UPTAKE CHARACTERISTICS OF TRACE ELEMENTS: LEAD, ZINC, CADMIUM AND MERCURY BY SELECTED FOOD CROPS GROWN ALONG NAIROBI RIVER

Thesis

By

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DECLARATION

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

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Dedicated

To

My wife Mary and our children: Mukhwana, Mulongo and Khisa.

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Summary list of symbols and abbreviations

IAEA	International Atomic Energy Agency
ng	nanogram
ppm	parts per million
Zn	Zinc
Pb	Lead
Cd	Cadmium
Hg	Mercury
WHO	World Health Organisation
NATO	North Atlantic Treaty Organisation
KSTW	Kariobangi Sewerage Treatment Works
AAS	Atomic Absorption Spectroscopy
EDXRF	Energy Dispersive X-ray Fluoresnce
Fe	Iron
Cr	Chromium
UNEP	United Nations Environmental Program
FAO	Food and Agriculture Organisation
mg	Milligram
HgS	Cinnabar
>	Greater Than
<	Less Than
DM	Dry Matter

ml	Millilitre
ZnS	Sphalerite
K_i	Relative excitation-detection efficiency
G_0	Geometrical constant
FET	Field Effect Transistor
KeV	Kiloelectron Volt
R_b	Background count-rate
T_b	Time on background counts
DL	Detection limit
h	Plank's constant
K	Boltzmann`s constant
T	Absolute temperature
I_o	Intensity of incident beam
I	Intensity of transmitted beam
Kms	Kilometres
%	Percentage
Hcl	Hydrochloric acid
MCA	Multi-Channel Analyzer
Dept.	Department
PbS	Galena
U.S	United States of America
U.K	United Kingdom
Yrs	Years

$PbSO_4$	Anglesite
$PbCO_3$	Cerrusite
$ZnCO_3$	Calamine
$HgCl_2$	Mercuric Chloride
$HgSb_2S_7$	Livingstonite
Hg_2Cl_2	Calomel
$\mu g/g$	Micro per gram
ρ	Density of the sample
ρ_i	Partial density of element i
Ω_1	Solid angle the source 'sees' the sample
Ω_2	Solid angle the detector 'sees the sample
ϕ_1	Angle formed by primary radiation
ϕ_2	Angle formed by secondary radiation
ε_i	Relative efficiency of the Si(Li) detector for element I
κ	Absorption jump
$\varepsilon(E_1)$	Relative efficiency of the detector for x-rays of energy E_1
ν	Frequency
j_k^i	Ratio between the value of the maximum and minimum photoelectric cross sections at the K-absorption edge of element 'i'
$1-\frac{1}{j_k^i}$	Relative probability for the photoelectric process to occur in the K-shell of element 'i'
ω_k^i	Fluorescence yield for 'K' X-ray of element 'i'
f_a^i	Relative transition probability for 'K' x-rays of element 'i'

$\mu_s(E_i)$ Total mass absorption coefficient of the sample for the characteristic E_i radiation

$\mu_s(E_i$ Total mass absorption coefficient of the sample for the primary E_i radiation

$\sigma_i^{ph}(E_i)$ Photoelectric cross section of element 'i'

Abstract

The relationship between the trace elements content of lead (Pb), zinc (Zn), cadmium (Cd) and mercury (Hg) in vegetable food crops samples and agricultural soil samples on which they are grown along the Nairobi River catchment were investigated in this study. Various biological plant samples which included 12 sugarcane (*saccharum offinaram*); 15 arrow roots (*Colocasia esculenta*); 10 kale (*Brassica olevacea*). In addition 12 soil and 19-river water samples were sampled and analysed from sampling sites.

Energy Dispersive X-ray Fluorescence (EDXRF) analytical technique was used to determine lead (Pb) and zinc (Zn) levels in sugarcane and arrow roots samples, while atomic absorption spectroscopy (AAS) analytical technique was used to determine cadmium (Cd) and mercury (Hg) in all sample types and also for lead and zinc levels in kale samples.

The concentration of most elements was observed to be at concentration levels normally observed in vegetables in uncontaminated soils. However, elevated concentration levels of lead and zinc were observed, particularly in arrow roots and kale leaf samples.

The dominant pathway for most trace elements in arrow roots was the soil on which these crops are grown. Arrow roots were found to accumulate more zinc than the other trace elements studied.

The levels of mercury and cadmium in river water samples were found to be below detection limits (<0.2 μg/ml and 0.0006) μg/ml, respectively). However, lead (Pb)

and zinc (Zn) levels in the raw water used for domestic purposes exceeded stipulated *WHO* limits, (> 0.05 μg/litre and 0.5 μg/litre respectively).

Mercury level in soil samples were below detection limit (0.2 μg/g), but the levels of cadmium observed in soil samples were within the concentration for uncontaminated soils (<2 μg/g). Lead and zinc levels in soil samples are as high as 228 μg/g and 400 μg/g, respectively. The 'available' levels of mercury and cadmium in the soil samples for plant absorption are below detection limits (0.2 and 0.0006 μg/g respectively), while the highest 'available' levels of lead and zinc account for less than 1% of the total soil content. The level of mercury in all food crop samples is below detection limit (<0.2 μg/g).

Sugarcane samples were found to readily absorb lead and zinc from the soil, but slowly absorb soil cadmium. It accumulates these elements more in the roots, than in leaves and the stem. The levels of lead, cadmium and zinc in the stems samples were observed to be within *WHO* recommended limits (<232 μg/day, 46 μg/g and 45 mg/day respectively), for human consumption.

Arrow roots readily absorb soil zinc, but slowly absorb lead and cadmium from the soil. Lead is accumulated more in the tubers than leaves, while cadmium and zinc are accumulated more in leaves than tubers. The levels of lead, cadmium and zinc found in the tubers in these studies are within *WHO* recommended limits for human consumption , the limits are <232 μg/day, 65 μg/day and 45 mg/day respectively.

Kale accumulate lead and zinc in the roots more than in the leaves and stems in levels which are within *WHO* limits (<232 μg/day, 46 μg/g and 45 mg/day respectively), for human consumption.

CHAPTER ONE

1.0 Introduction

Many industrial processes use compounds that contain elements such as lead, cadmium, mercury and zinc in large quantities, consequently leading to their distribution in the environment. The soil-plant system plays an important role in the dispersion of these metals in the ecosystem. The content of these elements in the uncontaminated soils depends largely on the soil forming parent rocks and varies between 5-1000 µg/g, of which 90% are inherent in the crystal lattice of clay, minerals and other silicates *(Vago et al, 1996; Bowen 1966; Ahrens, 1965; Vinogradov, 1959; Farb, 1960; Purves, 1977).*

A great deal of studies is directed towards contamination by potentially toxic elements on growing plants *(Purves, 1977; Lagerwerff, 1971; Turner, 1973).* For human beings, food constitutes a potential source of contamination by heavy metals besides exposure to industrial effluents and emission *(WHO, 1996).*

When present in traces, zinc is essential for growth in humans and animals but becomes toxic when present in large amounts. It plays an important role in the normal functions of some enzymes. It is non-cumulative and its absorption in the human body is thought to be inversely related to the amount ingested *(Goyer and Myron, 1977).* Its toxicity is primarily due to the presence of free metal ion and may not be directly related to the total concentration levels in the organ *(Shephard et al, 1980).* Zinc deficiencies in humans results in lesions of the skin and abnormalities of the skin. The toxic effects of zinc are characterized by increased lipase and amylase levels *(Burridge, 1969).*

Lead, cadmium and mercury are known to be poisonous and cumulative. When absorbed by plant tissues, these elements are passed onto the organisms consuming them.

although no known useful biochemical or structural functions have been established *(Pinta, 1978; Burridge, 1969; Nordberg, 1972; Haddow et al, 1964; Purves, 1977; Nicaud, 1942; Friberg, 1948/1950; Yamagata et al, 1971; D'itri, 1972; Fleming, 1968; Dowdy and Larson, 1975).*

For plants, the most important source of cadmium, mercury, lead and zinc uptake is the soil. The uptake of these elements varies and is determined by soil characteristics such as; pH value, clay mineral content, plant species, part of the plant, and the degree of maturity *(NATO Science Committee Conference, 1974; Burridge, 1969; Hahne and Krootje, 1973; Vago et al, 1996).*

The ever-increasing population of city dwellers, especially in slum areas located along the Nairobi river basin has exerted a high demand for some food crops such as arrow roots (*Colocasia esculenta*), sugarcane (*Saccharum offinaram*) and kale (*Brassica olevacea*) usually obtained from Kiambu and Kikuyu sub-urban of Nairobi city. Consequently, this has stimulated farming of these crops along the riverbanks and its catchment areas, for the purpose of consumption and also as a source of income. The Nairobi river catchment basin was selected as a case study because it combines a number of heavy metal and other toxic contamination elements from industrial and domestic activities in the city and, has also a high proportion of vegetable-based food crops such as bananas, cowpeas, spinach, cultivated within a distance of 1-2 Km away from the river.

Nairobi River originates from a swamp near Kikuyu town, about 24 Km west of Nairobi city centre and meanders across the city centre covering a stretch of about 30 Kms (Figure 1.1). Within the city area, the river basically carries runoff waters, untreated effluent from residential areas and small-scale industries, and a significant volume of treated waste

waters from Kariobangi Sewerage Treatment Works (K.S.T.W). Downstream, Mathare and the Rui-ruaka rivers join the Nairobi River which finally discharges its water into the Athi River.

Although the river water is not used for drinking purposes within the city environs, it is however, used by some people before and after it traverses the Nairobi city centre for various purposes including drinking, agricultural and industrial. The extensive use of river water for irrigation purposes has contributed to accumulation of the heavy metals in the soils through siltation and in crops grown along the river basin.

Most farmers in the city are increasingly using river water for irrigation, and might be exposing Nairobi residents to toxic substances and disease causing substances that thrive in sewage-contaminated soil and waters, such as cholera and amoebic dysentery. These waters are also rich in plant nutrients and serves as source of manure. Most often food crops grown in these conditions appear 'healthy' and attractive to consumers.

