz and Sperling, 2007).

The technique typically makes use of a flame to atomize the sample,but other atomizers such as a graphite furnaceor plasmas, primarily inductively coupled plasmas, are also used. A liquid sample is normally turned into an atomic gas in three steps; desolvation, vaporization, atomization. Hollow cathode lamps are the most common radiation source in atomic absorption spectroscopy. Inside the lamp, filled with argon or neon gas, is a cylindrical metal cathode containing the metal for excitation, and an anode. When a high voltage is applied across the anode and cathode, gas particles are ionized. As voltage is increased, gaseous ions acquire enough energy to eject metal atoms from the cathode. Some of these atoms are in excited states and emit light with the frequency characteristic to the metal (Skoog *etal*., 2007; Aceto *etal*., 2002). Atomic absorption spectroscopy can also be performed by lasers, primarily diode lasers because of their good properties for laser absorption spectrometry.The technique is then either referred to as diode laser atomic absorption spectrometry or since wavelength modulation most often is employed, wavelength modulation absorption spectrometry (Skoog *etal*., 2007;Welz and Sperling, 2007).

Based on cost, sensitivity and availability of the method, atomic absorption spectrometry was preferred as the technique of choice in this study.

2.8 Statistical Analysis

Mean concentrations of elements in soils, vegetables and sweet potato and their standard deviations for different sites were calculated using data from individual farms. Outlier values

from some farms were noted and filtered when calculating the mean of a site. The recorded data were subjected to two-way analysis of variance to assess the influence of different variables on the concentrations of heavy metals in the vegetables and sweet potatoes tested. All the statistical analyses were computed using SPSS software version 12.

CHAPTER 3

MATERIALS AND METHODS

3.0Description of Study Area

This study was carried out around Webuye and Mumias in Bungoma and Kakamega counties respectively. Mumias and Nzoia sugar companies located in Mumias and Webuye respectively serve farmers in the larger Bungoma and Kakamega counties with extensive company nucleus estates and out grower zones. Cultivation of sugarcane involve application of phosphate fertilizers at the initial stage of planting and top dressing with nitrogen fertilizers at the stage of two to nine months of growth. Farmers also grow other crops (maize, beans, cassava, millet, sweet potatoes and vegetables) beside sugarcane that involve fertilizer, manure and pesticides application. Industrial effluents from the two sugar factories and the pulp industry together with the municipal effluents from Mumias and Webuye urban centres which are possible sources of Pb, Cu, Cd, Zn and Cr as described in section 1.0 of this thesis characterise these study areas. The Mombasa-Uganda highway passes through Webuye, Bungoma County and is also characterized by heavy traffic flow. Kapkateny, an area characterized by no industrial activities, no municipal effluents, low fertilizer usage on farms and minimal vehicular emissions was chosen as a sampling control site. It is in Bungoma County and borders Mount Elgon.

Figure 3.0 is a map showing sampling areas.

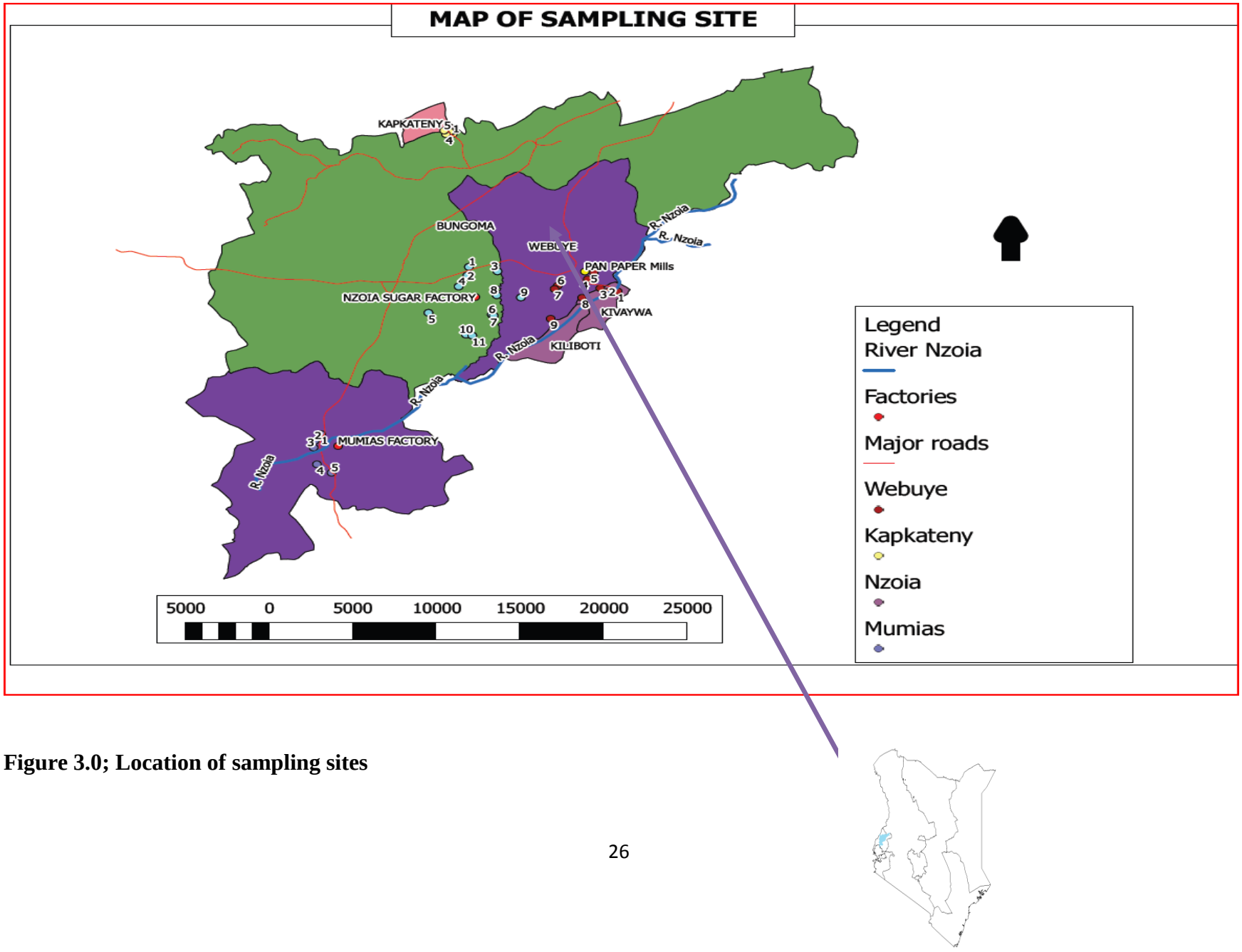


Figure 3.0; Location of sampling sites

Table 3.0a show the coordinates and sampling point descriptions around Mumias.

Table 3.0a: Description of Sampling Points around Mumias Site

Easting	Northing	Soil Ref No.	Sample identification No.
665632.33mE	42209.18mN	MSA	1
664853.31mE	41187.88mN	MSB	2
664720.49mE	40144.56mN	MSD	3
665117.42mE	37585.45mN	MSE	4
666866.24mE	36285.12mN	MSC	5

Co-ordinates and sample descripions around Nzoia are presented on table 3.0b.

Table 3.0b: Description of Sampling Points around Nzoia Site

Easting	Northing	Soil Refrence No.	Sample identification No.
683308.02Me	67863.90Mn	NSA	1
683135.51Me	66567.09mN	NSB	2
686726.43mE	67183.42mN	NSC	3
682079.74Me	64857.63mN	NSD	4
678469.28Me	60819.96mN	NSE	5
686048.19mE	60555.49mN	NSF	6
686270.45Me	60373.45mN	NSG	7
686635.55mE	63516.35mN	NSH	8
689534.13mE	63172.74mN	NSI	9
682950.03mE	57482.16mN	NSJ	10
683709.62mE	57326.04mN	NSK	11

Description of sampling points around Webuye is presented on Table 3.0c.

Table 3.0c: Description of Sampling Points around Webuye Site

Easting	Northing	Soil Refrence No	Sample identification No.
701115.99mE	64109.98mN	WSA	1
700054.17mE	64085.77mN	WSB	2
699027.27mE	64594.48mN	WSC	3
697533.04mE	65988.06mN	WSE	4
698265.09mE	67024.34mN	WSD	5
693932.33mE	64955.08mN	WSF	6
693563.41mE	64476mN	WSJ	7
696858.71mE	63131.04mN	WSI	8
693095.66mE	59912.64mN	WSP	9

Sample codes used in the study and there description is presented in Table 3.0d.

Table 3.0d; Sample Reference Numbers used to Identify Samples

Sample Ref. No.	Description
NSA to NSK	Nzoia soil samples during wet season
NSA-D to NSK-D	Nzoia soil samples during dry season
WSA to WSP	Webuye soil samples during wet season
WSA-D to WSP-D	Webuye soil samples during dry season
MSA to MSE	Mumias soil samples during wet season
MSA-D to MSE-D	Mumias soil samples during dry season
NS1 to NS14	Nzoia kales samples during wet season
NS1-D to NS14-D	Nzoia kales samples during dry season
WS1 to WS11	Webuye kales samples during wet season
WS1-D to WS11-D	Webuye kales samples during dry season
MS1 to MS12	Mumias kales samples during wet season
MS1-D to MS12-D	Mumias kales samples during dry season
NK1 to NK11	Nzoia cowpeas samples during wet season
NK1-D to NK11-D	Nzoia cowpeas samples during dry season
WK1 to WK10	Webuye cowpeas samples during wet season
WK1-D to WK10-D	Webuye cowpeas samples during dry season
MK1 to MK11	Mumias cowpeas samples during wet season
MK1-D to MK11-D	Mumias cowpeas samples during dry season
NP1 to NP8	Nzoia sweet potatoes samples during wet season
NP1-D to NP8-D	Nzoia sweet potatoes samples during dry season
WP1 to WP6	Webuye sweet potatoes samples during wet season
WP1-D to WP6-D	Webuye sweet potatoes samples during dry season
MP1 to MP6	Mumias sweet potatoes samples during wet season
MP1-D to MP6-D	Mumias sweet potatoes samples during dry season

3.1 Apparatus, Instruments and Reagents

The following apparatus, instruments and reagents were used in the study: Atomic absorption spectrometer (model spectra AA-10); Stainless steel scoop; Nitric acid(70%); Sulphuric acid (70%); Hydrochloric acid (37%); Perchloric acid (65%); Analytical balance (AG 204); Pippete; Burette; Beaker; Volumetric Flask; Distilled Water; Lead, Copper, Zinc, Cadmium And Chromium Metal Strips; Polythene Bags; Square Cardboard; Distilled Water; Alkaline detergent.

3.2 Sample Collection and Storage

The study was carried out during the months of November 2010 (wet season) and February 2011 (dry season). Random sampling procedure was used since it proved to be a practical method and a suggested technique for establishment of mean concentration where the site is suspected to be homogeneous with respect to the parameters to be monitored (ISO 10381-1, 2002). Soil and plant samples were collected from 25 sites within the agricultural and industrial areas of Webuye and Mumias. There were 5 sites sampled around Mumias town, 11 around Nzoia sugar factory, and 9 around Webuye town. The sites represented commercial vegetable farms and private residential vegetable gardens. Five sites were sampled around Kapkateny.

Soil Sampling was done using a stainless steel scoop. Soil was collected over a surface area of 10 cm by 10 cm and a depth of 20 cm. A square cardboard template measuring 10cm by 10cm was used to mark sampling areas. Samples of kales, cowpeas, and sweet potatoes were collected from each area. Only edible portions of the vegetables and sweet potatoes were collected, i.e., leaves in the case of kales and cowpeas while for sweet potato, tubers were collected. The sampled material was at harvest stage. A total of 50 soil samples, 74 kales samples, 64 cowpeas samples and 40

sweet potato samples were collected during both seasons. The samples were stored in clean polythene bags that had been rinsed with distilled water and transported to the laboratory for storage, preparation and analysis.

