LEAD, CADMIUM AND ZINC SPECIATION IN GARAGE SOILS, THEIR LEVELS IN KALES AND WATER ALONG KATOTHYANI STREAM, MACHAKOS TOWN, KENYA

BY

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SEPTEMBER, 2013
DECLARATION

I declare that this is my original work and has not been presented in for a degree in any other university.

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Reg No: I56/CE/11716/2007
Signature........................................................Date............................................

We as university supervisors confirm that the work reported in this thesis was carried out by the candidate.

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Signature........................................................Date............................................

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Department of chemistry
Signature........................................................Date............................................
DEDICATION

To the glory of God, my wife Salome. N. Mutua and to my sons Joshua and Caleb.
ACKNOWLEDGEMENTS

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# ABBREVIATIONS AND ACRONYMS

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<thead>
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<tbody>
<tr>
<td>AAS</td>
<td>Atomic absorption spectroscopy</td>
</tr>
<tr>
<td>ANOVA</td>
<td>Analysis of variance</td>
</tr>
<tr>
<td>BAL</td>
<td>British antilewisite</td>
</tr>
<tr>
<td>CDC</td>
<td>Center for disease control and prevention</td>
</tr>
<tr>
<td>EDTA</td>
<td>Ethylene diamine tetraacetic acid</td>
</tr>
<tr>
<td>EDXRF</td>
<td>Energy dispersive X-ray fluorescence</td>
</tr>
<tr>
<td>ICP</td>
<td>Inductively coupled plasma</td>
</tr>
<tr>
<td>ICP-AES</td>
<td>Inductively coupled plasma-atomic emission spectrometry</td>
</tr>
<tr>
<td>ICP-MS</td>
<td>Inductively coupled plasma-mass spectrometry</td>
</tr>
<tr>
<td>MCL</td>
<td>Maximum contamination levels</td>
</tr>
<tr>
<td>MF</td>
<td>Mobility factor</td>
</tr>
<tr>
<td>PPM</td>
<td>Parts per million</td>
</tr>
<tr>
<td>SNK</td>
<td>Student newman kuei’s test</td>
</tr>
<tr>
<td>UNEP</td>
<td>United nations environmental programme</td>
</tr>
<tr>
<td>WHO</td>
<td>World health organisation</td>
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ABSTRACT

Garage waste is a major source of environmental pollution since it contains heavy metals. These heavy metals end up being swept by rain water into rivers. When the water is used for drinking or irrigation the heavy metals end up in animal and human tissues causing adverse health effects. In soil, heavy metals exist in different forms which influence their mobility and bioavailability. These forms include those soluble in water, those exchangeable with other metal ions, the reducible forms (carbonate and oxides), and the oxidisable forms (organic and residual). The water soluble and the exchangeable forms are the most mobile and bioavailable while the oxidisable forms are the least mobile. In Machakos town Kenya, there are many garages situated next to each other and at close intervals. The waste from these garages is swept by rain water to the recipient Katothyani stream which is only 50 metres away. Water from this stream is used for irrigation and drinking hence posing as health risk to the community. The objective of the present study was to determine forms of Pb, Zn and Cd in garage soils of Machakos town and levels in the nearby Katothyani stream water and kales by Atomic absorption spectrometry. Nine composite soil samples each made of three replicates from depth intervals of 0-15, 15-30 and 30-60 cm of Kaunda, Industrial area and Mwangi sites were collected by stratified random sampling and extracted sequentially to determine forms. Forms of Pb and Zn were mainly oxides and organic type. The water soluble and exchangeable fractions were associated with the garage soils at relatively low concentrations with Pb and Zn in these forms contributing less than 5% and 2.6% respectively of the total of each metal extracted. Total heavy metal concentrations (ppm) in soils ranged between 1.61±0.02 to 69.19±0.14 for Pb, 1.61±0.02 to 11.51±0.01 for Zn and Cd was below detection limit. The mobility factors of lead in the top soil profiles ranged between 4.20% and 10.69% while those of zinc were between 9.20% and 15.71%. Levels of the metals in Katothyani stream obtained by random sampling and irrigated kales obtained purposively were also determined. In kales the highest mean concentrations of Pb, Cd and Zn were: 0.03±0.04, 0.01±0.01 and 1.62±0.02 ppm respectively. The mean Pb concentrations for water samples ranged between 0.01±0.01 and 0.14±0.04 ppm while Zn mean concentrations were between 0.00±0.01 and 0.92±0.01 ppm with Cd being below detection limit. ANOVA, SNK test showed significant differences in mean concentrations of Pb and Zn in Industrial area and Mwangi sites with respect to depth. This meant that activities at garage sites caused change in concentrations with depth. In Kaunda garage, the mean concentrations for lead were not significantly different while the mean concentrations for zinc were significantly different for the three soil profiles fractionated (p<0.05, Anova,SNK test). Pearson product moment correlation of water soluble and exchangeable fractions with the total metals showed negative correlation. This indicates that high concentration of heavy metals in garage soils does not necessarily infer their mobility and therefore their bioavailability. The stream and garage soils are slightly contaminated with respect to lead while the kales contained all metals within tolerable levels. Due to variation of mean concentrations of Pb and Zn with depth, as an evidence of surface pollution, there is not only need to relocate garages from the town centre but also to plant indigenous plant species on affected soils to mop up the bioavailable heavy metal forms.
CHAPTER ONE: INTRODUCTION

1.1 Background Information

In industrialized countries, a garage is an enclosed area of land set aside for repair of automobiles (Iwegbue, 2007). In Kenya, the concept of garages is however different as it refers to an open place where the activities of repair and maintenance of motor vehicles take place. Many of the open air garages are characterized by poor waste management practices. In Kenya, vehicle imports have been on the upsurge due to their increased demand with most of them being second-hand from Japan (UNEP, 2006). Garage soil pollution associated with spilling of automobile wastes has not been reported in Kenya. Studies reported have concentrated on emissions along busy highways (Onyari et al., 1991; Wanjala, 2009).

When an automobile is running, the engine oil, transmission oil and hydraulic fluid collect heavy metal debris due to frictional wears. The amount of frictional wear and tear however depends on the age and conditions of the engine and transmission systems. Recycling of engines and gear boxes further increase the amount of tear and wear resulting to increased concentration of heavy metals in used oil. Many of the automobiles in rural areas and middle level towns are old and are often repaired and serviced in open air garages (Cooke, 2000; Kumar et al., 2002).

Although many developing countries embrace the use of unleaded fuel, activities at automobile garages and service centres continue to add heavy metals to the environment. This is due to poor handling of garage waste and a number of vehicle maintenance operations that are harmful to the environment. Some of the waste generated from garages includes old paints, batteries, fluorescent tubes, waste electrical and electronic equipment, exhaust systems, spent
engine and transmission oil, worn out tyres and photochemical aerosols (Garcia and Millan, 1998).

Spent engine oil in particular is a mixture of several different chemicals that reach garage soils directly (Awofolu, 2005). These include low and high molecular weight aliphatic hydrocarbons, aromatic hydrocarbons, polychlorinated biphenyls, chlorodibenzofurans, lubricative additives, decomposition products and heavy metal contaminants such as aluminium, copper, chromium, iron, lead, manganese nickel tin and cadmium. Large amounts of spent engine oils are liberated into the environment as the motor is serviced, and disposed onto the ground (Garcia and Millan, 1998; Awofolu, 2005).

During the rain season, the waste from garage soils is swept to pollute water ways. If water from these water ways is used for irrigation, the irrigated crops bioaccumulate the contaminants and more especially heavy metals (Awofolu, 2005). Research has shown that kales accumulate highest quantities of heavy metals than other green vegetables (Githuku et al., 2010). In a research conducted in Kibera and Maili saba in Nairobi Kenya, it showed that irrigated kales had accumulated lead as high as 29.06mg/kg and cadmium as high as 5.78mg/kg in their leaves. Other irrigated leafy vegetables like black night shade and arrow roots had accumulated lower levels in their leaves on the same soils (Githuku et al., 2010).

The absorption of heavy metals by plants growing on polluted soils is closely related to the forms (chemical species) in the soil matrix (Annex, 2000). Depending on their origin, heavy metals are in different mineral forms and chemical speciation is of interest in environmental analytical chemistry because the behaviour of heavy metals in natural systems depends on forms as well as the amount present (Kabala and Sing, 2001). Since the heavy metals exist in different forms in the soil, their determination is usually performed using sequential extrac-
The procedures involve subjecting a solid sample (soil or sediment) to successive attacks with reagents possessing different chemical properties (acidity, redox potential, or complexing property) in which each extractant dissociates part of the heavy metal bound to it in order of increasing destructive ability (Wasay et al., 2001).

To assess the reactivity of the species or binding forms, of heavy metals in solid materials, de-ionised water, various extraction media electrolytes (CaCl₂ or MgCl₂), pH buffers of weak acids (acetic or oxalic acid), complexing agents (ammonium acetate, Ethylenediaminetetraacetic acid), Reducing agent (Hydroxylammonium chloride) and oxidising agents (Hydrogen peroxide, concentrated nitric acid) have widely been used (Bouchardon et al., 2005).

One of the most popular methods of operationally defined speciation is sequential extraction by Campbell and Tessier (1987). This consists of five steps in which the metals are distributed in the different phases. So far, a six step sequential extraction procedure which is a modified Campbell-Tessier procedure has been applied to soils and sediments to fractionate metals by using different reagents to obtain more useful information (Iwegbue, 2007; Yusuf, 2007). The fractions obtained in a six step extraction include: water soluble, the salt exchangeable part, the carbonate bound fraction, the oxides (easily reducible), the organic bound (easily oxidisable) and the residual fraction which is obtained using a strong oxidising agent (Iwegbue, 2007).

### 1.2 Problem Statement and Justification

Lead, zinc and cadmium can cause poisoning when taken at levels exceeding the defined maximum contamination levels (MCL) set by world health organisation (WHO). These heavy metals have been identified to be found in garage waste. All over the world, due to phenomenal increase in the number of autos, the number of garages has also multiplied. Many of these
garages do not have any elementary schemes for disposing off materials generated while servicing vehicles. Almost all waste is thrown directly to the environment to contaminate water either by percolation or surface runoff (Annex, 2000).

Machakos is a rapidly growing town. It has a high vehicle density as it is the major town in Machakos county and the main connection route to Kitui and Makueni counties. Many open garages have been set up for repair of automobiles as the demand for the service is high. Much of the land on which the open garages are situated is moderately sloppy and this encourages soil erosion. In the vicinity of the garages and about fifty metres away is Katothyani stream into which contaminated rain water from the garages is drained. This water is used for irrigation of kales grown along the stream. It therefore believed that the kales receive pollutants including heavy metals from these garages.

Study in Nairobi have shown high levels of these metals in garages with means ranging between 624 – 659 mg/kg (Onyari et al., 1991), however the chemical forms of these heavy metals have not been identified in garage soils hence the need for this study. The purpose of the present study was therefore to determine forms of lead, zinc and cadmium in the garage soils of Machakos town by sequential extraction as well as their levels in irrigated kales and water in Katothyani stream. It helped determine whether their levels exceed the defined MCL hence assessed the contribution of garage waste to environmental pollution.

1.3 Hypotheses

i. Levels of Pb, Cd, and Zn in Kaunda, Mwangi and Industrial area garage soils are high and in bioavailable forms.

ii. Katothyani stream and irrigated kales contain high levels of cadmium, lead and zinc.
1.4 Objectives

1.4.1 General Objective
To determine forms of selected heavy metals at garage sites of Machakos town and their levels in the nearby stream and irrigated kales.