However, these food crops are susceptible to accumulation of metals and when consumed, may transfer them to human beings, consequently poisoning the consumers. The critical levels of these elements, in order of decreasing toxicity, are listed in Table 1.1.

Figure 1.1 A MAP SHOWING NAIROBI RIVER AND ITS TRIBUTARIES

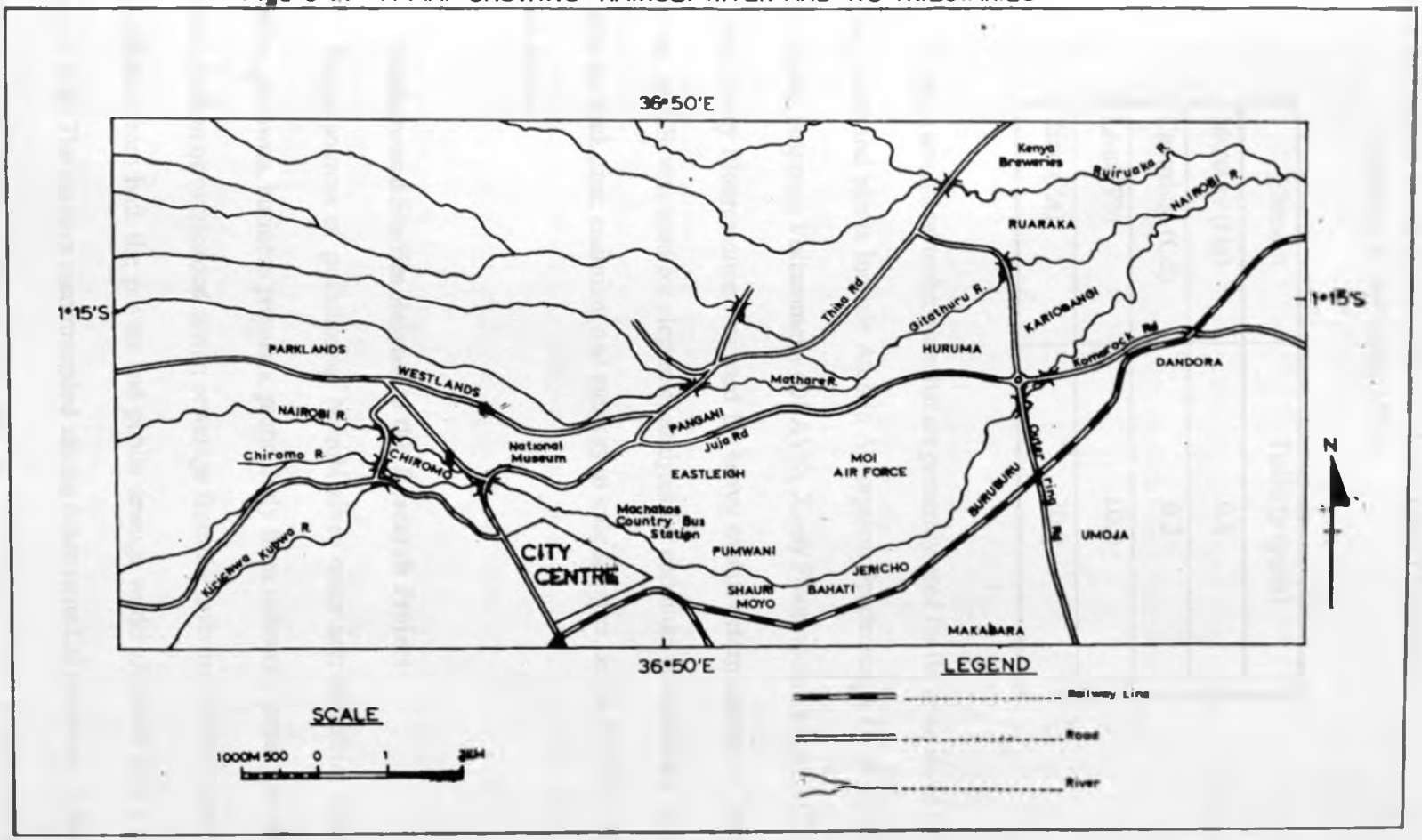


Table 1.1: Toxicity levels of some Heavy Metals (*NATO Science Committee Conference, 1974*).

Element	Toxicity (ppm)
Mercury (Hg)	0.1
Cadmium (Cd)	0.2
Lead (Pb)	10.0
Zinc (Zn)	20.0

Various analytical techniques that are presently used for the analysis of heavy metals in soils, water and plants include Atomic Absorption Spectroscopy (A.A.S), Differential Pulse Anodic Stripping Voltammetry (DPAVS), X-ray Fluorescence analysis (EDXRF). In this study X-ray Fluorescence was used for heavy metals determination of lead and zinc. However, A.A.S. was used for elemental analysis for cadmium and mercury in all samples and also for lead, zinc, cadmium and mercury in kale samples, as the EDXRF detector had broken down.

1.1 Background Studies Related to this Research Project

Major sources of pollution of Nairobi river water are: industrial effluents from factories, godowns, business premises, particularly from industrial areas; raw sewage from blocked, broken or overloaded sewer; sewerage from the informal sector, slums and others and; effluent from both the private and public sewage works *(Nairobi City Council Task Force, 1974)*. The surveys recommended among other remedial measures, which included treatment of effluents before disposal into the municipal sewers to acceptable levels by *WHO*. Likewise *Njuguna* (1978) observes that heavy metal pollution of River waters is

mainly due to domestic and industrial wastes and storm waters.

Njenga (1982) observed that the river water is not used for drinking purposes because it is heavily polluted with untreated industrial effluents. Results of analysis of sewage sludge from Kariobangi sewage treatment works and in cowpeas and spinach grown on sludge-amended soils reveal high concentration levels of heavy metals of chromium (Cr), nickel (Ni), lead (Pb), zinc (Zn), iron (Fe)*(Maina, 1984)*.

Similarly, *Masibo (1990)* found that chromium, cadmium, lead and zinc are the main pollutants found in River waters and, in general, the levels increased downstream. *Kinyua and Pacini (1991)* attributed the disappearance of some invertebrate taxa and effects of corroded and damaged edges of plant leaves in contact with river waters to toxicity of these metals, besides other chemical pollutants.

Availability and assimilation of heavy metals in the soil appears to be as much a function of the plant species as well as a physiochemical soil property *(Mitchell, 1964)*. Another proportion of the elements present is bound up in crystal lattices in the minerals in the soil, and remains quite unavailable to plants until released by weathering. A further proportion is combined in unavailable form in organic molecules in the organic matter in the soil. In areas of naturally high salinity such as where soil chloride levels have been enhanced as a result of use of chloride-containing fertilisers, or from drainage waters containing salt, there is a likelihood of increased availability of heavy metals *(Hahne and Krootje 1973)*. This was further confirmed by *Nderitu (1990)* who established a linear relationship between soils types and plant uptake of trace elements. However, he found that there is no relationship between the soil pH levels and 'available' heavy metals.

For any element, the concentration found in the plant depends not only on the level

'available' in the soil but also on the plant species and the degree of its maturity *(Burridge, 1969; Fleming, 1968).*

1.2 Statement of the Research Problem

At a time when environmental pollution and the quality of consumed food product are of major concern to man, a better understanding of the behaviours of trace elements in soil-plant system seems to be particularly significant. Trace metals pollution of the biosphere has reached such proportions that heavy metals rank as some of the factors degrading the environment. The main sources of trace elements to plants are their growth media (e.g. soil, air nutrient solution) from which they are taken up by the root or the foliage. Certain trace elements are essential in plant nutrition, (in micronutrients), but plants growing in polluted environments can accumulate trace elements to high proportions causing a serious risk to human health, when especially plant-based foodstuffs are consumed.

Current studies indicate that heavy metals contaminations are only second to pesticides on the pollution proportion and, the trend may increase in future *(UNEP, 1980).* It is therefore in the public interest that we should know to what extent potentially toxic trace elements are present in food crops grown in urban areas.

The ability of the plants to restrict the uptake of lead and mercury from contaminated soils is limited and, since contamination of the soil with most trace elements appears to be cumulative and largely irreversible, a point may eventually be reached when contaminant levels of these elements will render arable land permanently unsuitable for grazing or farming.

1.3 Aim of the Research Project

The aim of this study was to conduct a detailed study on the extent to which pollution of Nairobi river catchment by waste effluents has on soils and food crops grown on its basin. In particular, of interest were the levels due to cadmium, lead, zinc and mercury in the river waters.

1.4 Objectives of the Research Project

The objectives of the present study were as follows:

(a) to investigate the relationships between the trace elements; Pb, Zn, Cd and Hg in various food crops: sugarcane (*Saccharum offinarum*), arrowroots (*Colocasia esculenta*) and kale (*Brassica olevacca*) and in agricultural soil on which these crops are grown along the catchment of Nairobi River for total and 'available' elements and;

(b) to establish the uptake characteristics of these food crops from results of chemical analyses of (i) leaves, (ii) stalk/stem and (iii) roots/tuber.

1.5 Justifications and Significance of the Research Project

As a result of the high demand for food crops dwellers, Nairobi river basin provides farming grounds for arrowroots, potatoes, sugarcane and vegetables among others. The small-scale farmers found along the catchment use the river waters for irrigation purposes.

Previous studies indicate a high proportion of heavy metals pollution of River waters among other organic pollutants *(Njuguna, 1978; Njenga, 1982; Masibo, 1990; Kinyua and Pacini, 1991).* No similar studies have been done relating the concentrations of the heavy

metals content in soils and the various food crops grown along the Nairobi river basin. Plants assimilate and accumulate elements from the soil, water and air and thus serve as reservoirs through which the elements are transferred to animals and human beings *(Goyer and Myron, 1977)*. In order, therefore to establish the consumability of food crops grown on contaminated environment, it is important to establish the levels of heavy metal in these food crops.

Studies on toxic effects of these elements have been done in developed countries and the findings have resulted in laws being enacted to minimize and eliminate environmental pollution of the ecosystem. Few such studies have yet been conducted in Kenya, where laws on controlling environmental pollution have not been enacted due to lack of baseline data. It is hoped that the findings from this study will assist in future researches and management of the river waters in the country.

