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**ANALYSIS OF LEAD, ZINC AND COPPER LEVELS OF ROADSIDE SOIL
AND PLANTS ACROSS THIKA-NAIROBI HIGHWAY, KENYA //**

BY

MAGOTHE JACKSON MATHENGE
(B.E.D) (Sc.) (HONS.)
REG. NO: 156/5786/03

**A Thesis submitted in partial fulfilment for the requirements of the award of
the Degree of Master of Science in Applied Analytical Chemistry in the
School of Pure and Applied Sciences of Kenyatta University**

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Magothe, Jackson
*Analysis of lead,
zinc and copper*



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DECLARATION

This thesis is my original work and has not been presented for a degree in any other university or any award.

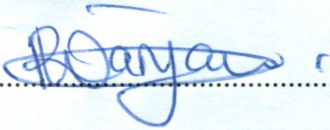


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MAGOTHE JACKSON MATHENGE
KENYATTA UNIVERSITY

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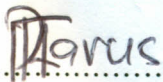
This thesis has been submitted in partial fulfilment of the requirements for the award of a degree of Master of Science in Applied Analytical Chemistry of Kenyatta University with our approval as supervisors.



6/5/09

DR. RUTH N. WANJAU
DEPARTMENT OF CHEMISTRY
KENYATTA UNIVERSITY

Date



6/5/09

PROF. PAUL K. TARUS
DEPARTMENT OF PHYSICAL SCIENCE
MASINDE MULIRO UNIVERSITY OF SCIENCE AND TECHNOLOGY
P.O. BOX 190
KAKAMEGA, KENYA.

Date

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DEDICATION

I dedicate this work to my beloved wife Monica and son, Brian for their true love and unfailing support throughout my academic endeavours.

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ABBREVIATIONS AND ACRONYMS

AAS	Atomic absorption spectroscopy
DNA	Deoxyribonucleic acid
GEMS	Global environmental monitoring system
IAEA	International atomic energy agency
ND	Not detected
OECD	Organization for economic co-operation & development
RNA	Ribonucleic acid
UNEP	United nation environment programme
WHO	World health organization
XRF	X-ray fluorescence
Ω_1	Solid angle the source 'sees' the sample in XRF analysis
Ω_2	Solid angle the detector 'sees' the sample in XRF analysis
Φ_1	Angle formed by primary radiation in XRF analysis
Φ_2	Angle formed by secondary radiation in XRF analysis
Go	Geometrical constant
$\mu\text{g/g}$	Microgram per gram
KeV	Kiloelectron Volt
m	Metre
cm	Centimetre

ABSTRACT

The importance of studying highway pollution has increased dramatically in recent years due to the rapid growth in the transportation sector which has resulted in environmental degradation. Increase of registered motor vehicles has been on the rise with 70 % being petrol driven while 30 % having diesel propelled engines. In the year 2000, the number of registered vehicles increased by 20,262. But due to improvement in economic growth and reforms in transportation sector that facilitated the reinforcement of traffic rules and regulations by Kenya government on January 2004, a major influx of motor vehicles on Kenyan roads increased by 42,634 which rose further by 85,324 in the year 2007. This rapid increase in transportation services is now a major source of heavy metals pollution, particularly along the busy urban highways. The exposure of man to these heavy metals has caused great concern due to their effect on human health. Therefore, there is need to continue monitoring the heavy metal inputs and levels in the environment. This study was undertaken to determine the levels of Pb, Zn and Cu in the soil and plants across the Thika-Nairobi highway which is one of the busiest road connecting Nairobi City and other provinces. The samples were collected from five different sites situated along the highway and their levels determined by X-Ray Fluorescence (XRF) technique. The soil and plants samples were investigated as a function of traffic density on the highway, distance from highway, and depth in soil profile. The results showed significant difference ($P < 0.05$) for Pb, Zn and Cu to increase with increase in traffic volume. There was gradual decrease in soil metal levels with increase in distance (5-80 M) from the highway. The mean average levels of Pb distribution on the top soil (up to 10 cm below surface) in the five sampling sites along the Thika-Nairobi highway ranged from 83.2 to 208.1 $\mu\text{g/g}$ during the dry season and 52.5 to 151.8 $\mu\text{g/g}$ during the wet season. Similarly, Zn values ranged from 94.4 to 267.2 $\mu\text{g/g}$ for the dry season and 57.5 to 212.6 $\mu\text{g/g}$ during the wet season. In addition, Cu recorded between 10.4 to 25.3 $\mu\text{g/g}$ during the dry season and 5.6 to 14.7 $\mu\text{g/g}$ during the wet season. The study also showed higher accumulation of Pb, Zn and Cu in the soil depth, 0-10 cm than in the soil depths 10-20 and 20-30 cm. The mean Pb levels on 0-10 cm ranged from 14.5 to 343.5 $\mu\text{g/g}$ and rapidly decreased with depth from ND to 167.6 $\mu\text{g/g}$ at 20-30 cm while Zn registered 21.5 to 376.9 $\mu\text{g/g}$ (0-10 cm) and ND to 194.3 $\mu\text{g/g}$ (20-30 cm) in addition to Cu recording ND to 56.8 $\mu\text{g/g}$ (0-10 cm) and ND to 19.2 $\mu\text{g/g}$ (20-30 cm) across the highway during dry and wet seasons. The levels of Pb, Zn and Cu in pasture grass (*Typha elephantina*) were higher than in napier grass (*Pennisetum purpureum*). This indicated that pasture grass posed greater hazard potential than napier grass since it is widely spread along the highway and is oftenly harvested by farmers to make hay to feed animals. The study findings would enable planning and decision making by the concerned stakeholders in resource management geared towards attainment of vision 2030 and thus making Kenyan highways pollution free and therefore creating a habitable ecosystem for all.

CHAPTER ONE

1.0 INTRODUCTION

1.1 Environmental pollution

Human beings have a great impact on the environment since they manipulate the environment for their own benefit. The components of the ecosystem namely, air, water and soil are greatly affected. The most noticeable way in which the ecosystem is affected is through pollution. Pollution in the world is a major health and environmental concern. This concern is increasing and should command high priority for action since environmental pollution affects the well being of all organisms in their habitats.

Environmental pollution could be defined as the addition of pollutants to the environment in quantities that are harmful to organisms and destructive to an ecosystem. These pollutants are released into the environment as a result of human activities such as combustion of fuels, use of pesticides and disposal of domestic sewage and industrial wastes. These pollutants range from toxic chemicals, motor vehicle particulates and noise, among others. They are usually released into the air, water bodies and soil, and depending on the amounts in the habitats they may modify the abiotic factors, which affect the food chains and food webs in the polluted habitat or ecosystem (Tolgate *et al.*, 2008). Pollutants include liquids, gases and solid particulates or chemicals. These pollutants contaminate air, water and soil (Michael, 1993).

1.1.1 Air pollution

Atmospheric air is supposed to be naturally pure. The moisture and gases it is composed of, are supposed to be original ones in their standard proportions. When the atmosphere is

contaminated with additional materials in solid or gases form, it is said to be polluted. Air pollution therefore, refers to the addition of pollutants into the air. These pollutants when taken in by living organisms interfere with their normal functioning causing injury or harmful effect and its ability to support life. The common air pollutants include oxides of sulphur, nitrogen, carbon, heavy metals and solid particulates. Poisonous gas pollutants arise from combustion of fuels, reaction of atmospheric nitrogen and oxygen and the decomposition of insecticides, perfume sprays and other substances (Andreas, 2001).

Air pollution is perhaps the most serious form of environmental change as this affects the atmosphere thus threatening to alter the climate and expose man to dangerous radiation. Air pollution is also increasingly becoming a major problem especially in the urban centres and near large population centers and industrial areas. Urban air is not clean because it contains a number of undesirable substances such as fumes from motor vehicles, dust and smoke from industries, mines and quarries, noise and other gases. When man and other living things breath, they take in the pollutants, which endanger the health and well being of living things (Marcus *et al.*, 2008).

1.1.2 Water pollution

Water pollution is the contamination of water bodies. Natural pollution of water occurs when materials like dust and salts are added to the water through natural processes such as erosion and wind deposition. Disposal of sewage and waste from homes into water sources like rivers or lakes also pollute the water. Dirty water and industrial effluents

discharged directly into water sources contaminate the water, resulting in deaths in developing countries and also affecting the aquatic life in water bodies (Philips, 1990).

Chemical substances are also known to contaminate water. Some industries discharge their effluent directly into water sources. This contaminates the water thereby affecting aquatic life in the water bodies. The first major international scare relating to toxic chemicals in water body occurred late in the 1950's when large numbers of people in Minamata Bay, Japan, began to contract an unusual disease (Wilson, 1995). It was later revealed that they were suffering from mercury poisoning as a result of waste that had been discharged into waterways and ingested by fish that were eventually consumed by human beings.

1.1.3 Soil pollution

Soil is a valuable and indispensable natural resource. It is in the soil that most of the food we eat grows. The water we drink seeps through the soil into the ground reservoirs or flows over it into the rivers. Soil is polluted by chemical inorganic fertilizers as well as sewage sludge which are added to it to improve its fertility and by industrial effluent which flows over it. Soil is also polluted by careless sewage disposal, heavy metal pollution and by the pesticides, fungicides and herbicides used to spray crops to keep away pests and diseases. These pollutants are absorbed by crops from the soil, which are then consumed indirectly when people eat fruits and vegetables grown on such soils (Ralston *et al.*, 1999).

1.2 Pollution due to human activities

Many human activities contribute to environmental pollution by adding harmful or unpleasant substances to the environment; the most pressing of the problems arising from man's exploitative approach to the natural environment is pollution. Thus, man's activities resulting in increased environmental pollution include agriculture, waste disposal, industrial activities and energy production and use (McBride, 1994).

1.2.1 Agriculture

Man depends on food derived from the soil and so the natural composition of the soil is of vital importance to him. In an effort to increase food productivity in farms, agricultural chemicals such as inorganic fertilizers, herbicides and pesticides have been incorporated as sprays on crops and in soils. As a result, the land becomes contaminated with these agrochemicals which are later washed into rivers during rain season and into the rivers and lakes. The fertilisers leads to eutrophication of the lakes or water bodies, which results in death and poisoning of fish and other animals. The enrichment of water with nitrogen and phosphorus lead to the massive growth of phytoplanktons such as algae. When the algae decays, it reduces the oxygen content in water (Hinnawi, 1990).

There are more than 80,000 chemicals in common use worldwide whose production and use generate large volumes of toxic waste (Hance, 2003). Chemical substances (biocides) such as herbicides used on plants and pesticides used on pests like tse tse flies, mosquitoes, weevils and ticks are all poisonous. They are potential environmental hazards if used in the wrong way or released accidentally into the environment since they

contaminate the soil and kill useful soil micro-organisms. Most biocides also tend to persist in the environment and are passed on through the food chain to tertiary consumers posing danger to health by being harmful to genetic materials. These biocides are composed of different grades of chemicals including heavy metals like mercury, lead, zinc and copper among others. These substances find their way into environmental systems such as water and soil, where some are absorbed by plants such as vegetables and fruits which are eventually eaten by humans (Edwards, 1991).

1.2.2 Waste disposal

Garbage waste is a big problem especially in urban areas where the population is increasing rapidly and services are inadequate. Garbage wastes include domestic waste, which is composed of scrap heavy metal matter in various forms (Stephen *et al.*, 1998). The dumping and accumulation of garbage, raw sewage, solid wastes and plastic menace in non-designated places even in residential areas result in pollution

1.2.3 Industry

Wastes from industries contain heavy metals such as lead, mercury, copper, zinc, nickel, chromium and cadmium. The industrial discharge also contains wastes from pesticides and chlorinated hydrocarbons depending on the industry (Arthur, 1997).

Chemical substances especially the heavy metals from industrial wastes accumulate in the bodies of aquatic organisms such as fish. If the aquatic organisms are eaten, the toxic

chemicals end in human bodies and because of the accumulative nature of these chemicals; they accumulate in human bodies sometimes resulting in death (Turk, 1998).

Industrial scrap metal wastes of Fe, Zn, Al, Cu, and Pb among others are non-biodegradable and undergo biogeochemical cycle with substantially different residence times in various spheres of the environment. During the biochemical cycling of these metals, man will take them up, mainly from food, air and drinking water (Conning *et al.*, 1983). In this respect, these metals at high concentrations constitute a health risk; although some are excreted, most have a tendency of accumulating in vital organs (Sephar *et al.*, 1987). The problem with heavy metals and their hazardous and deleterious effects are reported to be responsible for a number of health problems in humans and their accumulation in the environment is of great concern to environmentalists and health specialists (Berman, 1980).

1.3 Energy production

Energy harnessed from natural forces include wind, water, solar, geothermal steam and ocean tides. However, most of the energy used in the world today is derived from burning fuels such as coal and petroleum products (Daniel, 1993). The type of energy used to carry out various activities in a community has a bearing on the level of development in that society. Where animal and human energy is the most widely used form of power, the standard of living in that community is likely to be low and in rural areas. The use of more efficient forms of energy such as electricity and petroleum products enables output to be increased thus raising the material well being of the people, found mostly in towns.

Energy sources are normally classified into two groups, namely the renewable and non-renewable (Sodha *et al.*, 1990).

1.3.1 Renewable energy

Renewable sources of energy are those sources that can be regenerated and used over a long period of time; examples include the solar, wind, geothermal, biomass and water. Solar energy is a cheap, clean and also environmentally friendly form of energy and is inexhaustible. Wind energy also is a cheap source of energy that is harnessed using windmills, and does not pollute the environment (Hamrin, 1995), however it can not be relied upon due to limited technology available presently.

1.3.2 Non-Renewable energy

Non-renewable sources of energy include fossil fuel such as petroleum, coal and natural gas (Irwin, 1993). However, half of the energy used in the world today is derived from petroleum. Petroleum is also used in agriculture and in households for various purposes such as cooking, lighting and heating. About 50 % of the petroleum produced in the world is however used to make motor fuel used in the transport industry (Bansal, 1990). When petroleum is refined, several products and byproducts such as petrol, diesel, aviation fuel, liquefied gases, kerosene and lubricants are obtained. Petrol and diesel are used to fuel vehicles and machinery. The burning of petroleum pollutes the environment and contributes to global warming, and being the most widely used substance in the transport sector, it is mainly responsible for highway pollution (Daniel, 1993).

More than 70 % of Kenya's energy comes from wood fuel. This source of energy is an

environmental hazard because the gases emitted when wood is burnt pollute the environment. Wood fuel is also dirty due to the soot and smoke that is given off when wood is burnt. Indiscriminate cutting of trees for wood fuel leads to deforestation and other related problems such as soil erosion, interference with the ecosystem and disruption of rainfall patterns (Akatsa *et al.*, 2002).

1.4 Energy uses

The production and consumption of energy influence most aspects of both urban-rural life. Energy is required for cooking, heating, lighting, motorized transport and industrial processes. The rural population, which makes up about 85 % of the total population in Kenya, mainly uses firewood for cooking, lighting, heating and drying whereas in urban centres people with low incomes mainly use charcoal and kerosene for cooking, all of which produce harmful fumes contributing to environmental pollution (Akatsa *et al.*, 2002).

The manufacturing and processing industries use almost all forms of energy available, with most manufacturing industries using petroleum fuels. Fossil fuels meet most of the energy demands in cities throughout the world. Growing urban populations and levels of industrialization inevitably lead to greater energy demand which is usually reflected in increasing pollutant emissions of nitrogen oxides (NO and NO₂, collectively termed NO_x), carbon monoxide (CO) and suspended particulate of heavy metals (Karekezi *et al.*, 1997).

The transport industry is the largest consumer of petroleum products such as diesel and petrol which are used by motor vehicles. The rapid rate of industrialization and population has resulted in the rapid growth of the transport sector, leading to an increase in demand for petroleum fuels (Richard, 1995). This in turn results in more highway pollution.

1.5 Motor vehicle

Petrol fuelled motor vehicles are the principal sources of NO_x , CO and Pb among other heavy metals, whereas diesel fuelled engines emit significant quantities of particulates and SO_2 in addition to NO_x . The use of petroleum fuels in vehicles results in emission of large quantities of fumes, smoke and poisonous gases into the atmosphere from vehicles containing gases such as carbon dioxide, carbon monoxide, sulphur dioxide and nitrogen oxides (Faiz, 1996).

Urban centres have higher vehicle densities than rural areas and therefore are more likely to experience a higher contribution from motor vehicles to the total urban pollution load. In many developing countries, vehicle fleets tend to be older and poorly maintained. The corrosion of metal sheets and deterioration of paint, which appear as irregularly shaped and permanently etched, increase metal levels in the environment along the highway, a factor which will increase the significance of motor vehicles as a source of pollution. Since 1950, the global vehicle fleet has grown tenfold and is expected to double from the present total of 630 million vehicles within the next 20 years (UNEP, 1992). Much of the expected growth in vehicle numbers is likely to occur in developing countries and in Eastern Europe. In contrast, much of the demand for motor vehicles in the developed

countries will be for vehicle replacement. The contribution of motor vehicles to the traffic related pollution load is thus set to increase in these regions of the developing countries (UNEP, 1992) in which Kenya is one of them whose registered motor vehicle population stood at 1.3 million by the end of 2007 (Motor vehicle registry, 2008). Appendix 1 shows the growth of motor vehicles in Kenya for the last eight years.

1.6 Highway pollution

Motor vehicles in Kenya have recently become an issue of concern as a major source of environmental pollutants along the highways in the urban areas. This is so because of the marked increase of traffic in recent years. Increase of registered motor vehicles has been on the rise with the majority 70 % being petrol driven engines while a paltry 30 % have diesel propelled engines (Motor vehicle registry, 2005).

In the year 2000, the number of newly registered vehicles increased by 20,262. But due to good performance of economic growth during the year 2004, there was a major influx of motor vehicle use on Kenyan roads that increased by 42,634 that subsequently rose by 85,324 in 2007 (Motor vehicle registry, 2005). This continually rapid increase in transportation services is now a major source of heavy metals pollution, particularly along the busy highways in the urban environment. In addition, the use of unroadworthy vehicles, abrasion of tyres and brake linings and cheap fuel with lead additives contributed to a sharp increase of contamination of roadside soils and plants by heavy metals. Information concerning this source of contamination and data dealing with this subject in Kenyan roads is inadequate and scarce. This study therefore was aimed at

investigating the levels of Zn, Cu and Pb in soils and grass species found along Thika highway in Kenya as a function of distance from roadside, distance from Nairobi City Centre, soil depth profile and plants.

The heavy metals (Pb, Zn and Cu) contamination from motor vehicle materials end up in air, water and soil. The importance of air, water and soil cannot be over-emphasized. Man breath in air, drink water and eat food crop grown on soil. The crop may get some of these harmful elements from soil, water and air. People and animals are exposed to these pollutants when they eat food from such crops. As well, people living in cross proximity to highways have been found to be more exposed, for example, traffic police officers, garage attendants, drivers and petrol attendants are the most affected by motor vehicle highway pollution and they are more prone to developing respiratory diseases (Nicholas *et al.*, 2008).

In the year 2005, the Kenya government came up with a scheme to reduce petroleum based pollution. The country embraced the phasing out of leaded gasoline, which is considered harmful to the environment, besides being dangerous to human health and especially children. The Mombasa refinery stopped producing leaded fuel on November 30, 2005 (UNEP, 2005). This move was in line with the Dakar Protocol which required African countries to do so by December 2005 (ESMAP, 2001). As a result most of petrol stations have switched to the unleaded fuel called lead replacement petrol; however, some are reportedly still selling stocks of leaded products and other adulterated fuel after the expiry of a government directive against the sale of the latter (UNEP, 2005).

Motor vehicle pollutants can affect the environment, particularly the ecology of an area. The pollutants can alter the composition of air, contaminate water source, and pollute the soil (land). These pollutants can be harmful to animals and plants living on the soil. When these toxic chemicals contaminate crops and these crops are eaten by animals and even humans, it can lead to deformities and even death (Mark *et al.*, 2004).

Plants such as napier grass (*Pennisetum purpureum*), beans (*Phaseolus vulgaris*), maize (*Zeamays*), cabbages (*Brassica* spp.), kale (*Brassica oleracea*), arrowroots (*Maranta arundinacea*), carrots (*Baucaus carota* spp.), sweet potatoes (*Lopmoea batatus*), spinach (*Spinacia oleracea*) and tomatoes (*Lycopersicon esculentum*) grown on farms along the highway on contaminated soils tend to absorb high levels of heavy metals and when such crops are consumed as food by man, animals or aquatic organisms, lead to their (metals) accumulation in certain body organs where they induce toxicity if in higher concentrations than required. Presence of these metals at high concentrations can pose problems for consumers since they sometimes have synergetic effects. The toxicity of these metals when taken in excess may damage cells and inhibit enzyme activities (Berman, 1980). Appendices 4 and 5 show spinach and kales growing along the Thika-Nairobi highway respectively.

The atmosphere is very important since whatever is in it is either directly or indirectly in contact with water and soil, which are the man's livelihood. We must preserve it in a clean and acceptable state at all times and so the need for continuous analysis of motor vehicle related pollution and thus the necessity for this study.

1.7 Problem statement and justification

There has been an increase in the number of motor vehicles and traffic on Kenyan roads and consequently the consumption rate of petroleum fuel as well as the roadside heavy metals deposition load has extensively increased. Motor vehicle emissions into the environment require special attention and proper research to minimize their accumulation in the soil and in the plants. The study investigated the levels of Cu, Zn and Pb in soils and plants since these heavy metals were suspected to be contained in motor vehicles. Leaded fuel contained Pb. Zn is contained in rubber tyres and brake linings while Cu is found in electrical cables, body fittings and in radiator. Pb, Zn and Cu are a concern to the environmentalists because these heavy metals have health implication issues when they accumulate in living organisms beyond the required levels (Voleskey, 1990). It was therefore necessary to monitor and determine their pollution load levels along Thika-Nairobi highway as one of the busiest highway in East and Central Africa with an approximate carrying capacity of 70, 000 traffic per day.

As a result of improvement in economic growth and reforms in the transportation sector initiated by the Kenya government on January 2004 that enforced regulations governing motor vehicles on Kenyan roads (Kenya gazette, 2003), there was a major influx of both public and private vehicles on the urban roads. This inadvertently resulted in higher highway pollution load. In addition, long motor vehicles jams were witnessed during morning and evening peak hours on urban highways that exerted more pollution on the environment due to motor vehicle congestion as indicated in Appendix 2. Research in this area was therefore necessary in order to establish the levels of Pb, Zn and Cu in the

soil and plants along the highways. The data obtained would be used to sensitize and enlighten farmers who use the plant crops grown along the highways for human or livestock consumption on the potential hazard they are exposed to as per Appendix 3. There was therefore need to know the environmental pollution status of Kenyan highways.

1.8 Hypotheses

- (i) There is increased emissions from the high traffic density on Thika-Nairobi highway pollute soil and plants with heavy metals.
- (ii) Some plants found along the Thika-Nairobi highway have higher levels of heavy metals.

1.9 General objective of the study

To determine the levels of Pb, Zn and Cu in plants and soils along the Thika highway.

1.10 Specific objectives of the study

- (i) To determine the levels of Pb, Zn and Cu at selected sampling sites on Thika-Nairobi highway.
- (ii) To determine the levels of Pb, Zn and Cu in the soil depth on the Thika-Nairobi highway.
- (iii) To determine the seasonal variation of Pb, Zn and Cu at selected sampling sites on the Thika-Nairobi highway.
- (iv) To determine the levels of Pb, Zn and Cu in some plants found on the Thika-Nairobi highway.

1.11 Significance of study and anticipated outcome

The findings of the study will help all the stakeholders in the motor industry to give more focus on the issue of environmental pollution caused by the traffic on highways. This would alert the government and other agencies to seek intervention measures of curbing highway pollution. Knowledge of these trace elements and their extent of contamination may aid in seeking or determining remedial actions. Consequently, public awareness on the highway pollution on plants, soil, water and air would rise. The creation of awareness of the farmers who plant crops along the highways for human or livestock consumption and the potential hazards they are exposed to could be undertaken. The study will serve to provide local highway pollution data by motor vehicles. This is essential for development of policy strategies on highway pollution standards for motor industry in Kenya. Stakeholders in the transport sector would hence forth be enlightened on the best steps to take to reduce toxic heavy metals on the highways while humans would be enlightened on the precautionary measures to take to protect themselves from undue exposure to heavy metals from polluted air, soils, water, plants and animals. It would also provide base-line data for further studies on the toxicity and mobility of various heavy metals in soils and plants which humans and animals depend on. Finally, knowledge of the trace elements distribution in the soil is important for efficient soil treatment processes, which depend on trace metal concentration on soil and plants.