3.3 Sample Preparation and Analysis

3.3.1 Sweet Potato, Cowpeas and Kales Samples

Sampled leaves of cowpeas, kales and sweet potatoes tubers were chopped into small pieces. They were then dried in an oven at 70 degrees centigrade for 48 hours. The samples were then crushed using a stainless steel blender and passed through a 2 mm sieve.2.500±0.002g of each of the samples was accurately weighed using analytical balance and placed into 100ml beakers to which 20 ml of tri-acid mixture (HNO_3, $HClO_4$ and H_2SO_4) in a ratio of 5:1:1 was added. The mixture was then digested in a hot plate to a transparent liquid digest. The digest were separately cooled, filtered and diluted to 50 ml using deionised water for analysis of Cu, Zn, Cd, Pb and Cr using atomic absorption spectrometer.

3.3.2 Soil Samples

Soil samples were air dried at room temperature for 3 days. The dry soils were disaggregated with a porcelain pestle and mortar and passed through a 2 mm sieve. The samples were then oven dried at 105 degrees centigrade for 1 hour, and stored in a dry environment for further analysis.2.500±0.002g each of the samples was accurately weighed and placed into 100 ml beakers to which 20 ml of a mixture of HCl and HNO_3 in a ratio of 3:1 (V/V) was added. The mixture was then digested in a hot plate to a transparent liquid digest. The digest were separately cooled, filtered and diluted to 50 ml using deionised water for analysis of Cu, Zn, Cd, Pb and Cr using atomic absorption spectrometer.

3.4.0 Quality Assurance

Quality assurance procedures and precautions were taken to ensure the reliability of the results by minimizing contamination. Glassware were washed thoroughly in alkaline detergent, soaked in 3M nitric acid for 48 hours and rinsed thoroughly in distilled deionised water before use to leach out any trace metal contamination. Plastics were soaked in detergent and rinsed thoroughly in deionised water. Reagents were of analytical grade. Chemicals were obtained from Sigma, Kobian and Aldrich Chemical Company. Deionised water was used for all dissolutions and dilutions.

3.5 Analytical Procedures

3.5.1 Lead Analytical Procedures

1.000 g of lead metal strip was accurately weighed and dissolved in HNO_3 acid. It was diluted using distilled water to a volume of 1000 ml to make 1000 ppm lead. From 1000 ppm, dilution was made to give 100 ppm using dilution formula $c_1v_1=c_2v_2$ where c and v are concentration and volume respectively. From this 100 ppm a series of dilution was done to give working standards; 0.000 ppm,0.1000 ppm,0.250 ppm,0.5000 ppm and 1.000 ppm lead using dilution formula $c_1v_1=c_2v_2$.

The working conditions of the atomic absorption spectrometer for the analysis of lead were as follows: Lamp current (5 mA), wavelength (217.00 nm), slit width (1.00 nm), fuel (acetylene), oxidant (air) and detection limit (0.02 ppm). Table 3.5.1a shows the absorbance values for lead standards;

Table 3.5.1a; Absorbance Values for Lead Standards

	Concentration (ppm)	Absorbance
Standard 1	0.000	0.000
Standard 2	0.100	0.004
Standard 3	0.250	0.010
Standard 4	0.500	0.019
Standard 5	1.000	0.038

Figure 3.5.1 is a calibration graph of lead;

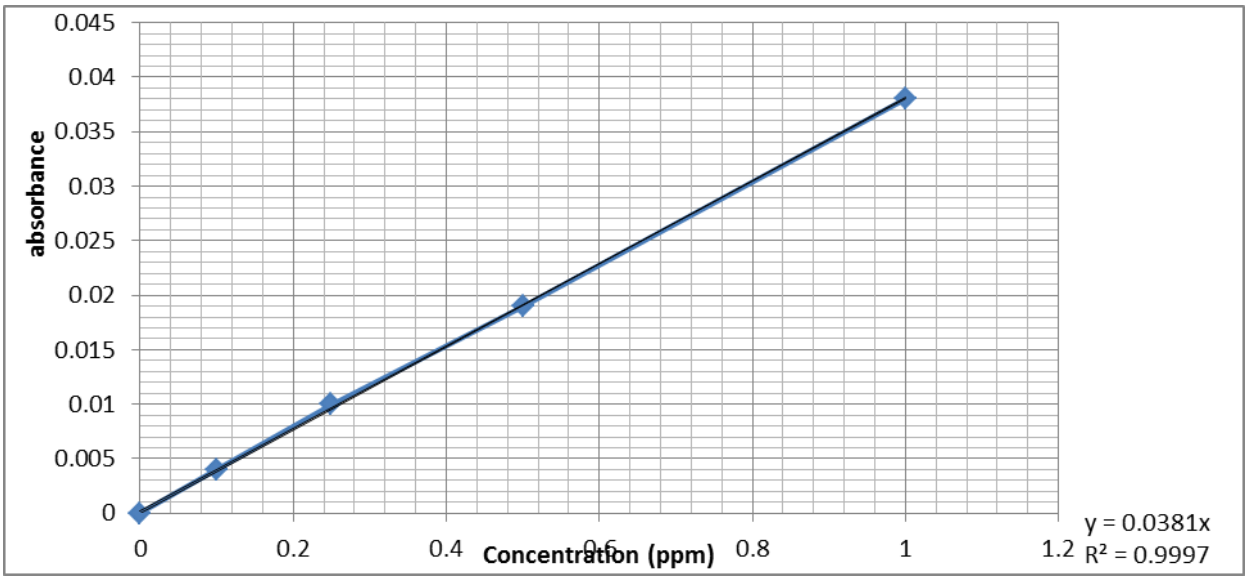


Figure 3.5.1; Calibration Graph for Lead

Percentage recovery and instrument sensitivity was checked by adding known amounts of Pb standard to selected samples. From the original sample (sample digest) 25 ml each of the selectedsamples pipette was transferred into 50 ml volumetric flask and 1 ml of 50 ppm lead

standard solution was added and topped up to the mark using de ionized water to make 50 ml. It was then analyzed using atomic absorption spectrometer for lead. Percentrecovery was calculated using the following formula and recorded in Table 3.5.1b;

Percent recovery = (spike result/expected result) x (spike volume/original volume) x 100%

Where, Expected spike result = sample result + standard conc.

Table 3.5.1b; Percentage Recovery (Lead)

Sample Code	Sample conc. (ppm)	Standard Conc.(ppm)	Spiked conc.(ppm)	Expected result (ppm)	% recovery
NSB	12.00	1.00	12.80	13.00	98.48
NSG	14.60	1.00	15.40	15.60	98.70
WSA	4.53	1.00	5.14	5.53	92.90
MSE	8.80	1.00	9.52	9.80	97.14
NS-5	43.90	1.00	44.52	44.90	99.13
WS 10-D	98.45	1.00	72.90	73.30	99.45
NK 2-D	97.70	1.00	31.98	32.40	98.70
WK 1-D	94.75	1.00	15.80	16.50	95.75
NP 2	95.72	1.00	12.70	13.13	96.72

3.5.2 Cadmium Analytical Procedures

1.000g of cadmium metal strip was accurately weighed and dissolved in HNO_3 acid. It was diluted using distilled water to a volume of 1000 ml to make 1000 ppm cadmium. From 1000 ppm, dilution was made to give 100 ppm using dilution formula $c_1v_1=c_2v_2$ where c and v are concentration and volume respectively. From this 100 ppm a series of dilution was done to give working standards; 0.000 ppm, 0.500 ppm, 1.000 ppm, 1.500 ppm and 2.000 ppm cadmium using dilution formula $c_1v_1=c_2v_2$.

The working conditions of the AAS for the analysis of Cd were as follows: lamp current (8 mA),

wavelength (228.8 nm), slit width (0.5 nm), fuel (acetylene), oxidant (air), and detection limit (0.0006 ppm). Absorbance values are recorded in Table 3.5.2a while Figure 3.5.2 shows the calibration curve. Percentage recovery is presented in Table 3.5.2b.

Table 3.5.2a; Absorbance Values for Cd Standards

	Concentration (ppm)	Absorbance
Standard 1	0.000	0.000
Standard 2	0.500	0.100
Standard 3	1.000	0.200
Standard 4	1.500	0.301
Standard 5	2.000	0.396

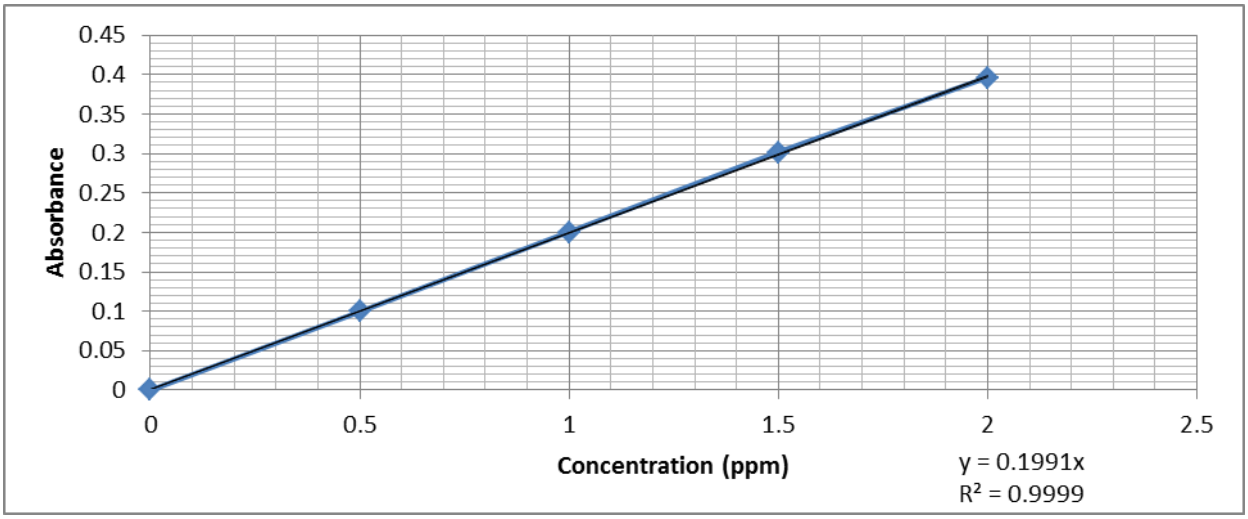


Figure 3.5.2; Calibration Graph for Cadmium

Percentage recovery, as well as instrument sensitivity was checked by adding known amounts of Cd standard to selected samples . From the original sample (sample digest) 25 ml each of

theselected samples pipette was transferred into 50 ml volumetric flask and 1 ml of 25 ppmcadmium standard solution was added and topped up to the mark using deionized water to make 50ml it was then analyzed using atomic absorption spectrometer for cadmium.

Table 3.5.2b; Percentage Recovery (Cadmium)

Sample code	Sample conc (ppm)	Standardconc (ppm)	Spiked result (ppm)	Expected Result (ppm)	% recovery
NSB	2.00	0.50	2.48	2.50	99.00
NSG	ND	0.50	0.49	0.50	98.00
WSA	1.80	0.50	2.26	2.30	98.20
MSE	2.20	0.50	2.52	2.70	93.30
NS-5	ND	0.50	0.47	0.50	94.00
WS 10-D	ND	0.50	0.48	0.50	98.00
WK 1-D	ND	0.50	0.46	0.50	92.00
NP 2	ND	0.50	0.49	0.50	98.00

3.5.3 Copper Analytical Procedures

1.000 g of copper metal strip was accurately weighed and dissolved in HNO_3 acid. It was diluted using distilled water to a volume of 1000 ml to make 1000 ppm copper. From 1000 ppm, dilution was made to give 100 ppm using dilution formula $c_1v_1=c_2v_2$ where c and v are concentration and volume respectively. From this 100ppm a series of dilution was done to give working standard; 0.000 ppm, 0.500 ppm, 1.000 ppm, 3.000 ppm and 5.000 ppm copper using dilution formula $c_1v_1=c_2v_2$.