1.4.2 Specific Objectives
i. To determine forms of Pb, Zn and Cd at garage soils of Machakos town by sequential extraction.
ii. To determine levels of Pb, Zn and Cd in nearby Katothyani stream and irrigated kales.

1.5 Scope of the Study, Limitations and assumptions
The study covered only specific garage sites of Machakos town, a nearby stream and irrigated kales. Analysis involved only three heavy metals in garage soils, water and the leaves of kales. Changes in forms and concentration due to seasonal variation were not studied. This was due to inadequate time and finance. It was assumed that pollution was only due to waste generated from the automobile garages and that the heavy metals were washed to Katothyani stream by surface run off.

1.6 Significance of the Study and Expected Output
The present study assessed the forms of heavy metals in soil as well as their availability in water and irrigated kales. The results obtained are not only relevant to the community in Machakos but also to the nation. It assessed the contribution of automobile waste to heavy metal pollution in garage soils and determined the forms in which these heavy metals are
found. Although the concentrations of Pb, Zn and Cd in kales were below their MCLs, the results indicated an increase in concentration of the various forms with depth hence an evidence of surface pollution with heavy metals by garage waste. These results are important as they suggest that activities at garages cause an increase in heavy metals in the soil and can assist in policy formulation and sensitisation of the community on harmful effects of poor automobile garage waste management. Necessary measures can therefore be taken to control the disposal of the garage waste to the environment and by instituting proper waste handling, disposal and recycling practices.
CHAPTER TWO: LITERATURE REVIEW

2.1 Introduction

Although total heavy metal content in soils provides a convenient means of expressing a measure of pollution, numerous reports have highlighted that such measures are deficient in predicting toxicity of metal pollutants (Yusuf, 2007). Heavy metals may be distributed among many components of the soil or sediment and may be associated with them in different ways (Harrison et al., 1981; Ma and Rao, 1997; Kabala and Singh, 2001). The nature of this association is referred to as speciation. Thus, the chemical form is of great significance in determining the potential bio-availability and remobilization of the soil metals to other compartments (such as water, plants and biota) when physicochemical conditions are favourable.

2.2 lead, Zinc and Cadmium in Soil, Water and Plants

Heavy metals once released to the environment can enter food chain and water. The Soil acts as long term sink for heavy metals which have residence times ranging from hundreds to thousands of years depending on the element and soil properties (Kaara, 1992). They are able to adapt to variable chemical properties of the environment. Figure 2.1 shows how heavy metals circulate by both natural and anthropogenic processes to reach air, soil and plants. Plants accumulate these heavy from soils and partly from water and air which later move to animals and especially to man causing adverse health effects (Cooke, 2000). As figure 2.1 shows, one of the sources of heavy metals for soil pollution is from motor vehicle emissions.
Natural uncontaminated soils contain between 15-40 ppm of lead with no detrimental health effects. The greatest concentration of lead is in the top one to two inches of the soil (Grosse, 1986; Denise and David, 2001). Particulate from automobile emissions of size less than 5 µm have the highest concentration of heavy metals and therefore of greatest hazard to health.
Water from different sources contain different levels of lead but drinking water level should not exceed 0.05 mg/l (Annex, 2000). Zinc is contained in soils at levels of approximately 50 ppm. Zinc levels in Kenya region soils have been found to be 36-290 µg/g and permissible levels of zinc in drinking water is about 50 mg/l (Ofuso et al., 1999; Annex, 2000). Cadmium in Kenya region soils has been found to be 0.25-2.5 µg/g (Ofuso et al., 1999). The levels of cadmium in drinking water should not exceed 0.005 mg/g (Annex, 2000).

A number of factors influence the concentration of heavy metals on and within plants. These factors include climate, atmospheric deposition, the nature of the soil on which the plant is grown and the degree of maturity of the plant (Lake et al., 1987; Grimanis et al., 1996; Scott and Keogh, 1996). The nature of the soil is one of the most important factors in determining the heavy metal content of food plants (Itanna, 2002; Bangira et al., 2002b). However the heavy metal content in plants can also be affected by other factors such as the application of fertilisers, sewage sludge or irrigation with wastewater (Mangwayana, 1995; Schmidt and Devkota, 2002; Frost and Ketchumen, 2002). Heavy metal contamination of agricultural soils can pose long-term environmental problems and is not without health implications (Chumbley, 1982; Ferguson, 1990; Cook et al., 1996). When the metals are derived from anthropogenic sources, this can strongly influence their bioavailability as is the case when metal contaminated water by garage waste is applied to agricultural land (Annex, 2000). Although the concentration of heavy metals in different plants growing in the same environment vary, the allowed concentrations of lead, zinc and cadmium in leafy vegetables are, 0.3 mg/kg, 50mg/kg and 0.2mg/kg respectively (USEPA, 2002).
2.3 Factors Affecting Toxicity of Heavy Metals

Metal toxicity is greatly influenced by intrinsic and extrinsic factors as well as the physiology and ecology of the organism (Nordberg, 2007). Extrinsic factors which may individually or collectively impact on the toxicity of a particular metal are temperature, dissolved oxygen, light, redox potential and salinity of the ambient environment. In addition to influencing the form of the metal, these factors may also contribute to impacts on the physiology of the organism. Concentration is another factor. In case of essential trace metals required for the formation of haemoglobin, both a deficiency and oversupply may prove to be detrimental or ultimately lethal to the organism. For non essential elements, their presence in low concentration may be tolerated by the organism but with increasing levels, it may eventually prove hazardous and lethal to the life cycle and development process. Extrinsic factors either individually or collectively decrease or increase the toxicity of a particular metal by changing the physiochemical nature of the metal in liquid or solid medium and thus changing its availability and consequently toxicity.

The condition of an organism and its environment may greatly influence or facilitate the toxic impact of a metal on a particular organism. Influential physiological variables of an organism impacted on by heavy metals include its entogenic stage, any major change in the life cycle or process, its age, size, gender, nutritional state, physical and metabolic activity and behavioural responses to contaminants (Luckey and Venugopal, 1978; Nordberg, 2007).

Intrinsic factors that influence the toxicity of metals are highly complex and include the synergistic and antagonistic effects. That is, the physiological state or form and how it acts synergistically with other heavy metals. Metal forms encompass inorganic and organic species and whether they are in soluble (ion, complex ion, chelate ion or molecular state) or particulate (colloidal, precipitated, adsorbed or absorbed) configuration. (Fergusson, 1990).
2.4 Health Effects of Zinc, Lead, Cadmium and Treatment

2.4.1 Lead

Lead poisoning primarily affects the chemistry of the nervous system when the MCL is exceeded. It also affects the red blood cells. Some of the effects of lead poisoning are reduced IQ, reduced physical development and neurological disorders (Narwal et al 1999; CDC, 2004). An increased level of lead in the body is the leading cause of anaemia. Although there is no safe and acceptable level of lead in the blood, tolerable levels in the blood samples of young children has been set at 10 µg/dl (Luckey and Venugopal, 1978; CDC, 2004). Lead has no biological role in the body. It mimics essential metals like iron and zinc when ingested allowing it to bind with vital molecules thus disrupting their functioning. It’s more pronounced in children under the age of six and can cause speech delay, hyperactivity, attention disorder, reading disability, behaviour disorder, stunted growth, and cognitive deficit which may persist to adulthood (Needle et al., 1979; CDC, 2004). Lead poisoning manifests itself in the following ways:

2.4.1.1 Lead as Enzyme Inhibitor

Lead coordinates with sulfhydryl groups in enzymes. This causes an inhibition of enzyme activity. The clearest manifestation of the inhibitory effect of lead is the disturbance in the biosynthesis of heme. The latter is the iron containing biomolecule that is precursor to hæmoglobin synthesis which is the oxygen carrying pigment of the red blood cells. Heme is also an essential constituent of the other respiratory pigments, the cytochromes which play key roles in energy metabolism. The decrease in heme biosynthesis leads at first to decrease in the lifespan of red blood cells and later to decrease in the number of red blood cells. However, the rate of production is less than the rate of disappearance. Therefore, in a person suffering
from lead poisoning, immature red cells called reticulocytes and basophilic stippled cells appear in circulation, causing anaemia (Brycesmith, 1972; Sodhi, 2006).

2.4.1.2 Effect of Lead on Kidney
Acute lead poisoning causes impairment of kidney functions. Lead tends to concentrate in the proximal renal tubules lining. There is an increase in the loss of amino acids, glucose and phosphates in the urine because the damaged tubular cells fail to absorb these substances as completely as normal tubular cells do. The energy storage system of the body suffers. Exposure to milder doses of lead causes chronic nephritis, a disease characterised by scarring and shrinking of kidney tissue (Brycesmith, 1972; Sodhi, 2006).

2.4.1.3 Lead and Neurological Disorders
Central nervous system effects are the most serious manifestation of lead poisoning. Continuous exposure to lead over a long period of time causes encephalopathy or brain damage by two mechanisms. Firstly, the blood capillaries reaching the brain start leaking and cause edema, that is swelling of the brain. There is not enough space to accommodate the swelled brain within the periphery of the rigid skull therefore the brain cells get damaged. Secondly, the cells constituting the motor nerve extremities are damaged and the condition of nerve impulse is impaired. Symptoms of encephalopathy initiate with the onset of vomiting, ataxia, periods of alternative stupor, and hyperirritability. Subsequently, these culminate in delirium, convulsions, coma and death (Brycesmith, 1972; Sodhi, 2006).

2.4.1.4 Behavioural Problems Associated with Lead Poisoning
When a person is exposed to milder doses of lead, the neurological damage manifests itself in form of behavioural problems. In such cases the symptoms include excitement, restlessness, insomnia, nightmares, impairment of memory and loss of concentration. In adults these ef-
Effects are reversed when the exposure to lead stops. The picture with children however is very different. In a few cases, childhood attacks of symptomatic lead poisoning can result to hostile, aggressive and destructive behavioural patterns so that there may eventually be need for institutionalization. In large number of cases children suffer because of dulling of mentation and chronic hyperkinesis. The former is followed by educational abnormalities, the latter by an impulse behaviour with a tendency to violence (Brycesmith, 1972; Sodhi, 2006).

2.4.1.5 Reproductive Problem of Lead

Women employed in pottery work where exposure to lead is high are more liable to be sterile than those in general population. If they become pregnant, the pregnancy is more likely to result to miscarriage or still birth. If the child is born alive, there is a higher infant mortality. Plumbism in father also affects the survival, vigour and fertilization of the offspring. This means that many of the males working in automobile garages are at risk of becoming sterile (Brycesmith, 1972; Sodhi, 2006).

2.4.1.6 Teratogenic Effects of Lead

Children born to women who are exposed to lead during pregnancy suffer from convulsions and a form of macrocephaly characterised by a square shaped head. It has also been observed that children born to women who suffered from plumbism, during their childhood may also show birth defects. This means that a girl growing up in a lead polluted environment might years later pass that lead to her offspring (Sodhi, 2006). During adolescence, the lead becomes concentrated in the girl’s bones. During pregnancy, calcium is removed from the woman’s bones and passed to the blood stream. It then enters the placenta to help build the developing embryo’s skeleton. In this process, lead also comes out of bones, crosses the placenta and enters the foetus where it elicits teratogenic effects (Brycesmith, 1972; Sodhi, 2006).
2.4.1.7 Treatment of Lead Poisoning

The treatment of lead poisoning is carried out with potent compounds called chemotherapeutic agents. These compounds tend to sequester lead from the body tissues and bind it in form of soluble complexes. In soluble form, lead is excreted through the kidney. Initially two agents are administered by injection: British antilewisite (BAL) and ethylenediamine tetraacetic acid (EDTA).