1.12 Limitations of the study

Pangani and Thika were the only sites that soil profile samples were analysed, and only three heavy metals (Pb, Zn and Cu) were considered in this study due to lack of finances.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Introduction

There are several routes through which heavy metals reach the environment; these are natural (vulcanicity and weathering) processes and anthropogenic sources which include effluent from domestic, sewage, motor vehicles emissions, industrial processes and agricultural activities as indicated in Figure 2.0. The uncontrolled action of these sources such as the production and usage of products with toxic metals without appropriate protection and safeguards against their hazards to man is at the moment an important concern in the pollution of the environment (Cooke, 2000).

The problem associated with heavy metals is their toxicity to biological organisms and accumulation in the environment. The soil acts as a long term sink for heavy metals such as zinc, copper, lead, nickel and cadmium, which have residence times that range from hundreds to thousands of years, depending on the element and soil properties (Kaara, 1992).

Heavy metals such as copper, chromium, zinc, manganese and molybdenum are essential trace elements for plants and animals but excessive concentrations become toxic to animals. Metals such as cadmium, copper, zinc and lead can have adverse effects on human and animal health if they are allowed to accumulate in the food chain. (IPCS, 1996).

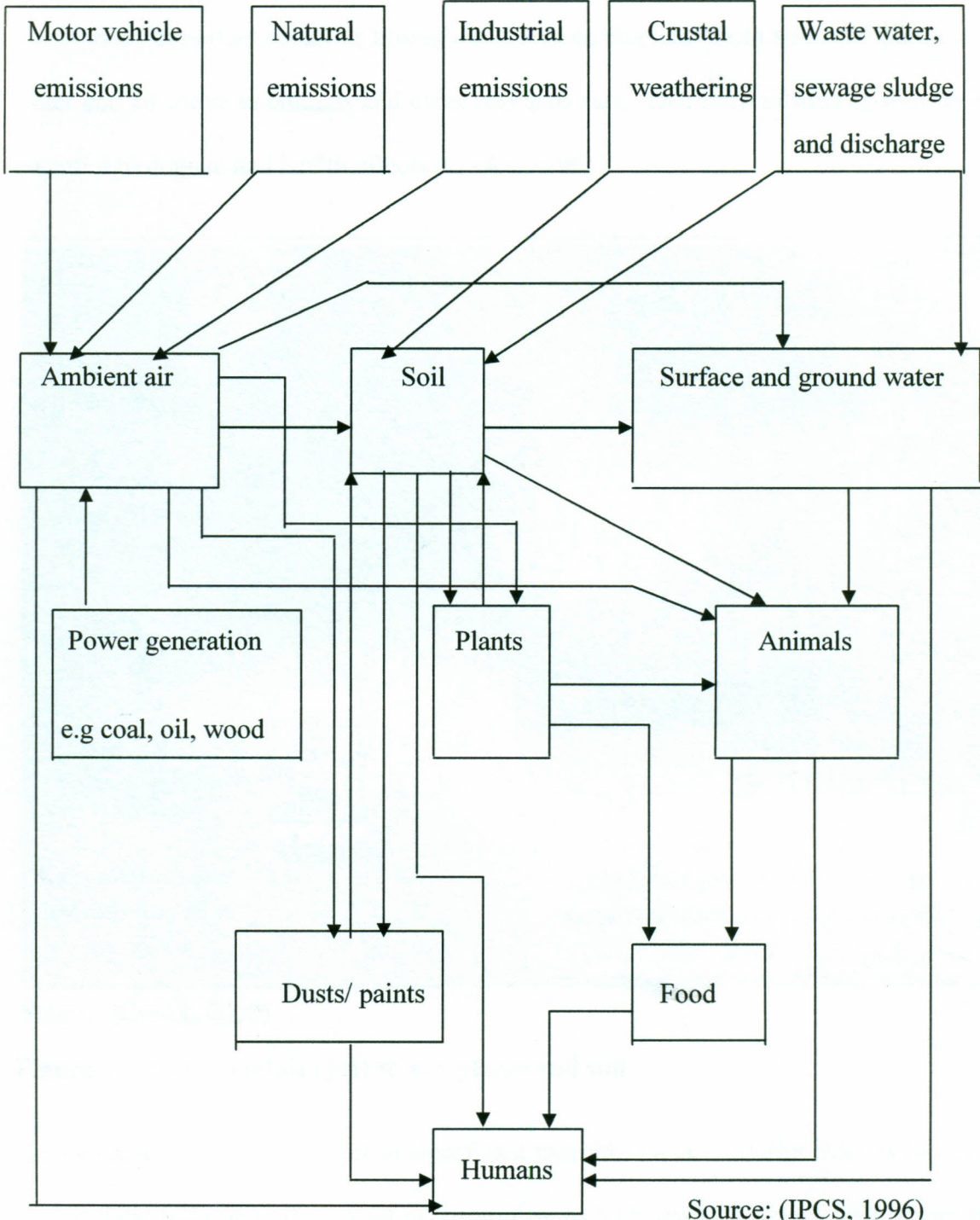
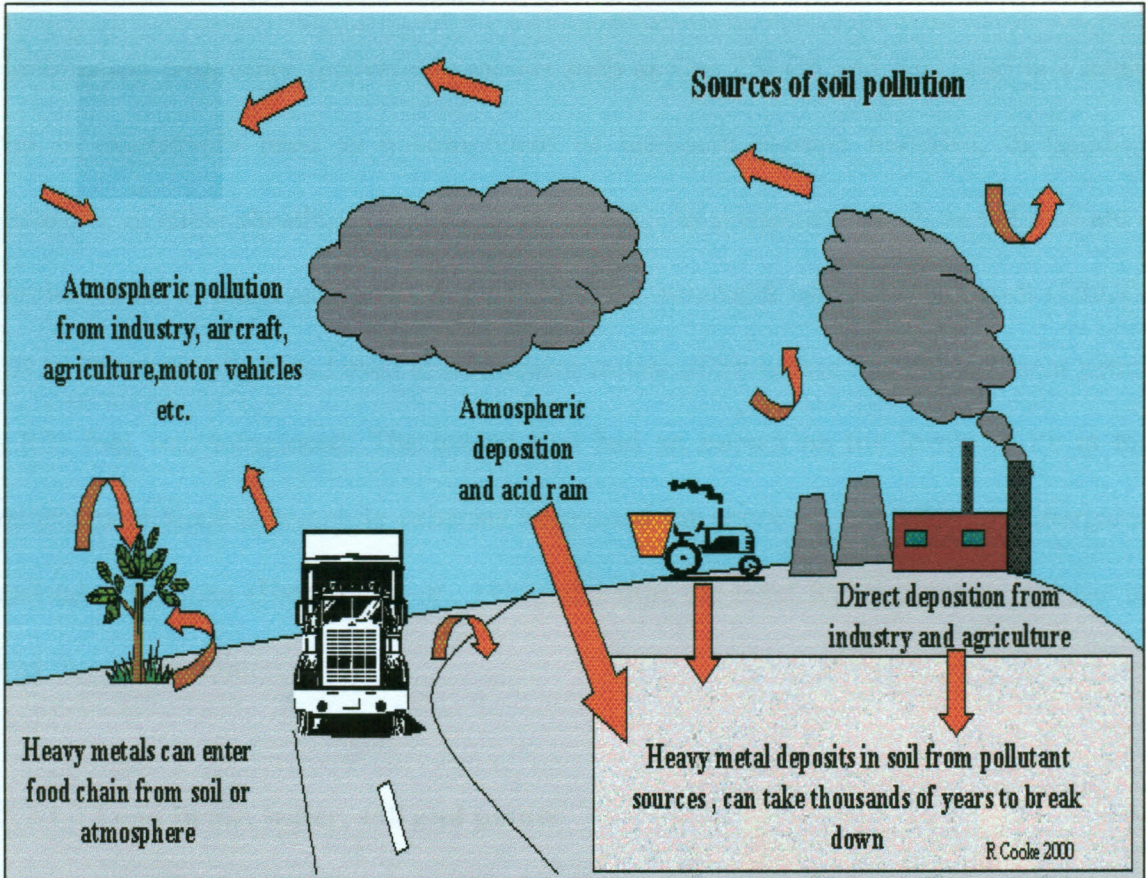


Figure 2.0 Pathways through which human may be exposed to heavy metals

The residence time of most heavy metals is long and they are available for plant uptake as indicated in Figure 2.1. Plants can accumulate elements especially heavy metals due to

their great ability to adapt to variable chemical properties of the environment. This makes plants to be important reservoir through which trace elements from soils and partly from water and air move to animals and especially into man. This form of metal pollution has potential biological and health effects (Cooke, 2000).



Source: (Cooke, 2000)

Figure 2.1 Heavy metals cycle in air, plants and soil

Heavy metal toxicity can result in significant morbidity and mortality. Metals like lead, copper, zinc and others if allowed to accumulate to high levels in plants, soils, water and air may cause toxicity. This is attributed to the role they play in biological processes as well as the way they interact with essential elements both at intestinal and organ level (Lucky, 1981). Research is therefore required to determine the varying distributions

levels of these heavy metals in plants and soils along the Kenyan highways. The heavy metals investigated in this study are discussed in the following sections.

2.2 Lead

Lead is obtained from its sulphide ore or galena (PbS). The ores are frequently found in combination with other recoverable metals such as Cu, Zn, Cd and Ag. Lead is a metal that is extensively used as a component of lead-acid storage batteries, in building materials, in cable sheathings and radiation shields. Its compounds such as red lead are a pigment used in paint and protective coatings for structural iron and steelwork (OECD, 1993). The tetra-alkyl lead used to be a major source of Pb before lead replacement petrol (LRP) fuel was introduced. The leaded fuel had an impact on the levels of Pb in the environment since automobile exhausts accounted for about 50 % of the total inorganic lead taken by man (Harrison *et al.*, 1989) and thus the need for continuous analysis of lead from the traffic.

2.2.1 Lead in air, water, soil and plants

A major source of Pb in the air is pollution from automobile exhaust. Tetra-alkyl lead is still added in substantial amount to gasoline to improve octane rating and as an antiknock. The concentration of Pb in the atmosphere of large cities, where there is heavy traffic, and near highways is so high as to cause toxic reactions in some particularly toxicity prone individuals (Mitei, 1996), hence motor vehicle emissions into the environment require special attention and proper research to minimize their accumulation on land and in plants along highway.

Concentrations of Pb in natural ground waters are generally low, with concentrations of less than 0.01 $\mu\text{g/l}$ being observed, however due to urban and industrial effluents seeping through into underground water. It has been reported that most of the underground water supplies are normally polluted by heavy metals especially in wells and boreholes in areas surrounding Nairobi (Kimei, 1996). He reported Pb levels ranging from 0.05-0.80 $\mu\text{g/l}$, with wet seasons recording a range of 0.01-0.38 $\mu\text{g/l}$ while dry seasons recorded a range of 0.01-1.00 $\mu\text{g/l}$, whose upper limits were above WHO maximum permissible level of 0.1 $\mu\text{g/l}$. The presence of lead at toxic levels revealed that these waters are occasionally contaminated and as such are not as safe as is usually assumed. Elevated levels of 6.02-69.39 $\mu\text{g/l}$ of Pb in Kenyan lakes arise principally from industrial discharges, sewage sludge and weathering processes (Kiilu, 1993).

The natural lead content of soil is inherited from the parent rocks, however, due to widespread Pb pollution; most soils are likely to be enriched with this metal, especially in the top soils. The approximate mean values of lead in soils have been reported as ranging between 15-25 $\mu\text{g/g}$ while the average levels of lead in the soil are in the range of 10-70 $\mu\text{g/g}$ (Laughler, 1992) with the stated upper limit for lead content of a normal soil being 70 $\mu\text{g/g}$ (Vernet, 1991), but higher lead levels of 45.4-263.8 $\mu\text{g/g}$ have been reported in garden soils from areas within and around Nairobi (Kaara, 1992). This probably reflects the impact of pollution and therefore the need for continuous monitoring of Pb levels in soils in urban areas. A positive linear correlation has been reported to exist between lead concentrations in plants and soil since lead present in the soil is transferred to the food

crops growing on the soil and thus food becomes contaminated with Pb either at the source or during preparation for consumption (GEMS, 1985).

Lead in plants growing on uncontaminated and unmineralised areas is quite constant, with a range of 0.1-10 $\mu\text{g/g}$ (Kaara, 1992), but, Mitei (1996) reported levels of Pb in tobacco leaves in Kenya to be between 7.40-25.00 $\mu\text{g/g}$. This indicates that tobacco uptakes heavy metals to varying degrees. These are high levels, which could be toxic to the health of the users. In analysis of vegetables intercropped with tobacco, Mitei (1996) found that spinach had a mean Pb content of 12.2 $\mu\text{g/g}$ in leaves with values ranging from 9.7-15.7 $\mu\text{g/g}$, while kale had lower levels of mean value of 9.1 $\mu\text{g/g}$ with a range of 6.4-10.8 $\mu\text{g/g}$. Ferguson (1990) stated that most of the lead taken up by plants seems to accumulate in the root system, and appreciable amounts are only translocated to the leaves at relatively high soil lead levels. There is some evidence that only a small fraction of lead absorbed on the surface of leaves can penetrate the protective cuticles and enter the plant tissues (Leeper, 1982). Since rains will eventually wash the contaminating material, surface contamination of leaves with lead is probably a temporary phenomenon.

The results obtained from analysis of heavy metals in sea plants along coastal regions of Kenya revealed presence of some toxic metals, for instance all species (except *Ulva* *elephantin* from Makupa Creek) were found to contain some Pb (Oyugi, 2000). The highest recorded level was 66.98 mg/l in *Chaetomopha* species from Makupa Creek (Oyugi, 2000), which was reported to be a dumping site for domestic and industrial wastes, hence the high levels of lead.

Man is exposed to varying degrees of lead in food, drink and air, and as a result there is a high degree of variability in dietary Pb intakes from individual to individual as well as country to country. The joint FAO/WHO experts committee (WHO, 1996) recommended that dietary intake of Pb should lie in the range of 100-200 $\mu\text{g}/\text{day}$ for adults, children and infants and 0.05 mg/l for raw water. There is therefore need for continuous research on the effect of heavy traffic presence and the leaching of the toxic metals to the soils, plants and our water bodies like oceans, lakes, aquifers and rivers.

2.2.2 Human and environmental effects of lead

Human exposure to Pb occurs through air, water, food and soil (Baker, 1982). Lead is taken and retained by living organisms and hence the lead content of the human body reflects the extent to which lead is present as a contaminant in the environment as it is a cumulative poison (Conning, 1983). This therefore requires that the levels of ingested Pb be investigated continuously since increasing amounts build up in the body and eventually a point is reached where symptoms of Pb poisoning occur. It normally accumulates in the liver, kidney and a higher percentage in the bones, where it produces a continuum of effects primarily on the haematopoietic systems, the nervous systems and the kidneys. It binds tightly to the sulfhydryl (SH), phosphate and carboxyl groups hence will bind tightly to proteins (Karin *et al.*, 2004).

Symptoms following prolonged exposure include abdominal discomfort and pain while on the other hand exposure to high levels of Pb for a short period of time can cause permanent brain damage in children. Exposure to low levels for a long period results in

loss of weight, body weakness and anaemia in children while severe cases may present colic, constipation, loss of appetite, nausea and vomiting, insomnia, headache, diarrhea, irritability and dizziness, coma and even death (Ferguson, 1990).

Lead uptake by plants is through roots and aerial deposition with most plants being lead tolerant. Plants with as much as 30 $\mu\text{g/g}$ of Pb in their roots have been reported, yet the plants showed no ill effects, but over deposition of lead from the air may be dangerous (Leeper, 1982) and thus a continuous assessment of Pb in the environment is necessary.

2.3 Zinc

Zinc is obtained from Zn ores such as zinc blende (ZnS), red zinc ore (ZnO) and calamine (ZnCO_3). Zinc metal is used to galvanize iron structures so as to prevent corrosion by attaching it as sacrificial anodes, industrial manufacture of batteries casing and brake linings. Zinc is also used in the manufacture of brass (Zn 30 % + Cu 70 %) which is a good conductor of electricity. As such it finds its use in electrical appliances, screws and in vehicles radiator steam condenser tubes. Also zinc (80 %) and aluminum (20 %) alloy becomes super-plastic at 270 °C and may be readily pressed into complex shapes, while on cooling, it becomes steel-like in hardness and therefore used for making car bodies that last longer. A compound of zinc oxide (ZnO) is used in manufacture of paints and as a reinforcing agent for rubber in tyres while zinc sulphide (ZnS) is used in making car paint as well (ILZSG, 1992).

2.3.1 Zinc in soil, water, plants and air

Zinc is widely distributed over the earth's surface. Estimates of its concentration vary from 0.02-0.005 % in earth's crust, 0.012-0.002 % in surface rocks and 0.001-0.0001 % in vegetable and animal matter (Gregory, 2000). The average concentration of zinc in soils ranges from 50-100 $\mu\text{g/g}$ though higher values have been reported elsewhere in cases of soil contamination while the mean total zinc contents in the surface soils of different countries range from 17-125 $\mu\text{g/g}$ (Kaara, 1992). Soluble form of zinc is readily available to plants as an essential element for growth and its uptake has been reported to be linear with its concentration (Robson, 1981). Normal zinc levels in plants are in the range of 25-150 $\mu\text{g/g}$ with concentrations above 400 $\mu\text{g/g}$ being toxic (Leeper, 1982).

Zinc dust may find its way into the air from industries manufacturing zinc and enters water by leaching from contaminated soils. The WHO maximum permissible level is 15 $\mu\text{g/g}$ (WHO, 1992). Kiilu (1993) reported Zn levels ranging between 2.54-265.2 $\mu\text{g/l}$ in Kenyan lakes. This implies that the metal may be leaching and accumulating in our water bodies which may be hazardous to both aquatic and human life. Zinc is an essential and beneficial element for the growth of both plants and animal life. However, concentrations above 5 mg /l can cause bitter taste and an opalescence in alkaline waters. The presence of zinc in fresh water is reported to have toxic effects of varying intensities to aquatic organisms with acute toxic conditions of above 500 $\mu\text{g/l}$ often killing fish by damaging the gill membrane as a result of restricted blood flow through the gill capillaries (Skidmone, 1984).

2.3.2 Human and environmental effects of zinc

Zinc is present within all body cells with a normal human body containing between 1.4-2.3 g, however, daily zinc intake range from 4.6-9.3 mg/day and that 6 mg Zn /day is adequate for normal needs of pre-adolescent girls (WHO, 1996). Zinc levels between 150-6600 mg/day have been established to be toxic to man and an excess of it in the body results in reduced growth, anaemia, poor production and reduced activity of the liver and cytochrome oxidase (Widdowson, 1983). Acute poisoning leads to vomiting, dehydration, severe nausea, fever, dizziness and muscular inco-ordination (Park, 1991).

Zinc is an essential nutrient for man as it is a constituent of many metallo-enzymes and plays a vital role in the biosynthesis of nucleic acids, RNA polymerases and DNA polymerases. The healing process of tissues in the body and physiological processes, including hormone metabolism, immune responses and stabilization of ribosomes and membranes require zinc (Ferguson, 1990).

Most plant species are zinc tolerant. However, some higher aquatic and terrestrial plants are badly affected by high levels of zinc, unless they happen to be the species possessing certain increasingly well-defined, heritable characteristics that permit their survival. Toxicity of zinc in plants is observed as reduced diversity, stunted growth and reduced growth rate and affect their abundance and productivity (Bradshaw, 1985). It is therefore important that zinc levels in soils and plants be monitored on regular basis since it could be a toxic pollutant along the highways.

2.4 Copper

Copper is found in nature in many forms. Most often, it occurs in chemical combination with sulphur and oxygen. For example, copper pyrites (CuFeS_2), malachite (CuCO_3), cupriate (CuO), chalcocite (Cu_2S), atacamite (CuCl_2), chrysocolla (CuSiO_3) and purple copper ore (CuFeS_3). Copper has been utilized for its ductibility, malleability and conductivity properties since ancient times. Copper plays a vital role in all branches of engineering and science. Copper is low in the reactivity series and therefore does not corrode easily and as such it is used in production of wire for wiring electrical cables circuits and radiators (cupronickel 80 % Cu + 20 % Ni) in cars, boilers and pipes. Copper is alloyed with various metals such as aluminum, zinc, lead, nickel and manganese and used in production of duralumin (Al 95 % + Cu 4 % plus other elements) which is popular in making airplanes parts, foils and window frames in cars. Also Bronze (Cu 90 % + Sn 10 %) is well suited for making tools and machinery (Peter, 1989). This means that traces of copper metal are likely to be found along roadside highways contributing to a significant of highway pollution depending on the traffic density, hence need for Cu analysis.

2.4.1 Copper in soil, plants, air and water

Copper is widely distributed geographically and geologically since the average levels of copper in the earth's crust is about 70 $\mu\text{g/g}$. Besides, much of the copper found in the environment is from man influenced sources which tend to have greater local impact and are quite significant. Much of the Cu pollution associated with industrial and urban activities is released from point sources from which dispersal is strongly dependant on local meteorological and topographical factors as evidenced in Europe where the

concentrations of Cu in soils near urban or industrial areas showed that regions quite distant from points of emission were also affected (Loneragan, 1981).

Copper is a relatively immobile element in soils, with the result that many soil profiles show little variation of total copper concentration with depth, however, a range of 2-250 $\mu\text{g/g}$ has been reported for the total Cu contents of all soils while the range in most agricultural soils from a number of countries is from 5-100 $\mu\text{g/g}$ (Bowen, 1979). The application of sewage sludge as a source of organic fertilizer in agricultural soils introduce levels that exceed the normal amounts of copper and other metals already present in the soils leading to contamination, however, Cu in soil rarely exceeds the concentrations of 100 $\mu\text{g/g}$ (Thornton, 1979), unlike other trace elements, copper content in the soil often does not correlate with its content in plants (Mitchell, 1984).

Copper alloys with other metals such as Pb, Zn, Ni, Sn, Al, and Mn is used in the production of wires, electrical cables, pipes and boilers. The corrosion of Cu containing alloys in metal fittings may introduce amounts of Cu into the soil and plants. The copper concentration in the street dusts and soils of urban parks frequently exceed 1000 $\mu\text{g/g}$. The combustion of wood products, fossil fuels and waste incineration within urban areas may also result in higher atmospheric emission of copper together with other elements but copper concentration in household dusts has been found to range from 700-900 $\mu\text{g/g}$ (Loneragan, 1981).

Copper is an essential nutrient for plants and is needed during complete life cycle for metabolic reactions or for maintaining the cytoplasmic structure on which metabolism is dependant. Hence most plants, contain between 5-15 $\mu\text{g/g}$ while crop plants contain between 5-20 $\mu\text{g/g}$ (Robson, 1981). Moreover, in soils where high levels of Cu contamination have been concentrated in the surface horizon, deep rooted perennial plant species are rarely affected unlike shallow rooted plant species (Goyer *et al.*, 1997).

Soluble copper levels in uncontaminated fresh water range from 0.5-10 $\mu\text{g/l}$ (Ferguson, 1988) while concentrations as low as 0.05-0.025 $\mu\text{g/l}$ are lethal to some invertebrates and fish specimens within four days (Magdalena *et al.*, 2004). However, Kiilu (1993) reported a significant increase of Cu levels ranging between 0.96-78.62 $\mu\text{g/l}$ in Kenyan lakes while Kimei (1996) reported a range of 0.01-1.30 $\mu\text{g/l}$ in wells and boreholes in areas surrounding Nairobi. There is little information about copper pollution in relation to the traffic density along Kenyan highways and consequently the need for continuous copper analysis to ensure controlled disposal and accumulation in the environment.

2.4.2 Human and environmental effects of copper

Copper is an essential trace element to healthy life of many plants and animals; usually occurring as part of the prosthetic group of oxidizing enzymes and as a key component in a number of important proteins including hemocuprein and hepatocuprein (Nriagu, 1979). The dietary content of most western diets is 2-5 mg of Cu/day with the total amount of copper in a normal adult being 72 mg (Norman, 1980). Copper is not acutely toxic to man but abnormally high copper levels orally ingested are characteristic of a number of

diseases in man including anaemia, herechromatosis, cirrhosis and yellow atrophy of liver and Wilson's diseases (Patterson, 1985).