CHAPTER TWO

LITERATURE REVIEW

2.1 Introduction

In present-day urban environment, sources of heavy metal contamination of the soil are numerous; fallout from atmospheric pollution and wind-blown dusts are some of the pollution sources found to concentrate in urban and industrial areas. There is also incidental contamination resulting from the corrosion of metal objects and from the dispersion of refuse and litter. Other pollution sources include; pollution resulting from the deliberate addition of wastes to the soil such as soot, fuel ash, sewage sludge, municipal compost, or even untreated domestic waste and use of both highly toxic inorganic compounds such as pesticides for agricultural purposes.

The heavy metal content of uncontaminated soil largely reflects the composition of the parent rocks from which the soil parent material was derived (*Mitchell,* 1964). In most soils, the content of any trace element is normally within limits dictated by geochemical considerations. In different soils, the content varies widely with a large proportion being chelated in organic compounds, ionically bound on clay surfaces or trapped inside mineral crystal lattices *(Mitchell, 1964).*

'Availability' of trace metals in soils appears to be as much a plant function as a physiochemical soil property. There is a tendency for the uptake of many trace elements to increase in poorly drained, waterlogged soils, when there is a reducing environment and when the soil is under conditions of continuous extraction (*Mitchell et al,* 1957). The soil pH value

also has a marked effect on the availability of elements. In areas of naturally high salinity, there is a likelihood of increased levels.

2.1.1 'Available' Cadmium soil Content and its Uptake Characteristics by Plants and Food Crops

Because of its high toxicity, cadmium in the environment has been viewed with increasing concern *(Page and Bingham ,1973)*. A monograph by Friberg *et al,* (1974) is a valuable source of information on the consequences of dispersion of this element in the environment.

Since cadmium is the adjoining member in the same sub-group as zinc in the periodic table, they have similar physical and chemical characteristics. Its high toxicity is, to some extent, due to similarities in atomic structure that allows it to replace zinc in enzyme systems in living organisms. For example, it has been reported that zinc can be replaced by cadmium in carboxypeptidase enzyme systems (catalyses peptide degradation) (*Mahler and Cordes, 1966)*. Cadmium is also geochemically associated with zinc and is found as an impurity (upto 3%) in zinc ores such as Zincblende and Sphalerite (ZnS) or Calamine ($ZnCO_3$). In uncontaminated soils, the Cd: Zn ratio varies between 1:100 to 1:1000 (*Fulkerson et al, 1973; Shephard et al, 1980*).

Cadmium is industrially used as an anti-friction agent, as a rust proofer in plastics manufacture; in alloys, as a colouring agent in enamels and paints, in alkaline storage batteries and for many other purposes (*Purves, 1977; Webber, 1973; WHO, 1972; Friberg et al, 1974*).

Plants take up cadmium in high amounts that could create a widespread toxic hazard for animals (*Purves, 1977*). *Huffman and Hodgson (1973)* have determined cadmium levels

in 153 wheat and perennial grass samples from rural areas in 19 states of the U.S. to be generally <0.3 ppm. However, it has been stated that cadmium is highly concentrated in the germ of wheat and that by contrast with most trace metals, relatively little loss occurs during the processes of flour-milling and rice-polishing. So these processes actually lead to enrichment of cadmium in food (*Underwood, 1971*).

The striking effects (*Itai-Itai* disease) of cadmium toxicity in Japan (*Yamagata et al, 1971*) arose from increased uptake of cadmium in locally consumed rice grown in paddy fields irrigated with cadmium contaminated river waters. The associated cadmium levels in rice diet were upto 3.4 ppm in brown rice and a mean level of 0.5 ppm in white rice. The use of cadmium-contaminated water from rivers for drinking purposes also appears to have been a factor (*Yamagata et al, 1971*). Uptake of cadmium by plants from contaminated soil is species-specific and cadmium is translocated differentially to different parts of the plant-preferentially to foliage *(John and Van Laerhoven, 1976)*.

Crops readily take up cadmium from the soil in which its content has been enhanced *(Purves, 1977; John, 1972/1973; Webber, 1973)*. Normal levels of cadmium in plants grown in uncontaminated soil are probably <1 ppm dry matter, but *John (1972)* has quoted a level of 66 ppm cadmium in dry matter of lettuce leaves from plants grown in cadmium contaminated soil. Although this level is exceptionally high, it is clear that cadmium is an element that can be readily taken up by plants to high concentrations in the plant without any phytotoxic symptoms. However, previous studies *(John, 1973; Webber, 1973)* present evidence that cadmium is quite phytotoxic for a number of crops. The adverse effect on plants appears to be largely a consequence of the ease with which cadmium enters the plant through the root system. Phytotoxicity has been ascribed to competition of cadmium with zinc active sites

without functional substitution *(Lake and Ulmer, 1972).*

Page (1972) has studied the relationship between cadmium uptake by a number of plant species grown in solution culture. The plant species studied were maize, tomato, beans, cabbage, lettuce and green peppers. The findings indicated that tolerance of different species varied to between cadmium levels (0.1-10) ppm in soil. Beans, beets were the most susceptible to cadmium toxicity and their growth was reduced by 50% at solution concentration of 0.2 ppm, whereas cabbages, the most tolerant species studied showed 50% growth retardation at 9 ppm. Even at cadmium level as low as 0.1 ppm, substantial amounts of cadmium were taken up by all the plants studied, although the concentration levels in the plant leaves varied widely- from 9 ppm in the bean leaves to 90 ppm in the maize leaves.

A number of toxic effects due to cadmium have been encountered and acute toxicity conditions have been reported in a variety of laboratory animals fed on diets containing cadmium in the range 60-400 ppm *(Burridge, 1969; Nordberg, 1972).* There is some evidence that cadmium is carcinogenic, for *Haddow et al,* (1964) were able to induce sarcoma in rats at the site of subcutaneous injection with cadmium sulfate. The finding was subsequently confirmed by *Gunn et al* (1967), who found that sarcoma could be induced by a single subcutaneous or intra-muscular injection of amounts of cadmium chloride equivalent to as little as 0.17 to 0.34) mg cadmium.

Toxic symptoms have been reported in man after taking contaminated beverages containing 15ppm cadmium *(Friberg, 1948).* Probably the most notorious case of cadmium toxicity was the disorder known as Itai-Itai disease that occurred in Japan after 2nd world war. This was essentially an *osteomalacia* associated with serious kidney damage *(Purves, 1977).* *Nicaud* (1942) has described changes in bones associated with cadmium toxicity and a

specific effect is *proteinuria* caused by damage to kidney tubules *(Friberg, 1950; Parizek and Zaher, 1956).* Acute necrosis of the testes has also been reported *(Friberg, 1950)* at relatively low doses of cadmium, although this effect does not seem to be a feature of chronic cadmium toxicity. Chronic bronchitis, hypertension and cardiovascular disease have also been reported as being associated with cadmium toxicity *(Friberg, 1950).*

Cadmium absorbed by the body is only slowly excreted *(Piscator, 1966)* and, as a consequence, cadmium toxicity is markedly cumulative so that there is the possibility of chronic cadmium poisoning among industrial workers regularly exposed to this metal or its compounds. Chronic cadmium poisoning can occur in factories that manufacture alkaline accumulators *(Piscator and Rhylander, 1971)* and a high incidence of kidney disease was reported in Glasgow among a group of Copper-smiths working with cadmium-containing solder *(Purves, 1977). Lauwerys et al* (1974), in an epidemiological survey of workers exposed to cadmium dust, found excessive *proteinuria* due to kidney damage in 68% of a group of male workers with over 20 years exposure, compared with an incidence of 15% in men with less than 20 years exposure. There have also been reports of a high incidence of cancer among workers exposed to cadmium oxide dust during the manufacture of alkaline batteries *(Lauwerys et al, 1974).*

According to *Schroeder et al* (1967) the estimated daily dietary intake of cadmium by adults is as high as 200-500 μg/day, *Friberg et al* (1974) have stated that in most countries, the daily dietary intake of cadmium is in the range (57-71) μg /day. It is of interest to note that the upper limit of the latter range is within the tolerable weekly dietary intake of cadmium (corresponding to about 70 μg/day) proposed in 1972 by a joint *FAO/WHO Expert Committee on Food Additives (WHO, 1972).*

Cadmium in air and drinking water is unlikely to increase the total intake substantially; cadmium inhaled in cigarette smoke is possibly a significant non-industrial source. *Tomita* (1972) has reported levels of (1.35-2.5) μg cadmium/cigarette on the basis of analyses of twelve different Japanese cigarette brands, and these levels are in agreement with data from other countries. Although there is some disagreement about the fraction of the total cadmium content likely to be inhaled, it is unlikely that cigarette smoking is a major source of cadmium intake, even in heavy smokers. Significant increases in cadmium levels in the renal cortex of guinea pigs experimentally exposed to cigarette smoke, have however, been demonstrated *(Piscator and Rhylander, 1971).*

The joint *FAO/WHO Experts Committee (WHO, 1993)* recommends an upper limit of 65 μg/day in dietary intake, and 0.005 mg/litre for raw water *(WHO, 1984)*

2.1.2 'Available' Mercury Soil Content and its Uptake Characteristic by Plants and Food Crops

The main source of mercury is Cinnabar ore (HgS) and Livingstonite ore ($HgSb_4S_7$), which are important sources for mercury *(Jonasson and Boyle, 1971).*

Currently, the extensive use of mercury is mainly industrial. Inorganic mercury is now employed in the chlor-alkali industry, where chlorine is produced by electrolysis of sodium chloride using a mercury cathode and in the production of electric batteries, mercury vapour lamps and electrical relays with liquid contacts. It is also used in paint manufacture and as a catalyst, in the form of mercuric chloride ($HgCl_2$) and in the manufacture of vinyl chloride, urethane plastics and acetaldehyde.

Inorganic compounds of mercury, such as Calomel (Hg_2Cl_2) and mercuric-chloride

($HgCl_2$), are used as fungicides in the paper-making industry to prevent fungal growth during storage.