With these complexing agents, very high tissue levels of lead are reduced to levels approaching normal and the adverse effects on metabolism are suppressed. After the lead level has been reduced, another chemotherapeutic agent D-penicillamine may be administered orally as a follow-up therapy (Jones and Pratt, 1976; Sodhi, 2006).

2.4.2 Cadmium

Cadmium ranks among the most toxic elements. It accumulates in the duodenum, liver and kidney tissues and is dangerous even in small quantities. Its accumulation in the body can cause cardiovascular, renal and reproductive dysfunctions. The acute effects on oral intake of cadmium are: excess salivation, nausea, vomiting, abdominal pains, diarrhoea and vertigo.
while large doses may lead to loss of consciousness (Sodhi, 2006). The dramatic toxic effect of cadmium is the development of itai itai disease, where the outcome is osteomalacia (softening of bones). The early signs of the problem are joints lumbago pains and pseudo fracturing of bones. Cases of high blood pressure have also been attributed to cadmium toxicity (Fergusson, 1990; Nordberg, 2007).

### 2.4.2.1 Cadmium Poisoning

Consumption of cadmium contaminated food causes enzyme poisoning. Cadmium displaces zinc in many vital enzymatic reactions resulting in disruption or cessation of activity. This leads to acute gastro-enteritis. Epideomologic studies indicate that workers engaged in cadmium related work are more likely to suffer from prostrate and nasopharynx cancers than their counter parts engaged in other activities (Fergusson, 1990).

### 2.4.2.2 Natural Removal of cadmium from the body

Nature has provided a mechanism to protect humans against chronic exposures to low levels of cadmium. Human bodies contain a chelating agent called metallothionein which removes cadmium and other metals from the body. It is a metal containing protein with normally copper and zinc on its structure. The metal free protein thionein, has a molecular weight of about 10,500 and 26 sulphhydryl residues for binding and subsequently removing toxic heavy metals. Cadmium as well complexes with metallothionein through sulphhydryl functions and is then quickly removed through urine (Sodhi, 2006).

### 2.4.2.3 Treatment of Cadmium Poisoning

If the ingested amount is too high, one can not solely rely on natural means of recovery. Unlike lead cadmium can not be removed using BAL. This is because the reagent coordinates to cadmium present in different tissues and transfers the entire complexed metal to the kid-
neys. Other than being eliminated from the body, the complex dissociates in the kidneys and damages this organ. As a result the condition of the person worsens. The most effective chelating therapeutic reagent for cadmium is EDTA. This reagent chelates with cadmium forming a stable and soluble complex that is rapidly eliminated from the body (Sodhi, 2006).

2.4.2.4 Control Measures for Cadmium Pollution

Modern zinc plants are endowed with electrostatic precipitators so as to capture cadmium rich particulates. The waste water from the extraction plant before being discharged into the aquatic system is passed through ion exchangers for removal of cadmium. In the ion exchange resin, cadmium exchanges with more soluble and non toxic cation. Phosphate based fertilizers are treated before being sprayed on agricultural lands to remove cadmium. Cadmium enters the vegetation only if the pH of the soil is within the acidic range. Liming of soil to increase its pH is an effective way of tying up cadmium as an insoluble hydroxide and metals. Unwanted cadmium containing utilities are now not directly incinerated, instead they are subjected to waste separation technologies to isolate the cadmium content. The cadmium free waste is incinerated while the separated cadmium is immobilised by vitrification (Alloway and Ayres, 1993)

2.4.3 Zinc

2.4.3.1 Zinc as an essential trace element

Zinc is required by both plants and animals in small concentrations. It is a component of enzymes which play key roles in growth, for example alkaline phosphatise and carboxy peptidase. In humans its deficiency can cause delayed sexual maturity (Sorenson and Tepper, 2000).
2.4.3.2 Effects of excess zinc in the human body

The free zinc ion is a very powerful Lewis acid. Stomach acid contains hydrochloric acid in which metallic zinc dissolves to give corrosive zinc chloride (Prasad, 2003). It can cause severe hemolytic anaemia as well as liver and kidney damage. Vomiting and diarrhoea are possible symptoms of zinc poisoning. Zinc can also damage nerve receptors in nose which can cause anosmia (Prasad, 2003; Hambidge and Krebs, 2007).

2.5 Sources of Heavy Metals for Garage Soil Contamination

Due to phenomenal increase in the number of autos, garage sourced waste is also on the increase. This waste includes waste oil, lubricants, discarded oil filters, tyres, acid batteries, paints, gas filters, brake pads, bearings and nuts. Heavy metals from the waste contaminate water through percolation or surface run off (Bowen, 1979; Annex, 2000). Bearings, races, nuts and bolts are cadmium coated and are used widely in the construction of cars. Cadmium also protects junctions between different metals (Fergusson, 1990). Alloys containing cadmium are also used in bearings; (Cd 99%, Ni 1%). Pigments containing CdS are also used in paints because they have high stability to heat and UV radiation and do not darken in H₂S atmosphere. Their colours range from yellow to red (Fergusson, 1990; Annex, 2000). The automobile industry uses large proportion of lead in car battery and in solder and the principal use of lead is in lead accumulators. Oil acquires too many impurities in the process of combustion or compression, including heavy metals. Cadmium is also used in certain exotic lubricants and finds its way to oil (Annex, 2000). The toxic effect of metals depends not only on total concentration but also the form of the metals. Soluble forms of the metals are more toxic than non soluble ones (Kabata and Pendias, 1992). Garage waste together with waste from other industries can contribute to high levels of these metals in soils and rivers hence need for this study.
2.6 Sequential Extraction Techniques

The analysis of heavy metal species in soil, dust or sediment, can be undertaken by either acid digestion or sequential extraction techniques. Analysis using acid digestion allows the analyst to ascertain the total content of heavy metal contamination. However, it is insufficient when assessing the environmental impact of the contaminated soil or sediment, since the chemical form which the metal is in will determine its behaviour and hence mobility and bioavailability. Although several extraction schemes for soil and sediments have been described, selective sequential extraction procedures are commonly used for studying chemical mobility and availability in soils since such procedures provide qualitative information on forms, associations, bioavailability and potential harmful effects of soil metals as well as a guideline in the choice of remediation technologies (Abolino et al., 2002). These heavy metals end up in water and are absorbed by plants when the water is used for irrigation (Sopper and Kerr, 1979; CDC, 2004).

Sequential extraction procedures, based upon Bisson *et al* (1979), Yusuf (2007), and Iwegbue (2007) are useful in assessing the relative geochemical forms that may be present in the sample being tested. Sequential extraction techniques use successive chemical extractants of various types in order of greater destructive ability and therefore possess greater sensitivity than a single extraction procedure. Specifically defined ‘speciation’ of soils and sediments is difficult due to numerous environmental variables (Kabala and Singh, 2001). Consequently, operationally defined ‘speciation’, using sequential extraction schemes have been developed for assessing geochemical forms in soil and sediment (Harrison *et al.*, 1981; Ma and Rao, 1997). Fractionation by selective chemical extraction removes or dissociates a specific phase with the associated metal bonded to it. The geochemical fractions most commonly analysed for are: water soluble, exchangeable, bound to carbonates, iron manganese bound, organic

2.7 Mobility and Bioavailability of Heavy Metals

It has been suggested that mobility and bioavailability of metals decrease apparently in order: water soluble > exchangeable > carbonate bound > Fe-Mn oxides bound > organic bound > residual (Wasay et al., 2001). The water soluble, exchangeable and carbonate bound fractions therefore indicate the forms in which metals are most available for plant uptake and metals retained in the residual fraction are expected to be immobile in the soil.

2.8 Methods of Analysis

Some methods used in heavy metal analysis are AAS, EDXRF and ICP (Fergusson, 1990; Abolino et al., 2002). For analysis of various fractions obtained by sequential extraction, AAS, ICP-MS and ICP- AES are used (Iwegbue, 2007). ICP-MS and AAS are most preferred because they are not prone to polyatomic interferences and are less affected by matrix suppression (Harrison et al., 1981). The method used in the present study for analysis was AAS due to its availability. AAS is simple, sensitive and selective and has the advantage of being a fast method of analysis (Katz, 1984).

2.8.1 Atomic Absorption Spectroscopy

This technique was introduced for analytical purpose by Walsh and Alleemade, Mihaz in the year 1956 under the designation Atomic absorption spectroscopy (Nordberg, 2007). It is found to be superior to other techniques as it can be used to determine 50-60 elements from trace to large quantities. It involves use of a flame to convert the sample into free atoms of the element being analysed. A beam of monochromatic radiation is passed through these atoms from a hallow cathode lamp source of a wavelength specific to each element. These at-
oms absorb radiation in proportion to the number in the flame. Absorbance is related to concentration by Beer-Lambert’s law in which absorbance is directly proportional to the concentration of absorbing species.

2.8.2 Principle
The sample is first converted into an atomic vapour and then the absorption of atomic vapour is measured at a selected wavelength characteristic of atoms of each element. The amount of light absorbed is determined because the absorption is proportional to the concentration of the element.

2.8.3 Instrumentation
2.8.3.1 Radiation Source
Hollow cathode lamp is widely used. It is a thick walled glass tube with a transparent window at one end. Tungsten wires are sealed into other end of the tube, which acts as anode. Other wire is attached to a hollow metal cylinder which acts as cathode. The tube is filled with helium or argon at 1-2 mm/Hg pressure.

![Figure 2.2 Radiation source. Hollow cathode lamp](image)
2.8.3.2 Atomizers

It is the one which introduces the spray into the flame. Atomization refers to breaking the sample in solution into gaseous atoms. There are various methods of atomization, the first one being flame atomization in which the burner and a nebulizer help in the atomization of the element. The flame is produced in the burner where the combustion occurs and an atomic vapour of the element to be analyzed is produced. The selection of flame temperature is important for atomization. When it is low, atomization will be incomplete. When it is high, the atoms may be ionized. A second type of atomization is graphite furnace atomization. It is used in graphite furnace atomic absorption spectroscopy. The atomizer may be elongated along its axis to increase the distance between the optical path and the sample deposition point. The elongation of atomizer increases the analytical sensitivity. Oxidants and fuel are also used to provide energy for atomization process. Fuels used are hydrogen, propane, butane, acetylene and natural gas and the one which is widely used is acetylene. Oxidants used are air enriched with oxygen, oxygen and nitrous oxide.

<table>
<thead>
<tr>
<th>Flame</th>
<th>Temperature</th>
<th>Examples of elements analysed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air – Coal gas</td>
<td>1800</td>
<td>Zn, Cu, Cd, Pb</td>
</tr>
<tr>
<td>Air – Propane</td>
<td>1900</td>
<td>Volatile and noble gases</td>
</tr>
<tr>
<td>Air – Acetylene</td>
<td>2300</td>
<td>Sn, Ba, Cr</td>
</tr>
<tr>
<td>N₂O – acetylene</td>
<td>2955</td>
<td>Al, V, Tp, Bi, Se</td>
</tr>
</tbody>
</table>

Table 2.1 Flame and Flame temperature requirement
2.8.3.3 Monochromator

It is important that this instrument be capable of providing a narrow band width to separate the line chosen for determination from other undesirable lines. Usually gratings or prisms are used.

2.8.3.4 Lenses and slits

They are used for the isolation of required spectral line from the total spectrum.

2.8.3.5 Detectors

Photo multipliers are commonly used as detectors. In some instruments two filters and two detectors are used to compensate the fluctuations in the output. The output of photomultiplier is taken to amplifier which helps in source modification.

2.8.3.6 Read out device

A chart recorder is used as a read out device. A schematic diagram showing the components of an atomic absorption spectrometer is given in figure 2.2.