Plant species differ appreciably in their tolerance to high levels of copper in soil. Certain families of Caryophyllaceae, Labiatae and some mosses are able to tolerate high accumulations of copper and have been used by mineral exploration companies to locate copper ore bodies (Purves, 1984). Toxicity of copper in plants is generally manifested as reduced shoot vigour, stunted growth, poorly developed and discoloured root systems and leafy chlorosis. High levels of Cu in the soil kills soil organisms such as the nitrogen-fixing bacteria (Robson, 1981).

2.5 Analytical techniques for trace element determination

Several techniques for determining trace levels of elements are currently in use. These include atomic absorption spectroscopy (AAS), X-Ray Fluorescence (XRF) (Andrew *et al.*, 2001), inductively coupled plasma-mass spectroscopy (ICP-MS) (Barry *et al.*, 2000), anodic stripping voltammetry (ASV) and neutron activation analysis (NAA) (Hamilton, 1996). In the present study XRF was the preferred analytical technique of choice due to its high accuracy, precision, availability and relatively low cost while the AAS was used for data comparison.

2.5.1 X-ray fluorescence

This is a multielement analytical technique, particularly suited for analysis of environmental samples. It can also be applied to biological (plant and animal tissues) and

soil samples analysis. It is based on the principle that when a sample is bombarded with energetic X-ray, it gives rise to a secondary radiation as electrons drop into vacant positions in the inner orbitals. The emitted X-rays have energies characteristic of the particular atom. The energy (wavelength) of the emitted radiation yields a qualitative analysis of the elements while the intensity of the radiation provides a quantitative analysis with reference to a standard sample (Anil, 1989).

2.5.1.1 Theoretical principles of X-ray fluorescence (XRF)

In X-ray analysis, the atoms in the sample are bombarded with energetic primary X-rays, to produce a positive ion with a valency in a inner electron shell. The ionized atoms return to the ground state by transition of electrons from an outer shell to the inner shell. As a result, there is emission of fluorescence X-rays equal in energy to the difference in electron energy levels. The energy of this fluorescence X-ray emission is a function of the atomic number of the element and therefore a characteristic of that element. This relationship serves as the basis for the quantitative analysis by XRF. X-rays interact with the atom of the material through processes such as photoelectric absorption, incoherent scattering and coherent scattering effects (Michette *et al.*, 1993). Each interaction has a certain probability of occurring, referred to as a cross-section. The fractions of the photons that pass through the material after the interaction is given by:

$$I = I_0 e^{-\mu\rho d} \dots\dots\dots (1)$$

where

I = Intensity of the photon beam after traversing an absorbing material

I_0 = Initial intensity of the photon beam

ρ = Density of the absorbing material (g cm⁻³)

d = Thickness of material

μ = Total mass absorption coefficient (sum of the scattering coefficients and the

photoelectric absorption coefficient).

For photoelectric absorption effect, the incident photon energy is completely absorbed by the electron leading to ejection of the electron from the sub-shell. The ejected electron is called a photoelectron. The incident photon must have enough energy, $h\nu$ to overcome its binding energy in a given shell for ejection to occur, “a hole” is created in the energy level from which electron is ejected. To restore stability, the atom must rearrange its electrons in the various electron shells. When an electron is transferred from a higher level to a lower energy level, the atom loses energy by emitting a characteristic X-ray radiation (Kump, 1993).

Incoherent scattering effect involves a photon of primary energy $h\nu$ colliding with a weakly bound electron assumed to be at rest. Thus, the part of the incident photon energy is converted into the kinetic energy of the struck electron with the original direction of the photon changing. Coherent scattering occurs when the low energy photons are scattered by elements with high atomic numbers, as more tightly bound atomic electrons are involved. The mass of the atomic nucleus is much higher than that of the incident photon, hence the photons do not undergo change in energy (Leyden, 1984).

2.5.1.2 Components of an XRF system

There are various excitation sources that are used in XRF. These include ^{55}Fe and ^{109}Cd among others. Quantitative analysis is performed by exciting the samples using a ^{109}Cd radioisotope source. The preamplifier converts the burst of electrons, resulting from the

absorption of X-rays, into a voltage signal which may be conveniently transmitted to the measurement system. It also minimizes any source of noise, which may degrade the resolution of the spectrum. The voltage amplifier converts voltage signals into 0–10 V range so that pulse height analysis can be performed. It also filters off low and high frequencies in order to improve signal to noise ratio and energy resolution. The detector is a 30 mm x 30 mm x 10 mm thick Canberra Si (Li) detector located inside a crystal and having a 25 mm beryllium window entrance. The resolution of the detector is 184 eV at 5.9 KeV Mn K_{α} line. The detector and the preamplifier assembly are mounted in the cooling system at liquid nitrogen temperature of 77 K to minimize electronic noises (Canberra, 1988).

Multichannel analyzer (MCA) measures heights of amplified output pulses and converts these amplitudes into an integer number in analog-digital converter. The number of times a pulse height has been detected is accumulated in the memory (channels) address to give a distribution of pulse heights. The pulse height distribution is converted to the X-ray energy spectrum by appropriate MCA calibration. The MCA also includes a microprocessor, which is pre-programmed to perform simple data analysis operations like energy calibration, integration and subtraction of background, for various qualitative and quantitative information. The software package for use in this study is S100 Canberra. It acquires, stores and retrieves spectral data for display. Other facilities include energy calibration, which enables peak identification and identity determination. The qualitative peak identification is facilitated by a generated chart, which has corresponding energy values of K and L lines for each element (Bruch *et al.*, 2008).

The background is calculated by the analysis of X-ray spectra by Iterative Least square fitting (AXIL) program that fits a polynomial function to the actual spectra (IAEA, 1992). Net areas of the elements of interest present in the sample are calculated after spectrum deconvolution. Excitation source holder is used as a sample holder, shielding and a collimator at the same time. Figure 2.2 indicates the schematic diagram of the components of X-ray (Kinyua, 1982).

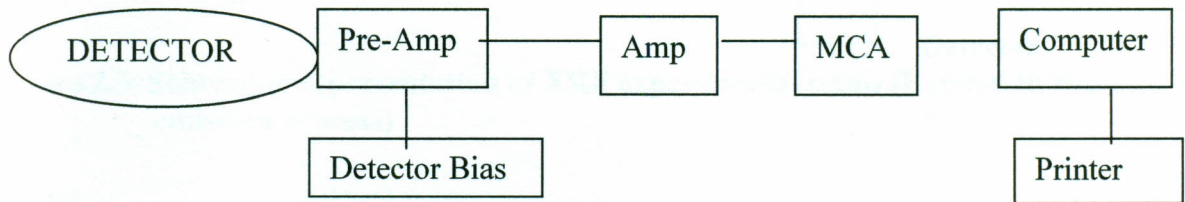


Figure 2.2 Schematic diagram of the components of X-ray

The basis of quantitative X-ray fluorescence analysis relates the measured intensity of characteristic X-rays from the analyte and their concentration. The analyte intensity and its concentration are related by an expression, which assumes a monochromatic excitation radiation on a homogenous sample;

$$I_i = G_0 \cdot K_i \cdot \varepsilon(E) \cdot (\rho d)_i \cdot \left[\frac{1 - \exp(-a \rho d)}{a \rho d} \right] \dots\dots\dots(2)$$

$$\text{and } K_i = \sigma_i^{\text{ph}}(E) \cdot (1 - 1/J_k)_i \cdot \omega_k^i \cdot f_k^{-1} \dots\dots\dots(3)$$

where, $G_0 = I_0 \cdot \Omega_1 \cdot \Omega_2$ is the geometrical constant (cps), I_0 is the intensity of primary radiation which is dependent on the activity of the excitation source, Ω_1 and Ω_2 are the solid angles of the source and the detector as seen from the sample in conformity with the geometry respectively (Kump, 1993) as indicated in Figure 2.3.

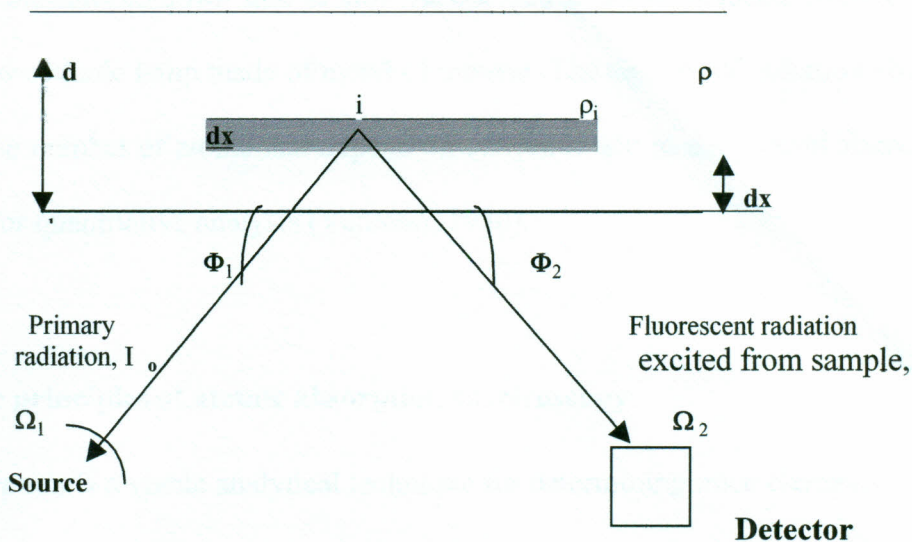


Figure 2.3 Schematic representation of XRF experimental setup (Excitation and emission process)

Where:

K_i is the relative detection efficiency,

$\sigma_i^{\text{ph}}(E)$ is the photoelectric mass absorption coefficient of element I at energy (E) .

$(1-1/J_k)_I$ is the relative probability for photoelectric effect in shell "K".

ω_k^i is the fluorescence yield for element I in shell "K".

f_k^i is the ratio of the intensity of a given K line to the intensity of the whole series.

$\varepsilon(E)_I$ is the relative efficiency of the detector for photons of energy E_i .

$(\rho d)_i$ is the mass per unit area of element I in the sample.

2.5.2 Atomic absorption spectroscopy (AAS)

The AAS is used in the quantitative analysis of various metals. The method is largely free from spectral or radiation interference because each metal has its own characteristic absorption wavelength and the source lamp is composed of the element being determined (Skoog *et al.*, 1992). The technique is based upon absorption of radiation by free atoms.

The first step is to introduce solution sample into a flame where aerosol atomization takes place. The solution is usually introduced into the atomization chamber by means of the pneumatic nebulizer, which produces a fine aerosol that is passed into the flame. The

flame breaks the sample down into atomic vapour that absorbs radiation from a source such as hollow cathode lamp made of metal of interest. The amount of radiation absorbed depends on the number of atoms that depend on concentration in the present study. AAS will be used for quantitative analysis (Vanloon, 1980).

2.5.2.1 Basic principles of atomic absorption spectroscopy

Atomic absorption is a viable analytical technique for determining trace elements because of its high specificity and relatively high sensitivity and has been used for trace elements analysis of environmental samples (Slavian, 1978). The determination of elements by AAS is based on the principle of absorption or emission of radiation by free atoms, for the excitation of ground state atom, R to R*



where h is Planck's constant and ν is the frequency of the absorption or emission of atoms associated with the process of transition of atoms from one steady state to the other. For the steady state m and n with energies E_m and E_n , respectively, absorption of light will take place when $E_n > E_m$, following the transition from m to n , while the transition n to m , results in the emission of radiation. The frequency ν_{mn} for m to n transition will be inversely proportional to the Planck's constant so that,

$$\nu_{mn} = \frac{E_n - E_m}{h} \dots\dots\dots (5)$$

Einstein's quantum theory of radiation suggests that between levels of steady states m and n , three types of transitions may take place:

- (i) emission ($n \longrightarrow m$), transition from an excited state to a lower energy state due to external radiation of the same frequency ν_{nm} .
- (ii) spontaneous emission ($n \longrightarrow m$), transmission from the excited state to a lower energy state, and
- (iii) absorption ($m \longrightarrow n$), transition from a lower energy state to a higher one due to external radiation with frequency ν_{mn} . This forms the basis of AAS.

Absorption involving ground state atoms result in the production of resonance lines characteristic of the element. However, the population of excited atoms to ground state atoms at a given temperature is governed by Boltzmann distribution (Tertian *et al.*, 1982).

$$\frac{N_n}{N_m} = \left\{ \frac{g_n}{g_m} \right\} \exp \left[\frac{E_n - E_m}{KT} \right] \dots\dots\dots(6)$$

Where;

N_n = number of atoms in excited state

N_m = number of atoms in ground state

g_n and g_m = statistical weights of excited and ground states respectively.

E_n and E_m = energies of excited and ground states respectively

$E_n - E_m$ = excitation energy

K = Boltzmann's constant $1.38 \times 10^{-23} \text{ J K}^{-1}$

T = absolute temperature

At a fixed value of g_n / g_m , the ratio N_n / N_m increases with temperature for a particular element at a particular spectral line. For an atomic gas consisting of atoms in thermal equilibrium capable of absorbing a quantum of energy $h\nu$, containing a radiation of frequency ν and intensity I_0 , passing through the atomic gas, the absorption of the incident radiation by neutral atoms is given by;

$$A = \log (I_0 / I) \dots\dots\dots(7)$$

The resulting emission I does not compensate the absorption I_0 because it is unidirectional. The absorption can be measured by classical spectrophotometric procedures. It permits the quantitative determination of the elements introduced into the atomizing source. A relation exists between I_0 and I that depends on the absorption (Slavian, 1978).

$$I = I_0 \cdot \exp - (K_n N_0 L) \dots\dots\dots(8)$$

Where;

I_0 = intensity of the incident beam

I = intensity of transmitted beam

K_n = absorption coefficient at the frequency, γ

N_0 = atomic population with a concentration of number of atoms per cm^3 in path.

L = length of sample cell.

2.5.2.2 Components of AAS

The most important components of a typical AAS are:

- (a) The spectral source which emits the radiation spectrum of the element of interest. The light source emits narrow resonance line profile with little background noise and stable and reproducible output of sufficient intensity to ensure high signal to noise ratios.
- (b) The atom cell, usually a flame furnace or graphite furnace, in which the atoms of the sample are formed by thermal dissociation. Atom cells produce atomic vapour of the metal to be determined. Commonly used atom cell atomizer for AAS is flame, although electrically heated graphite atomizers is used in significant amount of analytical work.
- (c) A monochromator for the spectral dispensation of the source radiation and an exit slit for selection of the wavelength of the analyte resonance line. Monochromator is a

wavelength selector that isolates the resonance line from the non-absorbing lines situated close to it in the spectrum as indicated in Figure 2.4. Such lines may originate from the metallic cathode or the lamp fill gas and molecular emission and background radiation that originate from flame.

- (d) A detector, normally a photo multiplier tube, to permit measurement of the radiation intensity at the resonance line. The photo multiplier having cathodes coated with photosensitive materials that amplifier optical signals received from the monochromators. The photons received strike the photosensitive material and eject electrons. Each electron produced repeats the process until an amplification factor of 10^6 or greater is achieved.
- (e) An amplifier and display unit for recording of the absorption values, where the signal is read out on an analogue or digital display. In modern instruments, read-out facilities may be handled by an inbuilt microprocessor (Skoog *et al.*, 1992).

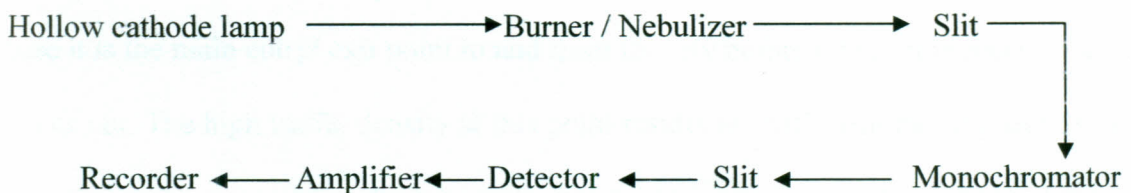


Figure 2.4 Schematic diagram of the components of AAS

Source: (Skoog *et al.*, 1992)

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Sampling sites

Samples for analysis were collected from five sites along the Thika-Nairobi highway. These sites were located at Pangani, Allsopps, Clayworks, Ruiru and Thika as indicated on a map in Appendix 6. The sites were chosen after the roundabout or a road branching off from the highway. It was hoped that these sites would have significant differences in the heavy metal concentrations because of varying traffic densities as there are other roads branching off from the highway, thus easing of the traffic concentration.

3.2 Description of the sampling sites

Site 1 – Pangani

The site is located within the outskirts area of the city center in about 3 kilometres and has a heavy traffic volume, probably the highest in all the sampling sites primarily because it is the main entry/ exit point to and from the city before other main feeder roads join in or out. The high traffic density at this point results in traffic jam moving slowly or being stationary especially during rush hours in morning and evening hours. Consequently, the highway at this point had shown signs of dilapidation in form of numerous potholes which further slowed down the traffic. This sampling site is sloppy.

Site 2 – Allsopps

This is located 7 kilometres from the City centre and 200 m after the GSU roundabout that forms the junction of the busy outer-ring road that branches from the Thika-Nairobi

highway to serve parts of Eastlands of Nairobi City. The site is located in a valley with no wind disturbances. The valley gently rises into a gradient that makes the ascending and descending of traffic slower. The traffic density in this site results in traffic jams during rush hours. Vehicles stalling in the middle of highway leading to obstruction and accidents are a common phenomenon in this site. There was evidence of pot-holed sections at the valley bed which slowed traffic in this section of the highway.

Site3 – Clayworks

It is located 14 kilometres from the town centre and 800 m after Roysambu roundabout at the junction towards Kasarani-Mwiki estates and Zimmermann-Kahawa west estates. The traffic density at this point is decreasing. This site is situated on a leveled flat ground on both sides of the highway with no visible trees resulting to strong winds blowing westward being experienced. There is fast motion of vehicles mainly because of the flatness of this section. However, the site does experience occasional traffic jams. There is evidence of Clay mining activities for brick making on the eastern side of the highway.

Site 4 - Ruiru

The site is situated about 20 kilometres from Nairobi City centre and 500 m after the junction branching towards Ruiru Township. It is a relatively raised, wide leveled area on both sides of the highway with no trees or buildings barriers on sight. However, violent winds blowing from east to west are experienced. There is fast motion of traffic.

Site 5 – Thika

This site is located 40 kilometres from Nairobi City centre and about 100 m just after the junction towards Thika town on the highway. It is a flat leveled area on both sides of the highway with some sparsely distributed trees and bushes lined along the site that act as a barrier to winds blowing from east to west. The traffic movement is fast since this section is smooth.

3.3 Sampling design

At each sampling site, samples were collected systematically across the dual-carriage Thika-Nairobi highway's transect. This meant collecting samples on the western, centre and the eastern side of the dual carriage highway were collected to provide a range in the composition of the samples representative of plants and soil. The centre sampling involved sampling the centre of the reserve zone between the two highways while at the same time, soils were sampled at 5, 20 and 80 m from the highway on both sides as indicated in Appendix 7. Plants' stems and leaves were sampled at centre as well as at the same distances comprising of 5, 20 and 80 meters away from the highway. Similarly, soils were sampled at the same distances from the highway but at different soil depth of 0-10, 10-20 and 20-30 cm. Soil depth sampling entailed making a cross section soil cut of soil slice from 0 to 10 cm. The same technique of depth sampling was carried at layers, 10-20 and 20-30 cm. A soil trowel and a tape measure were used for soil sampling. After sampling, the samples were placed in plastic containers and sealed to avoid contamination and taken to the laboratory for analysis. Sampling was done during the dry months of September-October 2004 and January-March 2005 as well as during the wet

months of December 2004 and April-May 2005 from the five sampling sites. A total of 368 samples were collected for analysis.

3.4 Cleaning of apparatus

All glassware used in this study were thoroughly washed with chromic acid and detergents, rinsed several times with distilled water then soaked in 1:1 nitric acid solution and finally rinsed with distilled de-ionized water, followed by oven drying at 80° C.

3.5 Sample treatment for XRF

The soil samples were first weighed and then oven dried at 85° C for 24 hours to remove the moisture content and then ground to fine particles sizes of less than 50 µm using a mortar and pestle. The plant samples were also oven dried at 70° C for 48 hours and later crushed and ground in a wily mill and made into fine particle sizes of less than 50 µm using a mortar and pestle. The ground samples for soils and plants were later pelletized using a 2.5 cm diameter die at an applied pressure of 10 tons/ inch² in a hydraulic press. Pellets of mass 0.05-0.08 g/cm² were prepared and ready for XRF analysis (Burke *et al*, 2008). For each sample, three replicates were prepared for analysis.

3.6 XRF samples analysis

In this study, the ¹⁰⁹Cd annular radioactive excitation source was used with an activity of 25 mCi and half-life of 453 days with photo-emission of 22 kev. The X-ray fluorescence spectrometer consisted of a sample holder and a ¹⁰⁹Cd excitation radiation source which produced a primary beam of energetic radiation which bombarded the

sample mounted as a thin layer, sample holder. A Si (Li) detector counted the resultant characteristic, secondary fluorescent monochromatic X-ray beam emitted radiation (Andrzej *et al.*, 2008).

The soil samples were irradiated for 2000 seconds using ^{109}Cd source and 1500 seconds for plants. The XRF experimental set up consisted of ^{109}Cd excitation source and Si (Li) detector with an area of 30 mm^2 and 5.9 keV. An amplifier Canberra joined to a high voltage bias supply-Type 459 together with a pre-amplifier Canberra model-1008. A dewar cryostat with coolant-liquid nitrogen regulated the high excessive heat generated while a computer based Multi Channel Analyzer (MCA) card (S-100, Canberra) was used for data acquisition and storage. Deconvolution and analyses of the spectra were performed using Analysis of X-ray spectra by Interactive Least squares fitting (AXIL) and Quantitative Analysis of Environmental Samples (QAES) software (Bruch *et al.*, 2008). The XRF instrument detection limits were $5.0\text{ }\mu\text{g/g}$ Pb, $4.3\text{ }\mu\text{g/g}$ Zn and $5.6\text{ }\mu\text{g/g}$ Cu. The WHO (2006) recommended tolerable levels for Pb, Zn and Cu are $70\text{ }\mu\text{g/g}$, $150\text{ }\mu\text{g/g}$ and $100\text{ }\mu\text{g/g}$ in normal soils while in plants, they are $10\text{ }\mu\text{g/g}$, $150\text{ }\mu\text{g/g}$ and $20\text{ }\mu\text{g/g}$ respectively.

3.7 Samples treatment for AAS

3.7.1 Plants

The pasture grass (*Typha elephantina*) and napier grass (*Pennisetum purpureum*) stems and leaves samples were dried at 70°C for 48 hours. These plant materials were crushed and ground in a wily mill using a 40-mesh delivery tube before being weighed. Then the

samples were stored in appropriate vials or plastic bags before being transferred into appropriate digestion flasks ready for acid digestion. Exactly 1.0 g of the plant material was weighed into 50 ml beaker or flask. Concentrated nitric acid and 70 % perchloric acid in the ratio of 2:1 were used. A 10 ml aliquot of concentrated nitric acid was added to the sample first and digested for 10 minutes at 110° C until brown fumes were produced. The digest was allowed cool before adding 5 ml of perchloric acid to complete the digestion. Further digestion at 110° C was carried out until white vapours of perchloric acid were liberated. The sample solution was finally cooled and filtered using whatman number 42 filter paper into 50 ml volumetric flask and volume made to the mark with distilled de-ionized water for AAS analysis (Lawrence, 1997).

3.7.2 Soil

Soils samples obtained from various sites were oven dried for 8 hours at 80° C and then crushed into fine powder and sieved to remove the coarse material. Further drying was done in the oven overnight at 80° C, homogenized by grinding and sieving before being stored in dry polyethylene bags awaiting acid digestion. Exactly 1.0 g of soil sample material was then weighed and put in appropriate digestion flasks. A 15 ml aliquot of concentrated nitric acid was added and digested at 110° C until brown fumes appeared. After cooling, 10 ml of 70 % perchloric acid was added and digestion continued until white fumes were liberated. The sample solution was then filtered into 50 ml volumetric flask and volume made to the mark distilled de-ionized water followed by analysis using AAS (Mitchell, 1984).