The working conditions of the AAS for the analysis of Cu were: lamp current (3 mA), wavelength (327.4 nm), slit width (0.1 nm), fuel (acetylene), oxidant (air) and detection limit (0.003 ppm). Table 3.5.3a shows the absorbance values for Cu standards;

Table 3.5.3a; Absorbance Values for Cu Standards

	Concentration (ppm)	Absorbance
Standard 1	0.000	0.000
Standard 2	0.500	0.060
Standard 3	1.000	0.121
Standard 4	3.000	0.360
Standard 5	5.000	0.599

The calibration graph for copper is presented in figure 3.5.3;

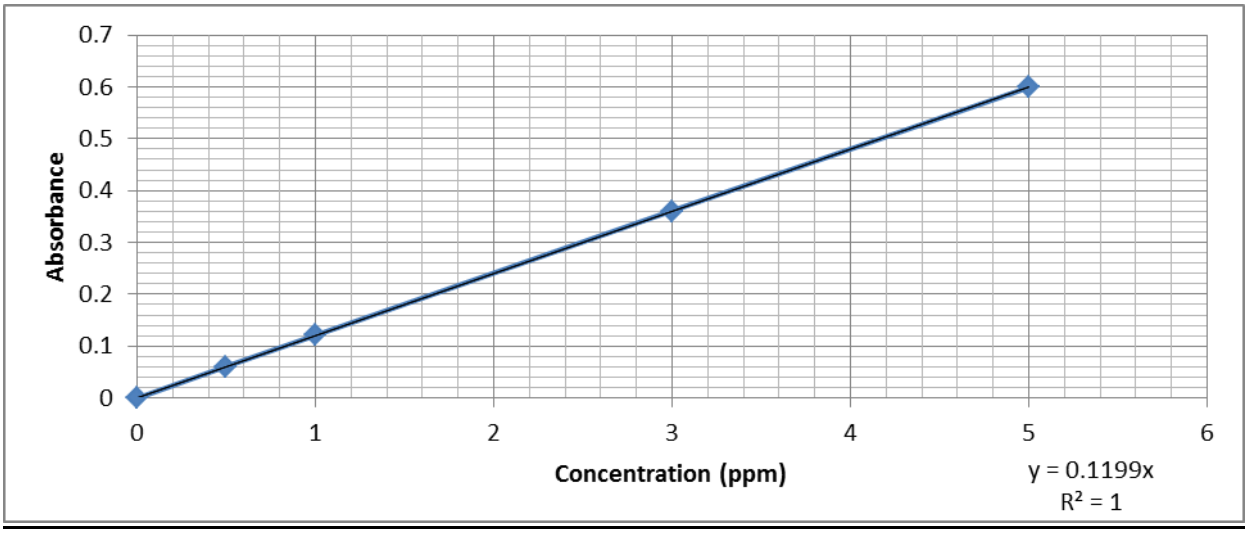


Figure 3.5.3; Calibration Graph for Copper

Percentage recovery and instrument sensitivity was checked by adding known amounts of Cu standard to selected samples. From the original sample (sample digest) 25 ml each of the selectedsamples pipette was transferred into 50 ml volumetric flask and 1 ml of 50 ppm copper standardsolution was added and topped up to the mark using de ionized water to make 50 ml. It

was thenanalyzed using atomic absorption spectrometer for copper. Table 3.5.3b show the percentage recovery for copper.

Table 3.5.3b; Percentage Recovery (Copper)

Sample code	Sample conc.(ppm)	Standard conc. (ppm)	Spiked conc. (ppm)	Expected result (ppm)	% recovery
NSB	8.20	1.00	9.0	9.20	97.80
NSG	6.20	1.00	7.10	7.20	98.60
WSA	2.60	1.00	3.58	3.60	99.40
MSE	6.66	1.00	7.60	7.66	99.20
NS-5	1.87	1.00	2.60	2.87	90.50
WS 10-D	4.00	1.00	4.90	5.00	98.0
NK 2-D	16.10	1.00	17.00	17.10	99.40
WK 1-D	4.10	1.00	5.00	5.10	98.03
NP 2	4.20	1.00	4.00	5.20	95.23

3.5.4 Chromium Analytical Procedures

1.000 g of chromium metal strip was accurately weighed and dissolved in HNO_3 acid. It was diluted using distilled water to a volume of 1000 ml to make 1000 ppm chromium. From 1000 ppm, dilution was made to give 100 ppm using dilution formula $c_1v_1=c_2v_2$ where c and v are concentration and volume respectively. From this 100 ppm a series of dilution was done to give working standard; 0.000 ppm,0.500 ppm,1.000 ppm,3.000 ppm and 5.000 ppm chromium using dilution formula $c_1v_1=c_2v_2$.

Chromium was analyzed under the following conditions of the AAS: lamp current (7 mA), wavelength (425.4 nm), slit width (0.1 nm), fuel (acetylene), oxidant (nitrous oxide) and detection limit (0.005 ppm). Absorbance values for Cr standards are presented in Table 3.5.4a;

Table 3.5.4a; Absorbance Values for Cr Standards

	Concentration (ppm)	Absorbance
Standard 1	0.000	0.000
Standard 2	0.500	0.030
Standard 3	1.000	0.061
Standard 4	3.000	0.180
Standard 5	5.000	0.301

Figure 3.5.4 show the calibration graph for chromium

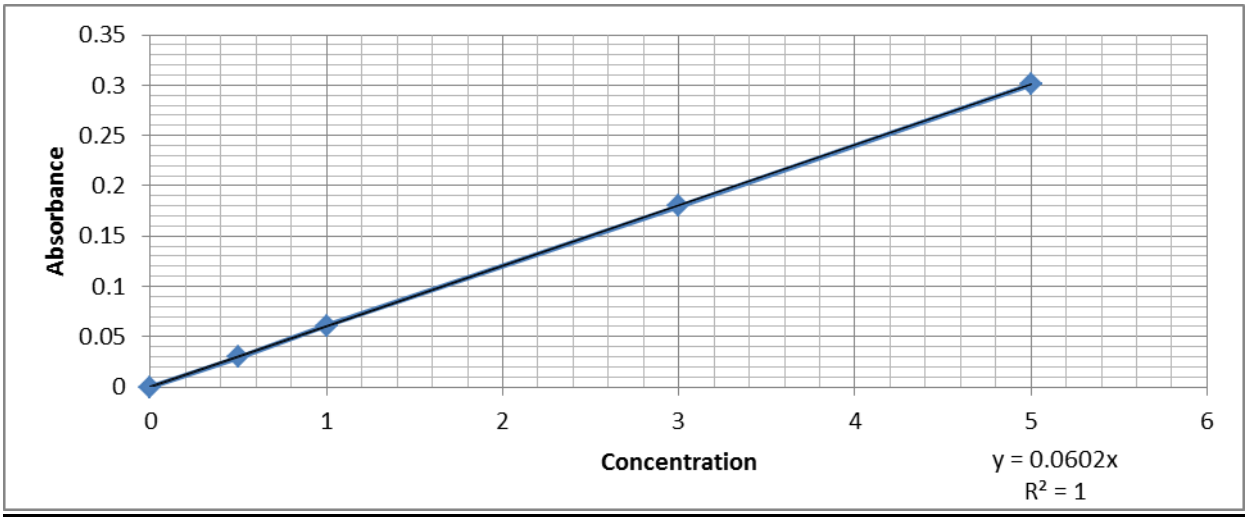


Figure 3.5.4; Calibration Graph for Chromium

Percentage recovery, as well as instrument sensitivity was checked by adding known amounts ofCr standard to selected samples. From the original sample (sample digest) 25 ml each of the selected samples pipette was transferred into 50 ml volumetric flask and 1 ml of 50 ppm chromium standard solution was added and topped up to the mark using de ionized water to make 50 ml. It was then analyzed using atomic absorption spectrometer for chromium. The

percentage recovery for chromium is presented in Table 3.5.3b;

Table 3.5.3b; Percentage Recovery (Chromium)

Sample code	Sample conc. (ppm)	Standard conc. (ppm)	Spiked conc. (ppm)	Expected conc. (ppm)	% recovery
NSG	24.60	1.00	25.0	25.60	97.27
WSA	37.40	1.00	37.9	38.40	98.69
MSE	59.80	1.00	60.0	60.80	98.50
NS-5	ND	1.00	0.95	1.00	95.00
WS 10-D	ND	1.00	0.98	1.00	98.00
NK 2-D	ND	1.00	0.96	1.00	96.00
WK 1-D	ND	1.00	0.98	1.00	98.00
NP 2	ND	1.00	0.97	1.00	97.00

3.2.5 Zinc Analytical Procedures

1.000 g of zinc metal strip was accurately weighed and dissolved in HNO_3 acid. It was diluted using distilled water to a volume of 1000 ml to make 1000 ppm zinc. From 1000 ppm, dilution was made to give 100 ppm using dilution formula $c_1v_1=c_2v_2$ where c and v are concentration and volume respectively. From this 100 ppm a series of dilution was done to give working standard; 0.000 ppm, 0.500 ppm, 1.000 ppm, 3.000 ppm and 5.000 ppm zinc using dilution formula $c_1v_1=c_2v_2$. Absorbance values for Zn standards are presented in table 3.5.5a while figure 3.5.5 shows the calibration graph for Zn.Working conditions of the AAS for the analysis of Zn were: lamp current (3mA), wavelength (213.9 nm), Slit width (0.1 nm), fuel (acetylene), oxidant (air) and detection limit (0.002).

Table 3.5.5a; Absorbance Values for Zn Standards

	Concentration (ppm)	Absorbance
Standard 1	0.000	0.000
Standard 2	0.500	0.266
Standard 3	1.000	0.533
Standard 4	3.000	1.601
Standard 5	5.000	2.640

Figure 3.5.5 is a calibration graph for zinc;

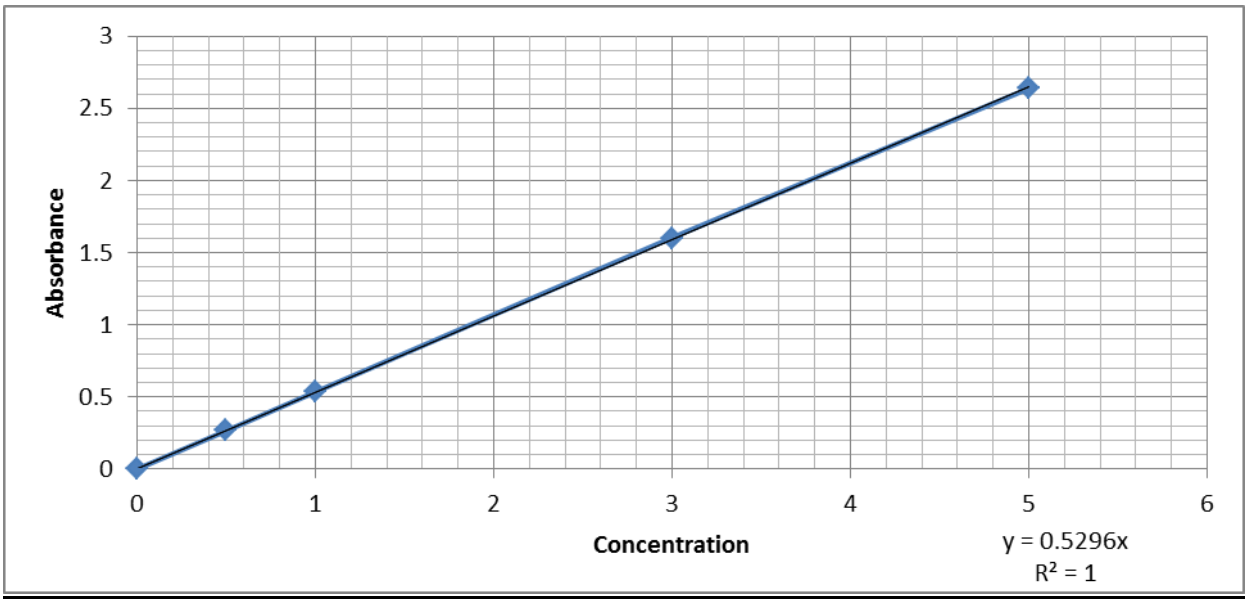


Figure 3.5.5; Calibration Graph for Zinc

Percentage recovery and instrument sensitivity was checked by adding known amounts of Znstandard to selected samples . From the original sample (sample digest) 25 ml each of the selectedsamples pipette was transferred into 50 ml volumetric flask and 1 ml of 25 ppm zinc standardsolution was added and topped up to the mark using deionized water to make 50 ml . It

then analyzed usin g atomic absorption spectrometer for Zinc. The percentage recovery for zinc is presented in Table 3.5.5b;