![Schematic diagram showing the components of an atomic absorption spectrometer](image)

Figure 2.3 Schematic diagrammatic representation of AAS

2.8.4 Working of the instrument

A blank solution is sprayed into the flame and the meter is adjusted for zero absorbance or 100% transmittance. Now the solution under investigation is sprayed, the atoms in excited
state absorb certain part of light resulting in decrease in transmitted light or increase in absorbed light falling on photomultiplier. This gives a deflection in the meter needle, with the help of standard graph, the concentration of a particular element in the sample can be determined.

2.8.5 Interferences

Though atomic absorption spectrophotometers are free from spectral interferences, they are prone to chemical interferences. Normally in AAS, chemical interferences could occur, due to the nature of the ions involved. For example, the phosphate ions interfere with the determination of calcium and magnesium. The reason is the formation of phosphates of calcium and magnesium, which prevents the easy breakage of Ca and Mg atoms into the flame. This interference could be reduced by the addition of salt of lanthanum or thorium. These salts will form a bond with phosphate ions. Therefore the calcium and magnesium ions can be determined easily. The second type of interference is ionization interference which also occur in AAS along with chemical interferences. Such interference occurs when the free metal atom undergoes ionization as follows:

\[ M_{(g)} \rightarrow M^+_{(g)} + e^- \]

This occurs with alkali metals as they need very low energy for their ionization. If a deionizer or a radiation buffer is added, then this type of interference may be overcome during analysis.
CHAPTER THREE: MATERIALS AND METHODS

3.1 Research Design

The study design was experimental. It aimed at determining forms of Pb, Cd and Zn in Kaunda, Mwangi and Industrial area garage soils as well as their levels in water and kales along Katotthyani stream of Machakos town. Soil sampling was done in the dry months of July to September by stratified random sampling, water sampling in the rainy months of October to December by systematic random sampling and kales in the dry months of January to March after they had been irrigated with water from katotthyani stream. Soil samples underwent sequential extraction to obtain six fractions per sample while the water and kale samples were subjected to acid digestion. Determination of heavy metal content in the samples was done using AAS and data analysed by ANOVA.

3.2 Sampling Sites

Samples for analysis were collected from Machakos main garage sites and along the nearby katotthyani stream. The garages were namely, Industrial area, Mwangi and Kaunda. These are the most spacious and the busiest garages. They have also served for over twenty years.

3.2.1 Industrial Area

This site is located to the western side of Machakos town. It has adequate parking space and moderate carrying capacity. Apart from the automobile repair work, a section of it is reserved for dumping of old damaged vehicle parts. It is on a flat surface of land.
3.2.2 Mwangi

This garage site is to the eastern side of Machakos town. It is on the entry point to Machakos from Mbooni and Kitui. It is the oldest garage in Machakos and has been in operation since the colonial era. Although it has a moderate parking space, it is usually a busy site owing to its proximity to the Machakos bus terminus. It is also on a moderate slope.

3.2.3 Kaunda

It is located to the eastern side of the town and adjacent to Mwangi site. It’s also on a moderate slope. It’s only fifty metres away from Katothyani stream and much of the discarded
waste end up in the stream. Soil had recently been spread and the ground flattened by the automobile garage owner before sample collection.

3.3 Sampling

At each garage site, samples were collected by stratified random sampling design. This involved subdividing each garage site into cells (10m by 10m) with each cell denoting a sampling point and soil samples collected at depths of 0-15 cm, 15-30 cm, and 30-60 cm. The samples at the same depths at each garage site were combined to form a representative sample for the horizon. This was done to avoid bias and give a good representation of each garage site. Soil sampling was done during the dry season of July to September to avoid rain washing of the heavy metals. A soil trowel and a tape measure were used for soil sampling. After sampling samples were placed in plastic containers and sealed to avoid contamination and taken to the laboratory for analysis.

Water sample were collected by random sampling along the Katothyani stream. This involved selecting a point near the source at random and water samples collected at intervals of 100m from each other downstream during the wet season of October to December (n=20). Kale samples were collected purposively at their growing points along the stream. This is because they were not evenly distributed at their growing points adjacent to the stream. Sampling was done during the dry spell January to March after they had been irrigated with the stream water.

3.4 Cleaning of Glassware and Sample Containers

All sampling containers and glassware to be used were washed in detergent then soaked in 50% nitric acid for 24 hours to leach out adsorbed metal ions (APHA, 1995). They were then
rinsed in tap water followed by de-ionised water before drying in a dust free area. The bottles were then packed and sealed in separate bags.

3.5 Chemicals/ Reagents.

The reagents used for chemical analysis were from (BDH Chemicals Ltd. Poole England) and were purely analytical grade.

3.6 Preparation of Standard Solutions

To make zinc stock solution, 1 g of analytical grade granulated zinc metal purity (99.9%) was dissolved in 30 mL of 5 molar hydrochloric acid. This was then diluted to 1 litre mark using distilled deionised water. The desired concentrations were prepared by serial dilution using the formula

$$C_1V_1 = C_2V_2$$

Where $V_1$ is the volume of the initial solution to be diluted and $C_1$ is its concentration. $V_2$ is the expected volume after dilution and $C_2$ is the expected concentration. For example to prepare 50 mL of 500 ppm from 1000 ppm we require 25 mL of the latter. That is:

$$1000\text{ppm} \times V_1 = 500\text{ppm} \times 50 \text{ ml}$$

$$V_1 = (500\text{ppm} \times 50\text{ml}) \div (1000 \text{ ppm})$$

$$V_1 = 25 \text{ ml}.$$  

Lead stock solution was obtained from spectroscopic grade lead nitrate (BDH Chemicals Ltd. Poole England). To prepare 1000 ppm, 1.598 g of lead nitrate was dissolved in 100 ml of deionised water. The solution was diluted to one litre in a volumetric flask using more deionised water. The desired concentrations were prepared by serial dilution as described for zinc. To prepare a stock solution of cadmium, 2.036 g of analytical grade cadmium chloride was dissolved in 250 ml deionised water. This was diluted to one litre in a volumetric flask. From the stock solution, standards were prepared which ranged from 0.01 to 100 ppm. In each of
these cases, the stock solutions were stored in polyethylene bottles to minimize loss of the metal through adsorption. Standards were freshly prepared each time an analysis was to be carried out.

### 3.7 Preparation of Solutions for Sequential Extraction

#### 3.7.1 Magnesium Chloride

One molar magnesium chloride solution was prepared by dissolving 95 g of magnesium chloride in 250 mL of deionised water and then diluting to one litre in a volumetric flask.

#### 3.7.2 Ammonium Acetate

One molar ammonium acetate was prepared by dissolving 77 g of ammonium acetate in 250 mL of deionised water and then diluting to one litre in a volumetric flask using deionised water.

#### 3.7.3 Hydroxy Ammonium Chloride

0.04 molar hydroxyl ammonium chloride was prepared by dissolving 2.78 g in 250 mL of deionised water and then diluting to one litre of solution in a one litre volumetric flask.

#### 3.7.4 Hydrogen Peroxide

30% hydrogen peroxide was prepared by diluting 300 mL of hydrogen peroxide to one litre of solution in a one litre volumetric flask using deionised water.

#### 3.7.5 Ammonium Acetate

3.2 molar ammonium acetate was prepared by dissolving 246.66 g of ammonium acetate in 250 mL of deionised water and then diluting to one litre in a volumetric flask using more deionised water.
3.7.6 Aqua Regia

This was prepared by mixing concentrated nitric acid and concentrated hydrochloric acid in the ratio 1:4 volumes respectively. 200ml was prepared for extraction and it involved adding 40 cm$^3$ of concentrated nitric acid to 160 cm$^3$ of concentrated hydrochloric acid.

3.7.7 Two Percent Nitric Acid

20 mL of analytical grade concentrated nitric acid were added to 980 mL of water in a one litre volumetric flask.

3.7.8 Two Molar Nitric Acid

126.78 mL of analytical grade concentrated nitric acid was added to 250mL of deionised water and the mixture diluted further in a one litre volumetric with more deionised water. The specifications of the acid were as follows:

- Molecular weight = 63.01
- Essay = 69 - 71
- Specific gravity = 1.42 g/ cm$^3$
- Mass of 1000 ml = 1000 × 1.42 = 1420 grams
- Moles of nitric acid in one litre = (70 ÷ 100) × (1420 ÷ 63.01) = 15.78
- Volume to be diluted to one litre = (2 × 1000) ÷ 15.78 = 126. 78 mL

3.8 Preparation of Blanks

In order to correct for background effects from the reagents used for sequential extraction, an empty centrifuge tube was used for the six steps of sequential extraction. For the vegetable and water blanks, 6% nitric acid solution used in the preparation of the samples was prepared and treated in a similar way as the samples These were used to calibrate the instrument before samples were introduced into the flame.
3.9 Sample Preparation

3.9.1 Soil Samples

All soil samples were air dried, ground and passed through a 2 mm sieve. They were further dried in an oven at 150 °C for 24 hours. Soil sample from each horizon at each garage site was used to separate metals into six operationally defined fractions through sequential extraction. (Kabala and Singh, 2001; Iwegbue, 2007). To obtain the water soluble fraction (F1), the soil sample was extracted with 20 mL of de-ionised water for two hours. For exchangeable fraction (F2), residue of (F1) was extracted with 20 mL of 1 mol L⁻¹ MgCl₂, pH 7 for 1 hour. The third fraction was the carbonate bound fraction (F3), which was extracted from residue of fraction (F2) with 20 mL of 1 mol L⁻¹ NH₄OAC pH 5 for 5 hours. Fe-Mn oxides bound fraction (F4) was obtained from residue of (F3) by extracting it with 20 mL of 0.04 mol L⁻¹ NH₂OH.HCl in 25% (v/v) HOAC at 96 °C with occasional agitation.

Organic bound fraction (F5) came from residue of (F4) which was extracted with 15 mL of 30% H₂O₂ at pH 2 (adjusted with nitric acid) for 5.5 hours (water bath, 85 °C). After cooling, 5mL of 3.2 Mol L⁻¹ NH₄OAC in 20% HNO₃ was added and shaken for 30 minutes before final dilution to 20 mL with de-ionised water. For residual fraction (F6), residue of (F5) was placed in a 250 mL glass beaker and digested with 8 mL, of aqua regia on a sand bath for 2 hours. After evaporation to near dryness, the sample was dissolved with 10 mL of 2% nitric acid, filtered and diluted to 50 mL with distilled water. The solid phases (with an exception of F6) were washed with 10 mL of de-ionized water before further extraction. The washes were collected and analysed with supernatant from previous fraction. After each extraction, the supernatant was separated by centrifugation for 30 minutes. To verify the sum of the metal recovered, in the sequential extraction, a separate total concentration, of Cd, Pb and Zn was determined on the sub samples after aqua regia digestion. Quality control was assured by use of triplicates and preparation of blanks (Fergusson, 1990; APHA, 1995; Iwegbue, 2007).
3.9.2 Water Samples

50 cm³ of water sample was filtered using a whatman No 41 (0.45 nm pore size) filter paper for estimation of dissolved metal content. 10 cm³ of analytical grade nitric acid was then added and the mixture heated on a digestion block to evaporate it to about 25 cm³ with occasional addition of few drops of analytical grade H₂O₂. After evaporation the solution was diluted in a 50 mL volumetric flask with distilled water and filled to the mark (Hunt and Wilson, 1986; Grande, 1996; Paar, 1998).

3.9.3 Vegetable Sample

Kale samples were washed with tap water to remove adhering soil particles and then rinsed with distilled water. The samples were then cut into small pieces, air dried for 2 days and finally dried at 100 ± 1 °C in hot air oven for 3 hours (Kabata and Pendias, 1992). The samples were then ground and passed through a 1 mm sieve. Digestion involved measuring 1g of the ground sample and placing it in a clean flask. To the flask, 5ml of analytical grade HNO₃ was added and the flask placed on a hot digestion block and H₂O₂ added drop wise. The mixture was then filtered and diluted to 50 mL in a volumetric flask (Paar, 1998).