While mercury is now a general urban contaminant and urban soils can be expected to contain about 5 or 6 times higher than uncontaminated soils, little is known about the effect this level has on plant uptake. According to *Goldwater (1971)*, this element does not seem to be readily taken up by plants from mercury-contaminated soils. *Hitchcock and Zimmermann (1957)* have reported that the roots of Roses do not take up mercury from soils treated with mercuric chloride ($HgCl_2$). There is some evidence, however, that at very high levels of mercury contamination of soil, mercury is taken up in relatively large amounts by plants. *Estes et al (1973)* have reported a level of 1.68 ppm of mercury of velvet-bent grass on soil containing 455 ppm mercury in the (0-5) cm layer. Even at this quite extraordinary high level of soil contamination no phytotoxic effects were observed. By contrast with inorganic-mercury, organically bound mercury appears to be readily taken up by plants, so that it can enter food chains. *Rao et al (1966)* have reported from work with labelled phenyl mercuric acetate, that pea roots take up mercury in this form, while *Haney and Lipsey (1973)* have demonstrated the concentration of mercury by tomato plants grown in nutrient solutions containing methyl mercury, and its subsequent translocation to aphids.

Although there is general lack of information on conditions in which mercury levels in plants are increased in mercury contaminated soils, no enhancement of levels in oat and barley plants grown from seeds treated with mercurial seed dressings have been observed. *Van Loon (1974)* has suggested that uptake of mercury from contaminated soils is more likely at acidic pH levels.

Gilmer and Miller (1973) have studied the fate of a mercurious-mercuric fungicide

added to turf grass and to bare soil and found that about half of the total mercury added was lost within 57 days. Plant uptake, however, did not account for this loss and these authors concluded that it was mainly due to volatilisation within the soil and subsequent transference to the atmosphere at the surface.

It appears that mercury applied to the soil in the form of organo-mercurial fungicides can enter food chains and be concentrated as biologically formed dimethyl-mercury. It is now known from experimental work with rabbits, that alkyl-mercury can readily pass through the placental barrier in mammals to the foetus *(D'itri, 1972)* and this is borne out by the fact that a number of children were born with symptoms of methyl mercury toxicity to women at Minamata who themselves were not evidently affected.

The first recorded incidences of industrial mercury poisoning were reported in 1557 *(D'itri, 1972)*. Exposure to the vapour of this relatively volatile element produced toxic effects on the nervous system, which include anxiety, depression, and lack of concentration and characteristic tremors affecting the hands.

D'Itri (1972) has stated that during the last two centuries, an estimated 1800-2000 people have been poisoned by some form of mercury, which has resulted in an estimated 120-150 deaths, and that most of the deaths could be ascribed to organo-mercurial compounds, which are generally more toxic than inorganic mercury. Among organo-mercurial compounds, alkyl mercury compounds such as methyl or ethyl mercury compounds are particularly dangerous and their use is now discouraged in several countries.

The 'Minamata disease' *(Yamagata et al, 1971)* which was caused by high incidences of methyl-mercury in the fish, was a neurological illness which affected fishermen and their families around Minamata Bay in Southern Japan in the period, 1953-61, and subsequently in

fresh water in Niigata in 1965. The symptoms were tragic *(Kurland et al. 1960)* and included muscular weakness, blindness, un-co-ordination, paralysis and in some cases, coma and death.

Mercury in elemental form can evidently enter the blood circulation directly from the inhaled vapour and its absorption leads to increased urinary excretion, which can be related to the airborne mercury level. A number of biological changes in laboratory workers have been observed as a result of occupational exposure to mercury vapour in air *(Lauwreys and Buchet, 1973)*. These include increased plasma *galactosidase* and *cataclase* activities and decrease in red blood corpuscle *cholinesterase* activity.

The normal levels of mercury in urine from unexposed subjects appears to be about 10 to 20 µg/litre, and levels as high as 425 µg/litre and 1150 µg/litre have been reported in urine specimens from two laboratory technicians regularly exposed to spilt mercury *(Harrington, 1974)*.

The joint *FAO/WHO Expert Committee (WHO, 1996)* recommends an upper limit of 46 µg/day in dietary intake and 0.001 mg/litre for raw water *(WHO, 1984)*.

2.1.3 'Available' Lead Soil Content and its Uptake Characteristics by Plants and Food Crops

Lead exists in both inorganic form as Pb(II), less often as Pb(IV), and in organic form (up to 4 lead-carbon bonds). The normal soil lead level is (0.1-20) mg/kg *(WHO, 1996)*. The main sources include ores that are mined as galena (PbS), cerrusite ($PbCO_3$), anglesite ($PbSO_4$) and from lead scrap.

It is an element that is extensively used in industry *(U.K. Dept. of Environ., 1974)*.

It is used in electrical batteries, cable sheathings, sheeting, radiation shielding and in water supply conduits, although its use is now becoming unpopular because of the toxicity associated with the increased levels of lead in drinking water. Red lead, calcium-plumbate and lead-chromate are widely used as paints pigments. Numerous compounds of lead are used in the manufacture of plastics, ceramic glasses and 'lead' glass.

Tetra-ethyl and tetra-methyl lead are added to petrol to increase the octane rating. Most of the lead introduced to the petrol for this purpose is eventually discharged into the atmosphere from the exhausts of motor vehicles. Contamination of herbage with lead from car exhausts is a well-established phenomenon. *Warren and Devault (1960)*, reported abnormally high concentration of lead in vegetation (greater than 1000 ppm in plant ash) in the vicinity of major highways in North America. *Cannon and Bowles (1962)* subsequently demonstrated that there was a concentration gradient of lead in herbage for a distance of 1000 feet from major highways in the US.

While lead appears to be 'significantly' absorbed by roots, only a small proportion is translocated to shoots *(Page, 1972)*. However, *Warren and Devault (1960)* have found that lead content in vegetables grown on lead polluted soils is ten times greater than normal. It seems that enhancement of plant lead levels in urban centres is largely due to foliar contamination with lead derived from tetra-ethyl lead in gasoline. But some evidence indicate that only a small fraction of lead absorbed on the surface of leaves can penetrate the protective cuticles and enter the plant tissues *(Page, 1972)*. Therefore surface contamination of leaves by lead is probably mainly temporal, since the contaminating material will eventually be washed off by rain. This seems to agree with the results of a study by *Cox and Rains, (1972)*, which indicated enhanced lead levels in vegetation in the 0-10 cm horizon in

soils downwind from a smelter to range (20-200) ppm and it appears much of this lead must have been taken by the roots, since the levels in the tops of five species of plant grown in greenhouse in soil from this horizon were in the range 13 to 78 ppm.

Purves (1977) has studied the effects of adding variable amounts of lead to soil in the form of lead acetate. The results indicate that there is no marked increase in translocation of lead to the aerial parts of the plants up to the two highest levels studied, but the plant lead content is markedly enhanced *(Purves, 1977)*. Much higher levels of lead, around 50 ppm dry matter (dm), have been found in oat plants grown on soil to which 400 ppm lead had been added *(Purves, 1977)*. These levels may have serious consequences on animal or human health. Therefore, apparently healthy plants, containing 50 times the lead levels (1 ppm dry matter, natural to plants), can grow in soils carrying the heavy burden of contamination, sometimes associated with old mining wastes *(Alloway and Davies, 1971)*. However, there is some evidence based on experimental work with maize and soybeans that both photosynthesis and transpiration are inhibited by the presence of high lead level in plants *(Bazzaz et al, 1974)*.

Rolfe (1973) has stated that most of the lead taken up by plants seems to accumulate in the root system, and an appreciable amounts are only translocated to the leaves at relatively high soil lead levels. There is some evidence that only a small fraction of lead absorbed on the surface of leaves can penetrate the protective cuticles and enter the plant tissues *(Arvik and Zimdahl, 1974)*. Since rains will eventually wash off the contaminating material, surface contamination of leaves with lead is probably a temporary phenomenon.

The *International Agency for Research on Cancer (WHO, 1996)* classifies lead as a category-2B carcinogen; evidence of *carcinogenicity* is shown in animals but not in humans.

The induction of renal *adenocarcinoma* by lead in rats and mice is dose-related but has not been reported at levels below that producing *nephrotoxicity*. Lead compounds stimulate the proliferation of renal tubular epithelial cells, and similar effects have been noted in rat livers.

Severe lead toxicity causes sterility, abortion and neonatal mortality and morbidity. *Gametotoxic* effects occur in both male and female experimental animals, but the potential for such effects in humans is unknown.

Lead poisoning is mostly gradual, silent and often hard to ascribe to a place, source or time *(WHO, 1987)*. There is a well-known association between lead toxicity and mental retardation or neurological illness in children *(Mueller, 1967)*. The primary routes of human exposure to lead are inhalation, ingestion and skin absorption. The toxicity of lead is based on the fact that it is a potent enzyme inhibitor because it binds the sulphurydryl (-sh) groups. It also inhibits utilisation of iron in the body. The pathological effects of lead are observed in the organ systems; the nervous system, kidney and hematopietic system. Other effects which may occur include endocrine and reproductive abnormalities *(Burrel, 1974)*.

The joint *FAO/WHO Experts Committee (WHO, 1996)* recommends that dietary intake of lead should not exceed 232 μg/day for adults, children and infants and 0.05 mg/litre *(WHO, 1984)* for raw water.

2.1.4 'Available' Zinc Soil Content and its Uptake Characteristics by Plants and Food Crops

Zinc occurs in the same sub-group as cadmium and is found in association with cadmium and is relatively rare in nature. Zinc is derived from sources such as zincblende and sphalerite (ZnS) or calamite ($ZnCO_3$) *(Shephard et al, 1980)*. Zinc is used in production of

steel products and galvanising iron, vulcanisation of natural and synthetic rubber, paints and wood preservation. The main sources of zinc pollution are industrial smoke. Most agricultural soil contain zinc in levels greater than 10 ppm *(Moore and Ramamoorthy, 1984).*

Zinc uptake and its accumulation vary widely in agricultural plants and is related to soil pH, soil organic matter content and crop species *(Nriagu, 1980).* Plants readily take up zinc from contaminated soils. Work with untreated pig slurry has shown that almost all the zinc added to the soil remains in the topsoil and as such, zinc levels in grass increases rapidly after the application of slurry to the soil *(Purves, 1977).*

Results of an experiment with oats, radishes and clovers indicate that adverse effects of acetic-acid extractable zinc on their growth begin to occur at levels in excess of 200 ppm zinc in the soil *(Purves 1977).* Lettuces appear to be considerably more susceptible to high levels of available zinc in the soil; inhibition of growth starts at around a level of 60 ppm available zinc.