Table 3.5.5b; Percentage Recovery (Zn)

Sample code	Sample conc. (ppm)	Standard conc. (ppm)	Spiked conc.	Spiked conc. Minus std conc.	% recovery
NSB	12.40	0.50	12.70	12.90	94.77
NSG	18.20	0.50	18.50	18.70	96.35
WSA	4.80	0.50	5.00	5.30	86.20
MSE	41.80	0.50	42.22	42.30	98.64
NS-5	125.63	0.50	125.90	126.13	99.40
WS 10-D	ND	0.50	32.00	32.50	96.96
NK 2-D	ND	0.50	17.88	18.90	92.14
WK 1-D	19.54	0.50	20.54	20.72	96.79
NP 2	ND	0.50	3.34	3.20	86.07

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Heavy Metal Levels in Geospatial Area During Wet Season

Cowpeas, kales, sweet potatoes and soil samples collected at Mumias, Webuye, Nzoia and Kapkateny during wet season were analysed for Cu, Pb, Cr, Cd and Zn. The results are presented in this section.

4.1.1 Soils

Table 4.1.1 shows the heavy metal levels in soils at Webuye, Mumias and Nzoia during wet season.

Table 4.1.1; Heavy Metal levels in Soils at Mumias, Webuye and Nzoia during wet season

Metal (ppm)	Webuye	Nzoia	Mumias
	M ± SD	M ±SD	M ±SD
Cd	1.74±0.90	1.77±0.79	1.76±0.98
Cu	2.52±1.06	6.67±2.62	6.97±1.16
Zn	10.86±4.78	16.10±5.17	27.72±12.04
Pb	13.85±4.91	11.36±4.01	6.17±1.86
Cr	26.67±10.04	22.09±8.67	44.4±22.50

SD-standard deviation, M- Mean

Soils at Webuye had lower copper level (2.52 ppm) compared to Nzoia (6.67 ppm) and Mumias (6.97 ppm), while zinc in soils at Mumias was higher (6.97 ppm) compared to Webuye (2.52 ppm) and Nzoia (6.67 ppm). Lead in soils at Webuye (13.85 ppm) was higher compared to Nzoia (11.36

ppm) and Mumias (6.17 ppm). Cadmium in soils at Webuye (1.74 ppm), Nzoia (1.77 ppm) and Mumias (1.76 ppm) was similar, while chromium was higher at Mumias (44.4 ppm) and lower at Nzoia (22.01 ppm).

4.1.2 Cowpeas

Table 4.1.2 shows the heavy metal levels in cowpeas at Mumias, Webuye and Nzoia during wet season.

Table 4.1.2; Heavy Metal levels at Mumias, Webuye and Nzoia during wet season

Metal (ppm)	Webuye	Nzoia	Mumias
	M ± SD	M ± SD	M ± SD
Cd	ND	N.D	N.D
Cu	13.34±6.30	8.17 ±3.46	11.48±5.09
Zn	34.16±12.61	19.26±9.36	63.49±30.19
Pb	20.13±8.78	24.51±11.64	49.81±24.18
Cr	ND	ND	ND

SD-standard Deviation, M- mean, ND- Not Detected

Levels of lead (49.81 ppm) and zinc (63.49 ppm) in cowpeas at Mumias were higher compared to Webuye and Nzoia, while copper was higher at Webuye (4.79 ppm) compared to Mumias and Nzoia. Cd and Cr were not detected at all the sites.

4.1.3 Kales

Table 4.1.3 shows the heavy metal concentration in kales at various sites during wet season.

Table 4.1.3; Heavy Metal levels in kales at various sites during wet season

Metal (ppm)	Webuye	Nzoia	Mumias
	M ± SD	M ± SD	M ± SD
Cd	ND	ND	ND
Cu	4.79±2.27	3.25±1.46	4.24±1.64
Zn	38.87±17.73	23.08±10.40	37.90±13.35
Pb	37.67±14.5	13.70±5.19	45.84±21.24
Cr	ND	ND	ND

SD-standard Deviation, M- mean, ND- Not Detected

Cd and Cr were not detected at all the sites, while lead was higher (45.84 ppm) at Mumias and lower at Nzoia (13.70 ppm). Zinc (38.87 ppm) and copper (4.71 ppm) concentrations were higher at Webuye compared to Nzoia and Mumias.

4.1.4 Sweet potatoes

Table 4.1.4 shows the heavy metal concentration in sweet potatoes at various sites during wet season.

Table 4.1.4; Heavy metal concentration in sweet potatoes at various sites during wet season

Metal (ppm)	Webuye	Nzoia	Mumias
	M ±SD	M ±SD	M ±SD
Cd	ND	ND	ND
Cu	3.8±1.40	3.93 ±1.7	5.14±1.72
Zn	7.66±2.80	5.89±2.90	5.16±1.98
Pb	13.18±4.52	15.08±1.94	12.03±6.01
Cr	ND	ND	ND

SD-standard Deviation, M- mean, ND- Not Detected

Zinc level in sweet potatoes was higher at Webuye (7.66 ppm) compared to Nzoia and Mumias while Cd and Cr were not detected at all the sites. Lead was higher at Nzoia (15.08 ppm) and lower at Mumias (12.03 ppm), while copper was higher at Mumias (5.14 ppm) and lower at Webuye (3.80 ppm).

4.2 Heavy Metal Levels in Geospatial Area During Dry Season

Cowpeas, kales, sweet potatoes and soil samples collected at Mumias, Webuye, Nzoia and Kapkateny during dry season were analysed for Cu, Pb, Cr, Cd and Zn. The results are presented in this section.

4.2.1 Soils

Table 4.2.1 shows the level of heavy metals in soils at various sites during dry season.

Table 4.2.1; Level of heavy metals in soils at various sites during dry season

Metal (ppm)	Kapkateny	Webuye	Nzoia	Mumias
	M ±SD	M ±SD	M ±SD	M ±SD
Cd	2.47±0.42	1.75±0.82	1.50±0.67	1.95±0.64
Cu	62.22±14.6	2.11±0.87	6.78±2.80	7.11±1.20
Zn	33.94±14.17	12.80±6.01	17.18±5.00	28.83±12.07
Pb	ND	14.80±5.21	11.05±4.78	6.34±0.84
Cr	19.14±8.80	25.26±8.04	19.80±7.90	44.0±21.28

SD- Standard Deviation, M- Mean, ND- Not Detected

Soils at Webuye had the highest level of lead (14.80 ppm) compared to Nzoia (11.05 ppm) and Mumias (6.34 ppm). Chromium was higher at Mumias (44.0 ppm) and lower at Nzoia (19.80 ppm). Both lead and chromium were not detected in soils at Kapkateny, while copper (62.22 ppm), Zinc (33.94 ppm) and Cd (2.47 ppm) were higher in soils at Kapkateny compared to Webuye, Mumias and Nzoia.

4.2.2 Kales

Table 4.2.2 shows the level of heavy metals in kales at various sites during dry season.

Table 4.2.2; Level of heavy metals in kales at various sites during dry season

Metal (ppm)	Kapkateny	Webuye	Nzoia	Mumias
	M ± SD	M ± SD	M ± SD	M ± SD
Cd	ND	ND	ND	ND
Cu	4.30±1.31	4.08±1.78	2.45±0.98	4.73±1.61
Zn	17.2±5.55	34.77±16.1	26.09±10.14	44.56±21.27
Pb	ND	34.85±17.28	16.67±5.13	33.33±16.73
Cr	8.40±2.74	ND	ND	ND

SD- Standard Deviation, M- mean, ND- Not Detected

Zinc in kales was higher at Mumias (44.56 ppm) and lower at Kapkateny (17.20 ppm), while lead was higher at Webuye (34.85 ppm) compared Nzoia and Mumias. Chromium was only detected at Kapkateny, while cadmium was not detected at all the sites. Copper was higher at Mumias (4.73 ppm) compared to Webuye and Nzoia.

4.2.3 Cowpeas

Table 4.2.3 shows the level of heavy metals in cowpeas at various sites during dry season.

Table 4.2.3; Heavy metals in cowpeas at various sites during dry season

Metal (ppm)	Kapkateny	Webuye	Nzoia	Mumias
	M ± SD	M ± SD	M ± SD	M ± SD
Cd	ND	ND	N.D	N.D
Cu	2.6±1.33	14.65±7.10	8.79±3.58	13.60±6.17
Zn	24.99±11.0	36.05±13.94	20.9±10.26	45.28±20.61
Pb	0.75±0.21	20.75±10.10	19.70±8.25	52.75±22.16
Cr	8.44±2.22	ND	ND	ND

SD- Standard Deviation, M- Mean, ND- Not Detected

Copper in cowpeas was higher at Webuye (14.65 ppm) and lower at Kapkateny while zinc was higher at Mumias (45.29 ppm) and lower at Nzoia. Cadmium was not detected at all the sites. Lead in cowpeas at kapkateny (0.75 ppm) was lower compared to Webuye (20.75 ppm), Nzoia (24.51 ppm) and Mumias (49.81 ppm) , while chromium was only detected at Kapkateny (8.44 ppm).

4.2.4 Sweet Potatoes

Table 4.2.4 shows the level of heavy metals in sweet potatoes at various sites during dry season.

Table 4.2.4; Level of heavy metals in sweet potatoes at various sites during dry season

Metal (ppm)	Kapkateny	Webuye	Nzoia	Mumias
	M ±SD	M ± SD	M ± SD	M ± SD
Cd	ND	ND	ND	ND
Cu	2.17±0.79	3.53±1.74	3.65±1.53	4.83 ±1.44
Zn	4.08±1.20	8.40±4.18	8.20±3.54	5.29±2.15
Pb	ND	15.23±5.14	15.83±3.68	10.78±5.34
Cr	ND	ND	ND	ND

SD- Standard Deviation, M- Mean, ND- Not Detected

Cd and Cr were not detected in sweet potatoes at all sites. Lead was higher at Nzoia (15.83 ppm) compared to Webuye (15.23 ppm) and Mumias (10.78 ppm) while it was not detected at Kapkateny. Zinc was higher at Webuye (8.4 ppm) compared to Nzoia (8.2 ppm) and Mumias (5.29 ppm) while copper was lower at Kapkateny (2.17 ppm) compared to Mumias, Webuye and Nzoia.