3.10 Determination of Pb, Zn and Cd in samples

Determination of Pb, Zn and Cd in samples was done using AAS technique (Spectr AA-10 Varian Techtron Pty Ltd. Australia) interfaced to a computer. Calibration curves were prepared from Zn, Pb and Cd standards by running different concentrations of the standard solutions. The spectrometer was set to zero by running the respective reagent blanks. Average values of the triplicates were taken for each determination. Samples were aspirated into a nitrous oxide acetylene flame. The detailed theory of AAS has been described in chapter 2. The experimental parameters that were used are presented in the table 3.1.
Table 3.1 AAS Operating conditions

<table>
<thead>
<tr>
<th>Operating parameters</th>
<th>cadmium</th>
<th>lead</th>
<th>zinc</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavelength (nm)</td>
<td>228.8</td>
<td>217.0</td>
<td>213.9</td>
</tr>
<tr>
<td>Slit width (nm)</td>
<td>0.2</td>
<td>0.3</td>
<td>0.2</td>
</tr>
<tr>
<td>Lamp current (mA)</td>
<td>3.0</td>
<td>4.0</td>
<td>3.0</td>
</tr>
<tr>
<td>Detection limit (ppm)</td>
<td>0.01</td>
<td>0.005</td>
<td>0.009</td>
</tr>
</tbody>
</table>

3.11 Statistical Analysis

ANOVA test was carried out to find out whether there was significant difference in the means of heavy metals at different levels of each garage site. Pearson product moment correlation was used for correlation analysis of the concentrations of heavy metals in soil, water and kales. For samples with values below the detection limit half of the respective limit quantification was used to perform statistical analysis (Miller and Miller, 1984).
4.1 Introduction

A sequential extraction procedure Salbu et al., (1998) which is a modified version of Bisson et al., (1979) was used to characterize how the heavy metals are retained in the soil. Heavy metals were analysed on the basis of elemental composition of each horizon per garage site. The results described in this chapter are for garage soils collected in the profiles of three main garages of Machakos and for water, and kale samples all collected from along nearby Kato-thyani stream. The garage sites are namely, Industrial area, Mwangi and Kaunda as described in chapter 3. The soil samples were sequentially extracted and analyzed for lead, zinc and cadmium based on two parameters per site: elemental composition per fraction in each horizon and that of depth in the three soil profiles considered. The analytical data for the three garage sites, water and kales are summarised in the tables 4.2.1 to 4.5.2 and graphical representations of mean levels are shown in figures 4.2.1 to 4.4.2.

4.2 Forms of Heavy Metals in the Soil Profiles of Garage Sites

The mean levels of the various forms in the various horizons were obtained as a result of calculating the average mean level of each horizon for the three horizons per garage site at depths of 0-15 cm, 15-30 cm and 30-60 cm for Kaunda, Mwangi and Industrial area respectively.

4.2.1 Forms of Lead in the Soil Profiles of the Three Garage Sites

From Table 4.1 the mean levels (ppm) in the various forms of the upper soil profiles (0-15cm) ranged from 0.01 ± 0.01 to 0.74 ± 0.02 for Kaunda site, 0.02 ± 0.02 to 44.08 ± 0.03 for Mwangi site and 0.00±0.00 to 17.92 ± 0.06 for Industrial area site as indicated. In the second profile (15-30cm), the various lead levels ranged from 0.00 ± 0.01 to 1.03 ± 0.01 for Kaunda
site, 0.02 ± 0.02 to 1.68 ± 0.02 for Mwangi site and 0.00 ± 0.00 to 9.27 ± 0.05 for Industrial area site. As far as the third profile is concerned, the various lead levels ranged from 0.02 ± 0.02 to 1.68 ± 0.02 for Kaunda site, 0.07 ± 0.01 to 3.02 ± 0.02 for Mwangi site and 0.00 ± 0.00 to 4.90 ± 0.02 for Industrial area. The forms of lead at the three garage sites are predominantly the Fe-Mn oxides bound and the organic layers with their highest concentrations being 1.68 ± 0.02 and 0.93 ± 0.04 for Kaunda site, 44.08 ± 0.30 and 15.56 ± 0.32 for Mwangi site and 17.92 ± 0.06 and 17.18 ± 0.28 for Industrial area.

The general trend is a decrease from the upper soil profile to the bottom profile with an exception of Kaunda site whose results depict a general increase. This could be due to the fact that it had been levelled with soil before soil sampling and the bottom profile therefore showed the highest concentration of the different forms of lead.

The garage with the highest mean levels of lead is the Mwangi garage recording the highest concentrations of 44.08 ± 0.30 and 15.56 ± 0.32 for Fe-Mn oxides bound and organic bound fractions respectively. The high concentration of lead at this garage site was probably due to its long time of operation and because of being preferred to other sites owing to its proximity to Machakos bus terminus.

The water soluble fractions and exchangeable fractions were relatively lower in ppm compared to the distribution of lead in the carbonate bound fraction for the soil profiles as depicted in the table 4.1. Water soluble fraction for the upper soil profile (0-15 cm) was as low as 0.01 ± 0.01 for Kaunda site, 0.02 ± 0.02 for Mwangi site and 0.05 ± 0.03 for Industrial area sites respectively. On the other hand, the exchangeable fraction was 0.1 ± 0.01 for Kaunda site, 0.14 ± 0.04 for Mwangi site and 0.00 ± 0.00 for Industrial area site for the top soil profiles respectively. Comparing these to the distribution of lead in the carbonate bound
fraction which was 0.06 ± 0.02 for Kaunda site, 5.93 ± 0.02 for Mwangi site and 1.57 ± 0.04 for Industrial area site for the same top soil profiles suggests very minimal contribution if any of these two phases to the mobility and bioavailability of lead. These results therefore suggest low mobility and bioavailability for lead because it is mainly distributed in the organic and Fe-Mn oxides bound fractions. Yusuf (2007) also found lead to be largely bound to the Fe-Mn oxides (reducible forms) as well as the organic fractions (oxidisable). Under oxidising conditions, metals present in both natural organic matter (due to complexation and peptization) and living organisms (as a result of bioaccumulation of metals) may be remobilised to the environment. Since the concentrations of these elements are not above their MCLs it therefore means that these favourable conditions of reduction and oxidation are not highly pronounced (Bisson et al., 1979).

The predominance of Fe-Mn oxides and organic bound fractions is in broad agreement with the results reported by Kabata and Pendias (1992) and Ramos et al. (1994) that found most lead associated with the oxides fraction in their study of spanish soils, with only very small amounts in the exchangeable and water soluble fractions. Although some lead was found in the residual fraction, there are low chances of this fraction being mobile. This is because the residual phase represents metals largely embedded in the crystal lattice of the soil fraction and should not be available for remobilization except under very harsh conditions. The results for the mean levels of the various forms of lead with depth profiles are shown in the table 4.1 and illustrated graphically in figure 4.1.
Table 4.1 Distribution of lead from different fractions of the garage soils with depth (ppm)

<table>
<thead>
<tr>
<th>Garage(n=3)</th>
<th>Depth(cm)</th>
<th>Water soluble (F1)</th>
<th>Exchange-able (F2)</th>
<th>Carbonate bound (F3)</th>
<th>Fe-Mn oxides (F4)</th>
<th>Organic (F5)</th>
<th>Residual (F6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaunda Site</td>
<td>0-15cm</td>
<td>0.01±0.01</td>
<td>0.1±0.01</td>
<td>0.06±0.02</td>
<td>0.74±0.02</td>
<td>0.43±0.04</td>
<td>0.25±0.04</td>
</tr>
<tr>
<td></td>
<td>15-30cm</td>
<td>0.00±0.01</td>
<td>0.10±0.01</td>
<td>0.01±0.02</td>
<td>1.03±0.01</td>
<td>0.51±0.06</td>
<td>0.28±0.04</td>
</tr>
<tr>
<td></td>
<td>30-60cm</td>
<td>0.02±0.02</td>
<td>0.12±0.03</td>
<td>0.16±0.02</td>
<td>1.68±0.02</td>
<td>0.93±0.04</td>
<td>0.51±0.04</td>
</tr>
<tr>
<td>Mwangi Site</td>
<td>0-15cm</td>
<td>0.02±0.02</td>
<td>0.14±0.04</td>
<td>5.93±0.02</td>
<td>44.08±0.30</td>
<td>16.56±0.32</td>
<td>2.46±0.02</td>
</tr>
<tr>
<td></td>
<td>15-30cm</td>
<td>0.07±0.01</td>
<td>0.98±0.02</td>
<td>0.77±0.07</td>
<td>7.12±0.02</td>
<td>5.37±0.04</td>
<td>0.67±0.02</td>
</tr>
<tr>
<td></td>
<td>30-60cm</td>
<td>0.07±0.01</td>
<td>1.01±0.08</td>
<td>0.63±0.03</td>
<td>3.02±0.02</td>
<td>2.23±0.06</td>
<td>0.41±0.04</td>
</tr>
<tr>
<td>Industrial Area site</td>
<td>0-15cm</td>
<td>0.05±0.03</td>
<td>0.00±0.00</td>
<td>1.57±0.04</td>
<td>17.92±0.06</td>
<td>17.18±0.28</td>
<td>1.81±0.03</td>
</tr>
<tr>
<td></td>
<td>15-30cm</td>
<td>0.06±0.02</td>
<td>0.00±0.00</td>
<td>1.48±0.03</td>
<td>9.27±0.05</td>
<td>7.18±0.04</td>
<td>0.74±0.02</td>
</tr>
<tr>
<td></td>
<td>30-60cm</td>
<td>0.05±0.02</td>
<td>0.00±0.00</td>
<td>0.26±0.05</td>
<td>4.90±0.02</td>
<td>1.68±0.04</td>
<td>0.27±0.03</td>
</tr>
</tbody>
</table>

4.2.2 Mobility Factors for Lead

Table 4.2 gives the mobility factors calculated for each soil profile at each garage site in terms of the percentage of mobile phases relative to the total heavy metal content for all phases in a horizon. The mobility factor of metals in soil samples may be assessed on the basis of absolute and relative of weakly bound fractions to soil components. The relative index of metal mobility was calculated as a mobility factor (MF; Kabala and Singh, 2001; Narwal et al., 1999; Salbu et al., 1998) on the basis of the following equation.

$$MF = \frac{(F1+F2+F3)}{(F1+F2+F3+F4+F5+F6)} \times 100$$

(Where F1 to F6 represents the various forms in the order given in table 4.1). Since some metal forms (extracted in F3) are relatively less mobile (more strongly bound to the soil components than those extracted in F1 and F2), the above index describes the potential mobility (Kabala and Singh, 2001). The soil samples had mobility factors of lead as presented on table 4.2 From the table, mobility factors of
10.99%, 8.80% and 4.20% for top most soil profile for Kaunda, Mwangi and Industrial area sites were obtained respectively. The MF values above 10% for this element Pb, is a symptom of moderate stability in the soil samples (Yusuf, 2007). Higher MF values have been interpreted as symptoms of high lability and biological availability of heavy metals in the soils (Ma and Rao, 1997; Kabala and singh, 2001). Mwangi site showed the highest MF in the lower soil profile and the order of MF increased in the order Industrial Area site<Kaunda site<Mwangi site with MF of 4.33%, 8.77% and 23.20% respectively. Due to erosion, the lower soil profiles can also be exposed to surface run off. Because of the loose soil on the upper profile of Kaunda site, the nearby Katothyani stream is at risk of receiving lead from Kaunda site due to its MF of near 10% in the lower profile. The site is also nearest the stream and on a moderate slope.