3.8 The AAS samples analysis

Digested plant and soil samples together with blanks prepared in the same way were analyzed. In order to account for the background effects from the acids and to correct for changes resulting from the digestion procedure, 6 % nitric acid was employed in the preparation of standards and the sample solutions. The same was also used to calibrate the instrument before introducing the samples into the flame for analysis. Standard solutions were run under the same conditions and calibration plots drawn so as to determine Pb, Zn and Cu concentrations in the samples. Each sample was analyzed in triplicates and the mean concentration determined. Standard solutions, samples and blank were analyzed using atomic absorption spectrophotometer model AA 680. Table 3.0 indicates the AAS operating conditions.

Table 3.0 The AAS instrument operating conditions

Operating parameters	Pb	Zn	Cu
Wavelength (nm)	217	313	324.7
Sensitivity ($\mu\text{g/g}$)	0.015	0.01	0.04
Detection limit ($\mu\text{g/g}$)	0.02	0.003	0.005
Flame	Air/acetylene		

3.9 Data analysis

The data was analyzed using t – tests by procedures of the Standard Statistical Package for Social Sciences (SPSS) to test whether significant differences between the means of various heavy metal samples (Pb, Zn and Cu) existed or not (Miller, 1988).

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

4.1 Introduction

The results of the analyses of the soil and plants samples that were collected during the dry and the wet seasons in the period from September of the year 2004 to May of the year 2005 from five different sites located along the Thika-Nairobi highway are presented in this chapter. These sites were located at Pangani, Allsopps, Clayworks, Ruiru and Thika.

The soil and plants samples were analyzed for Pb, Zn and Cu based on three parameters: along the highway, across the highway and in depth depth for the five sampling sites. Samples from each site were collected and analyzed in triplicate. The analytical data for the five sampling sites over the period of study are summarized in Tables 4.1 to 4.13. Graphical representations of mean levels are shown in Figures 4.1 to 4.9.

4.2 Levels of heavy metals in topsoil along Thika-Nairobi highway

The mean levels of Pb, Zn and Cu in this section were obtained as a result of obtaining the average mean levels of all the topsoil (0-10 cm) on western, centre and western sides at the sampling points (centre, 5, 20 and 80 m) for each of the sampling site, from Pangani upto Thika.

4.2.1 Levels of Pb in topsoil along Thika-Nairobi highway

The mean Pb levels of the topsoil (up to 10 cm below surface) ranged from 83.2 to 208.1 $\mu\text{g/g}$ during the dry season and 52.5 to 151.8 $\mu\text{g/g}$ during the wet season along the Thika-Nairobi highway as indicated in Table 4.1. The mean Pb in the topsoil concentration at

Pangani site during the dry season period was recorded as $208.1 \pm 43.5 \mu\text{g/g}$. Lesser amounts were recorded at Allsopps, Clayworks, Ruiru and Thika. This trend of Pb levels decreasing was probably so due to lower traffic density as the distance away from the Pangani sampling site increased towards Thika. The study revealed buildup of Pb levels during the dry season, which was attributed to the long dry spells, experienced during the start of the study in the month of September of year 2004 which had persisted since July of year 2004, thus providing an enabling environment for Pb accumulation.

Table 4.1 Mean values of Pb in the topsoil during dry and wet seasons as determined by XRF [$\mu\text{g/g} \pm \text{S.D}$, n =6] along the Thika-Nairobi highway

Sampling site	Dry season	Wet season
Pangani	208.1 ± 43.5	151.8 ± 19.9
Allsopps	172.4 ± 28.8	127.9 ± 15.6
Clayworks	155.1 ± 20.8	117.2 ± 15.5
Ruiru	98.3 ± 6.5	62.8 ± 8.1
Thika	83.2 ± 7.2	52.5 ± 4.3

However, a gradual decrease in Pb mean contents in the topsoil during the wet season were recorded throughout all the sampling sites. The study revealed that, some $151.8 \pm 19.9 \mu\text{g/g}$ were detected at Pangani down to $52.5 \pm 4.3 \mu\text{g/g}$ at Thika. The mean Pb levels were generally lower during the wet season than during the dry season. This could be attributed to the washing off the Pb from topsoil by rainwater and carried away as storm water and surface runoff during wet seasons.

The Pangani site registered the highest concentration of Pb both during the dry and wet seasons as shown in Figure 4.1. This could be due to the fact that this site was within

outskirts of the city centre and had a high traffic volume primarily because it was the main entry or exit point to the city before other feeder roads join in or out. The high traffic density at this point resulted in traffic jams, which at times remained almost stationary especially during morning and evening rush hours.

The trend portrayed in Figure 4.1 on the levels of Pb during dry and wet seasons was as a result of the traffic density decreasing as the distance from the City centre increased towards Thika which recorded the lowest Pb mean concentrations in topsoil during the dry and wet seasons. The Pb levels revealed that the traffic volume decreased gradually upto Clayworks beyond which, the levels seemed to level between Ruiru to Thika.

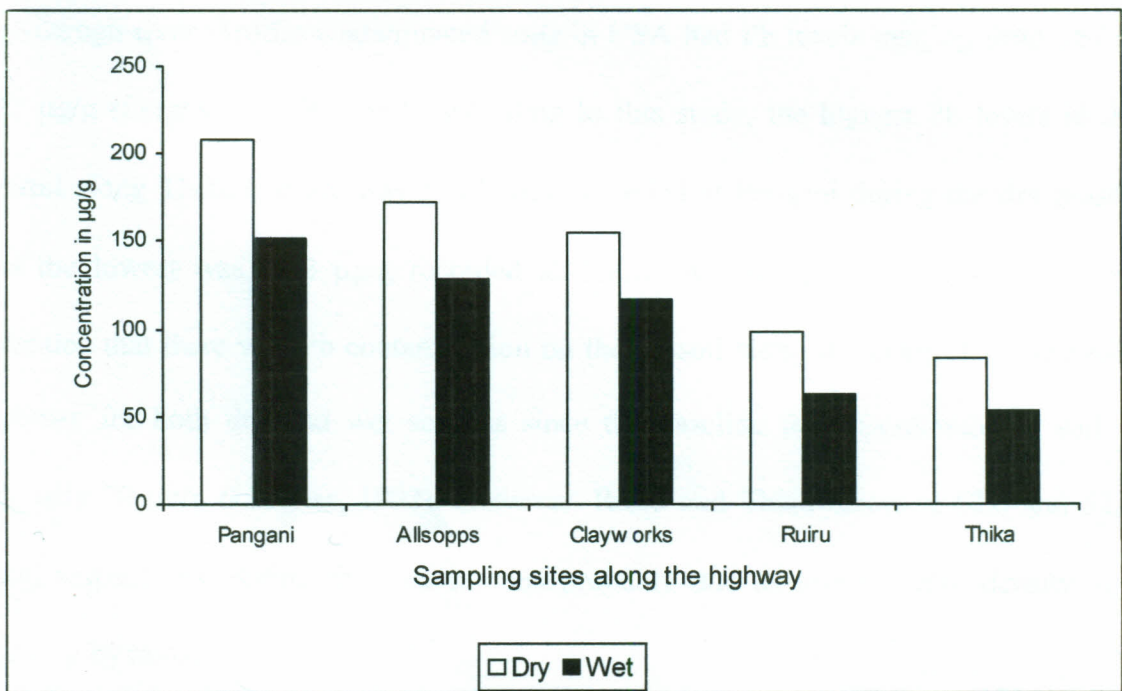


Figure 4.1 Variation of mean levels of Pb in the topsoil during the dry and wet seasons along Thika-Nairobi highway

Statistically, there was a significance difference in the mean Pb levels between the dry and the wet seasons in topsoil from Pangani to Thika sites ($t = 6.2666$, $d.f = 8$, at 95 %

confidence). This implied that rain pollutants wash of contributed to the difference. However, there was no significant difference in the mean Pb values for topsoil obtained between Pangani to Clayworks sites for both seasons ($t = 3.9819$ and 3.9282 , for dry and wet seasons respectively, $d.f = 1$, at 95 % confidence level).

The Pb values obtained compared well with those reported from other studies, for example, the Pb levels ranging from 45.4 to 263.8 $\mu\text{g/g}$ were reported in soils from areas within and around Nairobi (Kaara, 1992), while Oyaro (2002) reported soil Pb levels ranging from 6.6 to 395.1 $\mu\text{g/g}$ with a mean of $128.5 \pm 13.3 \mu\text{g/g}$ in Nairobi province and its environs. He reported 117.9 $\mu\text{g/g}$ at Ngara roundabout, ND at Juja town and 53.0 $\mu\text{g/g}$ at Ndarugu river. Traffic contaminated soils in USA had Pb levels ranging from 164 to 522 $\mu\text{g/g}$ (Ferguson, 1990) while according to this study, the highest Pb levels in the topsoil along Thika-Nairobi was 208.1 $\mu\text{g/g}$ recorded at Pangani during the dry season and the lowest was 83.2 $\mu\text{g/g}$ recorded at Thika site during the same season. This indicated that there was Pb contamination on the topsoil along the entire Thika-Nairobi highway for both dry and wet seasons since the baseline for uncontaminated soil is normally 70 $\mu\text{g/g}$ (Laughler, 1992). However, Ruiru and Thika recorded 62.8 and 52.5 $\mu\text{g/g}$, respectively during the wet seasons probably due to lower traffic density and leaching by rains.

4.2.2 Levels of Zn in topsoil along Thika-Nairobi highway

The mean Zn levels along the Thika-Nairobi for the topsoil analyzed were found to be within the range of 94.4 to 267.2 $\mu\text{g/g}$ during the dry season as indicated in Table 4.2.

The Zn values during the wet season ranged from 57.0 to 212.6 $\mu\text{g/g}$. The highest mean level was recorded at Pangani site for both the dry and wet seasons, probably because the effect of high traffic volume ascending and descending the Pangani sampling site could have led to a lot of tear and wear of motor vehicles rubber tyres and brake linings leading to a build up of Zn alongside the Thika-Nairobi highway. According to Huntzicker (1985), motor vehicle related particulates caused by tyre wear and brake wear accounted for 37 % and 28.5 %, respectively, while exhaust emissions vary widely with age, size and condition of vehicle which consisted of 54 % of other metallic substances such as Zn, Cu and Cd. Motor vehicles body fittings made of Zn could be other main sources of high levels of Zn in this site.

Table 4.2 Mean values of Zn in topsoil during the dry and wet seasons as determined by XRF [$\mu\text{g/g} \pm \text{S.D}$, n =6] along Thika-Nairobi highway

Sampling site	Dry season	Wet season
Pangani	267.2 \pm 37.6	212.6 \pm 24.1
Allsopps	238.8 \pm 29.2	178.2 \pm 20.4
Clayworks	187.1 \pm 17.7	141.4 \pm 10.3
Ruiru	101.9 \pm 8.0	63.3 \pm 4.2
Thika	94.4 \pm 11.6	57.5 \pm 4.7

The mean Zn concentrations along the highway reported in this study decreased during both dry and wet seasons as the traffic volume reduced from Pangani to Thika. Zinc levels reduced from 212.6 \pm 24.1 $\mu\text{g/g}$ at Pangani down to 57.5 \pm 4.7 $\mu\text{g/g}$ at Thika during the wet period. This could be due to the wash off of the Zn by rainwater and carried away as storm water and surface runoff during the wet season. A sharp decrease in Zn levels was noted at Ruiru and Thika sites during dry and wet seasons. This could be due to the traffic volume decreasing as the distance from the City increased and

remaining relatively unchanged at Ruiru to Thika. The Zn concentration trend along the Thika-Nairobi highway is shown in Figure 4.2.

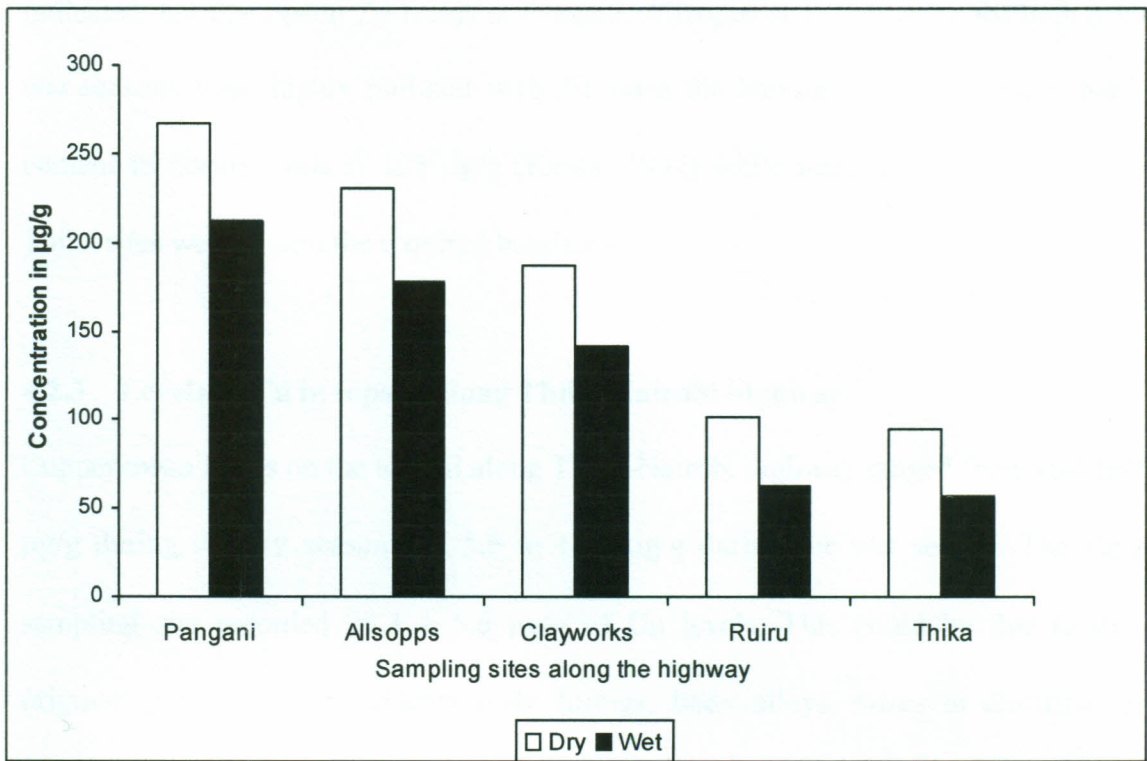


Figure 4.2 Variation of mean Zn levels in the topsoil during the dry and wet seasons along Thika-Nairobi highway

There was a significant difference in the mean Zn levels between the dry and the wet seasons in topsoil from Pangani to Thika sites ($t = 6.2515$, $d.f = 8$, at 95 % confidence), indicating that the low levels in Zn along the highway during the wet season could probably be due to washing away by surface runoff during rainy seasons.

The Zn levels cited in studies of other topsoils on most soils in the world ranged from 10-300 µg/g (Leeper, 1982) while the average concentration of Zn in soils range between 50-100 µg/g (Kaara, 1992). Zinc in sewage sludge topsoils ranged from 700-3000 µg/g (Leeper, 1982). Mitei (1996) reported 106.9 µg/g of Zn levels in topsoil at Kiserian and

243.4 $\mu\text{g/g}$ at Limuru while Oyaro (2002) reported 270.0 $\mu\text{g/g}$ at Ngara roundabout, 20.6 $\mu\text{g/g}$ at Juja and 87.8 $\mu\text{g/g}$ at Ndarugu river. The mean Zn values obtained in this study indicated that the topsoil Zn levels at Pangani, Allsopps and Clayworks for both dry and wet seasons were highly polluted with Zn since the baseline levels for mean total Zn content in normal soils is 125 $\mu\text{g/g}$ (Kaara, 1992) while mean Zn levels at Ruiru and Thika sites were within the required baselines.

4.2.3 Levels of Cu in topsoil along Thika-Nairobi highway

Copper mean levels on the topsoil along Thika-Nairobi highway ranged from 10.4 to 25.3 $\mu\text{g/g}$ during the dry season and 5.6 to 14.7 $\mu\text{g/g}$ during the wet season. The Pangani sampling site recorded 25.3 ± 5.6 $\mu\text{g/g}$ of Cu levels. This could be due to the Cu originating from motor vehicles body fittings, body alloys, wires in electrical cable circuits and motor car radiators. The other subsequent sites recorded lower mean Cu levels probably due to decrease in traffic volume. Allsopps registered mean levels of 23.4 ± 4.4 $\mu\text{g/g}$ and 14.1 ± 5.2 while Thika recorded 10.4 ± 1.9 and 5.6 ± 2.6 $\mu\text{g/g}$ during the dry and wet seasons, respectively as indicated in Table 4.3.

Table 4.3 Mean values of Cu in topsoil during the dry and wet seasons as determined by XRF [$\mu\text{g/g} \pm \text{S.D}$, n =6] along Thika-Nairobi highway

Sampling site	Dry season	Wet season
Pangani	25.3 ± 5.6	14.7 ± 3.0
Allsopps	23.4 ± 4.4	14.1 ± 5.2
Clayworks	17.9 ± 8.9	10.8 ± 3.4
Ruiru	12.3 ± 3.9	6.7 ± 1.5
Thika	10.4 ± 1.9	5.6 ± 2.6

The lower levels of Cu during the wet season showed that considerable amounts of the Cu was washed away from topsoil by rainwater and dispersed by storm water and surface runoff. The Cu values for both seasons indicated a gradual decrease from Pangani to Thika, probably due to decreasing traffic volume. The trend arising from the Cu concentrations indicated its lower distribution along the route than Pb and Zn (Figure 4.3).

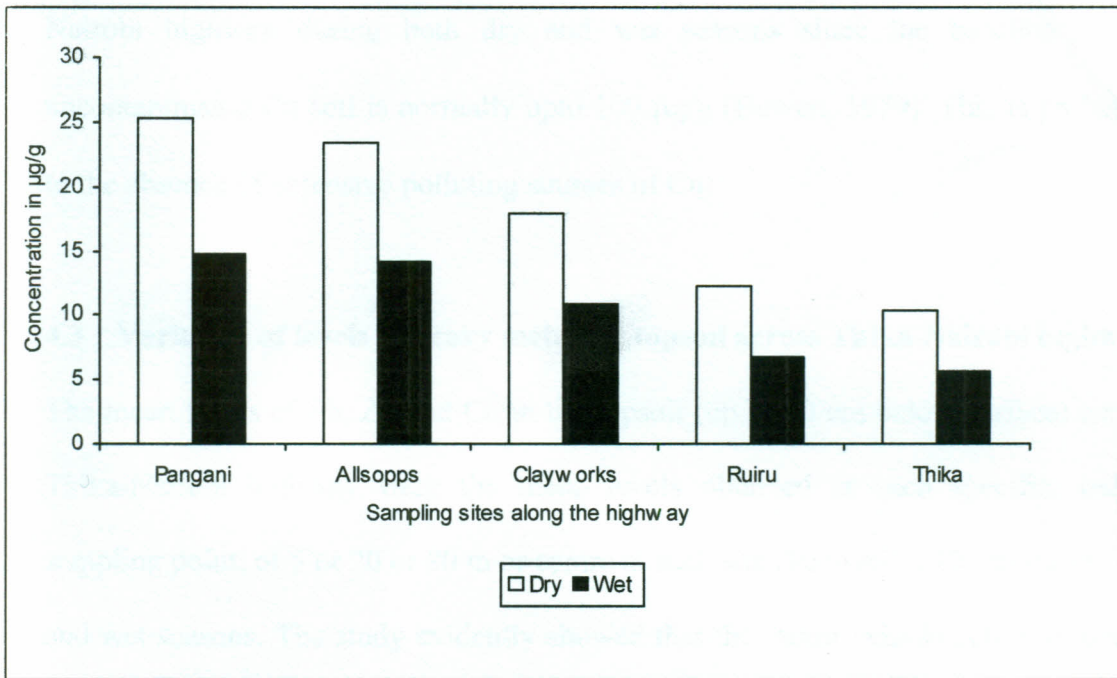


Figure 4.3 Mean Cu levels in the topsoil during the dry and wet seasons along the Thika-Nairobi highway

The study found out that a significant difference existed in the mean Cu values between the dry and the wet seasons in topsoil from Pangani to Thika sites ($t = 5.9057$, $d.f = 8$, at 95 % confidence), indicating that the traffic activities along the highway during the wet season were lower and could have caused the difference.

The Cu values obtained in this study compared with those reported in soils within Nairobi which ranged between 6.0-238.8 $\mu\text{g/g}$. Ngara roundabout recorded 36.5 $\mu\text{g/g}$ while 9.0 $\mu\text{g/g}$ was recorded at Juja town and 87.8 $\mu\text{g/g}$ at Ndarugu river (Oyaro, 2002). In this study the highest Cu levels of 25.3 $\mu\text{g/g}$ in the topsoil was recorded at Pangani sampling site during dry season while the lowest Cu level was 5.6 $\mu\text{g/g}$ recorded during the wet season at Thika site. This indicated that there was lower Cu levels along the entire Thika-Nairobi highway during both dry and wet seasons since the baseline levels for uncontaminated Cu soil is normally upto 100 $\mu\text{g/g}$ (Bowen, 1979). This is probably due to the absence of extensive polluting sources of Cu.

4.3 Variation of levels of heavy metals in topsoil across Thika-Nairobi highway

The mean levels of Pb, Zn and Cu in the topsoil (up to 10 cm below surface) across the Thika-Nairobi highway were the mean levels obtained at each specific, individual sampling point, of 5 or 20 or 80 m or centre at each site (Pangani to Thika) during the dry and wet seasons. The study evidently showed that the motor vehicle activities decreased as the distance from Pangani to Thika increased hence influencing the deposition of these heavy metals across the highway. Also, their mean concentrations decreased as the distance from the highway increased as discussed in sections 4.3.1, 4.3.2 and 4.3.3.

4.3.1 Variation of levels of Pb in topsoil across Thika-Nairobi highway

The mean Pb values in the topsoil across the Thika-Nairobi highway ranged from 26.2 to 343.5 $\mu\text{g/g}$ during the dry season and 14.5 to 250.3 $\mu\text{g/g}$ during the wet season as represented in Table 4.4. There was a significant difference in the mean Pb levels

between the dry and the wet seasons in topsoil across Pangani ($t = 5.4459$, $d.f = 12$, at 95 % confidence), Allsopps ($t = 4.1170$, $d.f = 12$, at 95 % confidence), Clayworks ($t = 5.5484$, $d.f = 12$, at 95 % confidence), Ruiru ($t = 5.3365$, $d.f = 12$, at 95 % confidence) and Thika ($t = 5.5996$, $d.f = 12$, at 95 % confidence) sampling sites. This meant that the heavy traffic activities could have influenced significantly the Pb levels in the topsoil across the highway during both seasons. This indicated that the higher Pb accumulation across the highway during dry season was probably due to the long dry spell that was experienced before the start of this study.

Lower amounts of Pb on the topsoil were recorded on the eastern side than on western side during both seasons in all the sites. The Pb levels on the topsoil across the highway ranged between 26.2 to 270.9 $\mu\text{g/g}$ and 14.5 to 199.3 $\mu\text{g/g}$ on the eastern side during dry and wet seasons, respectively. Similarly, average Pb levels ranged from 43.0 to 331.2 $\mu\text{g/g}$ and 22.1 to 237.2 $\mu\text{g/g}$ on western side during dry and wet seasons respectively as the distance from the highway increased. The centre and 5 m sites were more polluted than 80 m site as indicated in Figure 4.4. This could be attributed to the fact that the two sampling sites were located closest to the activities of the highway and since motor vehicles were the sources of the Pb pollutant, it therefore implied that those sites were exposed to higher levels of pollutants than the 80 m. The nearer the sites to the highway, the higher the rate of contamination. Also, the 5 m was observed to be mostly associated with motor vehicles activities such as overtaking during jams and packing vehicles that had stalled to avoid obstruction on the highway.