4.3 Distribution of Pb in Cowpeas, Kales, Sweet potatoes and Soils

4.3.1 Wet Season

Figure 4.3.1 shows the distribution of lead in kales, cowpeas, sweet potatoes and soils during wet season;

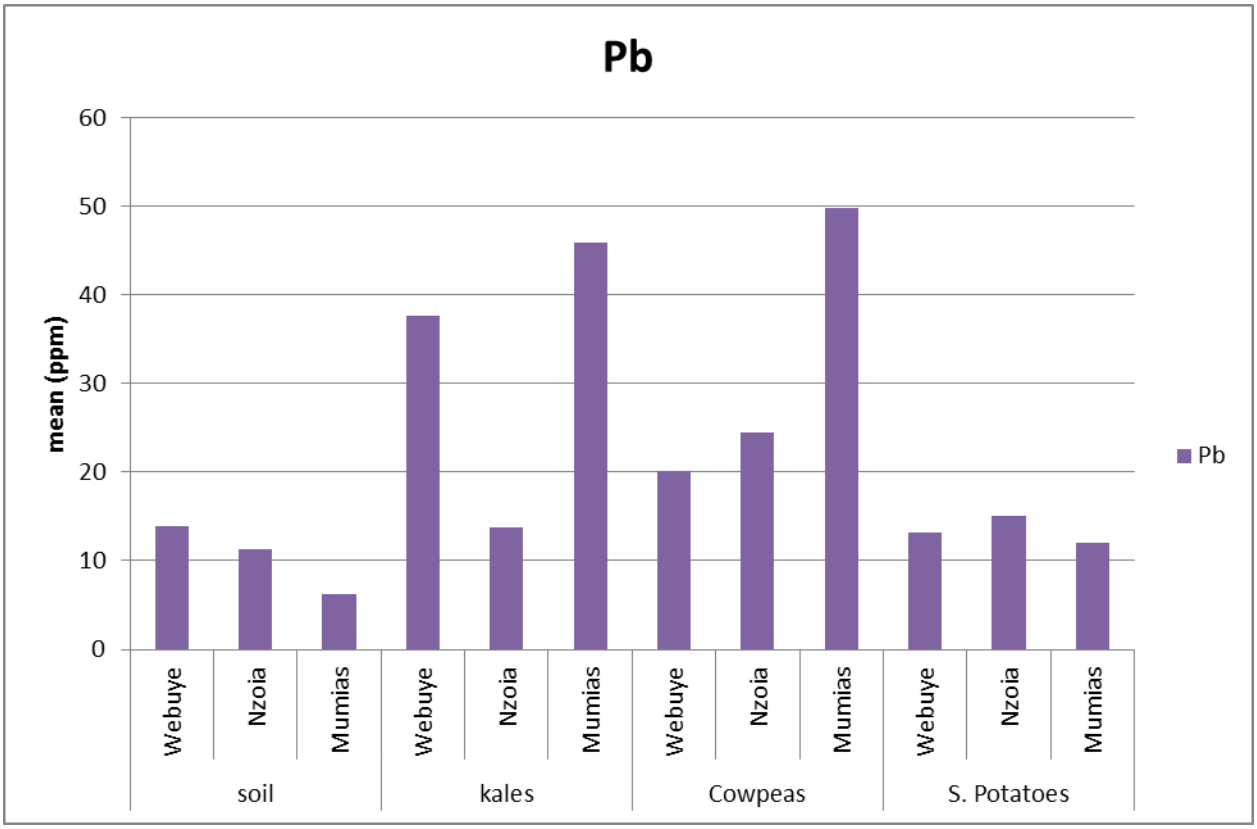


Figure 4.3.1; Distribution of lead in kales, cowpeas, sweet potatoes and soils during wet season.

Lead among the three food crops was higher in cowpeas at Mumias (49.81 ppm) and lower in sweet potatoes at Mumias (10.78 ppm). Lead in soils at all the sites was lower than the concentrations in kales, cowpeas and sweet potatoes.

4.3.2 Dry season

Figure 4.3.2 shows the distribution of lead in kales, cowpeas, sweet potatoes and soils during dry season.

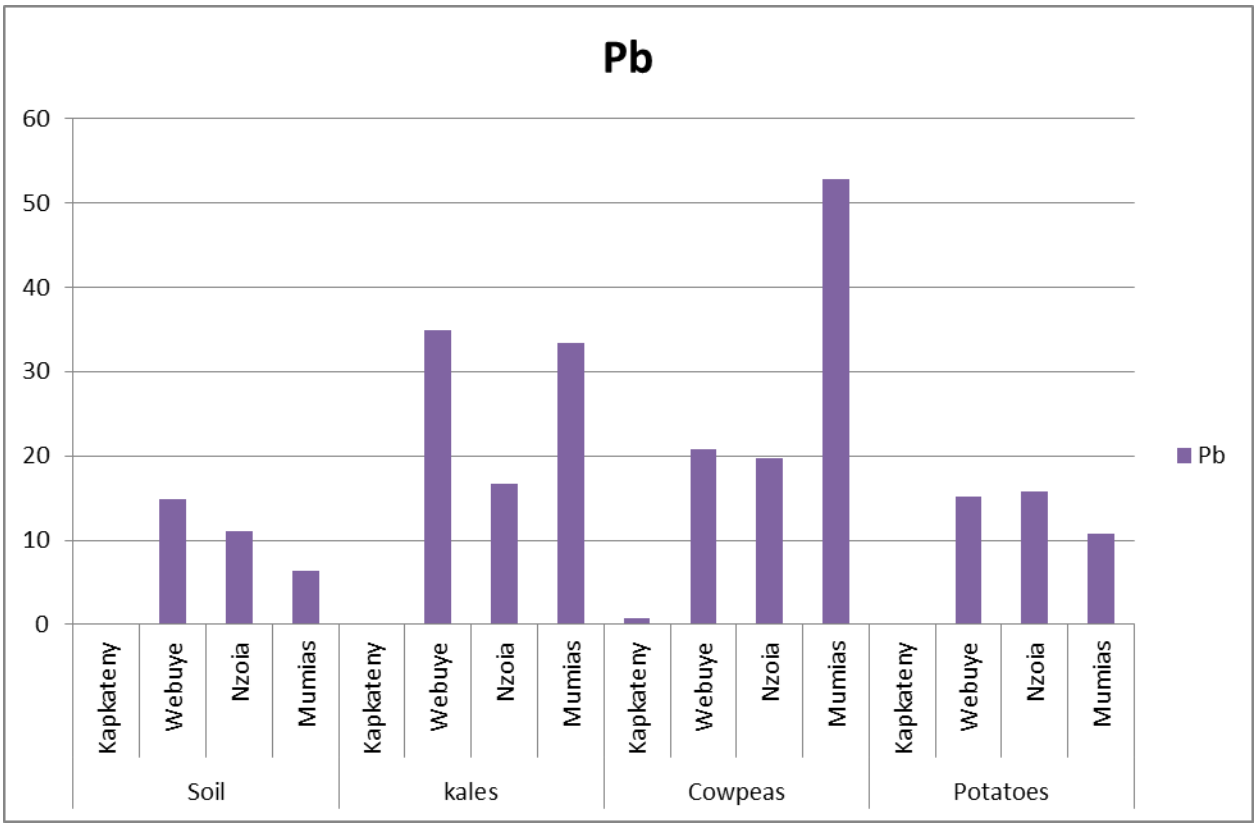


Figure 4.3.2; Distribution of lead in kales, cowpeas, sweet potatoes and soils during dry season

At Kapkateny, lead was only detected in cowpeas (0.75ppm). Among the three food crops, lead was higher in cowpeas at Mumias (52.75 ppm) and lower in sweet potatoes at Mumias(10.78 ppm). Lead in soils was also lower than the concentrations in kales, cowpeas and sweet potatoes at all the sites.

4.4 Correlation Analysis between Wet and Dry Season

There was a positive correlation ($p>0.5$) between wet and dry season concentrations in cowpeas [Cu ($r=0.81$), Pb ($r=0.92$), Zn ($r=0.87$)], Kales [Cu ($r=0.93$), Pb ($r=0.98$), Zn ($r=0.98$)], sweet potatoes [Cu ($r=0.91$), Pb ($r=0.90$), Zn ($r=0.89$)], and soils [Cu ($r=0.93$), Pb ($r=0.99$), Zn ($r=0.99$), Cd ($r=0.75$), Cr ($r=0.99$)], indicating insignificant seasonal variations(Table 4.4).

Table 4.4; Correlation analysis between wet and dry Season concentrations

Sample	R(Cd)	R(Cu)	R(Pb)	R(Zn)	R(Cr)
Cowpeas	N/A	0.81	0.92	0.87	N/A
Kales	N/A	0.93	0.98	0.98	N/A
Sweet potatoes	N/A	0.91	0.90	0.89	N/A
Soil	0.75	0.93	0.99	0.99	0.99

N/A; not applicable

4.5 Heavy metal Levels Verses Recommended Guidelines

Lead in 11 % of all the soil samples exceeded the range for unpolluted soils of 0.1 to 20 ppm. Copper in all the soil samples investigated were within the maximum recommended levels of 100 ppm. Mean zinc concentrations in soils were within the range of background values for unpolluted environment.

All kale samples had copper concentrations within the maximum recommended limit of 10 ppm. Zinc levels in kales were also within the safe limit of 99 ppm, while all kale samples had lead levels above the 0.3 ppm recommended guideline.

All cowpeas samples had lead levels exceeding the recommended limit of 0.3 ppm. Copper in 40 % of cowpeas samples exceeded the safe limit of 10 ppm. Zinc levels in Cowpeas were also within the safe limit of 99 ppm.

All the sweet potato samples had copper and zinc concentrations within the maximum recommended limit of 10 ppm and 99 ppm respectively. 95 % of Sweet potato samples exceeded the lead safe limit of 0.3 ppm.

4.6 Correlation Analysis Between Soil and Plant Concentrations

Soil concentrations were positively correlated (p>0.5) to zinc in kales [wet season (r=0.66), dry season (r=0.53)] and cowpeas [wet season (r=0.80), dry season (r=0.78)] indicating influence by soil concentrations on plant levels (Table 4.6a).

Table 4.6a; Pearson's correlation coefficients between soil and plant zinc levels

Concentrations (ppm)	Wet season	Dry season
Kales verses soil	R=0.66	R=0.53
Cowpeas verses soil	R=0.80	R=0.78
Sweet potatoes verses soil	R=-0.99	R=-0.11

There was negative correlation between copper concentrations in soils and in Cowpeas [wet season (r=-0.82), dry season (r=-0.52)] and Kales [wet season (r=-0.46), dry season (r=-0.80)] (Table 4.6b). Sweet potato copper concentrations were strongly correlated (p>0.5) [wet season (r=0.92), dry season (r=0.99)] to soil concentrations.

Table 4.6b Correlation coefficients between soil and plant copper levels

Concentrations (ppm)	Wet season	Dry season
Kales verses soil	r=-0.46	r=-0.80
Cowpeas verses soil	r=-0.82	r=-0.56
Sweet potatoes verses soil	r=0.92	r=0.99

There was a positive correlation (p>0.5) [wet season (r=0.78), dry season (r=0.63)] between soil concentrations and lead concentrations in sweet potatoes indicating influence by soil concentrations on plant levels (Table 4.6c).

Table 4.6c Correlation coefficients between soil and vegetable lead levels

Concentrations (ppm)	Wet season	Dry season	
Kales Verses Soil	r=-0.86	r=-0.99	
Cowpeas Verses Soil	r=-0.94	r=-0.97	
Sweet potatoes Verses Soil	r=0.78	r=0.63	

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Lead in 11 % of all the soil samples exceeded the range for unpolluted soils of 0.1 to 20 ppm.

All the cowpeas and kales samples had lead levels exceeding the recommended limit of 0.3 ppm while 95% of sweet potatoes samples exceeded the safe limit.

Copper in all the soil samples investigated were within the maximum recommended levels of 100 ppm. All the sweet potato and kale samples had copper concentrations within the maximum recommended limit of 10 ppm, while 40 % of the cowpeas samples exceeded the safe limit. The elevated levels of copper and lead may cause adverse health effects. Industrial effluents from the sugar factories and the paper mill and municipal effluents from the urban centres is a source for the high concentration of copper and lead. Pesticides, manure and fertilizer application on farms and vehicular emissions is also a possible source.

Mean zinc concentrations in soils were within the range of background values for unpolluted environment. Zinc in Cowpeas, kales and sweet potatoes were also within the safe limit of 99 ppm. This indicate no influence from athropogenic activities.

Chromium and cadmium were detected in soils but was not detected in cowpeas, sweet potatoes and kales. It could be attributed to concentrations of cadmium and chromium in plant available form being low in most soils.