Table 4.2 Mobility factors of lead for each soil profile at each garage

<table>
<thead>
<tr>
<th>Garages (n=3)</th>
<th>Depth (cm)</th>
<th>F1+F2+F3</th>
<th>F1+F2+F3+F4+F5+F6</th>
<th>MF (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaunda Site</td>
<td>0-15</td>
<td>0.17</td>
<td>1.59</td>
<td>10.69</td>
</tr>
<tr>
<td></td>
<td>15-30</td>
<td>0.11</td>
<td>1.93</td>
<td>5.70</td>
</tr>
<tr>
<td></td>
<td>30-60</td>
<td>0.30</td>
<td>3.42</td>
<td>8.77</td>
</tr>
<tr>
<td>Mwangi site</td>
<td>0-15</td>
<td>6.09</td>
<td>69.19</td>
<td>8.80</td>
</tr>
<tr>
<td></td>
<td>15-30</td>
<td>1.82</td>
<td>14.98</td>
<td>12.15</td>
</tr>
<tr>
<td></td>
<td>30-60</td>
<td>1.71</td>
<td>7.37</td>
<td>23.20</td>
</tr>
<tr>
<td>Industrial Area site</td>
<td>0-15</td>
<td>1.62</td>
<td>38.53</td>
<td>4.20</td>
</tr>
<tr>
<td></td>
<td>15-30</td>
<td>1.54</td>
<td>18.73</td>
<td>8.22</td>
</tr>
<tr>
<td></td>
<td>30-60</td>
<td>0.31</td>
<td>7.16</td>
<td>4.33</td>
</tr>
</tbody>
</table>
4.2.3 Forms of Zinc in the Soil Profiles of the Garage Sites

From table 4.3 the mean levels of zinc in the various forms of upper soil profile of the three garage sites ranged from 0.00 ± 0.00 to 0.72 ± 0.01 for Kaunda site, 0.00 ± 0.00 to 8.17 ± 0.00 for Mwangi site and 0.00 ± 0.00 to 5.18 ± 0.08 for Industrial area respectively. At the middle soil profile, the mean levels for zinc ranged from 0.00 ± 0.00 to 1.05 ± 0.00 for Kaunda site, 0.05 ± 0.01 to 2.04 ± 0.01 for Mwangi site and 0.00 ± 0.00 to 3.38 ± 0.01 for the Industrial area respectively. At the bottom soil profile, zinc means ranged from 0.00 ± 0.00 to 2.61 ± 0.01 for Kaunda site, 0.19 ± 0.01 to 2.75 ± 0.01 for Mwangi site and 0.00 ± 0.00 to 2.42 ± 0.00 for the Industrial area respectively.

Table 4.3 Distribution of Zinc (Mean ±SD) ppm from different fractions

<table>
<thead>
<tr>
<th>Garages (n=3)</th>
<th>Depth (cm)</th>
<th>Water soluble</th>
<th>Exchange-able</th>
<th>Carbonate bound</th>
<th>Fe-Mn oxides</th>
<th>Organic</th>
<th>Residual</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaunda</td>
<td>0-15</td>
<td>0.00±0.00</td>
<td>0.01±0.01</td>
<td>0.29±0.01</td>
<td>0.72±0.01</td>
<td>0.38±0.02</td>
<td>0.51±0.00</td>
</tr>
<tr>
<td></td>
<td>15-30</td>
<td>0.06±0.01</td>
<td>0.00±0.00</td>
<td>0.33±0.00</td>
<td>1.05±0.00</td>
<td>0.50±0.02</td>
<td>0.48±0.01</td>
</tr>
<tr>
<td></td>
<td>30-60</td>
<td>0.01±0.00</td>
<td>0.00±0.00</td>
<td>1.37±0.01</td>
<td>2.61±0.01</td>
<td>1.02±0.01</td>
<td>0.50±0.01</td>
</tr>
<tr>
<td>Mwangi</td>
<td>0-15</td>
<td>0.01±0.01</td>
<td>0.00±0.00</td>
<td>1.05±0.01</td>
<td>8.17±0.00</td>
<td>1.42±0.03</td>
<td>0.87±0.01</td>
</tr>
<tr>
<td></td>
<td>15-30</td>
<td>0.05±0.01</td>
<td>0.05±0.01</td>
<td>0.58±0.01</td>
<td>2.04±0.01</td>
<td>0.72±0.01</td>
<td>0.50±0.01</td>
</tr>
<tr>
<td></td>
<td>30-60</td>
<td>0.19±0.01</td>
<td>0.39±0.01</td>
<td>0.35±0.00</td>
<td>2.75±0.01</td>
<td>0.97±0.57</td>
<td>0.53±0.01</td>
</tr>
<tr>
<td>Industrial Area</td>
<td>0-15</td>
<td>0.11±0.01</td>
<td>0.00±0.00</td>
<td>1.29±0.01</td>
<td>5.18±0.08</td>
<td>1.63±0.01</td>
<td>0.70±0.01</td>
</tr>
<tr>
<td></td>
<td>15-30</td>
<td>0.12±0.01</td>
<td>0.00±0.00</td>
<td>1.04±0.01</td>
<td>3.38±0.01</td>
<td>0.73±0.01</td>
<td>0.42±0.01</td>
</tr>
<tr>
<td></td>
<td>30-60</td>
<td>0.13±0.01</td>
<td>0.00±0.00</td>
<td>0.62±0.01</td>
<td>2.42±0.00</td>
<td>0.94±0.01</td>
<td>0.16±0.01</td>
</tr>
</tbody>
</table>
The trend of abundance of zinc is also a decrease from the upper soil profile to the lower profile except for Kaunda site which shows a general increase from the upper profile to the lower soil profile. More zinc was extracted from Mwangi site than from Kaunda and Industrial area sites. This indicates that Mwangi site is more polluted with zinc than Kaunda and Industrial area sites. The dominant fractions in all the three sites were the Fe-Mn oxides (F4) and the organic bound fraction (F5) with Fe-Mn mean levels being 0.72 ± 0.01, 8.17 ± 0.00 and 5.18 ± 0.08 on the upper soil profile for Kaunda, Mwangi and Industrial area sites respectively. For the case of the organic bound fraction, the means of zinc distribution were 0.38 ± 0.02, 1.42 ± 0.03 and 1.63 ± 0.01 for Kaunda, Mwangi and Industrial area sites respectively. The water soluble and the exchangeable fractions were low compared to the other fractions this could have been due to their low concentration in the garage soils. Yusuf (2007) found zinc as largely bound to the Fe-Mn oxides fraction. The study also showed the same relationship. The oxide has high stability constant for the heavy metals to be concentrated in the fraction. In agreement with these results, several other workers have reported the dominance of Fe-Mn oxides bound fraction for zinc (Ahumada et al., 1999; Narwal et al., 1999; Yusuf, 2007).
The mobility factors suggest zinc is more mobile at the Kaunda garage site reaching a maximum of 23.0454% from the middle soil profile to the bottom soil profile. The three sites showed different mobilities of zinc with the order decreasing from Kaunda site > Mwangi site > Industrial area site as depicted the mobility factors in the lower soil profile. The Mobility of zinc from the top soil profile to the middle soil profile was higher at Mwangi site than for both Industrial area and Kaunda sites.

### 4.2.4 Mobility Comparison for Zinc and Lead

As the mobilities for the two metals suggest, zinc is more mobile than lead down the soil profiles. The mobility of lead is highest at Mwangi site while the mobility of zinc is highest at Kaunda site with mobility factors of 23.2022% and 23.0454% respectively.
4.2.5 Forms of cadmium in the soil profiles of the garage sites

The mean levels of the various forms of cadmium obtained are as given in table 4.5 Unlike the previous cases of lead and zinc which gave mean levels for statistical analysis, cadmium levels were mostly below the detection limit of the AAS machine (DL). Very little of it was bound to the exchangeable fraction and the residual fraction. Cadmium is very soluble and easily leached away or swept by rain water especially when the soil pH is within the acidic range. Its also released from tear and ware of rubber in small quantities and also from the waste engine oil in the small amounts. Apart from the low detection limit of the machine, it may have been low due to the slope of where the garages are situated due to possible occurrence of surface run off. Cadmium concentrations were therefore very low and did not yield enough data for studying its mobility down the soil profiles.

Table 4.5 Distribution of cadmium (Mean±SD) in ppm from different fractions

<table>
<thead>
<tr>
<th>Garage(n=3)</th>
<th>Depth cm</th>
<th>Water soluble</th>
<th>Exchangeable bound</th>
<th>Carbonate bound</th>
<th>Fe-Mn oxides</th>
<th>Organic</th>
<th>Residual</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaunda site</td>
<td>0-15</td>
<td>0.01</td>
<td>DL</td>
<td>DL</td>
<td>DL</td>
<td>0.01</td>
<td>DL</td>
</tr>
<tr>
<td></td>
<td>15-30</td>
<td>0.01</td>
<td>DL</td>
<td>DL</td>
<td>DL</td>
<td>DL</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>30-60</td>
<td>DL</td>
<td>DL</td>
<td>DL</td>
<td>DL</td>
<td>DL</td>
<td>DL</td>
</tr>
<tr>
<td>Mwangi site</td>
<td>0-15</td>
<td>DL</td>
<td>DL</td>
<td>DL</td>
<td>DL</td>
<td>DL</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>15-30</td>
<td>0.01</td>
<td>DL</td>
<td>DL</td>
<td>DL</td>
<td>DL</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>30-60</td>
<td>DL</td>
<td>DL</td>
<td>DL</td>
<td>DL</td>
<td>DL</td>
<td>DL</td>
</tr>
<tr>
<td>Industrial area site</td>
<td>0-15</td>
<td>DL</td>
<td>DL</td>
<td>DL</td>
<td>DL</td>
<td>DL</td>
<td>DL</td>
</tr>
</tbody>
</table>
4.2.6 Total Pb and Zn down the Soil Profiles

The results of total lead and zinc down the soil profiles are given in table 4.6. The total Pb and Zn showed a general trend of decrease down the soil profiles except for Kaunda site which showed a general increase. The total lead mean in the upper soil profile was highest at the Mwangi garage with a maximum of 69.19 ± 0.14 ppm followed by Industrial area site with a maximum of 38.53±0.21 ppm and lastly Kaunda site with a total of 1.61 ± 0.05 ppm. The extent of metal availability with respect to lead therefore decreased in the order Mwangi site > Industrial area > Kaunda site.

On the basis of six step sequential extraction, the total concentration of lead on the upper soil profile was higher than the mean for world soils as reported by Kabata and Pendias (1992) who reported a mean of 22 ppm. The total lead in the upper soil profile at Mwangi site was between the range of values reported by Kaara (1992) for soils within and around Nairobi which ranged between 45.4- 263.8 ppm. The total lead in the upper soil profile for all the sites was also between the range of lead reported for Nairobi and its environs in soils by Oyaro (2002). Oyaro reported lead levels ranging from 6.6 to 395.1 ppm for Nairobi province and its environs. The total lead on the upper soil profile especially at Mwangi site is considerably higher than the mean level obtained by Wanjala (2009) at some road side site with heavy traffic. The lead levels recorded for Nairobi Mombasa road at Cab were 34.6 ppm to 53.4 ppm (Wanjala, 2009). Wanjala’s findings also showed that lead was more concentrated at garage site than it was along the roads and parking places which showed a maximum 236.1±9.2 ppm at the garages which was higher than the total mean level obtained in the garage soils of Machakos town. From the results obtained for garage sites at Machakos, Mwangi site which is nearest to the Machakos bus terminus has the highest concentration of
lead. Although the total lead concentration at the garage site is lower than the threshold value given by Kari of 200 ppm (Kari, 2007), more research is needed to monitor the blood lead levels of the people working at the garages. The concentration of lead in normal blood should be below 10µg/dl (CDC, 2004).