Table 4.4 Mean levels of Pb in the topsoil during the dry and wet seasons across the Thika-Nairobi highway as determined by XRF [$\mu\text{g/g} \pm \text{S.D.}$, n =6]

Site	Sampling distance	Eastern side		Centre		Western side	
		Dry season	Wet season	Dry season	Wet season	Dry season	Wet season
Pangani	Centre			343.5 \pm 49.6	250.3 \pm 36.0		
	5 m	270.9 \pm 48.4	199.3 \pm 27.2			331.2 \pm 50.9	237.2 \pm 23.4
	20 m	210.3 \pm 31.3	151.1 \pm 16.4			241.1 \pm 12.8	197.5 \pm 31.2
	80 m	49.2 \pm 12.4	32.7 \pm 3.1			61.5 \pm 13.8	39.4 \pm 7.5
Allsopps	Centre			230.4 \pm 27.9	150.8 \pm 18.6		
	5 m	249.2 \pm 24.5	186.3 \pm 19.1			265.9 \pm 22.3	200.8 \pm 16.1
	20 m	171.2 \pm 14.2	138.8 \pm 10.6			180.1 \pm 20.3	147.3 \pm 12.4
	80 m	50.3 \pm 9.5	29.8 \pm 6.4			53.5 \pm 7.7	35.2 \pm 9.7
Clayworks	Centre			260.9 \pm 18.1	213.2 \pm 15.2		
	5 m	198.1 \pm 22.2	157.6 \pm 10.9			246.2 \pm 30.6	197.5 \pm 14.8
	20 m	132.6 \pm 6.7	88.7 \pm 4.3			148.5 \pm 18.7	102.3 \pm 13.9
	80 m	41.4 \pm 5.0	22.5 \pm 2.1			58.3 \pm 7.4	38.7 \pm 3.0
Ruiru	Centre			147.1 \pm 12.1	99.3 \pm 8.3		
	5 m	119.0 \pm 6.4	88.8 \pm 4.8			133.3 \pm 9.3	94.5 \pm 8.0
	20 m	84.6 \pm 7.2	55.1 \pm 3.5			114.9 \pm 7.8	62.7 \pm 4.2
	80 m	34.9 \pm 4.1	19.8 \pm 2.2			54.0 \pm 3.7	25.3 \pm 2.9
Thika	Centre			112.5 \pm 12.1	84.4 \pm 6.7		
	5 m	105.8 \pm 9.8	72.2 \pm 5.9			110.8 \pm 7.8	79.1 \pm 6.0
	20 m	75.4 \pm 4.5	33.8 \pm 3.3			86.4 \pm 5.2	55.0 \pm 3.9
	80 m	26.2 \pm 2.4	14.5 \pm 1.8			43.0 \pm 3.0	22.1 \pm 1.5

The highest mean amount of Pb on the topsoil across the highway was $343.5 \pm 49.6 \mu\text{g/g}$, which was recorded at Pangani in the centre during the dry period. This reflected the pollution impact on this site probably due to the convergence of Pb pollutants from both sides of the highway because their closer interaction that led to its higher deposition. Similarly, Pangani also recorded the highest Pb concentrations on the western side during both dry and wet seasons in all the sampling sites. They ranged from 32.7 to 270.9 $\mu\text{g/g}$ on eastern side and 39.4 to 331.2 $\mu\text{g/g}$ on western side. This was attributed to the fact that this hilly raised site experienced the highest traffic density coupled with mild wind disturbances despite it being lined with some buildings on the eastern side that prevented widespread of motor vehicle pollutants in eastern direction, thus leading to higher build up of pollutants on western side.

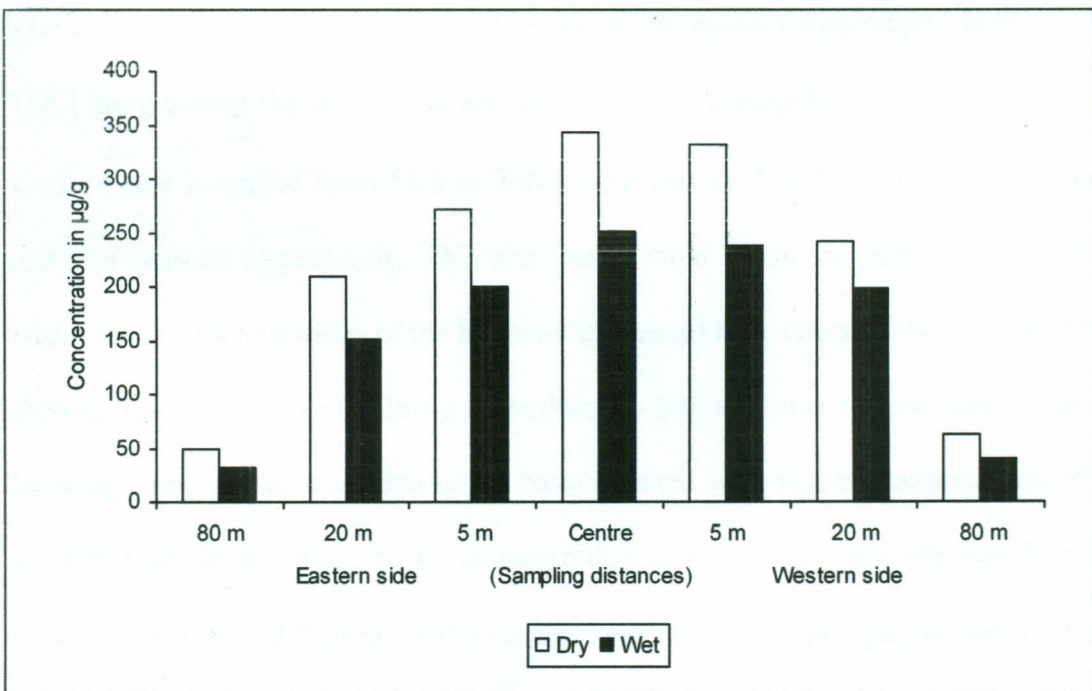


Figure 4.4 Mean levels of Pb in the topsoil during the dry and wet seasons at Pangani site

The mean Pb values on the eastern side across Allsopps sampling site ranged from 50.3 to 249.2 $\mu\text{g/g}$ during the dry season and 29.8 to 186.3 $\mu\text{g/g}$ during the wet season whereas on the western side, the mean values ranged between 53.5 to 265.9 $\mu\text{g/g}$ during dry season and 35.2 to 200.8 $\mu\text{g/g}$ during wet season. The highest mean concentration of Pb in the topsoil in this site was $265.9 \pm 22.3 \mu\text{g/g}$. This pattern of Pb deposition was attributed to heavily trafficked site mostly during morning and evening jams. The site was situated on a potholed section in a depressed valley that had little wind disturbances. The trend of Pb deposition levels at Allsopps was similar to that at Pangani. However, the centre at Allsopps was found to contain lower levels of Pb probably due to bigger portion occupied by the centre thus resulting in fewer convergences of the Pb pollutants from eastern and western sides of this site.

The amounts of Pb deposited at Clayworks on the eastern side ranged between 41.4 to 198.1 $\mu\text{g/g}$ during the dry season and 22.5 to 157.6 during the wet season while on the western side it ranged from 58.3 to 246.2 $\mu\text{g/g}$ and 38.7 to 197.5 $\mu\text{g/g}$ during both dry and wet seasons respectively. This site was located on an inclined ground punctuated with potholes on both sides of the highway that could have checked the flow of the traffic thereby leading to more build up of pollutants. The site also experienced strong winds blowing from east to west that could have resulted with higher accumulation of Pb on western side. In addition, the Pb concentration at Ruiru sampling site was found to lie between 34.9 to 119.0 $\mu\text{g/g}$ on the eastern side during the dry season and 19.8 to 88.8 $\mu\text{g/g}$ during wet season. Similarly, 54.0 to 133.3 $\mu\text{g/g}$ was deposited during dry season and a range of between 25.3 to 94.5 deposited during wet season on the western side.

This could be attributed to the fact that Ruiru sampling site had lower traffic activities besides having no trees or buildings barrier along the highway, thus this site experienced violent winds blowing from east to west resulting in more Pb pollutants being blown to the western side. The average Pb levels obtained on the topsoil at Thika sampling site registered a range of 26.2 to 105.8 $\mu\text{g/g}$ during the dry season and 14.5 to 72.2 $\mu\text{g/g}$ during the wet season on the eastern side while a range of between 43.0 to 110.8 $\mu\text{g/g}$ was deposited during dry season and 22.1 to 79.1 $\mu\text{g/g}$ deposited during the wet season on the western side. Similar deposition of Pb levels on both sides could be due to the location of this site on a potholed, leveled ground with some trees and bushes lined along both sides of the highway checked the spread of Pb pollutants.

A gradual decrease in the mean Pb contents in the topsoil during the wet season was registered across the highway in all the sites. The mean Pb levels ranged from 14.5 to 199.3 $\mu\text{g/g}$ on the eastern side and from 22.1 to 237.2 $\mu\text{g/g}$ on the western side as the distance decreased from 80 to 5 m. The rainwater and surface runoff were probably responsible for Pb dispersal during the wet season thus leading to the lower levels being recorded in all sites studied. The pattern of Pb variation at Thika and Ruiru showed similar trends to that of Pangani and Clayworks sampling sites though the amounts deposited were lower.

The Pb values obtained from other studies done in most topsoil were 200-220 $\mu\text{g/g}$ for 10 m, 100-160 $\mu\text{g/g}$ for 30 m and 60-80 $\mu\text{g/g}$ for 100 m from world trafficked highways in USA (Harrison, 1984). The highest Pb level in this study was 343.5 $\mu\text{g/g}$ recorded in the

topsoil at Pangani central site during the dry season while the lowest 14.5 $\mu\text{g/g}$ of Pb level was recorded during the wet season at 80 m on the eastern side in Thika. This indicated that there was Pb contamination across the Thika-Nairobi highway for both dry and wet seasons at the centre, 5 and 20 m in all sampling sites since the baseline for uncontaminated soil is normally upto 70 $\mu\text{g/g}$ (Laugher, 1992).

4.3.2 Variation of Zn in topsoil across Thika-Nairobi highway

The mean Zn levels on the topsoil across the Thika-Nairobi highway ranged from 36.8 to 376.9 $\mu\text{g/g}$ during the dry season and 21.5 to 300.8 $\mu\text{g/g}$ during the wet season as presented in Table 4.5. The statistical calculations indicated that there was a significant difference in the mean Zn levels between the dry and the wet seasons on topsoil across Pangani ($t = 5.6671$, $d.f = 12$, at 95 % confidence), Allsopps ($t = 6.2771$, $d.f = 12$, at 95 % confidence), Clayworks ($t = 7.4506$, $d.f = 12$, at 95 % confidence), Ruiru ($t = 5.0734$, $d.f = 12$, at 95 % confidence) and Thika ($t = 4.7439$, $d.f = 12$, at 95 % confidence) sampling sites. This implied that washing away by surface runoff during wet season could have caused fewer Zn levels in the topsoil. Generally the mean values for Zn during the dry season were higher in all the sites across the highway than during the wet season. The mean Zn levels on the topsoil during dry and wet seasons decreased on both sides of the highway as the distance from 5 m increased to 80 m. However, the western side topsoil was found to have been more contaminated with Zn than the eastern side. This is because the average Zn levels on eastern side ranged from 36.8 to 339.9 $\mu\text{g/g}$ while the western side ranged from 53.8 to 366.7 $\mu\text{g/g}$ at the 5 to 80 m during the dry

Table 4.5 Mean values of Zn in topsoil during the dry and wet seasons across the Thika-Nairobi highway as determined by XRF [$\mu\text{g/g} \pm \text{S.D.}$, n =6]

Site	Sampling distance	Eastern side		Centre		Western side	
		Dry season	Wet season	Dry season	Wet season	Dry season	Wet season
Pangani	Centre			376.9 \pm 41.5	300.8 \pm 36.2		
	5 m	339.9 \pm 32.7	265.3 \pm 15.3			366.7 \pm 34.9	299.7 \pm 24.8
	20 m	268.1 \pm 22.7	214.0 \pm 18.0			303.6 \pm 26.2	270.4 \pm 16.5
	80 m	99.1 \pm 16.3	58.6 \pm 6.8			116.2 \pm 15.0	79.1 \pm 11.0
Allsopps	Centre			299.1 \pm 28.5	252.8 \pm 23.0		
	5 m	306.8 \pm 21.9	259.1 \pm 15.6			313.3 \pm 31.1	268.6 \pm 22.7
	20 m	252.3 \pm 20.7	183.2 \pm 11.2			265.6 \pm 17.4	187.9 \pm 14.8
	80 m	78.1 \pm 7.5	43.5 \pm 3.7			100.1 \pm 7.1	55.8 \pm 6.2
Clayworks	Centre			281.7 \pm 28.4	237.1 \pm 17.2		
	5 m	219.7 \pm 20.3	159.4 \pm 11.3			272.9 \pm 30.5	224.9 \pm 25.6
	20 m	170.2 \pm 9.2	118.9 \pm 8.6			225.3 \pm 17.4	187.9 \pm 14.8
	80 m	75.4 \pm 7.5	40.1 \pm 4.0			90.7 \pm 6.6	55.1 \pm 4.7
Ruiru	Centre			164.6 \pm 13.5	102.2 \pm 10.4		
	5 m	137.8 \pm 7.9	93.4 \pm 6.2			153.7 \pm 11.2	97.4 \pm 6.4
	20 m	73.2 \pm 5.3	43.7 \pm 4.1			103.6 \pm 7.6	52.5 \pm 2.9
	80 m	43.5 \pm 3.0	25.6 \pm 2.8			57.2 \pm 3.7	28.5 \pm 3.0
Thika	Centre			150.2 \pm 14.2	89.8 \pm 5.4		
	5 m	135.4 \pm 9.8	75.5 \pm 6.7			147.4 \pm 11.2	82.9 \pm 8.4
	20 m	70.6 \pm 5.9	39.4 \pm 3.1			95.1 \pm 7.0	51.7 \pm 2.7
	80 m	36.8 \pm 2.2	21.5 \pm 1.5			53.8 \pm 3.6	25.6 \pm 1.8

season. The mean Zn mean levels across Pangani ranged from 99.1 to 339.9 $\mu\text{g/g}$ during the dry season and 58.6 to 265.3 $\mu\text{g/g}$ during the wet season for the eastern side while it ranged from 116.2 to 366.7 $\mu\text{g/g}$ during the dry season and 79.1 to 299.7 $\mu\text{g/g}$ during the wet season on western side as indicated in Figure 4.5. The highest Zn level recorded in this site was $376.9 \pm 41.5 \mu\text{g/g}$.

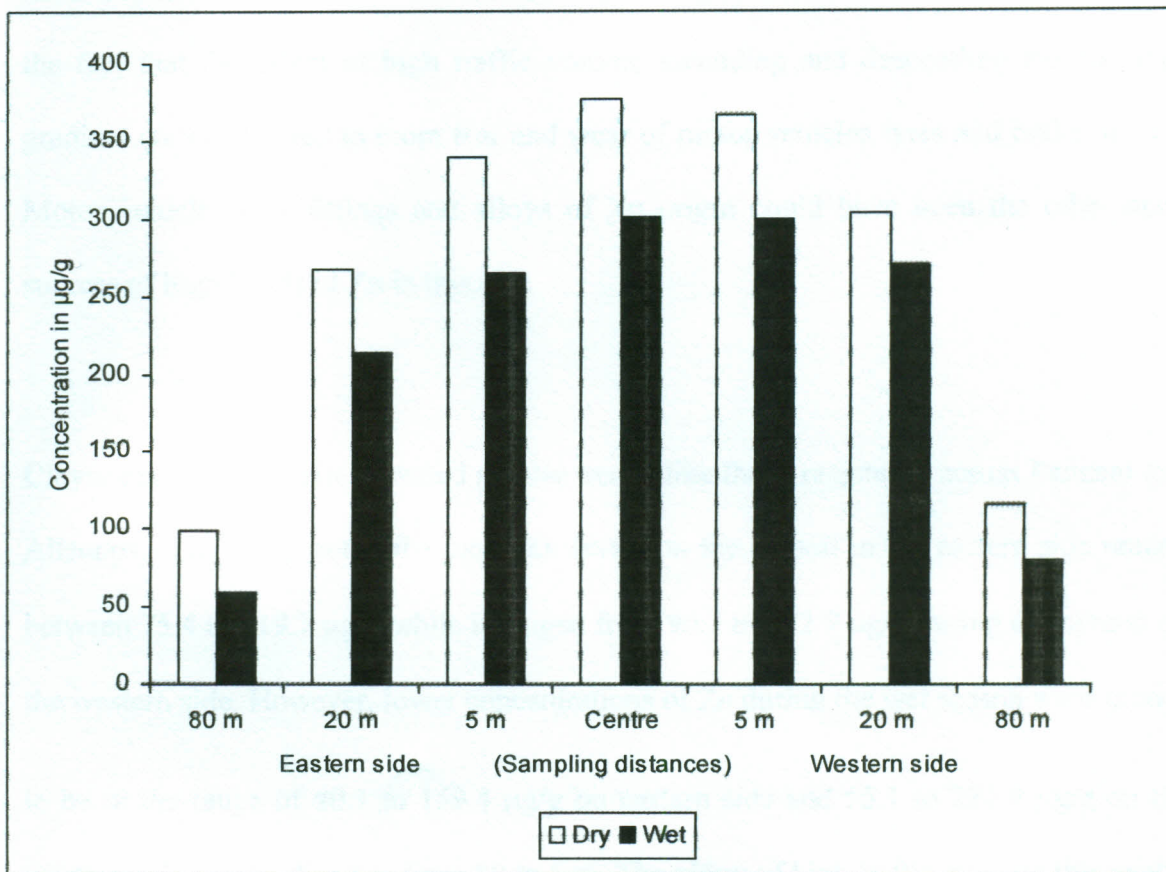


Figure 4.5 Mean levels of Zn in the topsoil during the dry and wet seasons at Pangani sampling site

As can be seen from Figure 4.5, the mean Zn levels on the topsoil across the Allsopps decreased gradually on both sides of the highway as the distance from the highway increased. But, the western side topsoil was found to have been more contaminated with Zn than the eastern side. The mean Zn levels for the eastern side in this site ranged from

78.1 to 306.8 $\mu\text{g/g}$ while the western side topsoil recorded a range of 100.1 to 313.3 $\mu\text{g/g}$ for the 80 to 5 m during the dry season. The higher deposition of Zn on the western side could have been contributed by a depressed valley with sparsely distributed vegetation cover that could have enhanced easier infiltration of Zn pollutants into the topsoil. The highest Zn level recorded at Allsopps was $313.3 \pm 31.1 \mu\text{g/g}$. This amount was detected at the 5 m on the western side of the highway during the dry season. This could be due to the fact that the effect of high traffic volume ascending and descending the Allsopps gradient could have led to more tear and wear of motor vehicles tyres and brake linings. Motor vehicle body fittings and alloys of Zn origin could have been the other main sources of high levels of Zn in this site.

Clayworks sampling site revealed similar trends like those registered across Pangani and Allsopps. The study noted the mean Zn levels on the topsoil in the eastern side ranged between 75.4 to 219.7 $\mu\text{g/g}$ while it ranged from 90.7 to 272.9 $\mu\text{g/g}$ during dry season on the western side. However, lower concentrations of Zn during the wet season were found to be in the range of 40.1 to 159.4 $\mu\text{g/g}$ on eastern side and 55.1 to 224.9 $\mu\text{g/g}$ on the western side for the distance from 80 to 5 m. The effect of high traffic flow on this gently inclined site might have led to more tear and wear of motor vehicles tyres and brake linings. Strong winds blowing from east to west of the highway were also suspected to have contributed to more Zn pollutants on the western side. The trends of mean Zn levels variation at Clayworks were found to be similar to that of Zn at Pangani (Figure 4.5).

The levels Zn detected on the topsoil across Ruiru during the dry season on eastern side ranged from between 43.5 to 137.8 $\mu\text{g/g}$ while on the western side, the topsoil ranged from 57.2 to 153.7 $\mu\text{g/g}$, respectively. However, lower concentrations of Zn during the wet season ranged between 25.6 to 93.4 $\mu\text{g/g}$ on eastern side and a range of 28.5 to 97.4 $\mu\text{g/g}$ on the western side. High traffic flow on this potholed and leveled site could have led to tear and wear of motor vehicles tyres and brake linings giving rise to Zn pollutants. The effect of having no trees or buildings barrier along the highway at this site might have resulted in violent winds blowing from east to west thereby dispersing more Zn pollutants on the western side. The trend of mean Zn levels at Ruiru was found to be similar to that of Pangani and Clayworks (Figure 4.5).

The study also found that the mean Zn levels on the topsoil across Thika sampling site ranged between 36.8 to 135.4 $\mu\text{g/g}$ on the eastern side while the western side recorded a range of 53.8 to 147.4 $\mu\text{g/g}$ during the dry season. The centre recorded 150.2 ± 14.2 $\mu\text{g/g}$, which was the highest during the dry season in this site. Lower concentrations of Zn during the wet season was recorded to be in the range of 21.5 to 75.5 $\mu\text{g/g}$ on eastern side while a range of 25.6 to 82.9 $\mu\text{g/g}$ on the western side was reported from 80 to 5 m. This site was located on a leveled ground. In addition, the site had some orderly planted trees and sparsely distributed bushes lined along the highway. The trees checked the wind blowing from east to west. The effect of trees and bushes along the highway prevented the wide spread of Zn pollutants.

The decrease in mean Zn content on the topsoil in all the sites across the highway during the wet season was evidently due to the mean Zn being leached by rainwater and carried away as storm water and surface runoff. The trend of Zn levels at Thika was found to be similar to that for Zn at Pangani, Clayworks and Ruiru. However, at Allsopps, the centre site registered lower amounts.

The mean Zn concentrations in topsoil in relation to traffic and distance from the heavily trafficked roads in Europe indicated a fall in Zn levels with distance from the roads. Therefore, studies on highway pollution reported 229 $\mu\text{g/g}$ of Zn being detected at 3 m and 152 $\mu\text{g/g}$ at 6 m from the highway while decreased Zn levels in soil as the distance increased were reported at 8 and 48 m as 162 $\mu\text{g/g}$ and 73 $\mu\text{g/g}$, respectively (Hamilton, 1996). The levels of Zn obtained across Thika-Nairobi highway study were significantly higher than those reported elsewhere in the literature. The study showed heavy pollution at the centre, 5 and 20 m during both seasons in this site by Zn compared to the baseline Zn levels of 125 $\mu\text{g/g}$ (Kaara, 1992).

4.3.3 Variation of Cu in topsoil across Thika-Nairobi highway

The mean Cu levels in the topsoil across the Thika-Nairobi highway were found to be within the range of between ND to 56.8 $\mu\text{g/g}$ during the dry season and ND to 38.7 $\mu\text{g/g}$ during the wet season as presented in Table 4.6. Statistics revealed that a significant differences existed in the mean Cu levels between the dry and the wet seasons in topsoil across Pangani ($t = 3.6459$, $d.f = 12$, at 95 % confidence), Allsopps ($t = 3.4549$, $d.f = 12$, at 95 % confidence), Clayworks ($t = 2.9985$, $d.f = 12$, at 95 % confidence), Ruiru ($t =$

Table 4.6 Mean values of Cu in topsoil during the dry and wet seasons across the Thika-Nairobi as determined by XRF [$\mu\text{g/g} \pm \text{S.D.}$, n =6]

Site	Sampling distance	Eastern side		Centre		Western side	
		Dry season	Wet season	Dry season	Wet season	Dry season	Wet season
Pangani	Centre			56.8 ± 7.5	38.7 ± 4.8		
	5 m	29.7 ± 4.9	16.1 ± 3.1			39.4 ± 11.3	32.3 ± 5.2
	20 m	12.2 ± 4.6	5.4 ± 1.7			19.6 ± 4.3	8.8 ± 2.0
	80 m	ND	ND			6.2 ± 1.7	ND
Allsopps	Centre			38.7 ± 6.0	23.8 ± 3.8		
	5 m	42.7 ± 5.9	26.4 ± 4.4			46.7 ± 7.1	30.5 ± 8.4
	20 m	21.8 ± 2.3	8.7 ± 1.7			23.6 ± 3.3	11.2 ± 2.1
	80 m	ND	ND			ND	ND
Clayworks	Centre			46.2 ± 7.5	23.1 ± 5.6		
	5 m	32.2 ± 6.1	16.9 ± 3.9			37.3 ± 6.0	19.7 ± 5.7
	20 m	13.2 ± 2.1	5.9 ± 0.7			19.2 ± 4.2	11.0 ± 3.5
	80 m	ND	ND			ND	ND
Ruiru	Centre			24.6 ± 3.3	14.5 ± 2.6		
	5 m	17.5 ± 2.0	9.6 ± 1.7			20.2 ± 2.9	13.1 ± 1.9
	20 m	9.3 ± 1.3	5.6 ± 0.8			12.4 ± 1.5	5.8 ± 0.4
	80 m	ND	ND			ND	ND
Thika	Centre			16.4 ± 2.0	9.3 ± 1.3		
	5 m	14.6 ± 1.8	6.1 ± 0.4			16.0 ± 2.1	8.5 ± 1.6
	20 m	5.6 ± 0.9	ND			9.9 ± 1.5	ND
	80 m	ND	ND			ND	ND

ND – Not Detected

3.2262, d.f = 12, at 95 % confidence) and Thika ($t = 3.3969$, d.f = 12, at 95 % confidence) sampling sites. This implied that the traffic activities across the highway had a significant impact on the Cu levels in the topsoil during the dry and wet seasons.