Most biochemical roles of zinc reflect its involvement in a large number of enzymes or as a stabiliser of the molecular structure of sub-cellular constituents and membranes. It also participates in the synthesis and degradation of lipid, carbohydrates, proteins and nucleic acids. It has recently been shown to play an essential role in polynucleoxide transcription and translation and thus in the process of genetic expression *(WHO, 1996).*

Zinc is non-cumulative and the amount absorbed is thought to be inversely related to the amount ingested *(Goyer and Myron, 1977).* Zinc is not harmful to man in 'small' quantities, but toxic to other organisms *(Moore and Ramamoorthy 1984).* Toxicity of cadmium and zinc is primarily due to the presence of free metal ion and as such may not be directly related to the total concentration level *(Shephard et al, 1980).* Its deficiency causes

lesions of the skin and abnormalities of the skeleton. Its moderately toxic effects are characterised by fever chills and pulmonary disorders *(Burridge, 1969)*, observed in industrial workers exposed to fumes. Casual ingestion of zinc sulphate causes drowsiness, lethargy and increased serum lipase and amylase levels, and has been observed, typically after ingestion of 4-8 grams equivalent of zinc *(WHO, 1996)*. Long-term exposure to high zinc intake substantially in excess of requirements has been shown to result in interference with the metabolism of other trace elements.

The upper limit of zinc intake recommended by the joint *FAO/WHO Expert Committee* should not exceed 45 mg/day in dietary intake *(WHO, 1996)* and 0.5 mg/litre *(WHO, 1984)* in raw water.

CHAPTER THREE

3.0 THEORY AND BASIC PRINCIPLES OF ANALYTICAL TECHNIQUES

In this section the principles of both EDXF and AAS analytical techniques are presented.

3.1 X-Ray Fluorescence Analysis

Following the discovery of x-rays by *Roentgen* in 1895, its developments in application fields such as medical and industrial radiography have since then increased tremendously *(Bertin, 1978)*.

Much of early x-ray spectrochemical analysis was done using photograph emulsion and crystal diffractometers. Commercial secondary emission and electron probe x-ray spectrometers were not used until late 1940s *(Burrel, 1974)*. The modern and widespread use of energy-dispersive spectrometry as opposed to wavelength-dispersive spectrometry using diffractometers and goniometers came about after the development of semi-conductor radiation detectors, particularly the Lithium-drifted Silicon detectors in the 1960's.

X-rays are electromagnetic radiation which may be propagated through space and which may interact with atoms and molecules. X-rays are generated from the disturbance of the electron orbital of stable atoms by bombarding a target element with high-energy electrons, x-rays or accelerated charged particles. In x-ray spectroscopy *(Leyden, 1984)*, x-ray tubes or radioisotopes (e.g. ^{109}Cd, ^{241}Am, and ^{55}Fe) are used as primary sources of x-ray radiation for the excitation of the target atoms. When an x-ray beam passes through a material, the photons (or electromagnetic fields) may interact with electrons in the orbital of the target elements to result in photoelectric ejection of electrons, or scatter of x-ray beam.

The resulting vacancies or holes represent high energy, unstable states. If these orbital vacancies are in the innermost shells, electrons from outer shells cascade to fill them, resulting in a lower energy, more stable state. The energy released by the process may be emitted as x-rays radiation. Each of the transitions which occur leads to the emission of sharp x-ray lines, which are characteristic of the target element, and the transition involved *(Leyden, 1984; Sparks, 1975)* which forms the basis of EDXRF analysis technique.

The EDXRF analytical technique is suited for the trace elements determination in environmental samples; food products, soils, minerals ores, water, sediments, aerosols, plant materials, animal tissues, whole blood etc. However, the analytical technique compliments other instrumental and classical analytical methods and presents the following characteristics *(Kump, 1993)*:

- very simple sample preparation procedures;
- simultaneous analysis of many elements (>20) beyond aluminum;
- low detection limits for most elements in the range of few 10 μg/g and down to less than 1 μg/g;
- simple and automated instrumental analysis procedure;
- relatively low cost.

3.1.1 Basic Principles of Quantitative XRF by Fundamental Parameter Method

For quantitative analysis one needs to correlate elemental concentration with observed x-ray fluorescence intensities. This correlation is presented by the basic equations derived using fundamental parameters. In general, the equations used represent a basis for quantitative analysis, and whose derivations is based on the following assumptions *(Sparks, 1975; Kinyua, 1982; Mangala, 1987)*:

- a monochromatic primary radiation source is used to excite characteristic x-rays from the sample,
- the sample is homogeneous i.e., the density is well defined and constant throughout the sample volume,
- a fixed geometry of sample, source and detector orientation is maintained during measurement *(Bertin, 1978; Kinyua, 1982).*

The geometry assumed, (Appendix 1), to relate the intensity, I_i, of fluorescent radiation from the element "i" within the sample, excited by primary radiation of energy E_1; assumes the basic 'intensity' equation (1), *(Leyden, 1984; Kinyua, 1982; Sparks, 1975).*

$$I_i = G_o \cdot K_i \cdot (\rho_i d) \cdot \left(\frac{1 - \exp(-a\rho d)}{a\rho d} \right) \text{----------(1)}$$

valid for transparent samples, $0.1 < a\rho d < 2$.

In which the factors G_o, K_i and a are defined as:

$$G_o = I_i \cdot \Omega_1 \cdot \Omega_2 \cdot \csc \phi_1 \text{ ----------(2)}$$

G_o= the geometrical constant (cps)

$$K_i = \sigma^{ph}(E_1) \cdot f_{\alpha}^{i} \omega_k^{i} \left(1 - \frac{1}{j_k^{i}}\right) \varepsilon(E_i)\ cm^2 \quad \text{----------(3)}$$

Where

$a = \Sigma\mu(E_1) \csc\phi_1 + \Sigma\mu_1) \csc\phi_2$

K_i = relative excitation-detection efficiency (cm^2/g);

I_i = fluorescent intensity of the element of interest (cps);

a = combined absorption coefficient for primary and fluorescent x-rays in the sample;

Ω_1 and Ω_2 = solid angles, for the source and detector 'sees' the sample respectively;

ρ and ρ_i = density of the sample and partial density of element 'i' within the sample, respectively;

$\sigma_i^{ph}(E_1)$=the photoelectric cross-section of element 'i' for primary radiation (cm^2/g);

$\mu_s(E_i)$ and $\mu_s(E_1)$ are the total mass absorption coefficients of the sample for the characteristic E_i, and the primary radiation, E_1, respectively, (cm^2/g;

k= absorption jump;

j_k^{i}= ratio between the value of the maximum and minimum photoelectric cross-section at the 'K' absorption edge of element 'i';

$1-1/j_k^{i}$ is the relative probability (fraction) for the photoelectric process to occur in the K-shell of element 'i';

ω_k^{i}= is the fluorescent yield for 'K' x-rays of element 'i';

$$f_{\alpha}^{i} = \frac{p(K_{\alpha})}{p(K_{\alpha}) + p(K_{\beta})} \quad \text{----------(4)}$$

f_{α}^{i} = relative transition probability for 'K' x-rays of element 'i', where p's are transition probabilities.

$\varepsilon(E_I)$= is the relative efficiency of the detector for x-rays of energy E_I

The last factor in equation (1), i.e. $\left(\frac{1 - \exp(-a\rho d)}{a\rho d}\right)$, called the absorption correction factor, is responsible for attenuation of the measured fluorescence intensity I_i, because of:

a) Absorption of primary x-rays, which are therefore less and less effective in exciting atoms deeper within the sample, and;

b) Absorption of the fluorescent x-rays especially those emitted within the sample and absorbed along their way out in the direction of the detector. If this factor is known, the absorption of x-rays in the sample can be determined.

For thick samples, the measured intensity of fluorescent x-rays, I_i, is a function of the combined absorption coefficient 'a' in the sample, which implicitly depends on the concentration of all the elements composing the sample.

The absorption correction factor depends strongly on the value of the product (aρd). When aρd is much smaller than one, assumes a thin samples and whose useful equation is given as:

$$I_i = G_O \cdot K_i \cdot (\rho_i d) \text{----------(5)}$$

On the other hand very large values of aρd characterize thick samples via equation

$$I_i = G_O \cdot K_i \cdot \alpha_i \cdot \frac{1}{a} \text{----------(6)}$$

Measured intensities of x-rays emission lines do not depend any more on sample thickness 'd' when the sample is thick as seen from equation (6). This means that deeper layers of the sample do not contribute any more to the measured intensity, because the very much-reduced number of x-rays emitted in those layers do not succeed to penetrate out of the sample.

The enhancement effects characterise thick samples and in such a case, the necessary correction procedures must be performed to properly relate the analyte lines with the concentration. The enhancement and absorption of analyte intensities are usually referred to as matrix effects. Equation (2) does not, however, include enhancement which occurs in cases when fluorescent radiation of element 'i' is excited not only by excitation radiation but also by fluorescent radiation of other elements in the sample. The enhancement effect is a second order process and depends on the concentration of elements, whose characteristic radiation could enhance measured intensity. For practical purposes, the effect is negligible if concentrations of those elements are below 3%, and the sample is considered thin or transparent (<100 mg/cm^2).

The relative excitation-detection efficiency for different elements and for a particular excitation source are determined using the tabulated values of Fundamental Parameters Technique (FPT) such as photo effect, cross-section and fluorescent yields *(Storm and Israel, 1970; Bambynek, 1972).*

3.1.2 Experimental evaluation of the Si(Li) detector dead layer and its relative efficiency $\varepsilon_{rel}(E_i)$.

The relative efficiency of an x-ray Si (Li) detector, $\varepsilon_{rel}(E_i)$, is defined as a ratio between x-rays detected and the total number of x-rays emitted in the direction of the detector

i.e., $$\varepsilon_{rel}(E_i) = \frac{\text{no. of detected x-rays at full energy peak (FEP)}}{\text{no. of x-rays impinging on the detector}} \quad \text{-(7)}$$

The relative efficiency of the Si(Li) detector would be one if it were not for the attenuation of x-rays on their path into the sensitive volume of the detector through air, thin beryllium window, gold contact and detector dead layer .