Total zinc down the soil profiles as obtained by six steps sequential extraction was low compared to the mean for the world soils which is reported to be 45 ppm (Kabata and Pendias, 1992). The total concentration of zinc on the upper soil profile was highest at Mwangi garage and the range was 1.91 ± 0.02 to 11.51 ± 0.01ppm for the upper soil profiles of the garage sites. In the middle and lower profile the ranges were 2.42 ± 0.00 to 11.51 ± 0.01 ppm and 4.26 ± 0.00 to 5.51 ± 0.00 ppm respectively. These concentrations were far much below the ones reported by Wanjala (2009) from a study conducted along busy roads in Nairobi and its environs. He reported zinc levels of between 75.9 ± 5.0 to 337 ± 18.2 ppm. Another study gave the upper soil profile (0-10 cm) levels ranging from 94.4 to 267.2 ppm during the dry season (Wanjala, 2009). The low levels of zinc extracted could be due to its low concentration in the soil of Machakos area. Yusuf (2007) reported zinc as low as 1.62 ppm for some sites near ojota waste site of Nigeria. Kabata and Pendias (1992) reported a higher value of 53 ppm in the soils of Poland.
Table 4.6 Comparison of total heavy metal distribution across the soil profiles

<table>
<thead>
<tr>
<th>Garage Site</th>
<th>Depth(cm)</th>
<th>Pb (Mean±SD) ppm</th>
<th>Zn (Mean ±SD) ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaunda site</td>
<td>0-15</td>
<td>1.61±0.05</td>
<td>1.91±0.02</td>
</tr>
<tr>
<td></td>
<td>15-30</td>
<td>1.94±0.04</td>
<td>2.42±0.00</td>
</tr>
<tr>
<td></td>
<td>30-60</td>
<td>3.42±0.06</td>
<td>5.51±0.00</td>
</tr>
<tr>
<td>Mwangi site</td>
<td>0-15</td>
<td>69.19±0.14</td>
<td>11.51±0.01</td>
</tr>
<tr>
<td></td>
<td>15-30</td>
<td>14.98±0.02</td>
<td>3.95±0.00</td>
</tr>
<tr>
<td></td>
<td>30-60</td>
<td>7.36±0.07</td>
<td>5.18±0.33</td>
</tr>
<tr>
<td>Industrial area site</td>
<td>0-15</td>
<td>38.53±0.21</td>
<td>8.91±0.04</td>
</tr>
<tr>
<td></td>
<td>15-30</td>
<td>18.73±0.01</td>
<td>5.69±0.01</td>
</tr>
<tr>
<td></td>
<td>30-60</td>
<td>7.16±0.03</td>
<td>4.26±0.00</td>
</tr>
</tbody>
</table>

The lead and zinc of Mwangi and Industrial area sites showed a general decrease down the soil profiles. This in perfect agreement with other researches carried out in other countries by the procedure of six steps sequential extraction procedure (Kabata and Pendias, 1992; Ma and Rao, 1997; Yusuf, 2007). Kabata and Pendias found that the concentrations changed in the same order only that zinc was more concentrated than lead in Poland (concentration of zinc was 53 ppm while that of lead was 31 ppm). Yusuf (2007) also found that lead and zinc were strongly bound to Fe-Mn oxides and the Organic soil fractions just as it was the case in Machakos. The Kaunda garage site showed a general increase for the concentrations of the two heavy metals down the soil profiles which may have been attributed by levelling of the site with soil.

4.2.7 Comparison of Concentrations of Pb and Zn at Soil Profiles of Each Garage Site

The results for variation of mean concentrations of lead and zinc down the soil profiles of each garage site are illustrated graphically in figures 4.1 and 4.2 respectively. The means were compared using one-way ANOVA followed by students Newman kuels test (SNK test). For lead metal concentrations, it was found that the means of the three levels at both
Kaunda and Mwangi garage sites were significantly different from each other while the lead mean concentrations of the the three levels of Industrial area were not significantly different (p < 0.05, Anova, SNK test).

Figure 4.1 comparison of lead in the profiles of garage sites

Site A: Kaunda site       Site B: Mwangi site       Site C: Industrial area site.

Bars with the same cluster followed by different small letters are significantly different (p<0.05, Anova, Snk test).
Zinc showed significant differences for the three profiles of all the three garage sites. These differences are shown by different small letters a, b, and c for each garage site in figure 4.2.

**Figure 4.2 Comparison of zinc in the soil profiles of garage sites**

Site A: Kaunda site  Site B: Mwangi site  Site C: Industrial area

Bars within the same cluster followed by different small letters are significantly different (p<0.05, Anova, SNK test)
Table 4.7 Mean percentages of lead and zinc across soil profiles.

<table>
<thead>
<tr>
<th>Heavy metal</th>
<th>Water soluble</th>
<th>Exchangeable</th>
<th>Carbonate bound</th>
<th>Fe-Mn oxides</th>
<th>Organic</th>
<th>Residual</th>
<th>Total mean fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb mean</td>
<td>0.04±.01</td>
<td>0.28±.08</td>
<td>1.21±.34</td>
<td>9.97±2.57</td>
<td>5.78±1.24</td>
<td>0.82±.14</td>
<td>18.10±4.15</td>
</tr>
<tr>
<td>% fraction</td>
<td>0.44±.07</td>
<td>4.09±.87</td>
<td>5.20±.50</td>
<td>51.71±1.64</td>
<td>30.69±1.36</td>
<td>7.87±1.00</td>
<td></td>
</tr>
<tr>
<td>Zn mean</td>
<td>0.08±.01</td>
<td>0.05±.02</td>
<td>0.77±.08</td>
<td>3.15±.42</td>
<td>0.92±.08</td>
<td>0.52±.04</td>
<td>5.48±0.56</td>
</tr>
<tr>
<td>% fraction</td>
<td>1.56±.25</td>
<td>1.05±.46</td>
<td>14.62±.95</td>
<td>53.21±1.84</td>
<td>17.84±.76</td>
<td>11.72±1.34</td>
<td></td>
</tr>
</tbody>
</table>

Percentage mean fractions followed by small letter(s) within the same row are significantly different (P<0.05, Anova, Snk test).

**Mean Percentages of Lead and Zinc Down the Soil Profiles**

The mean percentages of lead and zinc down the soil profiles for different forms are shown on table 4.7. The percentage mean fractions suggest that there is no significant difference for water soluble, exchangeable and the carbonate bound fractions which are the fractions most mobile and bioavailable to plants (Iwegbue, 2007). The results also show that the percentage average mean of the iron- manganese oxides bound lead is significantly different from that of water soluble, exchangeable and carbonate bound fractions already mentioned as well as the residual fraction. For zinc, the water soluble percentage mean fraction is not significantly different from the percentage mean of the water soluble fractions. The study also suggest that the percentage average mean of the carbonate bound zinc is not significantly different from that bound to the organic fraction. The Fe- Mn percentage mean fraction is significantly different from all the other five fractions while the residual percentage mean of zinc is not significantly different from the first three fractions.
4.3 Pearson correlation of fractions with the total Pb and Zn

4.3.1 Correlation of mobile and most soluble fractions with the total Pb and Zn

The correlation of mobile and most soluble fractions with the total lead and zinc is given in table 4.8. Correlation for lead was significant for the three mobile fractions that is, the water soluble, the exchangeable and the carbonate bound fraction when the three fractions were correlated with the total for the six fractions (p<0.05, 99% confidence limit). However the correlation was negative for water and exchangeable fraction and positive for the carbonate bound fraction meaning that the availability of soluble lead to water and bioavailability of lead to plants may or may not be influenced by the garage waste lead. For the case of zinc, the correlation was not significant for the three soluble fractions when correlated with the total zinc. The correlation was however negative meaning that when the concentration of water soluble zinc was high the concentration of the total zinc was low. This means that not every time zinc was high in the soil the soluble zinc was high in the same garages (p>0.05, 99% confidence limit).

4.3.2 Correlation of the low soluble fractions with the total Pb and Zn

The low soluble fractions refer to the oxides, organic and residual forms which were also correlated with the total lead and zinc. The results are given on table 4.8. For the Fe-Mn oxides, the organic and residual fractions, it was only the residual fraction lead which had a significant correlation with the total lead which was negative (p<0.05, 99% confidence limit). The other two fractions had a positive correlation with the total lead at the sites which was not significant. Zinc on the other hand showed significant negative correlation for the three phases when compared with the total zinc in all the six phases (p<0.05, 99% confidence limit). This indicates that zinc was strongly bound to the low water soluble fractions. This means that not every time we are talking about high levels of zinc, the same is mobile and bioavailable to plants.
Table 4.8 Pearson correlation coefficients of total heavy metal with the six fractions

<table>
<thead>
<tr>
<th></th>
<th>F1</th>
<th>F2</th>
<th>F3</th>
<th>F4</th>
<th>F5</th>
<th>F6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb(r*)</td>
<td>-0.520*</td>
<td>-0.492*</td>
<td>0.489*</td>
<td>0.346</td>
<td>0.156</td>
<td>-0.560*</td>
</tr>
<tr>
<td>P-VALUE</td>
<td>0.005</td>
<td>0.009</td>
<td>0.010</td>
<td>0.077</td>
<td>0.436</td>
<td>0.020</td>
</tr>
<tr>
<td>Zn(r*)</td>
<td>-0.279</td>
<td>-0.116</td>
<td>-0.240</td>
<td>-0.852*</td>
<td>-0.509*</td>
<td>-0.622*</td>
</tr>
<tr>
<td>p-value</td>
<td>0.159</td>
<td>0.565</td>
<td>0.228</td>
<td>0.000</td>
<td>0.007</td>
<td>0.001</td>
</tr>
</tbody>
</table>

*correlations are significant at α=0.01(two-tailed).

4.4 Concentrations of Lead, Zinc and Cadmium in Water

The results for the levels of lead and zinc in water are given in table 4.9. The mean concentrations of lead in the water samples ranged between 0.01±0.01 to 0.14± 0.04 ppm.