There was positive correlation ($p>5$) between the wet and dry seasons, indicating insignificant seasonal variations in soils, sweet potatoes and vegetable heavy metal concentrations.

There was a positive correlation ($p>0.5$) between zinc levels in soils and in kales, zinc levels in

soils and in cowpeas; Copper levels in soils and in sweet potatoes and lead levels in soils and in sweet potatoes. This indicate bioavailability of heavy metals in soils to plants.

5.2 Recommendations

This dissertation has significantly advanced our understanding of the level of heavy metals in soils, cowpeas, sweetpotatoes, kales in Bungoma and Kakamega counties, and the possible infuence of agricultural and industrial activities on the level of various heavy metals. In a larger study, considerably more resources should be devoted to understanding the concentrations of heavy metals in fertilizers and pesticides used on farms and industrial and municipal effluents discharged to the environment. A risk assessment needs to be carried out to establish how these elevated levels of heavy metals have affected the population feeding on these vegetables.

REFERENCES

Aceto, M., Abollino, O., Bruzzoniti, M.C., Mentasti, E., Sarzanini, C., Malandrin, M. (2002). Determination of metals in wine with atomic spectroscopy (flame-AAS, GF-AAS and ICP-AES); A review. Food additives and contaminants 19 (2): 126–33.

Antosiewicz, D.M. (1992). Adaptation of plants to an environment polluted with heavy metals. Acta Soc. Bot. Polon. 61:281-299.

ATSDR (Agency for Toxic Substances and Disease Registry). (2008). Toxicological Profile for Cadmium.U.S. Department of Health and Human Services Public Health Service.

ATSDR (Agency for Toxic Substances and Disease Registry). (2005). Toxicological Profile for Zinc. U.S. Department of Health and Human Services, Public Health Service

ATSDR (Agency for Toxic Substances and Disease Registry). (2004). Toxicological Profile for Copper. U.S. Department of Health and Human Services, Public Health Service.

Bartlett, R.J and James, B.R. (1988).Mobility and bioavailability of chromium in soils.J.Environ.Qual. 8 : 31-35

Berry, W.J., Cantwell, M.G., Edwards, P.A. (1999). Predicting toxicity of sediments spiked with silver. Environ Toxicol Chem 18(1):40-48.

Breslin, V.T. (1999). Retention of metals in agricultural soils after amending with MSW and MSW-biosolids composite. Water Air Soil Pollut 109:163-178.

CDA (Copper Development Association). (1988). Copper in Plant, Animal and Human Nutrition CDA Publication TN35, pg 20-80

Chaney, R.L. (1993). Zinc phytotoxicity. In: RobsonAD, ed. Zinc in soil and plants. Dordrecht, the Netherlands: Kluwer Academic Publishers, 135–150.

Chang, A.C., Hinesly, T.D., Bates, T.E. (1987). Effects of long-term sludge application on accumulation of trace elements by crops. In: Page AL, Logan TJ, Ryan JA, eds. Land application of sludge - food chain implications. Chelsea, MI: Lewis Publishers Inc., 53-66.

Chuan, M., Shu, G.Y., Liu, J.C. (1996). Solubility of heavy metals in a contaminated soil: Effects of redox potential and pH. Water Air Soil Pollut 90:543-556.

Chaney, R.L., Mielke, H.W., Sterret, S.B. (1988). Speciation, mobility and bioavailability of soil lead. Environ Geochem Health 9:105-129.

CIA (Central Intelligence Agency). (2012). World Factbook. Geographical coordinates of countries. https://www.cia.gov/library/publications/the-world-factbook/index.html

Cook, M. E., and Morrow, H. (1995). Anthropogenic Sources of Cadmium in Canada, National Workshop on Cadmium Transport Into Plants, Canadian Network of Toxicology Centres, Ottawa, Ontario, Canada, June 20-21.

Davies, B.E. (1995). Lead and other heavy metals in urban areas and consequences for the health of their inhabitants. In: Majumdar SK, Miller EW, Brenner FJ (eds), Environmental Contaminants, Ecosystems and Human Health, pp.287-307. The Pennsylvania Academy of Science, Easton PA, USA.

DH. (1991). Department of Health. Dietary Reference Values for Food and Energy and Nutrients for the United Kingdom, Report of the Panel on Dietary Reference Values of the Committee on Medical Aspects of Food Policy, Report on Health and Social Subjects 41, Department of Health. Available from the Stationery Office, PO Box 29, Norwich NR3 1GN.

Duffus, J.H .(2002). ""Heavy metals" a meaningless term? (IUPAC Technical Report)" Pure and Applied Chemistry, 2002, Vol. 74, pp. 793–807

ECMC (Environmental Cost Management Centre). (2004). Environmental Audit Report for Mumias Sugar Company. Effluent discharge by Mumias Sugar Company. Sacha Journal of environmental studies vol 1 pp 1-30

Eggenberger, U. and Waber, H.N. (1998). "Cadmium in Seepage Waters of Landfills: A Statistical and Geochemical Evaluation, "Report of November 20, 1997 for the OECD Advisory Group on Risk Management Meeting, February 9-10, 1998, Pads.

Frenzel, W. (1998). Highly sensitive semi-quantitative field test for the determination of chromium(VI) inaqueous samples. Fresenius' Journal of Analytical Chemistry**361**(8) 774–779.

Garbarino JR, Hayes H, Roth D, Antweider R, Brinton TI, Taylor H (1995). Contaminants in the Mississippi River, *U. S.* Geological Survey Circular *1133,* Virginia, U.S.A. (www.pubs.usgs.gov/circ/circ1133/)

GOK (Government of Kenya). (2009). Population & Housing census Results. Ministry of State for Planning, National Development and Vision 2030. Kenya Census 2009.

GOK (Government of Kenya). (2002). District Development Plan for Butere/Mumias (2002-2008). Government printers, Nairobi.

Godzik, B. (1993). Heavy metal contents in plants from zinc dumps and reference area. Pol. Bot. Stud. 5:113-132.

Hawkes, J.S. (1997). Heavy Metals, J. Chem. Educ. 74(11): 1374.

Huang, J.W., Chen, J., Berti, W.R., Cunningham, S.D. (1997). Phytoremediation of lead-contaminated soil: role of synthetic chelates in lead phytoextraction. Environ. Sci. Technol. 31:800–805.

Inoti, K.J., Kawaka, F., Orinda, G., and Okemo, P. (2011). Assessment of heavy metal concentrations in urban grown vegetables in Thika Town, Kenya. African Journal of Food Science Vol. 6(3), pp. 41-46, Available online at http://www.academicjournals.org/AJFS DOI: 10.5897/AJFS10.072 ISSN 1996-0794 ©2012 Academic Journals

ISO 10381-1. (2002). Soil quality Sampling, Part 1: Guidance on the design of sampling programmes

Jensen, A., and Bro-Rasmussen, F. (1992). "Environmental Contamination in Europe," Reviews of Environmental Contamination and Toxicology, Volume 125, pages 101-181.

Jumba, O., Kisia, S.M., Kock, R. (2006). Animal Health Problems Attributed to Environmental Contamination in Lake Nakuru National Park, Kenya: A Case Study on Heavy Metal Poisoning in the Waterbuck Kobus ellipsiprymnus defassa (Ruppel 1835). Arch. Environ. Toxicol. 52, 270-281

Kachenko, A., Singh, B. (2004). Heavy metals contamination of home grown vegetables near smelters in NSW. 3rd Australian New Zealand Soils Conference, 5-9 December 2004, University of Sydney, Australia. 2004.

Khan, M., Kalsoom, U., Mahmood, T., Riaz, M., and Khan, R. (2003). Characterization and Treatment of industrial effluents from sugar industry. Journal Chem.Soc.Pak. vol. 25, No.3, 2003

King, M., Ramachandran, V. (1995). Lead. In: Kirk-Othmer encyclopedia of chemical technology. 4th edition. New York, NY: John Wiley & Sons, 69-113.

Kumar., Dushenkov., Motto, H., Raskin, I. (1995). Phytoextraction: the use of plants to remove

heavy metals from soils. Environ. Sci. Technol. 29:1232-1238.

Lane, T.W., Morel, F.M. (2002).A biological function for cadmium in marine diatoms. Department of Geosciences, Princeton University, Princeton, NJ 08544-1003, USA. tlane@princeton.eduHYPERLINK "mailto:tlane@princeton.edu"Proc Natl Acad Sci U. 2000 Apr 25;97(9):4627-31

Lasat, M.M., Kochian, L.V. (2000). Physiology of Zn hyperaccumulation in Thlaspi caerulescens. In: TerryN, BañuelosG, eds. Phytoremediation of contaminated soil and water. Boca Raton, FL, USA: CRC Press LLC, 159–169.

Lee, S.Z., Chang, L., Yang, H.H., Chen, C.M., Liu, M.C. (1998) .Absorption characteristics of lead onto soils. J. Haz. Mat. 63:37-49.

Lenntech. (2004). Water Treatment, Published by Lenntech, Rotterdamseweg, Netherlands. (www.excelwater.com/thp/filters/Water-Purification.htm).

Marschner, H. (1995). Mineral nutrition of higher plants, 2nd edn. London, UK: Academic Press.

McLaughlin, M. J., Parker, D. R. and Clarke, J. M. (1999), Metals and micronutrients – food safety issues. Field Crops Res. 60, 143–163.

McBride, M. B. (2003). Toxic metals in sewage sludge-amended soils: has promotion of beneficial use discounted the risks? , *Adv. Environ. Res.* 8, 5–19.

McDonald, J.A., Potter, N.U. (1996). Lead's legacy, Early and late mortality of 454 lead-poisoned children. Arch Environ Health 51:116-121.

McGrath, S.P. (1995). Chromium and nickel. In Heavy Metals in Soils, 2nd edn, ed Alloway BJ, BlackieAcademic & Professional, London.

Mulhern, S.A., Stroube, W.B., Jacobs, R.M. (1986). Alopecia induced in young mice by exposure to excess dietary zinc. Experientia 42:551-553.

Nair, M., Balachandran, K.K. Sankarnarayan, V.N.and Joseph, T. (1997). Heavy metals in fishes from coastal waters of Cochin, South West Coast of India. Indian Journal of Marine Science. 26:98-100.

NRBMI (Nzoia River Basin Management Initiative). (2006). A public private partnership. (www.unep.org/training). Accessed August 5, 2007

Nriagu, J.O., Pacyna, J.M. (1988). Quantitative assessment of worldwide contamination of air, water and soils by trace metals. Nature 333:134-139.

OECD (Organisation for Economic Co-operation and Development). (1994). Risk Reduction Monograph No. 5: Cadmium OECD Environment Directorate, Paris, France.

Ogwuegbu, M.O.C, Muhanga, W. (2005). Investigation of Lead Concentration in the Blood of People in the Copperbelt Province of Zambia, J. Environ. (1): 66 – 75.

Omwoma, S., Lalah, J.O., Ongeri, D.M. and Wanyonyi, M.B. (2010). Impact of fertilizers on heavy metal loads in surface soils in Nzoia nucleus Estate Sugarcane Farms in Western Kenya. Bull Environ Contam Toxicol. 85(6), 602-8.

Olaguibel, J.M., Basomba, A. (1989). Occupational asthma induced by chromium salts. Allergol Immunopathol (Madr) 17(3):133-136.

Oyaro, Nathan. (2000). Heavy metal content in Amaranthus Hybridus, Bidens Pilosa and Pennisetum as environmetal pollution indicators in Nairobi City.MSc Thesis. Kenyatta University, Kenya. Kenyatta University Moi Library. QH 541.15. M64 O96

Pendias, A.K., Pendias, H.K. (2001). Trace Elements in Soils and Plants, 3rd edn, CRC Press, Boca Raton, FL.pp 1-200

Peplow D (1999). Environmental Impacts of Mining in Eastern Washington,
Center for Water and Watershed Studies Fact Sheet, University of Washington, Seattle.