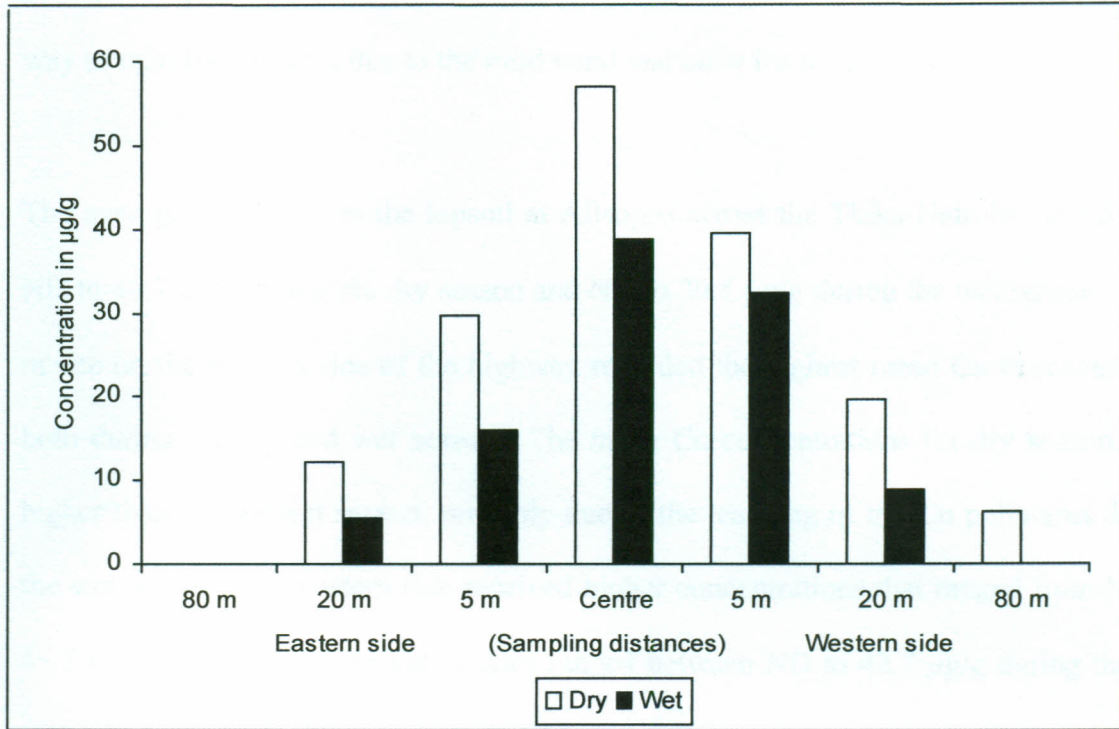


Figure 4.6 Mean levels of Cu in the topsoil during the dry and wet seasons at Pangani sampling site

From Table 4.6, lower Cu concentrations were noted throughout all the sampled sites during the wet season, probably because the rainwater leached most of the Cu pollutants. The centre site, at Pangani recorded the highest Cu amount for both seasons. This could probably be due to closeness of this site to the highest traffic density and hence the pollution was maximum. The average Cu levels in this site were found to be decreasing gradually from the highway on both sides. The Cu values in topsoil on the western side was recorded as ranging from 6.2 to 39.4 µg/g which was slightly higher than the eastern

side which ranged from ND to 29.7 $\mu\text{g/g}$ from 80 to 5 m as shown in Figure 4.6. The western side had more elevated Cu levels than the eastern side as depicted in Figure 4.6 probably because the Cu which was thought to be originating from motor vehicles body fittings, body alloys, wires in electrical cable circuits and motor car radiators found its way to this site probably due to the mild wind that blew from east to west.

The average Cu values in the topsoil at Allsopps across the Thika-Nairobi ranged from ND to 46.7 $\mu\text{g/g}$ during the dry season and ND to 30.5 $\mu\text{g/g}$ during the wet season. The 5 m site on the western side of the highway recorded the highest mean Cu concentrations both during the dry and wet seasons. The mean Cu concentrations for dry season were higher than for the wet season, probably due to the leaching of the Cu pollutants during the wet season. The western side received higher concentrations that ranged from ND to 46.7 $\mu\text{g/g}$ while the eastern side values ranged between ND to 42.7 $\mu\text{g/g}$ during the dry season, respectively. Allsopps sampling site was situated in a valley and the western side had sparse vegetation cover that enhanced easier deposition of Cu pollutants into the topsoil than on eastern side. Further, this site was more prone to motor accidents due to its location in a valley drift that slowed the motion of the high traffic density thereby making this site that experienced calm wind to receive more Cu deposition on both sides of the highway than that at Pangani.

The Cu levels across Clayworks in the topsoil ranged between ND to 37.3 $\mu\text{g/g}$ on the western side which were slightly higher than those on the eastern side whose mean concentration ranged within between ND to 32.2 $\mu\text{g/g}$ from 80 to 5 m during the dry

season. This was attributed to strong winds blowing from east to west of the highway thus accelerating deposition of Cu pollutants into the topsoil than on the eastern side. Meanwhile, the mean Cu values on the topsoil at Ruiru across the Thika-Nairobi varied between ND to 20.2 $\mu\text{g/g}$ during the dry season and ND to 13.1 $\mu\text{g/g}$ during the wet season as indicated in Table 4.6. The higher levels of Cu during the dry season than wet season was attributed to the leaching of the Cu pollutants during the wet season. Also, Cu levels on the western side recorded a range of between ND to 20.2 $\mu\text{g/g}$, which was slightly higher than on the eastern side whose values ranged between ND to 17.5 $\mu\text{g/g}$ from 80 to 5 m during the dry season probably because this site was situated on a leveled potholed section without trees or buildings, therefore strong violent winds blew from east to west thus enhancing more deposition of Cu into the topsoil on western side than on the eastern side. The highest levels of Cu in this site was $24.6 \pm 3.3 \mu\text{g/g}$ that was accumulated at the centre during the dry season probably because the centre was more closer to the sources of Cu pollutants than the other sides.

Thika sampling site received the lowest Cu concentrations in the topsoil among all the sites. The western side in this site registered a range of between ND to 16.0 $\mu\text{g/g}$ while the eastern side had a range of ND to 14.6 $\mu\text{g/g}$ from 80 to 5 m during the dry season. These similar trends could be attributed to the fact that this leveled site was surrounded by some trees and bushes lined along the highway and thus prevented wide spread of Cu pollutants. This could have led to almost similar Cu levels in the topsoil on both sides of the highway. The highest Cu concentration recorded in this site was $16.4 \pm 2.0 \mu\text{g/g}$ that was found at the centre during the dry season simply because of its closeness to the

sources of Cu pollutants hence higher Cu accumulation. There was no or little mean Cu levels detected at 80 m on both sides of the highway probably because the Cu concentrations were below detection limit of the XRF instrument.

The Cu levels along the roadside topsoil in a study around Nairobi were reported to have a mean value of 37.8 $\mu\text{g/g}$ and a range of 3.4 – 238.8 $\mu\text{g/g}$ (Oyaro, 2002). The mean levels of Cu obtained in this study across the Thika-Nairobi highway ranged from ND – 56.8 $\mu\text{g/g}$. These Cu levels were comparable to the baseline levels of Cu content in the surface soils reported to be 100 $\mu\text{g/g}$ (Bowen, 1979) for uncontaminated soils. This indicated that topsoil from all the sampling sites across the highway were not contaminated with Cu though elevated levels were noted at the Centre and 5 m on both sides of the highway.

4.4 Variation of heavy metals in soil profiles across Thika-Nairobi highway

The results of the analyses of Pb, Zn and Cu in the soil profiles that were collected during the dry and wet seasons across the Thika-Nairobi highway are presented in sections 4.4.1, 4.4.2 and 4.4.3. The soil depths samples were analyzed in two sites, namely the Pangani and Thika sampling stations. The study recorded reduced mean concentrations of Pb, Zn and Cu across the horizons from the top layer to the bottom layer as the distance from the highway increased.

4.4.1 Variation of Pb in soil depth across Thika-Nairobi highway

The amount of mean Pb in the soil depths at all sampling sites across the highway ranged from ND to 343.5 $\mu\text{g/g}$ during the dry season and ND to 250.3 $\mu\text{g/g}$ during the wet season for the layers 20-30 to 0-10 cm as indicated in Table 4.7. A significant difference was registered in the mean Pb levels between the dry and the wet seasons in the soil depth across the highway at Pangani ($t = 8.2328$, d.f = 40, at 95 % confidence) and at Thika ($t = 6.1583$, d.f = 40, at 95 % confidence) sampling sites. This was due to rain wash off resulting with surface run off and storm water. Figure 4.7 indicates the Pb trend levels decreasing with increase in the soil depth. The 0-10 cm, soil depth had elevated levels of Pb than in 10-20 cm and even lower in 20-30 cm at all sampling points (centre, 5, 20 and 80 m) across the highway at Pangani during dry season. This was attributed to the limited downward movement caused by formation of insoluble compounds that could not be easily leached.

The mean concentration of Pb in 80 to 5 m distance at Pangani ranged from 19.8 to 280.9 $\mu\text{g/g}$ on the eastern side and 24.0 to 331.2 $\mu\text{g/g}$ on the western side during the dry season while similar sampling sites at Thika recorded a range of between ND to 105.8 $\mu\text{g/g}$ on the eastern side and 11.4 to 110.8 $\mu\text{g/g}$ on the western side for the bottom layer 20-30 to 0-10 cm as indicated in Table 4.7. The highest Pb values of 343.5 ± 49.6 $\mu\text{g/g}$ were found on the topsoil layer (0-10 cm) at the centre in Pangani whereas the lowest was ND $\mu\text{g/g}$ registered at 80 m in Thika on the bottom layer (20-30 cm). A decrease in Pb levels was noted in the soil depth in all the sites during the wet season. The Pb levels at Pangani sampling site from 80 to 5 m on the eastern side ranged from 6.3 to 199.3 $\mu\text{g/g}$

Table 4.7 Mean values of Pb in soil depth during the dry and wet seasons across the Thika-Nairobi as determined by XRF [$\mu\text{g/g} \pm \text{S.D.}$, n =6]

Site	Sampling distance	Soil depth (cm)	Eastern side		Centre		Western side	
			Dry	Wet	Dry	Wet	Dry	Wet
Pangani	Centre	0-10			343.5 \pm 49.6	250.3 \pm 36.6		
		10-20			233.9 \pm 30.8	135.5 \pm 12.7		
		20-30			167.6 \pm 21.6	76.7 \pm 6.6		
	5 m	0-10	280.9 \pm 48.4	199.3 \pm 27.2			331.2 \pm 50.9	237.2 \pm 23.4
		10-20	207.7 \pm 28.0	141.6 \pm 11.5			227.1 \pm 24.5	181.4 \pm 18.0
		20-30	145.3 \pm 17.6	87.2 \pm 8.7			142.7 \pm 13.3	122.7 \pm 9.7
	20 m	0-10	210.3 \pm 31.3	151.1 \pm 16.4			241.1 \pm 12.8	197.5 \pm 31.2
		10-20	147.6 \pm 12.5	88.5 \pm 8.3			151.1 \pm 13.8	122.9 \pm 7.9
		20-30	109.8 \pm 7.8	38.0 \pm 4.0			108.9 \pm 7.5	72.6 \pm 10.4
	80 m	0-10	49.2 \pm 12.4	32.7 \pm 3.1			61.5 \pm 13.8	39.4 \pm 7.5
		10-20	30.6 \pm 5.2	14.9 \pm 2.7			39.6 \pm 3.9	32.7 \pm 1.9
		20-30	19.8 \pm 1.8	6.3 \pm 0.6			24.0 \pm 2.1	9.4 \pm 0.3
Thika	Centre	0-10			112.5 \pm 12.1	84.4 \pm 6.7		
		10-20			71.9 \pm 9.6	38.1 \pm 4.1		
		20-30			49.0 \pm 6.7	16.9 \pm 2.0		
	5 m	0-10	105.8 \pm 9.8	72.2 \pm 5.9			110.8 \pm 7.8	79.1 \pm 6.0
		10-20	63.1 \pm 5.2	26.2 \pm 3.6			65.4 \pm 5.9	38.3 \pm 4.5
		20-30	34.6 \pm 2.8	13.5 \pm 1.9			39.6 \pm 4.7	20.4 \pm 2.3
	20 m	0-10	75.4 \pm 4.5	33.8 \pm 3.3			86.4 \pm 5.2	55.0 \pm 3.9
		10-20	41.5 \pm 3.9	20.2 \pm 1.8			50.7 \pm 4.9	27.7 \pm 3.4
		20-30	22.8 \pm 2.7	9.0 \pm 0.4			33.2 \pm 4.0	14.0 \pm 0.8
	80 m	0-10	26.2 \pm 2.4	14.5 \pm 1.8			43.0 \pm 3.0	22.1 \pm 1.5
		10-20	11.1 \pm 1.9	ND			18.4 \pm 4.1	8.1 \pm 0.4
		20-30	ND	ND			11.4 \pm 2.5	ND

ND – Not Detected

and 9.4 to 237.2 $\mu\text{g/g}$ on the western side in soil depth 20-30 to 0-10 cm. Similarly, the same distances at Thika on the eastern side ranged from ND to 72.2 $\mu\text{g/g}$ and ND to 79.1 $\mu\text{g/g}$ on the western side for 20-30 to 0-10 cm during the wet season. The trend of Pb

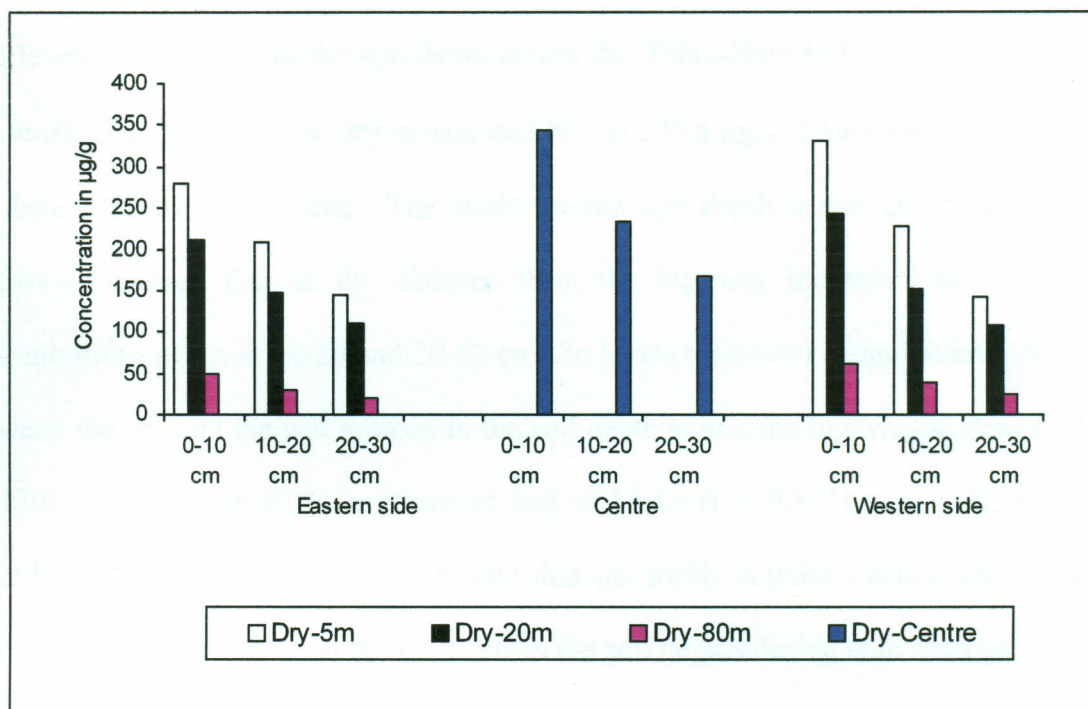


Figure 4.7 Mean levels of Pb in the soil depths during the dry season at Pangani sampling site

deposition in soil depth at Thika during both seasons were similar to that at Pangani sampling site as shown in Figure 4.7. The Pb amounts in soil depth studies in relation to sampling distances indicated that in a distance of 5 m and 8-10 cm soil depth, the amount of Pb was 350 $\mu\text{g/g}$ (Ferguson, 1990). Harrison (1989) reported 200-220 $\mu\text{g/g}$ of Pb in the topsoil (0-10 cm) at 10 m, 100-160 $\mu\text{g/g}$ at 30 m and 60-80 $\mu\text{g/g}$ at 100 m while Hamilton (1996) reported 252 $\mu\text{g/g}$ for 5-10 cm at 7.6 m, 42-172 $\mu\text{g/g}$ for 15-31 cm at 7.6 m, 30-171 $\mu\text{g/g}$ at 22 m and 26-229 $\mu\text{g/g}$ for 15-31 cm at 68 m. The values for mean Pb obtained at Pangani and Thika in this study ranged from 22.8 to 343.5 $\mu\text{g/g}$ during the

dry season for 20-30 to 0-10 cm at 20 m to Centre which were found to compare with those recorded in the literature.

4.4.2 Variation of Zn in soil depth across Thika-Nairobi highway

The levels of mean Zn in the soil depth across the Thika-Nairobi highway ranged from 9.3 to 376.9 $\mu\text{g/g}$ during the dry season and ND to 300.8 $\mu\text{g/g}$ during the wet season for the layers 20-30 to 0-10 cm. The study on the soil depth across the Thika-Nairobi highway indicated that as the distance from the highway increased, the lower the concentrations of Zn in 10-20 and 20-39 cm. Zn levels registered a significant difference between the dry and the wet seasons in the soil depth across the highway at Pangani ($t = 10.1701$, d.f = 40, at 95 % confidence) and at Thika ($t = 9.3851$, d.f = 40, at 95 % confidence) sampling sites. This indicated that the traffic activities across the highway had a significant influence on the Zn levels in the soil depths during both seasons.

The average Zn at 80 to 5 m distance at Pangani ranged from 47.8 to 339.9 $\mu\text{g/g}$ on the eastern side and 60.0 to 366.7 $\mu\text{g/g}$ on the western side during the dry season as indicated in Table 4.8. Similarly, levels of Zn in the soil profiles from 80 to 5 m within Thika ranged from 9.3 to 135.4 $\mu\text{g/g}$ on the eastern side and 11.4 to 147.4 $\mu\text{g/g}$ on the western side during the dry season for the horizon 30-20 to 0-10 cm.

In addition, the soil profile at the centre across the highway at Pangani was found to contain Zn levels in range of between 194.3 to 376.9 $\mu\text{g/g}$ more than both eastern and western sides during the dry season. This is because the site was situated in a densely

Table 4.8 Mean values of Zn in soil depth during the dry and wet seasons across the Thika-Nairobi as determined by XRF [$\mu\text{g/g} \pm \text{S.D.}, n=6$]

Site	Sampling distance	Soil depth (cm)	Eastern side		Centre		Western side	
			Dry	Wet	Dry	Wet	Dry	Wet
Pangani	Centre	0-10			376.9 \pm 41.5	300.8 \pm 38.6		
		10-20			271.3 \pm 24.9	199.3 \pm 19.7		
		20-30			194.3 \pm 19.6	118.2 \pm 7.4		
	5 m	0-10	339.9 \pm 32.7	265.3 \pm 24.0			366.7 \pm 34.9	299.7 \pm 28.5
		10-20	246.6 \pm 25.9	168.2 \pm 10.6			247.5 \pm 30.1	178.9 \pm 22.2
		20-30	169.0 \pm 13.3	96.3 \pm 8.8			158.7 \pm 12.6	115.7 \pm 11.3
	20 m	0-10	268.1 \pm 22.7	214.0 \pm 14.9			303.6 \pm 26.2	270.4 \pm 18.7
		10-20	162.8 \pm 15.5	114.7 \pm 10.1			186.6 \pm 20.5	142.9 \pm 10.1
		20-30	84.8 \pm 8.2	45.1 \pm 5.0			103.2 \pm 7.5	59.3 \pm 2.1
	80 m	0-10	99.1 \pm 16.3	58.6 \pm 4.6			116.2 \pm 15.0	79.1 \pm 8.0
		10-20	65.8 \pm 7.4	34.6 \pm 2.8			81.3 \pm 8.9	46.0 \pm 4.4
		20-30	47.8 \pm 5.9	20.9 \pm 3.7			60.0 \pm 6.5	25.3 \pm 2.5
Thika	Centre	0-10			150.2 \pm 18.4	89.8 \pm 8.2		
		10-20			107.8 \pm 9.9	66.3 \pm 9.5		
		20-30			65.5 \pm 8.0	36.7 \pm 2.0		
	5 m	0-10	135.4 \pm 16.9	75.5 \pm 7.5			147.4 \pm 28.2	82.9 \pm 9.7
		10-20	94.6 \pm 14.8	52.9 \pm 9.1			101.0 \pm 17.0	57.1 \pm 5.1
		20-30	47.2 \pm 4.7	22.4 \pm 4.9			44.4 \pm 9.6	25.2 \pm 8.6
	20 m	0-10	70.6 \pm 5.2	39.4 \pm 6.0			86.4 \pm 8.8	51.7 \pm 7.8
		10-20	57.1 \pm 6.4	28.2 \pm 2.5			50.7 \pm 4.9	36.2 \pm 4.4
		20-30	15.9 \pm 3.0	5.2 \pm 0.7			33.2 \pm 4.0	13.2 \pm 2.2
	80 m	0-10	36.8 \pm 7.1	21.5 \pm 3.8			43.0 \pm 3.6	25.6 \pm 3.0
		10-20	19.1 \pm 4.9	11.0 \pm 1.6			18.4 \pm 4.1	15.6 \pm 1.9
		20-30	9.3 \pm 0.8	ND			11.4 \pm 2.5	5.8 \pm 0.3

ND – Not Detected

motorized site and closest to sources of Zn contaminants. From Table 4.7, it is clear that higher accumulation of Zn in the upper layer than in the lower sub-layers was evident in all sampling sites. This was attributed to lower downward movement of Zn in soil depth as a result of precipitated insoluble compounds. The trends of Zn deposition in the soil depth at Thika across the highway resembled that portrayed by Pb deposition at Pangani.

Studies done on Zn concentration in soil depth on trafficked highway in Alexandria-Egypt indicated that at 5 m and 0-10 cm soil depth, the amount of Zn ranged from 370-498 $\mu\text{g/g}$, 300-390 $\mu\text{g/g}$ for 10-20 cm and 170-185 $\mu\text{g/g}$ for 20-30 cm. At 20 m, 300 $\mu\text{g/g}$ for 10-20 cm, 250 $\mu\text{g/g}$ for 10-20 cm and 160 $\mu\text{g/g}$ for 20-30 cm (Vernet, 1991). Hamilton (1996) reported 48-73 $\mu\text{g/g}$ of Zn in the topsoil at 48 m while a range of 93-498 $\mu\text{g/g}$ for 0-10 cm at zero distance from the highway. The values for mean Zn obtained at Pangani during dry season ranged between 47.8 to 376.9 $\mu\text{g/g}$ and which compared with those mentioned in studies above for 20-30 to 0-10 cm soil depth.