The concentration of lead along katotothani stream from the source to about 200m was slightly higher than the maximum contamination levels reported to be 0.015 ppm by WHO (1996) while at a distance exceeding 900m away from the source the concentrations were lower. A research conducted in Nairobi by Kimei (1996) showed lead levels ranging between 0.05-0.80 ppm for Nairobi water. The mean concentration in katotothani stream was therefore within the range obtained by Kimei. Elevated levels of between 6.02- 63.39 ppm of lead in Kenyan lakes have been reported principally from industrial discharges, sewage sludge and weathering process (Kiilu, 1993). The concentrations of lead were relatively higher near the source of katotothani stream which is 50m away from Kaunda garage site than they were downstream. This may be due to the upstream being nearest the source of the contaminants, the garages. At the lower end of katotothani stream, the higher concentrations than the middle of the stream may be attributed to farming carried out on sloppy farms adjacent to katotothani stream.
### 4.9 Results for the concentrations of lead and zinc in water

<table>
<thead>
<tr>
<th>Sampling point</th>
<th>Distance from the source (Metres)</th>
<th>Pb (Mean ± SD) ppm</th>
<th>Zn(Mean ± SD) ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0.11±0.01</td>
<td>0.46±0.01</td>
</tr>
<tr>
<td>2</td>
<td>100</td>
<td>0.11±0.03</td>
<td>0.68±0.01</td>
</tr>
<tr>
<td>3</td>
<td>200</td>
<td>0.14±0.04</td>
<td>0.65±0.01</td>
</tr>
<tr>
<td>4</td>
<td>300</td>
<td>0.02±0.02</td>
<td>0.31±0.02</td>
</tr>
<tr>
<td>5</td>
<td>400</td>
<td>0.01±0.01</td>
<td>0.92±0.01</td>
</tr>
<tr>
<td>6</td>
<td>500</td>
<td>0.02±0.00</td>
<td>0.80±0.02</td>
</tr>
<tr>
<td>7</td>
<td>600</td>
<td>0.01±0.01</td>
<td>0.74±0.02</td>
</tr>
<tr>
<td>8</td>
<td>700</td>
<td>0.02±0.02</td>
<td>0.52±0.02</td>
</tr>
<tr>
<td>9</td>
<td>800</td>
<td>0.01±0.01</td>
<td>0.71±0.02</td>
</tr>
<tr>
<td>10</td>
<td>900</td>
<td>0.02±0.02</td>
<td>0.51±0.02</td>
</tr>
<tr>
<td>11</td>
<td>1000</td>
<td>0.04±0.02</td>
<td>0.13±0.01</td>
</tr>
<tr>
<td>12</td>
<td>1100</td>
<td>0.09±0.02</td>
<td>0.12±0.02</td>
</tr>
<tr>
<td>13</td>
<td>1200</td>
<td>0.08±0.01</td>
<td>0.04±0.00</td>
</tr>
<tr>
<td>14</td>
<td>1300</td>
<td>0.07±0.04</td>
<td>0.06±0.02</td>
</tr>
<tr>
<td>15</td>
<td>1400</td>
<td>0.02±0.02</td>
<td>0.03±0.01</td>
</tr>
<tr>
<td>16</td>
<td>1500</td>
<td>0.06±0.01</td>
<td>0.03±0.01</td>
</tr>
<tr>
<td>17</td>
<td>1600</td>
<td>0.03±0.04</td>
<td>0.01±0.01</td>
</tr>
<tr>
<td>18</td>
<td>1700</td>
<td>0.05±0.02</td>
<td>0.01±0.01</td>
</tr>
<tr>
<td>19</td>
<td>1800</td>
<td>0.10±0.02</td>
<td>0.07±0.01</td>
</tr>
<tr>
<td>20</td>
<td>1900</td>
<td>0.04±0.04</td>
<td>0.04±0.02</td>
</tr>
</tbody>
</table>
Figure 4.3 Variation of mean concentrations of lead down the stream.

Figure 4.4 Variation of mean concentrations of zinc down the stream.
These mean concentrations are represented graphically in figures 4.3 and 4.4 for lead and zinc respectively. Near garage sites (0-200M) the higher concentrations of lead and zinc could be due to proximity to the source of contaminants. Sampling points 12, 13 and 19 could be having higher levels of lead due to contamination from farming near them on sloppy farms adjacent to Katothyani stream. Zinc mean concentrations on the other hand ranged between 0.01- 0.92 ppm. This is below the acceptable levels of zinc in drinking water and therefore the water is deficient of this important mineral element. The acceptable level of zinc in drinking water is below 50 ppm and higher concentrations are detrimental to health (WHO, 1996). Kiilu (1993) reported Zn levels ranging between 2.54 – 265.2 ppm in Kenyan lakes. Zinc is an essential and beneficial element for growth of both plants and animals. However, concentrations above 5 mg/l can cause bitter taste and an opalescence in alkaline waters. The trend of zinc was that higher concentrations were found near the source of Katothyani stream than downstream. This means zinc was more available near the garage sites than away from the sites. The reason for lower levels of Zn than Pb in the stream water could be due to its higher mobility.

4.5 Concentration of lead, zinc and cadmium in kales

The mean levels of Pb, Zn and Cd in kales are given in table 4.10. The lead mean levels in kales ranged between 0.02 ± 0.03 to 0.03 ± 0.04 ppm while the zinc mean levels ranged between 0.59 ± 0.02 to 1.62 ± 0.02 ppm. The levels of cadmium ranged between ND to 0.01 ± 0.01 ppm. The permissible MCL of lead in leafy vegetables is 2 ppm while that one of zinc is 50 ppm (USEPA, 2002). This shows that neither the lead nor the zinc in the kales had levels exceeding the defined MCL. USEPA (2002), recomends that the MCL for Cd in leafy vegetables should not exceed 0.3 ppm hence the kales are not contaminated with cadmium.
The Pearson moment correlation of mean concentrations of lead and zinc in kales with the mean concentrations of the respective metal in water sampled from the nearest point to the kale growing areas was also done. Lead showed weak positive correlation which was not significant (p>0.05) at 99% confidence limit. Zinc on the other hand showed negative correlation which was also not significant at 99% confidence limit. This means that there may be other factors influencing the concentration of these heavy metals in kales other than the use of water contaminated with these heavy metals by garage waste.

**Table 4.10 Mean concentrations of lead, zinc and cadmium in kales (ppm)**

<table>
<thead>
<tr>
<th>Sampling point</th>
<th>Distance from source (M)</th>
<th>Pb</th>
<th>Cd</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0.03±0.04</td>
<td>0.01±0.01</td>
<td>1.62±0.02</td>
</tr>
<tr>
<td>5</td>
<td>400</td>
<td>0.03±0.03</td>
<td>0.01±0.01</td>
<td>0.81±0.06</td>
</tr>
<tr>
<td>6</td>
<td>500</td>
<td>0.02±0.03</td>
<td>0.01±0.01</td>
<td>0.59±0.02</td>
</tr>
<tr>
<td>8</td>
<td>700</td>
<td>0.03±0.03</td>
<td>0.01±0.01</td>
<td>0.63±0.01</td>
</tr>
<tr>
<td>12</td>
<td>1100</td>
<td>0.03±0.03</td>
<td>0.00±0.01</td>
<td>1.01±0.04</td>
</tr>
</tbody>
</table>

**Table 4.11 Correlation of Pb and Zn concentrations in kales with concentrations in water**

<table>
<thead>
<tr>
<th></th>
<th>Pb</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>pearson correlation</td>
<td>0.055</td>
<td>-0.41</td>
</tr>
<tr>
<td>p-Value</td>
<td>0.846</td>
<td>0.129</td>
</tr>
</tbody>
</table>
CHAPTER FIVE: CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSION

The forms of heavy metals present at garage soils were mainly the Fe-Mn oxides bound and the organic bound fractions. The forms which are most bioavailable, that is, the water soluble and exchangeable fractions were present in relatively small amounts for both lead and zinc. The garage soils at Machakos had therefore a low potential of polluting water resources and biosystems. The abundance of lead in garage soils followed the order Fe-Mn oxides > organic > residual > carbonate > exchangeable > water soluble. Availability of zinc on the other hand followed the order Fe-Mn oxides > organic > residual > carbonate > water soluble > exchangeable. The forms of cadmium at Machakos garage soils were below the detection limit of the AAS machine. This could be attributed to its low concentration and distribution in the different forms that were fractionated. Cadmium could also have been solubilised and moved because it does so especially at low pH (Yusuf, 2007). The residue fraction, the least mobile was present at a lower concentration than the Fe-Mn oxides and the organic fractions. The dominance of the Fe-Mn oxides could be attributed to the fact that oxides exist in nodules, concretions, cement between particles or as a coating on particles and are excellent scavengers for trace elements (Ikem et al., 2003). Sorption by these oxides tend to control the solubility of heavy metals (Pickering, 1986).

The immediate Katotthyani stream had lead mean levels slightly above the defined MCL of 0.015 ppm by WHO (1996) especially the upper parts nearest the garage sites. The zinc mean levels were below its MCL. The kales grown along the Katotthyani stream by irrigation contained lead, zinc and cadmium below their MCL of 2 ppm, 50 ppm and 0.03 ppm respectively (WHO, 1996) hence not polluted with the heavy metals.
5.2 Recommendations

a) The variation of lead levels down the soil profiles is an evidence of accumulation of lead due to anthropogenic activities at the garage sites. There is therefore need to plant local phytoremediation plants and grass on the garage soils to help counteract the accumulation of the toxic lead. According to Bouchardon et al. (2005), indigenous plant species predominant in an area are usually preferred for the phytoremediation process. This is because the plant species can easily adapt to relocations and cope with local conditions in a phyto- restoration programme. Fakayode and Onianwa (2002) also obtained strong correlation between heavy metal concentration in the soil and local guinea grass (Panicum Maxicum) hence planting of guinea grass can help in the reduction of lead and other heavy metals from the garage soils.

b) Due to variation of heavy metal concentration with depth as an evidence of surface pollution, garages should be relocated away from Machakos town centre to isolated land reduce the extend of surface pollution. Although the forms at present are of low mobility, with time, increased volume of automobiles and changes in prevailing chemical environment the heavy metals may slowly be leached to the nearby stream polluting it as well as the nearby vegetation.

c) The water flowing in Katothyani stream should not be used for drinking purpose or irrigation. This is because some points contained lead levels exceeding the defined MCL. These include sampling points 1, 2, 3, 12, 13, 14 and 16.
d) The kales grown along the vicinity of Katathyani stream may be used as food. Care should however be taken to ensure that the stream does not receive other contaminants from the populated Machakos town. There should also be continuous monitoring of the water in the stream and irrigated vegetables to assess the changes of heavy metal pollution with time.

e) As the results indicate high levels of heavy metals in the soil does not necessarily infer mobility and bioavailability. It is therefore important to determine not only the total heavy metal content of polluted soils but also the forms in which these heavy metals are in order to assess their toxicity.

5.3 Areas of Further Research

Although there are tolerable levels of lead and zinc in the vegetables grown along Katathyani stream, Zinc levels happen to be of concern because they are much lower than the recommended levels. It is therefore necessary to research on levels of zinc in farm soils and other food crops of Machakos area. The concentration of heavy metals in underground water systems need also be studied. This is because apart from surface run off heavy metals can also be leached to pollute underground water ways.

Other elements which may be present in garage waste like copper, manganese and iron need also to be fractionated and their total content determined in the garage soils to assess their distribution. This is because apart from zinc, lead and cadmium the other metals mentioned above can also be present at automobile garages due to pollution.

The concentration of lead in the blood of the people working at the automobile garages should also be determined to assess the bioaccumulation of this toxic heavy metal and assess
the implication of garage waste heavy metals on health risks. There is also need for the
determination of total heavy metal content in the garage soils and find the percentage of each
metal extrated in the sequential extraction procedure. The background concentration of these
heavy metals in unpolluted soils was not considered in the present study. There is therefore
need to determine this background concentration for comparison purpose because the extent
of pollution for a particular place can also be judged on the basis of this comparison.

Since there are several sequential extraction schemes, it is also needful to carry out research
to compare these methods to find out which extractants and with which sequential extraction
steps there is maximum extraction of the desired metals. The soil was only sampled during
the dry season to avoid surface run off. There is need for further research on seasonal
variation on forms and total concentration of these heavy metals. Determination of soil type
and fractionation of the soil into size that is, the course (1000-500 µm), medium (500-
125µm), fine (125-53µm) and silt (< 53µm) is also an important study to find out the
distribution of of heavy metals in the different size fractions. This is because the distribution
of the heavy metals in the various fractions vary with the highest concentration being
associated with the smallest sized particulates.
REFERENCES


APPENDICES

APPENDIX 1: Graphs of total Pb and Zn fractions for three profiles

A: kaunda B: mwangi C: industrial area. Fractions from top to bottom: water soluble to residual
APPENDIX 2: Photographs of sampling sites.

a) A Photograph showing part of Kaunda garage

b) A photograph showing part of Mwangi site
c) A Photograph showing part of Industrial area site

d) A photograph showing a section of katothyani stream
e) Photograph showing kales grown along Katothyani stream