Accordingly, $\varepsilon_{rel}(E_i)$, is calculated as probabilities for transmission through air, beryllium window, gold contact, detector dead layer and the absorption in a sensitive volume of the crystal by the following equation,

$$\varepsilon_{rel}(E_i) = \exp-\{(\mu\rho d)_{air} + (\mu\rho d)_{Be} + (\mu\rho d)_{Au} + (\mu\rho d)_{Si-Det}\} * \{1 - \exp(-\mu\rho d)\}_{crystal} * \{1 - P_{esc}\} \quad \text{------(8)}$$

The last factor takes into account probability of escape, P_{esc}, of silicon characteristic x-rays from the detector, after de-excitation of vacancies produced by interaction of incoming x-rays. When x-rays interact with the crystal, its energy is transferred partly to photoelectrons and auger electrons and silicon characteristic x-rays in de-excitation process.

The characteristic x-rays can escape out of the crystal and the energy of the incoming original x-ray deposited in the detector wall, therefore, be reduced by the energy of the escaped x-ray. The probability of escape of characteristic x-ray in silicon is relatively small, just above the K-absorption edge (1.836 kev) reaches 1.5%.

The probability of escape has a maximum value at K-absorption edge and decreases with increased energy. This phenomenon is caused mainly by the decreasing photo-effect interaction probability at the increasing energies of x-rays.

The overall efficiency and the dead layer thickness of a Si (Li) detector can be determined by comparing the ratio of efficiencies at two energies obtained experimentally and by calculations. This ratio is sensitive to dead layer thickness especially at low energies and near the absorption edge of the detector material (equation 8). Thick samples of annular grade KCl, K_2SO_4 and K_2CrO_4 were used in order to obtain efficiency ratios at the energy peaks of the characteristic x-rays of measurable constituent elements in the compounds (Table 5.1.1).

The efficiency ratio is related to the ratio of the respective intensities of x-rays by the equation:

$$\frac{\varepsilon(E_1)}{\varepsilon(E_2)} = k\frac{I_1^k}{I_2^k} \qquad \text{----------(9a)}$$

in which

$$k = \frac{k_2}{k_1(1 + \Delta_{1,2}^{enh})} \qquad \text{----------(9b)}$$

Where I_1^k and 1_2^k are the intensities corresponding to element 1 and 2 in the components of the compound sample. $\left(1 + \Delta_{1,2}^{enh}\right)$, accounts for the enhancement effect of the element whose characteristic energy is lower than the other components, a phenomena characteristic of thick samples. The parameters of the right hand term of equation (9b) are constants, hence equation (9a). The 'k' values, using ^{109}Cd-radioisotope source, for KCl, K_2SO_4 and K_2CrO_4 are 0.84, 7.46 and 1.92 respectively. And using ^{55}Fe-radioisotope source, 1.16 and 6.69 for KCl and K_2SO_4 respectively (*Kinyua, 1982).*

The x-ray fluorescence Spectrometer (appendix 2) used consists of the following:

- Si (Li) detector-Canberra Series 7300
- spectroscopy amplifier-Canberra Model 2026
- High voltage bias supply-EG&G Ortech Type 459
- Preamplifier-Canberra Model 1008
- Coolant-liquid nitrogen in a dewar cryostat
- ADC-Canberra Model 8075
- A canberra S-100 PC-based MCA card used for data acquisition and storage.

The detector is a crystal of silicon in the form of a diode. When operated under reverse bias, electron-hole pairs produced by interaction of x-rays are swept out of the crystal by applied electric field. In practice, when operating normally the detector requires that other sources of charge carriers be minimized. This is accomplished in large crystals by compensating for impurities in silicon with lithium (Li) in the process called lithium drifting. The Si (Li) detector must be maintained at liquid nitrogen temperature at all times for the lithium to remain in place and also to reduce thermal noise.

The detector pre-amplifier converts the burst of electrons resulting from absorption of x-rays into a voltage signal, which may be conveniently transmitted to a measurement system. It is also required to minimize any source of noise that may degrade the signal. This is achieved through use of FET input charge sensitive pre-amplifier. The pre-amplifier is located next to the detector to reduce capacitance of the leads, which can degrade the signal and also serves to provide a match between a high impedance of the coaxial cables to the amplifier.

The amplifier serves to shape the pulses as well as to amplify it linearly and make the pulses suitable for the precise pulse-height analysis by Multi-Channel Analyser. This function is achieved by 'pulse-shaping' technique in order to obtain the optimum in energy resolution

and count-rate performance. A near gaussian shape is produced with a time constant 6-12 μsec.

The Multi-Channel Analyser performs the sorting of pulses from the amplifier according to their pulse heights and accumulates the respective pulse-height distribution in its memory (1024 channels). It also includes a microprocessor that is pre-programmed to perform simple data analysis operations like energy calibration, integration, subtraction of background etc.

To achieve the optimum in spectral line resolution and count-rate performance, the stability and linearity of the electronic spectrometer modules is very important. Stability was maintained by having the spectrometer systems permanently powered.

3.1.3 Sensitivity Calibration of the Si(Li) Detector for Quantitative analysis by Quantitative Analysis of Environmental Samples (QAES)

The QAES, a modular program of the IAEA's QXAS was calibrated for quantitative analysis. Calibration for sensitivity involved determining the distribution of x-ray source and intensity measurements of pure metal samples or annalar compounds.

The following standards were irradiated by ^{109} Cd source for 1000 seconds each and their intensities measured for sensitivity calibration of the system using pure elements and compounds.

(a) Thin deposit mylar standards (Whatman): gold (Au), copper(Cu), diasporium fluoride (DyF_3,), lanthanum fluoride (LaF_3), molybdenum(Mo), lead (Pb), titanium(Ti), uranium fluoride (UF_4), and tungsten oxide(WO_3)

(b) thin cellulose substrates standards of (Whatman): copper(Cu), molybdenum(Mo), and titanium(Ti)

(c) pure metal foils (copper, iron, cobalt, zinc and zirconium)

3.1.4 Detection Limits

In general, the detection limits may be improved by *[Bertin, 1978]* lowering the background intensity, increasing the analyte intensity and increasing the counting time. The detection limits for analyses measured by the EDXRF was improved by increasing the counting times for irradiation of the samples.

The detection limits for elements of interest were determined from equation (10)

$$DL = \frac{3}{m}.\sqrt{\frac{R_b}{T_b}} \quad \text{----------(10)}$$

where

m = Sensitivity (c/s/μg/g)

R_b = background count rate (c/s)

T_b = time on background (seconds)

DL = detection limit (μg/g)

3.2 Flame Atomic Absorption Spectroscopy (A.A.S)

Atomic absorption is a viable analytical technique for determining trace elements, because of its high specificity and relatively high sensitivity when compared with other methods *(Pinta, 1978; Slavin, 1978)*. Atomic absorption spectroscopy has been widely used

for trace element analysis of environmental samples. Detailed reviews of flame and non-flame atomic absorption techniques have been published *(Slavin, 1978; Segar and Gilli, 1973; Welz, 1976).*

One of the main advantages of atomic absorption spectrophotometry, as an analytical technique, is that absorption by atoms takes place within very narrow spectral regions and only those involving the ground state are normally observed, yielding extremely simple spectra, and as such there is very little possibility of coincidence of spectral lines and spectral interference *(Varian Techtron, 1989; Pinta, 1978).*

The most important components of a typical AAS are:

a) The spectral source which emits the spectrum of the element of interest,

b) The atom cell, usually a flame furnace or graphite furnace, in which the atoms of the sample are formed by thermal dissociation,

c) A monochromator for the spectral dispersion of the source radiation and an exit slit for selection of the wavelength of the analyte resonance line,

d) A detector, normally a photo multiplier tube, to permit measurement of the radiation intensity at the resonance line,

e) An amplifier and display units for recording of the absorption values

3.2.1 Basic Principles of Quantitative Atomic Absorption Spectroscopy

The determination of elements by AAS is based on the principle of absorption or emission of radiation by free atoms,

a) emission of spectral line of frequency υ;

b) absorption of the same line;

For the excitation of a ground state atom, R to R*

$R+h\nu=R^*$----------(11)

Where h is planck's constant and ν is the frequency of the absorption or emission of atoms associated with the process of transition of atoms from one steady state to the other. The type of transition between the steady states will depend on the magnitude of the energies involved.

For the steady states m and n with energies E_m and E_n, respectively, absorption of light will take place when $E_n > E_m$, following the transition from m to n, while the transition n to m, results in the emission of light.

The frequency υ_{mn} for m to n transition will be inversely proportional to the Planck's constant so that;

$$\nu_{mn} = \frac{E_n - E_m}{h} \text{ ----------(12)}$$

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

i) emission (n-------->m), transition from an excited state to a lower energy state, due to external radiation of the same frequency n_{nm},

ii) spontaneous emission (n------>m), transmission from the excited state to lower energy state, and,

iii) absorption (m------>n), transition from a lower energy state to a higher one due to external radiation with frequency υ_{nm}. This is the basis of AAS.

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

$$\frac{N_n}{N_m} = \left(\frac{g_n}{g_m}\right). \exp- \left[\frac{En - Em}{KT}\right] \text{----------(13)}$$

where

N_n = number of atoms in excited state

N_m = number of atoms in ground state

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

E_n and E_m = energies of excited and ground states respectively

E_n-E_m = excitation energy

K = Boltzmann's constant = 1.38×10^{-23} JK^{-1}

T= absolute temperature

At a fixed value of g_n/g_m, the ratio N_n/N_m increases with temperature for a particular element at a particular spectral line.