Sauve, S., McBride, M.B., Hendershot, W.H. (1997). Speciation of lead in contaminated soils. Environ Pollut 98(2):149-155.

Seregin, I.V., Shpigun, L.K., Ivaniov, V.B. (2004). Distribution and toxic effects of cadmium and lead on maize roots. Russ. J. Plant Physiol. 51:525-533.

Sharma, R.K., Agrawal, M., Marshall., F.M. (2006). Heavy metals contamination in vegetables grown in wastewater irrigated areas of Varanasi, India. Bull. Environ contamination 77:312-318

Singh, B.R. (1994). Trace element availability to plants in agricultural soils, with special emphasis on fertilizer inputs. Environ Rev 2:133-146.

Skoog D.A, Holler F.J, Crouch S.R. (2007). *Principles of Instrumental Analysis* (6th ed.). Belmont, CA: Thomson Brooks/Cole. pp. 169–173. ISBN 9780495012016.

Snyder, C.A., Valle, C.D. (1991). Immune function assays as indicators of chromate exposure. Environ Health Perspect 92:83-86.

Sutherland, C.A., Milner, E.F. (1990). Lead. In: Elvers B, Hawkins S, Schulz G, eds. Ullmann's encyclopedia of industrial chemistry. 5th edition. New York, NY: VCH Publishers, 193-236.

Todd, G.C. (1996). Vegetables Grown in Mine Wastes. Environmental Toxicology and Chemistry. 19 (3): 600-607.

Trupheme, V., Bousquet, M., Montrejaud-Vignoles, J. L., Lacout, J. P., Fortune, T. (2000). Mineralogical and physicochemical methods to differentiate between natural and anthropogenic sources of chromium in soils. Water Environment Research **72**(5) 516–522.USEPA

UNEP/GPA (United Nations Environmental Protection/Global Program of Action) . (2004). Why The Marine Environment Needs Protection from Heavy Metals, Heavy Metals 2004, UNEP/GPA Coordination Office (http://www.oceansatlas.org/unatlas/uses/uneptextsph/wastesph/2602gpa.).

Vema, V.K, Gupta, R.K and Rai, J.P.N. (2005). Biosorption of Pb and Zn from pulp and paper industry effluent by water hyacinth.Journal of Scientific and industrial research. Vol. 64. Pp 778-781.

Vitale, R.J.,Mussoline, G. R., Rinehimer, K. A., Moeser, K. L., Petura, J. C.(2000). An evaluation of a technical holding time for the preparation and analysis of hexavalent chromium in soils/sediments. Soil and Sediment Contamination 9(3) 247–259.

Welz, B., Sperling, M. (2007). Atomic Absorption Spectrometry, Wiley-VCH, Weinheim, Germany. Third Edition. Published Online: 13 DEC 2007 DOI: 10.1002/9783527611690.fmatter

Whatmuff, M. S. (2002). 'Applying biosolids to acid soil in New SouthWales: Are guideline soil metal limits from other countries appropriate?', *Aust. J. Soil Res*. **40**, 1041–1056.

WHO. (2001). Zinc. Environmental Health Criteria 221. Geneva, Switzerland: World Health Organization. http://www.inchem.org/documents/ehc/ehc/ehc221.htm. June 11, 2003.

Yousef, M.I., El-Demerdash, F.M., Kamil K.I. (2006). Ameliorating effect of folic acid on chromium(VI)-induced changes in reproductive performance and seminal plasma biochemistry in male rabbits. Reprod Toxicol 21(3):322-328.

APPENDIX 1; HEAVY METAL CONCENTRATIONS IN SOILS

Table 4.1a; Concentration of Elements in Soils around Nzoia during Wet Season (ppm)

SAMPLE REF. NO.	Cd	Cu	Pb	Zn	Cr
NSA	0.6			16.8	
NSB	2	8.2	12	12.4	
NSC	2	7.8	19.8	20	
NSD	2.5	2.5	8	29	ND
NSE	2	6.73	7.47	15.2	
NSF	2	7.2	8.67	10.4	27.4
NSG	ND	6.2	14.6	18.2	24.6
NSH	2.27	2.47	15.2	15.6	23.6
NSI	2.67		8.73	10.9	4.76
NSJ	1.67	9.47	8.8	14.9	28
NSK	1.8	9.5	10.33	13.8	24.2
Mean	1.77	6.67	11.36	16.1	22.09
Standard dev.	±0.79	±2.62	±4.01	±5.17	±8.67

Table 4.1b; Concentration of Elements in Soils around Nzoia during Dry Season (ppm)

SAMPLE REF. NO.	Cd	Cu	Pb	Zn	Cr
NSA-D	0.5			19.2	
NSB-D	1.7	6.2	14.2	15.2	
NSC-D	2.2		17.1	23	
NSD-D	2.1	2.6	5.6	26	
NSE-D	2.2	5.1	8.6	17.1	
NSF-D	1.4	6.8	6.5	8.6	21
NSG-D	0.3	5.3	19.1	20.1	22.4
NSH-D	1.6		13.1	13.3	19
NSI-D	2.3		6.6	11.8	5.6
NSJ-D	1.8	11.3	7.5	18.9	30
NSK-D	1.2	8.8	12.2	15.8	21
Mean	1.57	6.58	11.05	17.18	19.80
Standard dev.	±0.68	±2.82	±4.78	±5.01	±7.90

Table 4.1c: Concentration of Elements in Soils around Webuye Town during Wet Season (ppm)

SAMPLE REF. NO.	Cd	Cu	Pb	Zn	Cr
WSA	1.8	2.6	4.53	4.8	37.4
WSB	2.5	4	14.5		20.4
WSC	2.4	3	15.8	19	16.4
WSE	0.4		16.06	13	
WSD	2.2	1.8		9	44
WSF	2	1.6	10.33	10.4	19.2
WSJ	2.2	3.86	21.6		32.4
WSI	0	2.33	13.4		19.6
WSP	2.2	1	14.6	9	24
Mean	1.74	2.52	13.85	10.86	26.67
Standard dev.	±0.90	±1.06	±4.91	±4.87	±10.04

Table 4.1d: Concentration of Elements in Soils around Webuye Town during Dry Season (ppm)

SAMPLE REF. NO.	Cd	Cu	Pb	Zn	Cr
WSA-D	0.9	3.1	5.1	5.6	36.7
WSB-D	1.4		16.3	26	18.5
WSC-D	2.1	2.4	12.3	24.5	18.4
WSE-D	0.6		18.2	9.5	
WSD-D	1.8	1.4	41.3	11.2	37.2
WSF-D	2.9	2.5	13.5	13.4	23.4
WSJ-D	2.8	3.1	23.4		28.5
WSI-D		1.1	15.4	46.7	17.4
WSP-D	1.5	1.2	14.2	12.3	22
Mean	1.75	2.11	17.74	12.80	25.26
Standard dev.	±0.82	±0.87	±10.09	±6.01	±8.04

Table 4.1e: Concentration of Elements in Soils around Mumias Town during Wet Season (ppm)

SAMPLE REF. NO.	Cd	Cu	Pb	Zn	Cr
MSA	ND	6	4.47	15.1	11.4
MSB	2.2		5.4	33.2	121.4
MSD	2.2	8.26	6		17.4
MSE	2.2	6.66	8.8	41.8	59.8
MSC	2.2		28.466	20.8	53
Mean	1.76	6.97	6.17	27.72	44.40
Standard dev.	±0.98	±1.16	±1.86	±12.04	±22.50

Table 4.1f: Concentration of Elements in Soils around Mumias Town during Dry Season (ppm)

SAMPLE REF. NO.	Cd	Cu	Pb	Zn	Cr
MSA-D	1.11	6.34	5.83	16.7	9.23
MSB-D	2.8		6.9	31.9	118.67
MSD-D	1.83	6.5	5.43	104.32	19.45
MSE-D	1.71	8.5	7.21	44.32	57.34
MSC-D	2.31		32.78	22.43	55.21
Mean	1.95	7.11	11.63	43.93	44.0
Standard dev.	±0.64	±1.20	±11.05	±35.34	±21.28

Table 4.1g: Concentration of Elements in Soils around Kapkateny during Dry Season (ppm)

Sample Ref. No.	Cu	Pb	Zn	Cr	Cd
KSA	80.4	ND			2
KSB	55.6	ND	52.4	31.4	
KSC	42.3		36.14	11.52	2.61
KSD	61.51	ND	18.92	19.43	
KSE	71.3		28.31	14.21	2.8
Mean	62.22	ND	33.94	19.14	2.47
std dev	±14.61		±14.17	±8.80	±0.42

APPENDIX 2; HEAVY METAL CONCENTRATIONS IN COWPEAS, KALES AND SWEET POTATOES

Table 4.2d; Concentration of Elements in Sukuma wiki Samples on Farms aroundNzoia during Wet Season (ppm)

SAMPLE REF. NO.	Cd	Cu	Pb	Zn	Cr
NS1			18.33	16.5	ND
NS2	ND	3.17	15.83	33.25	ND
NS4		1.8	8.2	10.6	ND
NS5	ND	1.87			ND
NS6	ND	1.16		18.25	ND
NS7				36	ND
NS8	ND	5.67	8.33	28.5	ND
NS9		5	22.5	37	ND
NS10		3.67	10.56	35	ND
NS11	ND	3.66		13.67	ND
NS12		2.33	10.13	17.7	ND
NS13	ND		15.73	8.46	ND
NS14	ND	4.16		22	ND
Mean		3.25	13.70	23.08	
Standard. dev.		±1.46	±5.19	±10.40	

Table 4.2e; Concentrations of Elements in Sukuma wiki Samples on Farms around Nzoiaduring Dry Season (ppm)

SAMPLE REF. NO.	Cd	Cu	Pb	Zn	Cr
NS1-D			20.1	22.6	ND
NS2-D	ND	2.8	17.2	36.7	ND
NS4-D		2.1		14.5	ND
NS5-D		1.6			ND
NS6-D	ND	0.9		20.2	ND
NS7-D				38.1	ND
NS8-D	ND		11.35	31.2	ND
NS9-D		3.9	23.5	39	ND
NS10-D		3.4	8.5	38.3	ND
NS11-D	ND	2.9		15.3	ND
NS12-D		1.5	18.6	16	ND
NS13-D	ND		17.5	14.5	ND
NS14-D	ND	3		26.7	ND
Mean		2.45	13.70	26.09	
Std deviation		±0.98	±5.19	±10.14	

Table 4.2f; Concentrations of Elements in Sukuma Wiki Samples on Farms around Webuye Town During Wet Season (ppm)

SAMPLE REF. NO.	Cd	Cu	Pb	Zn	Cr
WS1	ND	2	32.17	17.33	ND
WS2	ND	2.5		34.5	ND
WS3	ND	6.5	37	59.5	ND
WS4	ND	6.5	36.16	26.5	ND
WS5	ND	8.5		27	ND
WS6				58	ND
WS7	ND		66	67	ND
WS8	ND	4.33	30		ND
WS10	ND	5		30	ND
WS9		3	24.67	30	ND
WS11					ND
Mean		4.79	37.67	38.87	
Std dev.		±2.27	±14.58	±17.73	

Table 4.2g: Concentrations of Elements in Sukuma Wiki Samples on Farms around Webuye Town During Dry Season (ppm).