4.4.3 Variation of Cu in soil profiles across Thika-Nairobi highway

The mean Cu amount in the soil depth across Thika-Nairobi highway varied between ND to 56.8 $\mu\text{g/g}$ during the dry season and ND to 38.7 $\mu\text{g/g}$ during the wet season for the soil depth 20-30 to 0-10 cm as indicated in Table 4.9. Statistical calculations done in the study showed that significant differences occurred in the mean Cu levels between the dry and the wet seasons in the soil depth across the highway at Pangani ($t = 4.8801$, $d.f = 40$, at 95 % confidence) and Thika ($t = 3.8672$, $d.f = 40$, at 95 % confidence) sampling

Table 4.9 Mean values of Cu in soil depth during the dry and wet seasons across the Thika-Nairobi as determined by XRF [$\mu\text{g/g} \pm \text{S.D.}, n=6$]

Site	Sampling distance	Soil depth (cm)	Eastern side		Centre		Western side	
			Dry	Wet	Dry	Wet	Dry	Wet
Pangani	Centre	0-10			56.8 \pm 7.5	38.7 \pm 6.0		
		10-20			31.9 \pm 4.6	18.4 \pm 2.7		
		20-30			19.2 \pm 3.0	10.6 \pm 1.5		
	5 m	0-10	29.7 \pm 4.9	16.1 \pm 3.7			39.4 \pm 11.3	32.3 \pm 7.2
		10-20	14.1 \pm 2.1	7.0 \pm 1.8			18.0 \pm 3.9	8.7 \pm 1.4
		20-30	6.7 \pm 1.7	ND			9.1 \pm 2.0	ND
	20 m	0-10	12.2 \pm 4.6	5.6 \pm 0.9			19.6 \pm 4.3	8.8 \pm 1.6
		10-20	5.6 \pm 1.3	ND			6.9 \pm 1.8	ND
		20-30	ND	ND			ND	ND
	80 m	0-10	ND	ND			6.2 \pm 1.7	ND
		10-20	ND	ND			ND	ND
		20-30	ND	ND			ND	ND
Thika	Centre	0-10			16.4 \pm 4.8	8.7 \pm 0.7		
		10-20			9.5 \pm 2.1	ND		
		20-30			ND	ND		
	5 m	0-10	14.6 \pm 2.9	6.1 \pm 1.3			5.6 \pm 4.7	8.5 \pm 1.9
		10-20	8.2 \pm 1.5	ND			1.2 \pm 3.5	ND
		20-30	ND	ND			ND	ND
	20 m	0-10	9.9 \pm 3.2	ND			5.6 \pm 0.3	ND
		10-20	ND	ND			ND	ND
		20-30	ND	ND			ND	ND
	80 m	0-10	ND	ND			ND	ND
		10-20	ND	ND			ND	ND
		20-30	ND	ND			ND	ND

ND – Not Detected

sites. This indicated that the traffic activities across the highway had significant influence on the Cu levels in the soil depths during both dry and wet seasons. The concentration of average Cu at 80 to 5 m for the soil depth 20-30 to 0-10 cm on eastern side of the Pangani sampling site ranged from ND to 29.7 $\mu\text{g/g}$ and ND to 39.4 $\mu\text{g/g}$ for the western side during the dry season whereas Cu values at Thika varied between ND to 14.6 $\mu\text{g/g}$ on the eastern side and ND to 16.0 $\mu\text{g/g}$ on western side during the dry season. This is because prevailing wind could have facilitated more Cu deposition on western side than on eastern side. The study in the soil profiles across the highway found that at 80 m, there was no Cu detected in the layers 0-10 to 20-30 cm on the eastern and western sides probably due to inability for the XRF instrument to detect Cu levels due to its low concentrations in those sites.

The study also reported decreased levels of Cu in soil depths during the wet season than during dry season. It was found that at 80 to 5 m the Cu levels on the eastern side during wet season ranged from ND to 16.1 $\mu\text{g/g}$ and ND to 32.3 $\mu\text{g/g}$ on the western side for soil depth 20-30 to 0-10 cm at Pangani while similar soil depths had Cu levels ranging from ND to 6.1 $\mu\text{g/g}$ and ND to 8.5 $\mu\text{g/g}$ on eastern and western sides at Thika, respectively. However, at 80 m, there was no Cu detected on both eastern and western sides for 0-10 to 10-20 cm soil depths as indicated in Table 4.9. This indicated that considerable amounts of the Cu were concentrated on the upper soil layer. The amount of Cu levels deposited in top layer (0-10 cm) was higher than that deposited in the sub-layer (10-20 cm) but the amount in the bottom layer (20-30 cm) was even lower than in the middle layer. This had been confirmed by Bowen (1979) who reported that Cu is an immobile

element in soils, and as a result, many soil depth show little variation of total Cu concentration with depth. The trend of Cu levels obtained across the highway was similar to that for Pb at Pangani, however, lower amounts of Cu were deposited.

The Cu levels in roadside topsoils in a study done around Nairobi reported a mean value of 37.8 $\mu\text{g/g}$ and a range of 3.4-238.8 $\mu\text{g/g}$ (Oyaro, 2002). The Cu concentration in the topsoil profile at Ngara roundabout was 36.5 $\mu\text{g/g}$ (Oyaro, 2002). The mean levels of Cu obtained in this study ranged from ND to 56.8 $\mu\text{g/g}$ during the dry season and ND to 38.7 $\mu\text{g/g}$ during the wet season in the top horizon 0-10 to 20-30 cm at Pangani.

4.5 Variation of heavy metals in grass across Thika-Nairobi highway

The analyses of Pb, Zn and Cu found in grass (stems and leaves) collected across the Thika-Nairobi highway during the dry and wet seasons are presented in sections 4.5.1, 4.5.2 and 4.5.3. The grass samples were analyzed in two sites namely; Allsopps and Thika. The pasture grass at Allsopps was sampled at the centre and on both sides of the highway, but the napier grass was sampled on the eastern side only. On the other hand, all sampling sites at Thika were sampled with pasture grass, but no napier grass was samples in that site as indicated in Table 4.10. The study noted decreasing mean values of Pb, Zn and Cu in grass as the sampling distance from the roadside increased.

4.5 Variation of Pb levels in pasture grass (*Typha elephantina*) and napier grass (*Pennisetum purpureum*) across Thika-Nairobi highway

The effect of Pb emissions originating from the high traffic density on Thika-Nairobi highway and deposited or biosorped on grass at Allsopps and Thika sampling sites were

noted in this study. The average Pb levels contained in pasture grass across the highway ranged from 5.1 to 154.7 $\mu\text{g/g}$ during the dry season and ND to 109.7 $\mu\text{g/g}$ during the wet season as shown in Table 4.10. The pasture grass on western side across the highway had elevated levels of mean Pb since they ranged between 5.8 to 154.7 $\mu\text{g/g}$ during the dry season and ND to 109.7 $\mu\text{g/g}$ during wet season for the 80 to 5 m distance than on the eastern side which ranged from 5.1 to 148.0 $\mu\text{g/g}$ during dry season and ND to 100.7 $\mu\text{g/g}$ during the wet season for similar sampling distances. The washing of Pb from pasture grass by rainwater was attributed to be the main reason behind this reduction in levels.

The mean amounts of Pb deposited on pasture grass at Allsopps varied between 20.8 to 154.7 $\mu\text{g/g}$ and was more than that found at Thika which ranged between 5.1 to 32.6 $\mu\text{g/g}$ during both seasons across all the sites. These levels could have originated from the high traffic density and deposited on grass at Allsopps than at Thika. The levels of Pb in pasture grass at Allsopps on the eastern side was detected to vary from 20.8 to 148.0 $\mu\text{g/g}$ during the dry season and 6.9 to 100.7 $\mu\text{g/g}$ during the wet season for 80 to 5 m as shown in Figure 4.8 compared to the lesser amounts of napier grass that ranged from 14.7 to 124.6 $\mu\text{g/g}$ and 5.2 to 63.9 $\mu\text{g/g}$ during the dry and wet seasons, respectively in similar sampling distances. This showed that pasture grass had accumulated more Pb levels because of its adaptive and resistant nature to dry conditions.

Table 4.10 Mean values of Pb in the pasture grass and napier grass during the dry and wet seasons across the Thika-Nairobi highway as determined by XRF [$\mu\text{g/g} \pm \text{S.D.}$, n=6]

Site	Sampling distance	Plant	Eastern side		Centre		Western side	
			Dry	Wet	Dry	Wet	Dry	Wet
Allsopps	Centre	Pasture grass			131.2 \pm 8.5	92.6 \pm 4.7		
	5 m	Pasture grass	148.0 \pm 12.1	100.7 \pm 8.1			154.7 \pm 13.2	109.7 \pm 6.5
		Napier grass	124.6 \pm 9.2	63.9 \pm 5.6				
	20 m	Pasture grass	82.2 \pm 7.9	52.7 \pm 6.6			100.8 \pm 7.2	67.0 \pm 4.8
Napier grass		68.2 \pm 8.8	19.9 \pm 2.5					
80 m	Pasture grass	20.8 \pm 3.6	6.9 \pm 1.2			25.4 \pm 3.0	9.7 \pm 1.4	
	Napier grass	14.7 \pm 1.8	5.2 \pm 0.7					
Thika	Centre	Pasture grass			32.6 \pm 5.9	17.8 \pm 2.4		
	5 m	Pasture grass	25.5 \pm 3.8	12.9 \pm 2.2			31.3 \pm 4.5	16.0 \pm 2.0
	20 m	Pasture grass	12.4 \pm 2.6	5.7 \pm 0.9			15.5 \pm 2.3	6.6 \pm 0.8
	80 m	Pasture grass	5.1 \pm 1.4	ND			5.8 \pm 1.7	ND

ND – Not Detected

On the other side, napier grass was more likely to be harvested for animal consumption as a fodder and thus could have absorbed less Pb than the pasture grass. The pasture grass and napier grass at Allsopps were contaminated with Pb especially at 5 and 20 m since their levels were higher than the base levels of 10 $\mu\text{g/g}$ required in the normal health plants as reported in the literature.

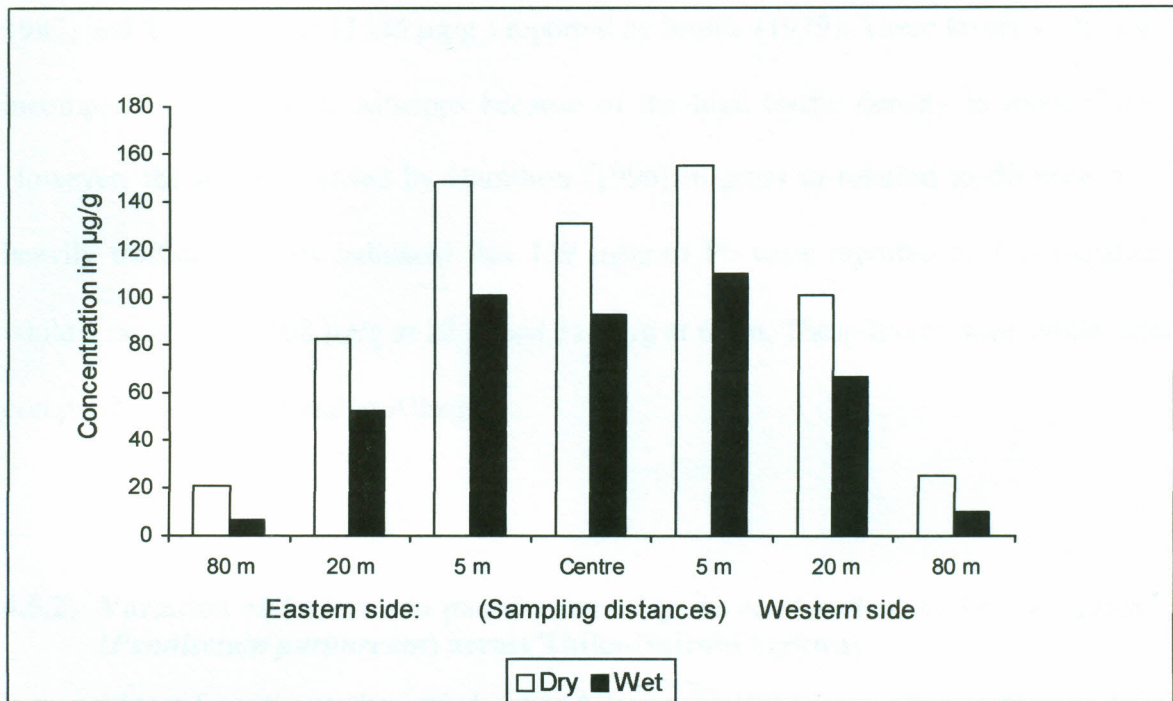


Figure 4.8 Mean levels of Pb in the pasture grass during the dry and wet seasons at Allsopps

Statistically, there was a significant variation registered in the mean Pb levels between the dry and the wet seasons in pasture grass ($t = 4.9372$, $d.f = 12$, at 95 % confidence) and in the napier grass ($t = 2.8653$, $d.f = 4$, at 95 % confidence) found at Allsopps sampling distances. Similarly, a significant difference existed in the mean Pb levels in pasture grass ($t = 4.7713$, $d.f = 12$, at 95 % confidence) found across Thika sampling site between the dry and the wet seasons. This meant that the motor vehicle activities across the highway

had a significant influence on the Pb levels in the pasture grass and napier grass in both seasons.

The highest level of Pb recorded in pasture grass at Allsopps was 154.7 $\mu\text{g/g}$, lower than the highest levels of 991 $\mu\text{g/g}$ of Pb in grass reported in Hong Kong City (Ho *et al.*, 1987) and Vancouver City (1545 $\mu\text{g/g}$) reported by Smith (1979). These levels of Pb were incomparable to those at Allsopps because of the high traffic density in those Cities. However, the levels reported by Hamilton (1996) in grass in relation to distance from heavily trafficked roads indicated that 139 $\mu\text{g/g}$ of Pb were reported at 7 m distance, while a range of 66-198 $\mu\text{g/g}$ at 22 m and 31 $\mu\text{g/g}$ at 68 m. These levels were similar and comparable to those found at Allsopps.

4.5.2 Variation of Zn levels in pasture grass (*Typha elephantina*) and napier grass (*Pennisetum purpureum*) across Thika-Nairobi highway

It was evident from the study carried out at Allsopps and Thika sampling stations that the mean Zn levels on pasture grass ranged from 14.2 to 208.4 $\mu\text{g/g}$ during the dry season and 5.3 to 147.8 $\mu\text{g/g}$ during the wet season as shown in Table 4.11. The pasture grass on western side at Allsopps had higher levels of mean Zn. They ranged from 58.6 to 208.4 $\mu\text{g/g}$ during the dry season and 28.6 to 147.8 $\mu\text{g/g}$ during wet season for 80 to 5 m distance than on the eastern side whose values ranged from 48.8 to 199.2 $\mu\text{g/g}$ during dry season and 20.9 to 125.6 $\mu\text{g/g}$ during the wet season. Meanwhile, the pasture grass at Thika ranged from 14.2 to 45.9 $\mu\text{g/g}$ and 5.3 to 28.1 $\mu\text{g/g}$ on eastern side against a range

Table 4.11 Mean values of Zn in the pasture grass and napier grass during the dry and wet seasons across Thika-Nairobi highway as determined by XRF [$\mu\text{g/g} \pm \text{S.D}$, n =6]

Site	Sampling distance	Plant	Eastern side		Centre		Western side	
			Dry	Wet	Dry	Wet	Dry	Wet
Allsopps	Centre	Pasture grass			147.2 \pm 6.8	103.3 \pm 6.2		
	5 m	Pasture grass	199.2 \pm 14.1	125.6 \pm 7.7			208.4 \pm 20.9	147.8 \pm 16.2
		Napier grass	173.1 \pm 18.5	106.5 \pm 5.9				
	20 m	Pasture grass	120.9 \pm 4.6	71.8 \pm 6.2			139.1 \pm 14.7	94.8 \pm 8.4
Napier grass		100.4 \pm 7.0	52.5 \pm 3.0					
80 m	Pasture grass	48.8 \pm 3.5	20.9 \pm 2.1			58.6 \pm 2.9	28.6 \pm 3.7	
	Napier grass	28.8 \pm 2.4	12.4 \pm 0.6					
Thika	Centre	Pasture grass			57.3 \pm 7.3	39.0 \pm 5.2		
	5 m	Pasture grass	45.9 \pm 4.7	28.1 \pm 3.1			52.9 \pm 6.0	32.7 \pm 4.9
	20 m	Pasture grass	26.3 \pm 3.6	16.5 \pm 2.9			38.7 \pm 5.5	18.1 \pm 2.7
	80 m	Pasture grass	14.2 \pm 2.5	5.3 \pm 0.4			25.1 \pm 4.0	9.6 \pm 1.6

of 25.1 to 52.9 $\mu\text{g/g}$ and 9.6 to 32.7 $\mu\text{g/g}$ on western side during dry and wet seasons, respectively. These levels were lower than those at Allsopps due to lower traffic activities at Thika. The average Zn values contained in pasture grass obtained on eastern side during both seasons were higher compared to the lesser amounts in napier grass that ranged from 28.8 to 173.1 $\mu\text{g/g}$ during the dry season and 12.4 to 106.5 $\mu\text{g/g}$ during the wet season for 80 to 5 m as indicated in Table 4.11. The higher accumulation of mean Zn in pasture grass than in napier grass could have been caused by its tolerance and resistance to the dry weather conditions than the napier grass thus higher accumulation. Similarly, napier grass was frequently and regularly harvested as a fodder for animals.

The Zn levels in pasture grass sampled from Thika ranged from 14.2 to 57.3 $\mu\text{g/g}$ during the dry season and 5.3 to 39.0 $\mu\text{g/g}$ during the wet season as indicated in Table 4.11. The pasture grass on western side had higher levels of average Zn since it ranged from 25.1 to 52.9 $\mu\text{g/g}$ during the dry season and 9.6 to 32.7 $\mu\text{g/g}$ during wet season for 80 to 5 m than the eastern side whose Zn levels ranged from 14.2 to 45.9 $\mu\text{g/g}$ during dry. The reduction of Zn pollutants levels both in pasture grass and napier grass during the wet season was caused by rainwater washing. The trend of the mean Zn levels in pasture grass during the dry and wet seasons was similar to that of Pb at Allsopps although the amount of Zn at the centre was more than on its sides.

Statistical calculations done on sampled plants showed that significant variations existed in the mean Zn levels between the dry and the wet seasons in pasture grass ($t = 5.5507$, $d.f = 12$, at 95 % confidence) found on both sides and in napier grass ($t = 2.8099$, $d.f = 4$,

at 95 % confidence) on the eastern side at Allsopps as well as in the pasture grass ($t = 6.0303$, $d.f = 12$, at 95 % confidence) at Thika sampling site. This could be attributed to rain wash off as well as having fewer motor vehicles during the wet seasons hence leading to this reduction and subsequently a significant difference.

The detected Zn levels recorded in pasture grass at Allsopps varied between 48.8 to 208.4 $\mu\text{g/g}$ during the dry season. These mean Zn levels in grass were comparable to those reported in Hong Kong that ranged from 43-276 $\mu\text{g/g}$ and higher than those reported in Belgium that ranged from 37-114 $\mu\text{g/g}$ (Ho *et al.*, 1987). Hamilton (1996) reported 219 $\mu\text{g/g}$ of Zn in grass at 6 m and 72 $\mu\text{g/g}$ at 16 m which were within the same range to those obtained at Allsopps in this study.

4.5.3 Variation of Cu levels in pasture grass (*Typha elephantina*) and napier grass (*Pennisetum purpureum*) across Thika-Nairobi highway

The mean Cu concentrations in pasture grass across the Thika-Nairobi highway varied from ND to 39.2 $\mu\text{g/g}$ during the dry season and ND to 19.2 $\mu\text{g/g}$ during the wet season as shown in Table 4.12. The pasture grass on western side at Allsopps registered higher levels of mean Cu that ranged from ND to 39.2 $\mu\text{g/g}$ during the dry season and ND to 19.2 $\mu\text{g/g}$ during wet season for 80 to 5 m than on the eastern side which ranged from ND to 34.1 $\mu\text{g/g}$ during dry season and ND to 15.8 $\mu\text{g/g}$ during the wet season. However, much lower Cu concentrations were deposited in pasture grass at Thika that ranged from ND to 15.9 $\mu\text{g/g}$ on western side during the dry season and ND to 9.2 $\mu\text{g/g}$ during the wet

Table 4.12 Mean values of Cu in the pasture grass and napier grass during the dry and wet seasons across Thika-Nairobi highway as determined by XRF [$\mu\text{g/g} \pm \text{S.D.}$, n =6]

Site	Sampling distance	Plant	Eastern side		Centre		Western side	
			Dry	Wet	Dry	Wet	Dry	Wet
Allsopps	Centre	Pasture grass			33.4 ± 3.3	13.3 ± 2.9		
	5 m	Pasture grass	34.1 ± 3.5	15.8 ± 2.6			39.2 ± 3.7	19.2 ± 2.0
		Napier grass	25.2 ± 2.8	10.5 ± 1.5				
	20 m	Pasture grass	17.8 ± 0.7	7.9 ± 1.9			21.9 ± 2.2	9.7 ± 1.4
		Napier grass	12.5 ± 0.4	5.6 ± 0.3				
80 m	Pasture grass	ND	ND			ND	ND	
Thika	Centre	Pasture grass			20.7 ± 3.6	15.1 ± 1.1		
	5 m	Pasture grass	13.6 ± 1.5	8.5 ± 0.7			15.9 ± 2.8	9.2 ± 0.6
	20 m	Pasture grass	5.7 ± 0.3	ND			8.8 ± 2.2	ND
	80 m	Pasture grass	ND	ND			ND	ND

ND – Not Detected

season against a range of ND to 13.6 $\mu\text{g/g}$ obtained during dry season and ND to 8.5 $\mu\text{g/g}$ during the wet season for similar distances. The washing of Cu from pasture grass by rainwater was the reason for having lower amounts during wet season. The pasture grass at Allsopps on both sides during dry and wet seasons contained elevated mean Cu levels compared to the lesser amounts contained in napier grass that ranged from ND to 25.2 $\mu\text{g/g}$ during the dry season and ND to 10.5 $\mu\text{g/g}$ during the wet season in similar sampling distances. This was attributed to a more recent growth in napier grass than in a more resistant pasture grass thus resulting in higher accumulation.

There was a significant difference in Cu levels between the dry and the wet seasons in pasture grass ($t = 3.2774$, d.f = 12, at 95 % confidence) and in the napier grass ($t = 2.7903$, d.f = 4, at 95 % confidence) at Allsopps. Similarly, napier grass ($t = 3.3676$, d.f = 4, at 95 % confidence) on the eastern side at Thika registered a significant difference too. This evidently indicated that the rain wash off during wet season could have caused this significant variation.

The amount of mean Cu recorded in pasture grass at Allsopps ranged from ND to 39.2 $\mu\text{g/g}$ during the dry season and ND to 19.2 $\mu\text{g/g}$ during the wet season. These mean Cu levels of grass at Allsopps were found comparable to those reported in grass found growing by motorway interchange in Auckland, New Zealand which ranged between 16-31 $\mu\text{g/g}$ (Ward, 1977). Oyaro (2002) reported a mean of 24.28 $\mu\text{g/g}$ and a range of 0.4-74 $\mu\text{g/g}$ of Cu levels in napier grass in Nairobi and its environs which fell within the range of 0 to 25.2 $\mu\text{g/g}$ found in napier grass during the dry season at Allsopps.

4.6 Comparison of XRF and AAS analytical methods

The comparative studies of the mean levels of Pb, Zn and Cu in the topsoil were measured using XRF and AAS techniques and presented in the Table 4.13. The topsoil from Pangani sampling site was selected for comparison of XRF and AAS analytical methods since the site had the highest traffic density and all the sampling sites within Pangani covered a wide range of concentrations which is desirable in comparative studies of instrumental methods (Miller, 1988). The mean values of Pb, Zn and Cu for the two analytical methods (XRF and AAS) were statistically tested by being plotted on a regression line which is a sensitive tool for comparing analytical methods (Miller, 1988). The XRF mean values were assigned to the y-axis and the AAS values to the x-axis. By using linear regression equation: $y = bx + a$, the intercept (a), slope (b) and the r (correlation coefficient) was computed and line of best fit drawn as shown in Figures 4.9.

From these values it became clear that the calculated slope and intercept did not differ significantly from the ideal values of 1 and 0 respectively and thus, there was no evidence for significant differences between XRF and AAS techniques. The slope and the intercept were much closer to the values expected for the part of the graph closer to the origin. The r value obtained indicated that the linear regression was about as good a fit of the points of the two methods since the r value for topsoil at Pangani ($r = 0.9998$) was statistically high and closer to the ideal value of 1 hence the mean Pb, Zn and Cu values were in a close agreement for the two methods.