For an atomic gas consisting of atoms in thermal equilibrium capable of absorbing a quantum of energy hυ, containing a radiation of frequency υ and intensity I_o, passing through the atomic gas, the absorption of the incident radiation by neutral atoms is given by A = log (I_o/I).

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

$$I = I_o.\exp-(K_n N_o L) \text{----------} (14)$$

where

I_o = intensity of incident beam

I = intensity of transmitted beam

K_n=absorption coeff. at the frequency ν

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

L = length of absorbant

CHAPTER FOUR

4.0 MATERIALS AND METHODS

4.1 General Description of the Project Area: Nairobi River and its Catchment

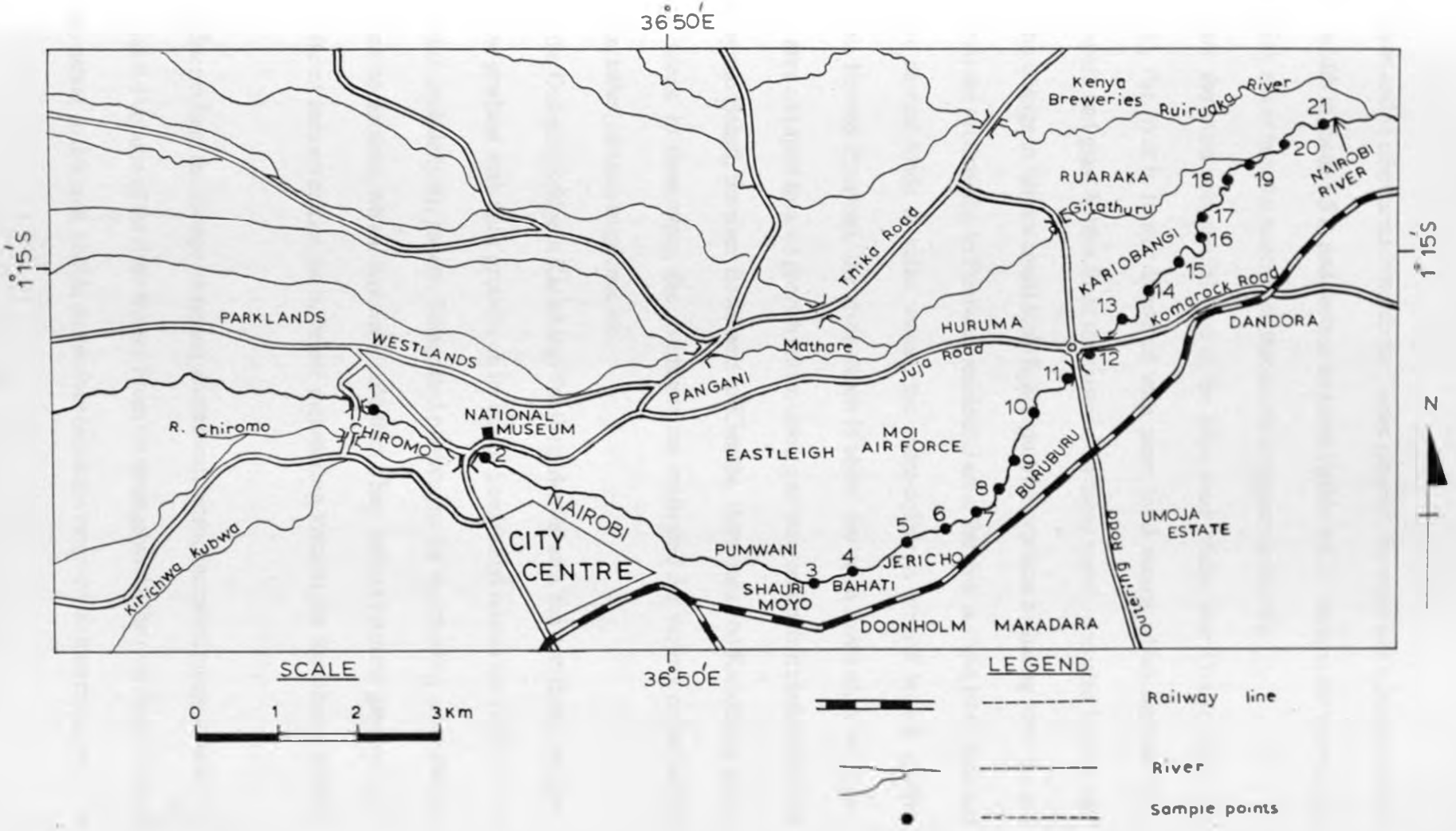
Nairobi River has its source located at Kikuyu and is joined by its first tributary at Dagoretti (Figure 4.1). The stream waters become more turbid and brown after its confluence at Dagoretti.

Apart from siltation due to cultivation along the river basin, there is no evidence of waste disposal into the river upto Chiromo, onwards along the river course; domestic wastes including bottles and paper are visible in the waters as the stream flows through a series of residential areas.

The river traverses the city commercial area at Kijabe Street, whereby a few solid wastes are visible floating in its waters, which upto now is brown in colour due to siltation. The river waters begin to change its colour from brown to grey after Kijabe street, where streams of domestic effluents from several kiosks are discharged into the river.

The discharges carry an increasingly heavier load of suspended solids, which include garbage, tin cans, glass and plastic bottles and waste paper.

Figure 4.1 A MAP SHOWING SAMPLING SITES ALONG NAIROBI RIVER



In these areas and in other areas towards the 'Globe cinema', the water has a pungent smell. The river width is about 3.5 m and there is so many visible solids waste in the waters, that forms a thick cover over the water such that the flow appears immobile.

After the main commercial area at the Digo road bridge near Country Bus Site (Machakos), the river is further burdened with more solid wastes which include tyres, plastics, papers and glass bottles from the surrounding areas mainly occupied by 'Jua kali' artisans who engage in various small scale light industrial practices including furniture and steel fabrications at Gikomba. In Pumwani residential area, the river is about 10 m wide and still carries several loads of solid wastes, the water-colour is greyish brown. Further downstream beyond Pumwani, the river which is about 6m wide flows close to Bahati residential area and apart from its greyish brown colour and pungent smell, it carries few solid wastes. Beyond Bahati, the river flows next to Kimathi, Buru buru and Kariobangi South residential areas. In these areas, the riverbanks are cultivated for various crops mainly arrow-roots, kales, tomato, sugarcane etc.

At the Outering Bridge in Kariobangi South residential area, the river flows through a place of low gradient with thick growths on its banks. Some solid wastes are visible in the waters, which include tyres, papers, foliage and plastics. In the surrounding areas various activities are undertaken, which may cause pollution. They include open-air garages and a dumping site of motor vehicles parts, before meandering towards the Kariobangi sewage works.

Effluents from the sewage treatment plants contribute to increased pungent smell, the turbidity and the volume of the river waters. From the sewage works the river flows close to Korogocho estate. In this area, visible on the river banks are extensive human excrement. On

leaving Korogocho the river is joined by a stream of effluent discharge from an abandoned solid waste disposal site. The stream discharges a large mass of lather foam into the river resulting from detergents accumulated in the waste disposal site. Further downstream, from Ngomongo estate, the Mathare stream joins the river.

The colour of Mathare river water is nearly black and has a pungent smell. About 1km further downstream the river is joined by the Ruiruaka stream, whereby a visible amount of lather foam in the river increases after the confluence.

4.2 Description of the Sampling Sites for this Study

The following is a brief description of the sampling sites (Figure 4.1): -

Site 1

This sampling site is located at the bridge along a pathway joining Riverside drive Road and Westlands Shopping Centre, about 200m west of Chiromo campus hostels. The water colour was pale brown, probably due to siltation upstream.

Site 2

This is located 20m downstream, east of the National Museum roundabout. This roundabout forms the junction of the busy Uhuru highway and Chiromo road. The riverbed is mainly covered by Nairobi phonolites. At this point, the water colour had changed to pale grey, an effect that could be attributed to effluent discharges from Riverside residences, Chiromo campus hostels, International Casino and the Chiromo river.

Site 3

This is located 40 m downstream of the bridge of a road junction between Pumwani and Makongeni estate; this road has a light traffic flow. By this point the river water was so dirty and oily and appeared grey in colour. There was evidence of domestic and burst sewage effluents discharging into the river, open garages and vehicle washing.

Site 4

This is located 1 km downstream of site 3 in Shauri Moyo estate. Here most of discharges into the river were domestic effluent, of so high volume that appears like a swamp. There is no evidence of human activities along the river and the soils are mainly clay.

Site 5

This is also within Shauri Moyo but about 500 m downstream of site 4. Here 'small streams' of effluents from domestic, burst sewer and open garages discharge into the river, and a substantial farming of arrowroots and sugarcane is evident.

Site 6

This is located 700 m downstream of site 5 in Bahati estate and on the outward side of the river bend. There are farming activities of bananas, sugarcane, arrowroots etc. Further, burst sewage, domestic and open garage effluents discharge into the river. The soils are clay.

Site 7

This is located 1 km downstream of site 6, and due to the flatness of this section the river flow is slow. The proportion of iron-rich pebbles mixed in clay soil is significant. These pebbles are derived from the weathering pyrites, which partly defines the river course. There are more discharges of sewage and domestic effluents into the river.

Site 8

This is about 500 m downstream of site 7, at the contact with a stream emanating from the Moi Air base, Eastleigh. Basically the iron-rich pebbles overly clay and there is extensive farming of bananas and sugarcane.

Site 9.

This is about 600 m downstream of site 8 and on the bend of the river course. It marks the contact of the pyrite and the Nairobi phonolite rocks. Burst sewage, domestic effluents from the Moi Air base quarter's discharge into the river. There is also significant farming of arrowroots, bananas and sugarcane.

Site 10

This is about 500 m downstream of site 9, in Buru Buru estate. Open garages and vehicle washing points are located adjacent to the river. The soils are black cotton, as the riverbed becomes basaltic. More farming activities become evident with bananas dominating.

Site 11

This is located about 500 m downstream of site 10; the soils are still black cotton. There are massive discharges of sewage effluents from Huruma and Buru Buru estates. Here, besides the bananas, sugarcane and arrowroots farming, there are also cultivations of sweet potatoes and 'slum' on the Buru Buru side of the river.