SAMPLE REF. NO.	Cd	Cu	Pb	Zn	Cr
WS9-D		2.4	27.4	28.6	ND
WS11-D		3.4		13.2	ND
WS1-D	ND	3.1	35.2	19.5	ND
WS2-D	ND	1.5		37.5	ND
WS3-D		5.6	39	62.6	ND
WS4-D	ND	5.9	31.4	28.6	ND
WS5-D	ND	7	4.6	31.3	ND
WS6-D			49.6	62.6	ND
WS7-D	ND		63.6		ND
WS8-D	ND	3.8	28	31.8	ND
WS10-D	ND	4		32	ND
Mean		4.08	34.85	34.77	
Std. Dev.		±1.78	±17.28	±16.19	

Table 4.2h; Concentrations of Elements in Sukuma wiki Samples on Farms around Mumias During Wet Season (ppm)

SAMPLE REF. NO.	Cd	Cu	Pb	Zn	Cr
MS1	ND	3.125	18.95	18.75	ND
MS2			43.6	32	ND
MS3	ND	2.34	23.75	30	ND
MS4		3		40.6	ND
MS5	ND	6.88	41.67	30	ND
MS6	ND		73.33	49	ND
MS7	ND	5	64	38	ND
MS8	ND		70.66		ND
MS9	ND	5.62		65.63	ND
MS10		3.75	30.83	37.19	ND
MS11	ND				ND
MS12	ND				ND
Mean		4.24	45.84	37.90	
Std dev.		±1.64	±21.24	±13.35	

Table 4.2i: Concentration of Elements in Sukuma wiki Samples on Farms around Mumias Town During Dry Season (ppm)

Sample Ref.	Cd	Cu	Pb	Zn	Cr
MS1-D	ND	2.92	23.9	12.78	ND
MS2-D			47.11	38.66	ND
MS3-D	ND		17.8	27.34	ND
MS4-D		2.82		48.9	ND
MS5-D	ND	5.21	48.38	34.23	ND
MS6-D	ND			42.45	ND
MS7-D	ND	5.9	59.04	44.2	ND
MS8-D	ND	7.3		89.45	ND
MS9-D	ND	4.1		68.21	ND
MS10-D		4.87	36.67	39.34	ND
MS11-D	ND		17.89		ND
MS12-D	ND		15.9		ND
Mean		4.73	33.33	44.56	
Standard dev.		±1.61	±16.73	±21.27	

Table 4.2j: Elemental Concentrations in Sukuma Wiki Samples from Kapkateny area During Dry Season (ppm).

Sample Ref. No.	Cu	Pb	Zn	Cr	Cd
KS1	1.33	ND	16	10	ND
KS2	5.2	ND	26.1	7.1	ND
KS3	2.8		18.1	6.8	
KS4	4.9	ND	14.5	12.41	ND
KS5	1.7		11.3	5.7	
Mean	4.30	ND	17.2	8.40	ND
std dev.	±1.31		±5.55	±2.75	

Table 4.2k; Concentrations of Elements in Cowpeas Samples on Farms around Nzoia During Wet Season (ppm)

SAMPLE REF. NO.	Cd	Cu	Pb	Zn	Cr
NK1		4.2		4.2	ND
NK2	ND	12.39	28.43	12.39	ND
NK3	ND	5.8	12.8	5.8	ND
NK4	ND	6.33		6.33	ND
NK5	ND		15.8		ND
NK6	ND	4.3		4.3	ND
NK7	ND	14.66	29.32	14.66	ND
NK8		6.16	17	6.16	ND
NK9	ND	9.67		9.67	ND
NK10		8.75	43.75	8.75	ND
NK11	ND	9.5		9.5	ND
Mean		8.17	24.51	19.26	
Std deviation.		±3.46	±11.64	±9.36	

Table 4.2l; Concentration of Elements in Cowpeas Samples on Farms around Nzoia During Dry Season (ppm)

SAMPLE REF. NO.	Cd	Cu	Pb	Zn	Cr
NK1-D		4.5		8.2	ND
NK2-D		16.1	31.4	18.4	ND
NK3-D	ND	6.2	14.2	9.4	ND
NK4-D	ND	8.1		28.7	ND
NK5-D			17.2	6.9	ND
NK6-D	ND	5.6		21.8	ND
NK7-D	ND	12.14	27.2	38.2	ND
NK8-D	ND	5.5	19	19.3	ND
NK9-D	ND	10.1		27.3	ND
NK10-D		9.5		33.1	ND
NK11-D	ND	10.2	9.2	18.6	ND
Mean		8.79	19.70	20.9	
Standard deviation.		±3.58	±8.25	±10.27	

Table 4.2m; Elemental Concentrations in Cowpeas Samples on Farms around Webuye Town During Wet Season (ppm)

SAMPLE REF.	Cd	Cu	Pb	Zn	Cr
WK1	ND	3.8	13	18.47	ND
WK2	ND	20		23	ND
WK3	ND	13.83	21.5	25	
WK4	ND	8.33		63.33	
WK5	ND	15	32	33.3	ND
WK6	ND	20		41	ND
WK7	ND	22		32	ND
WK8	ND	15		28.5	ND
WK9	ND	5.5	14	37	ND
WK10	ND	10		40	ND
Mean		13.34	20.13	34.16	
Std dev.		±6.30	±8.78	±12.61	

Table 4.2n; Elemental Concentrations in Cowpeas Samples on Farms around Webuye Town During Dry Season (ppm)

SAMPLE REF.	Cd	Cu	Pb	Zn	Cr
WK1-D	ND	4.1	15.5	20.22	ND
WK2-D		23		26.4	ND
WK3-D	ND	15.5	18.7	21.5	
WK4-D		11.4		66.7	
WK5-D	ND	14.5	36.1	32	ND
WK6-D	ND	24.6		45	ND
WK7-D	ND	25.2		37.5	0.5
WK8-D	ND	11.4		27.4	ND
WK9-D	ND	4.5	12.7	39.4	ND
WK10-D	ND	11.7		44.4	ND
Mean		14.59	19.2	36.05	
Std dev.		±7.64	±19.00	±13.94	

Table 4.2o; Elemental Concentrations in Cowpeas Samples on Farms around Mumias Town During Wet Season (ppm)

SAMPLE REF. NO.	Cd	Cu	Pb	Zn	Cr
MK1	ND	6	39.16	102.5	ND
MK10	ND	16	62		ND
MK11	ND		32.5	42	ND
MK2	ND		33.67	21.33	ND
MK6	ND		34.83	43	ND
MK8	ND			68.33	ND
MK4	ND	14	78	86.33	ND
MK7	ND	20	75	99.66	ND
MK3		6.67	11.5	44.8	ND
MK9					ND
MK5	ND	6.25	81.67		ND
Mean (11 samples)		11.48	49.81	63.49	
Std dev.		±5.09	±30.19	±30.19	

Table 4.2p; Elemental Concentrations in Cowpeas Samples on Farms around Mumias Town During Dry Season (ppm)

SAMPLE REF. NO.	Cd	Cu	Pb	Zn	Cr
MK1-D	ND	9.6	38.2		ND
MK10-D		22.6	59.4		ND
MK11-D	ND	6.5	29.3	36	ND
MK2-D	ND		38.9	26.9	ND
MK6-D	ND	12.2	39	45	ND
MK8-D	ND	21.4		80.3	ND
MK4-D	ND	20.5			ND
MK7-D	ND		79.1		ND
MK3-D		7.9		38.2	ND
MK9-D					ND
MK5-D	ND	7.9	85.4		ND
Mean		13.60	52.75	45.28	
Std dev.		±6.17	±22.16	±20.16	

Table 4.2q; Elemental Concentrations in Cowpeas Samples on Farms around KapkatenyDuring Dry Season (ppm)

Sample Ref. No.	Cu	Pb	Zn	Cr	Cd
KK1	2.2	ND	40.33	11	ND
KK2	3.4	ND	18.5	8.5	ND
KK3	1.7	0.6	12.22	7.1	
KK4	4.5	ND	31.5	10.11	ND
KK5	1.2	0.9	22.41	5.5	
MEAN	2.6	0.75	24.99	8.44	ND
Std dev.	±1.34	±0.21	±11.06	±2.22	

Table 4.2r; Elemental Concentrations in Sweet potatoes on Farms around Nzoia During Wet Season (ppm)

SAMPLE REF. NO.	Cd	Cu	Pb	Zn	Cr
NP1	ND	3.93		4.2	ND
NP2	ND	3.2	12.13	2.8	ND
NP3	ND	4.73	18	9.2	ND
NP4	ND	3.4	16	4.8	ND
NP5	ND	2	15.2		ND
NP6	ND	6.8	15	9.4	ND
NP7	ND	2		2.4	ND
NP8	ND	5.4	14.2	7.8	ND
Mean		3.93	15.08	5.89	
Std dev.		±1.66	±1.94	±2.90	

Table 4.2s; Elemental Concentrations in Sweet potatoes on Farms around Nzoia DuringDry Season (ppm)

SAMPLE REF. NO.	Cd	Cu	Pb	Zn	Cr
NP1-D	ND	3.01	1.2	5.5	ND
NP2-D	ND	2.8	16.21	3.5	ND
NP3-D	ND	5.41	23	12.1	ND
NP4-D	N.D	2.5	15	5.4	ND
NP5-D	ND	2.2	13.1	1.1	ND
NP6-D	ND	5.2	14.2	11.6	ND
NP7-D	N.D	2.3	0.7	4.2	ND
NP8-D	ND	5.8	13.5	10.4	ND
Mean		3.65	12.11	6.72	
Std dev.		±1.54	±7.56	±4.10	

Table 4.2t; Elemental Concentrations in Sweet potatoes Samples on Farms around Webuye Town during Wet Season (ppm)

SAMPLE REF. NO.	Cd	Cu	Pb	Zn	Cr
WP1	ND	5.8	17.6	10.2	ND
WP2	ND	3.93	5.87	3.6	ND
WP3	ND	2.6	14.13	6.6	ND
WP4	ND	4.87	16.73	10.2	ND
WP5	ND	3.6	15.13	5.6	ND
WP6	ND	2	9.67	9.8	ND
Mean		3.8	13.18	7.66	
Std dev.		±1.40	±4.52	±2.80	

Table 4.2u: Elemental Concentrations in Sweet potatoes Samples on Farms around Webuye Townduring Dry Season (ppm)

SAMPLE REF. NO.	Cd	Cu	Pb	Zn	Cr
WP1-D	ND	6.3	19.7	12.6	ND
WP2-D	ND	4.5	6.8	3.1	ND
WP3-D	ND	2	15.5	4.2	ND
WP4-D	ND	3.7	18.1	7.2	ND
WP5-D	ND	3.2	19.7	4.6	ND
WP6-D	ND	1.5	11.6	12.9	ND
Mean		3.53	15.23	7.43	
Std dev.		±1.74	±5.15	±4.33	

Table 4.2v; Elemental Concentrations in Sweet potatoes Samples on Farms around Mumias Townduring Wet Season (ppm)

SAMPLE REF. NO.	Cd	Cu	Pb	Zn	Cr
MP1	ND	5.8	15.07	8	ND
MP2	ND	4.3	12.27	3.8	ND
MP4	ND	7.1	12.13	3.6	ND
MP3	ND	5.0	12.13	6	ND
MP6	ND	3.4	1.2	3	ND
MP5	ND	3.4	19.4	6.6	ND
Mean		4.83	12.03	5.16	
Std dev.		±1.44	±6.01	±1.98	

Table 4.2w: Elemental Concentrations in Sweet potatoes Samples on Farms around Mumias Town During Dry Season (ppm)

SAMPLE REF. NO.	Cd	Cu	Pb	Zn	Cr
MP1-D	ND	5.5	12.34	8.61	ND
MP2-D	ND	4.65	9.41	4.3	ND
MP4-D	ND	8.1	16.12	3.11	ND
MP3-D	ND	5.6	8.51	6.63	ND
MP6-D	ND	3.11	2.1	3.21	ND
MP5-D	ND	3.92	16.21	5.9	ND
Mean		5.14	10.78	5.29	
Std dev.		±1.72	±5.34	±2.16	

Table 4.2x: Elemental Concentrations in Sweet Potato Samples from Kapkateny Area during Dry Season (ppm)

SAMPLE REF. NO	Cu	Pb	Zn	Cr	Cd
KP1	1.95	ND	5.8	ND	ND
KP2	2.2	ND	2.6	ND	ND
KP3	1.4	ND	4.6	ND	ND
KP4	1.8	ND	3.5	ND	ND
KP5	3.5	ND	3.9	ND	ND
Mean	2.17		4.08		
std dev	±0.79		±1.20		