Table 4.13 Mean values of Pb, Zn and Cu in the topsoil during the dry season across Pangani site as determined by XRF and AAS [$\mu\text{g/g} \pm \text{S.D.}$, n =6]

Method	Metal	Eastern side distance			Centre	Western side distance		
		80 m	20 m	5 m	Centre	5 m	20 m	80 m
XRF	Pb	49.2 \pm 12.4	210.3 \pm 31.3	270.9 \pm 48.4	343.5 \pm 49.6	331.2 \pm 50.9	241.1 \pm 12.8	61.5 \pm 13.8
AAS	Pb	47.4 \pm 7.2	207.1 \pm 19.8	268.1 \pm 17.7	339.0 \pm 33.8	325.7 \pm 41.2	236.5 \pm 17.7	54.3 \pm 6.6
XRF	Zn	99.1 \pm 16.3	268.1 \pm 22.7	339.9 \pm 32.7	376.9 \pm 41.5	366.7 \pm 34.9	303.6 \pm 26.2	116.2 \pm 15.0
AAS	Zn	93.7 \pm 10.7	265.4 \pm 18.5	330.1 \pm 29.3	371.8 \pm 36.8	358.0 \pm 31.0	297.4 \pm 21.9	112.7 \pm 10.4
XRF	Cu	ND	12.2 \pm 4.6	29.7 \pm 4.9	56.8 \pm 7.5	39.4 \pm 11.3	19.6 \pm 4.3	6.2 \pm 1.7
AAS	Cu	ND	9.8 \pm 3.2	26.3 \pm 5.2	50.4 \pm 10.8	33.5 \pm 8.0	15.7 \pm 4.2	5.9 \pm 1.3

ND – Not Detected

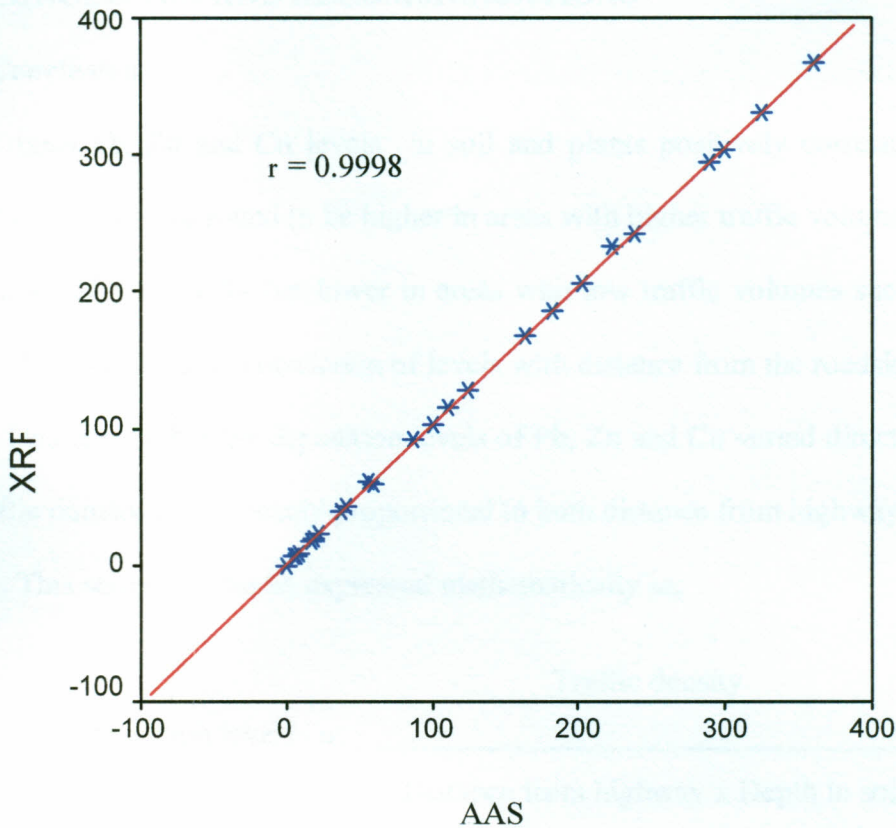


Figure 4.9 Comparison of XRF and AAS for levels of Zn in topsoil at Pangani

The detection limits for AAS were lower as indicated in Table 3.0 than the detection limits for XRF as indicated in section 3.6. For this particular study, XRF would be the most preferred technique because during the AAS analysis some silica (sand sediments) contained in the sample composition due to the nature of soil type found along the Thika-Nairobi highway were left undigested, hence the AAS values were slightly lower. However, the two sets of values for XRF and AAS did not show any significant difference ($t = 2.1617$, $d.f = 12$ at 95 % confidence levels).

CHAPTER FIVE

5.0 CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The mean Pb, Zn and Cu levels in soil and plants positively correlated with traffic density. Levels were found to be higher in areas with higher traffic volumes like Pangani, Allsopps and Clayworks but lower in areas with low traffic volumes such as Ruiru and Thika. Further negative correlation of levels with distance from the roadside and depth of soil. This means that the deposition levels of Pb, Zn and Cu varied directly proportional to traffic density and inversely proportional to both distance from highway and in the soil depth. This statement can be expressed mathematically as;

$$\text{Amount of deposition levels} \propto \frac{\text{Traffic density}}{\text{Distance from highway} \times \text{Depth in soil}}$$

$$\text{Amount of deposition levels} = \frac{K \times \text{Traffic density}}{\text{Distance from highway} \times \text{Depth in soil}}$$

where $K = \text{constant}$

The average levels of Pb on topsoil along the Thika-Nairobi from Pangani to Thika sampling sites ranged from 83.2 to 208.1 $\mu\text{g/g}$ during the dry season and 52.5 to 151.8 $\mu\text{g/g}$ during the wet season. These levels were higher than the recommended Pb levels of 70 $\mu\text{g/g}$ (Laugher, 1992) while mean Zn levels ranged from between 94.4 to 267.2 $\mu\text{g/g}$ during the dry season and 57.5 to 212.6 $\mu\text{g/g}$ during the wet season along the highway. Most sites had Zn levels being above the maximum allowed concentrations of 125 $\mu\text{g/g}$

recommended in normal soils (Kaara, 1992). In addition, the mean Cu levels varied between 10.4 to 25.3 $\mu\text{g/g}$ during the dry season and 5.6 to 14.7 $\mu\text{g/g}$ during the wet season. This meant that most Cu levels were found to be within the comparable levels of 100 $\mu\text{g/g}$ required in the soil (Bowen, 1979).

Decrease in mean Pb, Zn and Cu levels on the topsoil layer (0-10 cm) was noted with increasing distance from the roadside to 80 m across the highway in this study. The mean Pb levels across the Thika-Nairobi highway from Pangani to Thika varied between 26.2 to 343.5 $\mu\text{g/g}$ during the dry season and 14.5 to 250.3 $\mu\text{g/g}$ during the wet season. These levels in most sites exceeded the recommended maximum levels of 70 $\mu\text{g/g}$ (Laughler, 1992). The Zn levels ranged from 36.8 to 376.9 $\mu\text{g/g}$ during the dry season and 21.5 to 300.8 $\mu\text{g/g}$ during the wet season. Most sites were contaminated since they exceeded the recommended maximum levels of 125 $\mu\text{g/g}$ (Kaara, 1992). The levels of Pb and Zn that were registered in this study could be dangerous to human health, in view of the toxicity of these (Pb and Zn) pollutants as discussed earlier in literature section. The study also revealed that the effect of traffic activities could be achieved for a longer distance of more than 80 m for Pb and Zn on both sides of the Thika-Nairobi highway. However, the mean Cu levels across the highway ranged from ND to 56.8 $\mu\text{g/g}$ during the dry season and ND to 38.7 $\mu\text{g/g}$ during the wet season. These levels fell within the recommended levels of 100 $\mu\text{g/g}$ (Kabata-Pendias *et al.*, 1992), meaning that there was little or no Cu pollution in the topsoil across the highway.

There was higher accumulation of Pb, Zn and Cu concentrations in the soil depth (0-10 cm) than in the bottom subsoil layers (10-20 and 20-30 cm) from the centre to 80 M across the Thika-Nairobi highway. The mean Pb levels in the soil profiles (from 0-10 to 20-30 cm) across the Thika-Nairobi highway ranged from 14.5 to 343.5 $\mu\text{g/g}$ in 0-10 cm and rapidly decreased with depth from ND to 167.6 $\mu\text{g/g}$ in 20-30 cm while mean Zn levels in the 0-10 cm ranged from 21.5 to 376.9 $\mu\text{g/g}$ and reduced from ND to 194.3 $\mu\text{g/g}$ in 20-30 cm. Moreover, the mean Cu concentrations in the soil profile across Thika-Nairobi highway ranged from ND to 56.8 $\mu\text{g/g}$ in 0-10 cm and decreased from ND to 19.2 $\mu\text{g/g}$ in 20-30 cm. The lower levels of Pb, Zn and Cu contaminants in inner soil layers (10-20 and 20-30 cm) was due to limited downward movement of these pollutants as a result of their conversion into insoluble compounds.

The study also showed evidence of elevated levels of Pb on pasture grass across the Thika-Nairobi highway whose mean levels ranged from 5.1 to 154.7 $\mu\text{g/g}$ during the dry season and ND to 109.7 $\mu\text{g/g}$ during the wet season. The mean Pb values in napier grass varied between 14.7 to 124.6 $\mu\text{g/g}$ during the dry season and 5.2 to 63.9 $\mu\text{g/g}$ during the wet season. Most of the sites that were sampled across highway had Pb levels above the maximum recommended amounts of 10 $\mu\text{g/g}$ of Pb required in plants. The mean Zn levels in the pasture grass ranged from 14.2 to 208.4 $\mu\text{g/g}$ during the dry season and 5.3 to 147.8 $\mu\text{g/g}$ during the wet season. The Zn values in napier grass ranged from 28.8 to 173.1 $\mu\text{g/g}$ during dry season and 12.4 to 106.5 $\mu\text{g/g}$ during the wet season. The Zn concentrations in pasture grass and napier grass in some sites were found in this study to lie within while some had slightly above the recommended value of 150 $\mu\text{g/g}$ (Kaara,

1992). The mean Cu values registered in pasture grass varied between ND to 39.2 $\mu\text{g/g}$ during the dry season and ND to 19.2 $\mu\text{g/g}$ during the wet season while the range in napier grass was ND to 25.2 $\mu\text{g/g}$ during the dry season and ND to 10.5 $\mu\text{g/g}$ during the wet season. The recommended upper limit of Cu in normal plants is 20 $\mu\text{g/g}$ (Bowen, 1979). This therefore meant that there was little or no Cu pollution in both pasture grass and napier grass across the highway. It was clear from the study that considerable contamination of pasture grass by Pb and Zn had occurred in mostly at centre, 5 and 20 m while Cu to some extent had polluted pasture grass at the centre and 5 m across the Thika-Nairobi highway.

Finally, it was clear from the study that the mean levels of Pb, Zn and Cu in pasture grass across the Thika-Nairobi highway were considerably higher than in napier grass in both seasons. The study also indicated that pasture grass was widely spread out along and across the Thika-Nairobi highway and had elevated levels than in napier grass. This could probably be attributed to the fact that pasture grass could easily tolerate dry weather conditions for longer period.

5.2 Recommendations

From the results of the study, the following recommendations have been made:

- (i) Introduction of cheaper and efficient public transport system in the urban centres and cities such like Nairobi metropolitan transport system so that people would be discouraged from using personal cars more often. Fewer cars on the road would mean less pollution on highways. This would ease traffic congestion in Nairobi and its environs thus curbing environmental pollution.
- (ii) Enactment of motor vehicle emission policies to control environmental pollution due to poor vehicle maintenance. The number of years the vehicles should be in use on the Kenyan roads should be enforced. This would ensure that vehicles do not emit smoke, unburnt gases, oily substances and solid particles. For example, in United Kingdom, specific regulations of levels of Pb and S (sulphur) in vehicle fuels are provided in law as vehicle emission standards.
- (iii) There is need for strict enforcement of road rules. Vehicle tare weight should be enforced to prevent excessive tear and wear on highways and bridges by heavy commercial vehicles as a result of damage caused by overloading. Over weight vehicles should be fined on the spot. Enforcing this law by ensuring effective surveillance would result in reduction of highway dilapidation which in turn would lead to lower pollution.

- (iv) Alternative fuels which are environmentally friendly should be sought such as the use of hydrogen fuel as is the case at State of California in USA. Also, the need to use Methylcyclopentadienyl Manganese Tricarbonyl (MMT) to replace octane numbers lost in allowable Pb concentrations. The concentration of manganese in petrol to which MMT has been added is very low and it is photochemically unstable thus decomposing rapidly in sunlight hence it is environmentally friendly. Moreover, the use of bio-diesel or bio-fuel from some plants such as *Jatropha curcas* needs to be encouraged to substitute the organic fuel since it is cheaper to produce and free from green house gases.
- (v) The study showed that soils and plants (adsorped) along the busy urban highways accumulate high levels of heavy metal pollutants and therefore it is recommended that people should be discouraged from roadside cultivation and living along the urban highways.
- (vi) The Kenya Roads Board (KRB) which is charged with the responsibility of building and maintaining roads needs to improve on surveillance and monitoring of roads and ensure that they are passable and in good order to minimize dilapidation and hence controlling motor vehicle pollution.

5.3 Further research

- (i) Further studies should be done to establish the cross-contamination of soils and plants by other pollutants besides the traffic across the Thika-Nairobi highway and in other highways in urban areas.
- (ii) There is need for a research to be conducted on contamination of surface water run off and storm water by the traffic on the highways in order to establish the levels of heavy metals in them.
- (iii) In this study, the total concentration of the heavy metals Pb, Zn and Cu was determined. The speciation forms in which they occur were not determined and therefore speciation studies need to be carried out to ascertain the chemical forms of these metals in the soils-plants interaction system. This is because toxicity of heavy metals is governed by processes such as complexation with organic and inorganic metal ligands, adsorption to organic particulates and hydrous metal oxides which require chemical speciation analysis technique which was lacking. It is therefore recommended that future studies should incorporate this analysis.
- (iv) Finally, there is need to determine the levels of Pb, Zn and Cu in cooked foods sold by traders at Githurai as well as other pollutants originating from lorries found packed at Juja town along the Thika-Nairobi highway.

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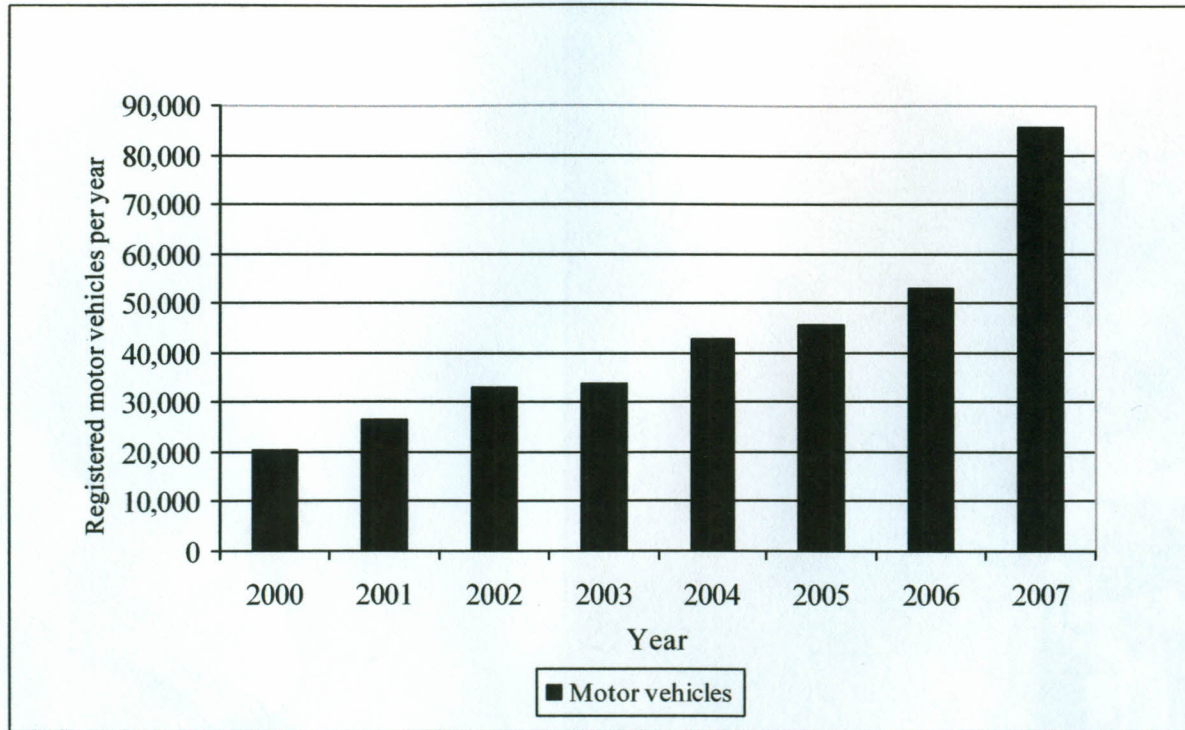
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APPENDICES

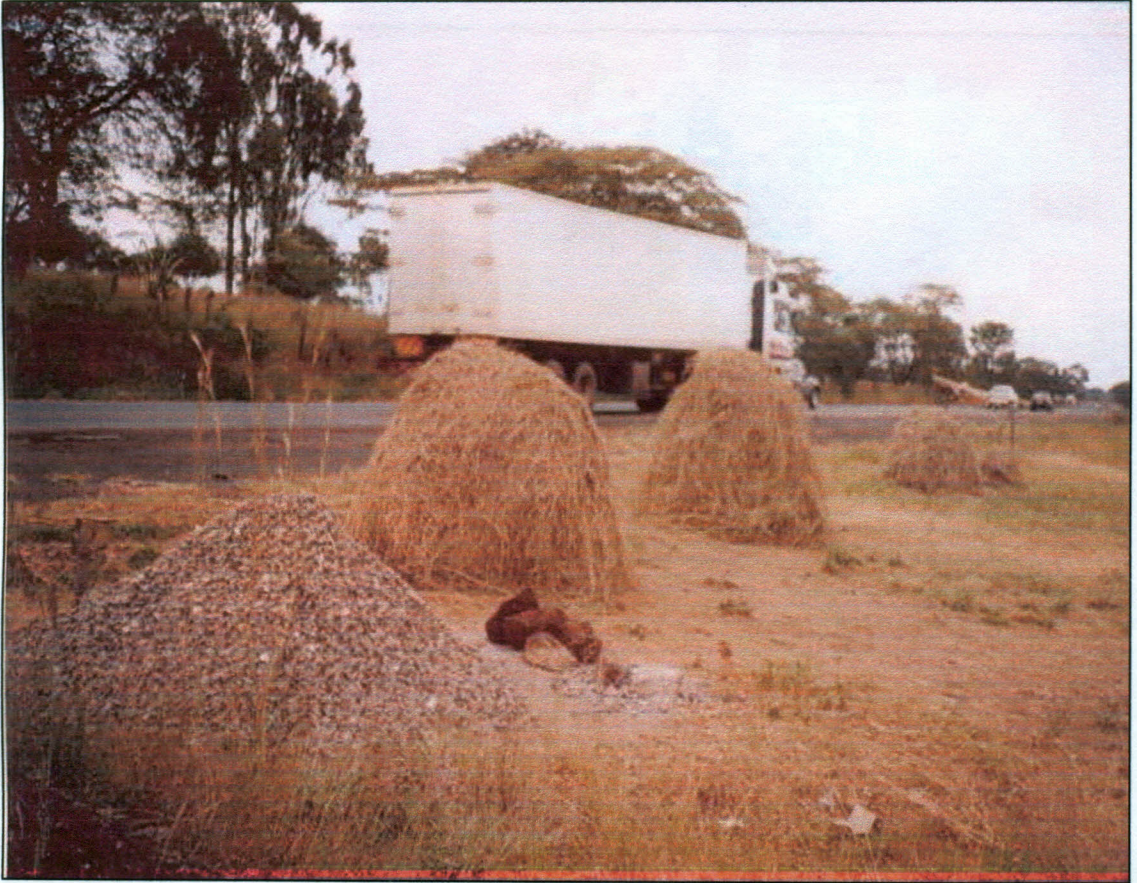
Appendix 1 Growth of motor vehicles in Kenya for the last eight years



Appendix 2 A plate showing congestion of motor vehicles along Thika-Nairobi highway



Appendix 3 A plate showing heaps of pasture grass gathered on a cleared field awaiting transportation to be fed on animals



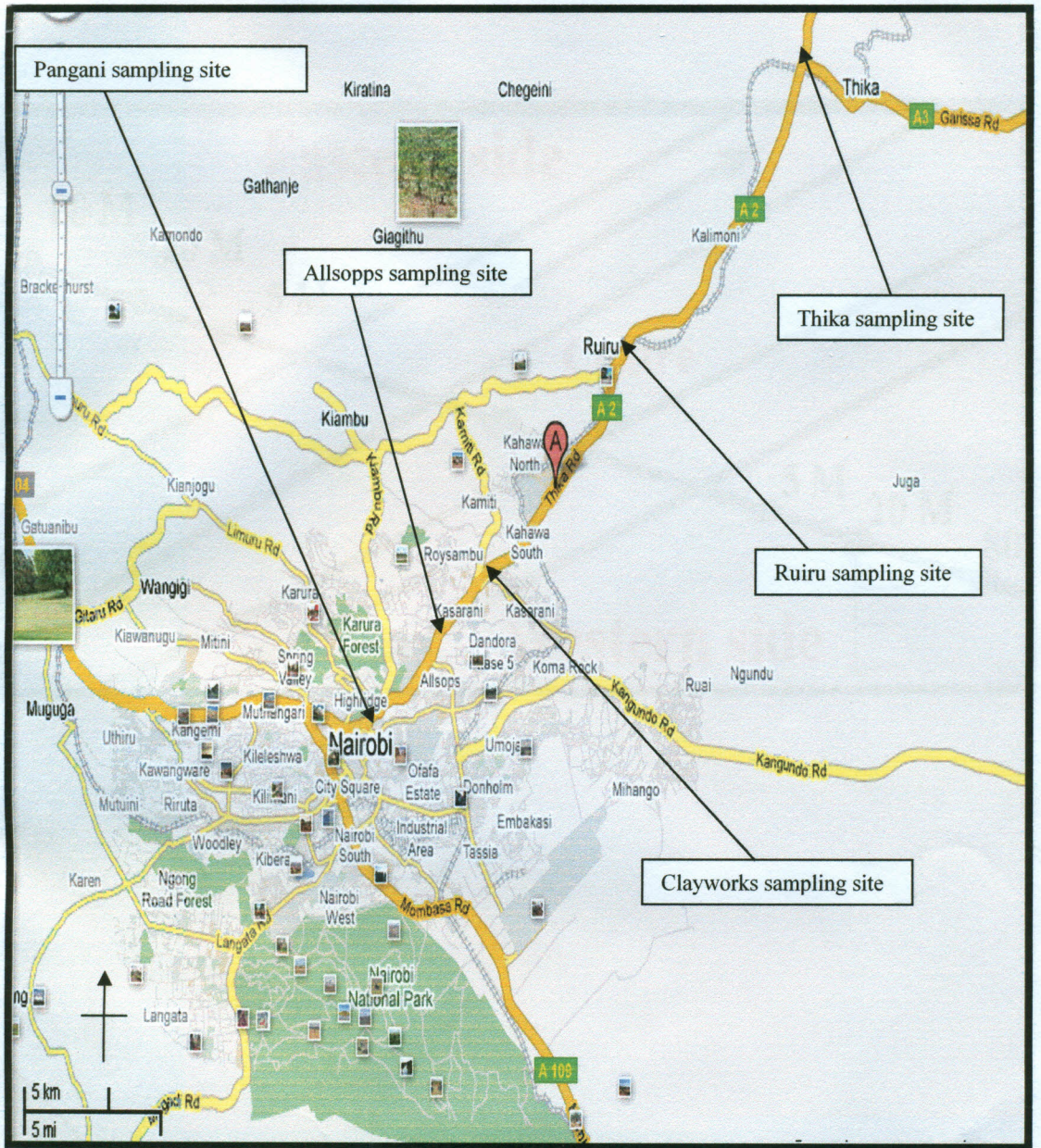
Appendix 4 A plate showing vegetables (spinach) growing along Thika- Nairobi highway



Appendix 5 A plate showing kales growing along Thika-Nairobi highway



Appendix 6 A map of Thika-Nairobi highway showing the sampling sites



Appendix 7 A Thika-Nairobi highway transect established for sampling across the highway