Site 12

This is located 800 m downstream of site 11 and marks the change from black cotton soil to clay. More effluents from Buru Buru estate discharges into the river, which now overflows the phonolites. The land here is mainly used for grazing of livestock and farming of bananas, sugarcane and arrowroots. is being practised

Site 13

This is a swampy location about 400 m west of a bridge along the busy Outering road and about 600 m south-west of the busy Huruma roundabout joining Outering and Juja roads. Both domestic, sewage effluents and from several open garages adjacent to the river discharges into the river. There are also discharges from a light factory with processes animal feeds from animal bones.

Site 14

This is located between Outering and Komarock roads, and east of Huruma roundabout. A lot of sewage and open garages effluents from Kariobangi south discharges into the river. It is also a dumping ground of motor vehicles. However, there is plenty of

farming especially of sugarcane and arrowroots through irrigation of wastewaters.

Site 15

This is about 500 m downstream from the bridge along Komarock road, in the middle of Korogocho slum open-air market, and there is a lot of effluent discharge into the river. In fact the river seems the only dumping site available for the slum dwellers in addition to farming of arrowroots and sugarcane.

Site 16

This is at the junction with a stream draining out of the Kariobangi Sewage Treatment Works (K.S.T.W). The water has pungent smell as the treated sewage discharges into the river. There is also domestic and burst sewage discharges from the eastern side of the river from Dandora phase 1 and Kinyako slums.

Site 17

This is about 500 m downstream of site 16 and just after the bend in river course. Here is a junction with a stream emanating from a massive garbage-dumping site in Dandora phase 2. The stream introduces a lot of foam into river waters. There are plenty of sugarcane and arrowroots farming.

Site 18

This is about 400 m downstream of site 17 and there is a big 'dam' formed by an abandoned quarry, where water is used for domestic purposes besides substantial crop farming activities around the 'dam'. The 'dam' also receives massive discharges from

Kariobangi North estate.

Site 19

This is located about 300 m downstream of site 18 at the junction with a small stream draining through Baba Dogo estate. It is also the boundary of Korogocho, Dandora and Lucky Summer slums. Around here sugarcane, arrowroots etc. are grown in plenty and the river overflows the phonolite rocks.

Site 20

This is located about 500 m downstream of site 19 and within Dandora phase 4, whereby burst sewage and domestic effluents discharge into the river makes river volume increases. Also evident is extensive farming of sugarcane, arrowroots and to less extent bananas.

Site 21

This is at the confluence of Nairobi and Gitathuru rivers. Farming of sugarcane, arrowroots and bananas is extensive and the crops appear much healthier, apparently due to an enhanced by an overloaded and leaking major sewage line to the main treatment works at Ruai.

4.3 Sampling

Water, soil and various food crops samples were collected, between mid January to late April 1997, at several sites along the course of Nairobi river, within the environs of

Nairobi city (Figure 4.1). The sites had been established during a reconnaissance survey done in November 1996, within the city and its suburbs. Sampling sites were chosen on basis of availability of the sampled food crops, accessibility and other human activities.

4.3.1 Water Samples

These were 22 water samples collected from 21 sites along the river course. Water samples were taken at two or three points across the river at each sampling site, then was mixed together in one-litre pre-cleaned polyethylene bottles. This was acidified with a few drops of nitric acid (analar grade) to avoid metal adsorption on the container walls and was then stored at 4°C for 48 hrs prior to preparation for analysis.

4.3.2 Soil Samples

Soil samples were basically of clay mineral all along the river course. A total of 34 samples were collected. Sampling was done by uprooting the food crops and then picking about 0.5 kg of the soils at a distance of 5 cm below the roots. The samples were placed in polythene bags for storage at 4°C to retard compositional changes due to biological activity (*Holysnka, 1993*). In cases where the food crops were found intergrown, as in some of sugarcane and arrowroots, the collected soil samples were considered representative for all food crops sampled there. However, a separate soil sample was collected for each food crop where food crops were not intergrown, particularly for kale.

4.3.3 Plant Samples

A wide range in the ages of food crops sampled was evident. This was probably as a result of a prolonged rain failure leading a dry spell and early harvesting as soon as the crop appeared to be mature.

A total of 37 food crops samples were collected from the aforementioned site 3-19. They were 12 sugarcane, 15 arrowroots, and 10 kale samples, and then separated in to roots/tubers, leaves and stems/stalks and placed in polythene bags for later preparation for analysis.

4.4 Sample Preparation

In this section sample preparation procedures for analysis using EDXRF and AAS techniques are presented.

4.4.1 Analysis with X-Ray Fluorescence Method

The sample preparation for x-ray fluorescence analysis varies depending on the nature of the sample (*Bertin, 1978; Holysnka, 1993).*

a) Biological Samples

About 5 g of each plant sample were carefully washed in double distilled water to get rid of external dirt such as dust, then dried at temperatures of 25-30° centigrade for 24 hrs. These were then oven-dried at temperatures of 100° centigrade for 48 hrs to a constant weight. An aliquot of approximately 3 g of dried plant material were ground and pulverised to fine powder of 75 μm particles size and 5 pellets each weighing approximately 250 mg were prepared for each sample.

b) Soil Samples

Soil samples were oven dried overnight at 100° centigrade, then ground to pass through a 2 mm sieve. Further pulverisation was done to reduce the particle size to less than 75 μm using a pestle and mortar. Portions of soil samples were diluted with starch binder in ratios of 1:5 and thoroughly mixed for homogeneity. Five pellets each weighing approximately 250 mg were prepared for each sample for XRF analysis.

c) Water Samples

Since water samples collected were dirty and had a lot of organic matter, wet digestion was done to rid of the organic matter. The procedure followed was as follows: to 100 ml of water sample in a round bottom flask, 30 ml of HNO_3 (analytical grade) was added, then 10 ml of HCl (analytical grade) were added. The solution was then heated till all brown fumes were completely expelled and cooled. After cooling, double distilled water was added so that the total volume was 100 ml. Since the solution is very acidic, its pH value was adjusted by adding NH_4OH solution until the desired pH of 5-6 value was obtained. Pre-concentration of metal ions was achieved by adding a solution of 10 ml of freshly prepared 2% sodium diethyldithiocarbamate NaDDTC. The resulting precipitate was allowed to stand for about 30 minutes and then filtered on Millipore filters (0.4 μm) and air-dried for XRF analysis. For each water sample, 5 replicate thin substrates were prepared.

4.4.2 Analysis with Atomic Absorption Spectroscopy.

(a) Plant Samples

Three (3) grams of oven dried plant material were put into round bottom flask, 30ml of nitric acid (A.R) was added and the sample heated at about 100° centigrade, until brown fumes appeared. This was then followed by the continued heating until all the fumes disappeared. After cooling, 10ml of 70% perchloric acid ($HClO_4$) were added and the solution heated again until white fumes appeared. The digestion was considered to be complete when the solution became clear and colourless. This was then transferred into a beaker and double distilled water added to 100ml volume mark.

(b) Soil Samples (Total Content)

For soil samples, 0.5 g of the sample was put into graduated test-tube, and then 0.75 ml nitric acid and 2.25 ml HCl were added and shaken. The mixture was then heated to about 80° C for about 1 hour, dissolving completely, on the aluminium-heating block. After cooling, 11.5 ml of double distilled water was added and mixed well. After settling, a portion of the solution was centrifuged for measurement.

(c) Water Samples: The procedure used was as described earlier in section 4.4.1(c).

4.4.3 Extraction Procedure for 'Available' Element Content in Soil Samples for XRF and AAS analyses

After determining the pH value of soil samples, extractions of the 'available' heavy metals were done as follows: 50ml of 0.1M HCl (analytical grade) acid were added to 5g of soil in bottles while a blank was prepared by adding only the acid, (50 ml). The bottles and their contents were shaken on a reciprocal shaker for about 1 hr. The suspension was then filtered through a pre-washed filter paper (Whatman No.2) and the solution containing the 'available' elements were subjected to appropriate preparation procedures for x-ray fluorescence and atomic absorption spectroscopy analysis procedures as outlined earlier.

4.4.4 Soil pH Measurement

Approximately 20 g of air-dried soil were transferred into a 1000 cm^3 plastic shaking bottle. A blank containing only distilled water was also prepared. 50 cm^3 of distilled water were added to the bottles to give a ratio of 1: 2.5 soil to water suspension. This was then shaken for 2 hrs in a reciprocal shaker. The suspension was then homogenised by short vigorous manual shaking and its pH value determined. For each sample, the procedure was repeated and 4-5 determinations of the soil pH value evaluated.

4.5 Sample Analyses

In this study both EDXRF and AAS techniques were used for analysis for element content of samples.

a) X-Ray Fluorescence Method

The set up used for EDXRF spectrometer consisted of ^{109}Cd excitation source (Isotope Products Laboratories, USA) and a Si(Li) detector (Canberra Industries, USA) with an active area of 30 mm^2, thickness of 3 mm and FWHM of 165ev at 5.9 kev coupled to a personal computer based MCA (Multi Channel Analyser) card (S-100, Canberra). Deconvolution and analyses of the spectra were performed using AXIL-PC and QAES (Quantitative Analysis of Environmental Samples) software (Canberra Industries) as described by *(Kump 1993).* The instrumentation used in this work is shown in Appendix 2.

The soil samples were irradiated for 1000 seconds while the plant/ water samples were irradiated 2000 and 3000 seconds respectively.

b) Atomic Absorption Spectroscopy (AAS)

The following optimum instrumental parameters as described by (*Varian Techtron, 1989)* were adopted.

Table 4.1 Optimum parameters for AAS method

Spectra	Cd	Pb	Zn	Hg
Lamp current (mA)	4	10	5	3

Spectral band pass (nm)	0.7	0.7	0.2	0.2
Wavelength (nm)	38.3	283.3	213.9	253.7
Oxidant flow rate (l/min)	7.5	19.5	-	-
Acetylene flow rate (l/min)	1.0	1.3	-	-
Detection limit (μg/ml)	0.0006	0.02	0.002	0.2

CHAPTER FIVE

5.0 RESULTS AND DISCUSSION

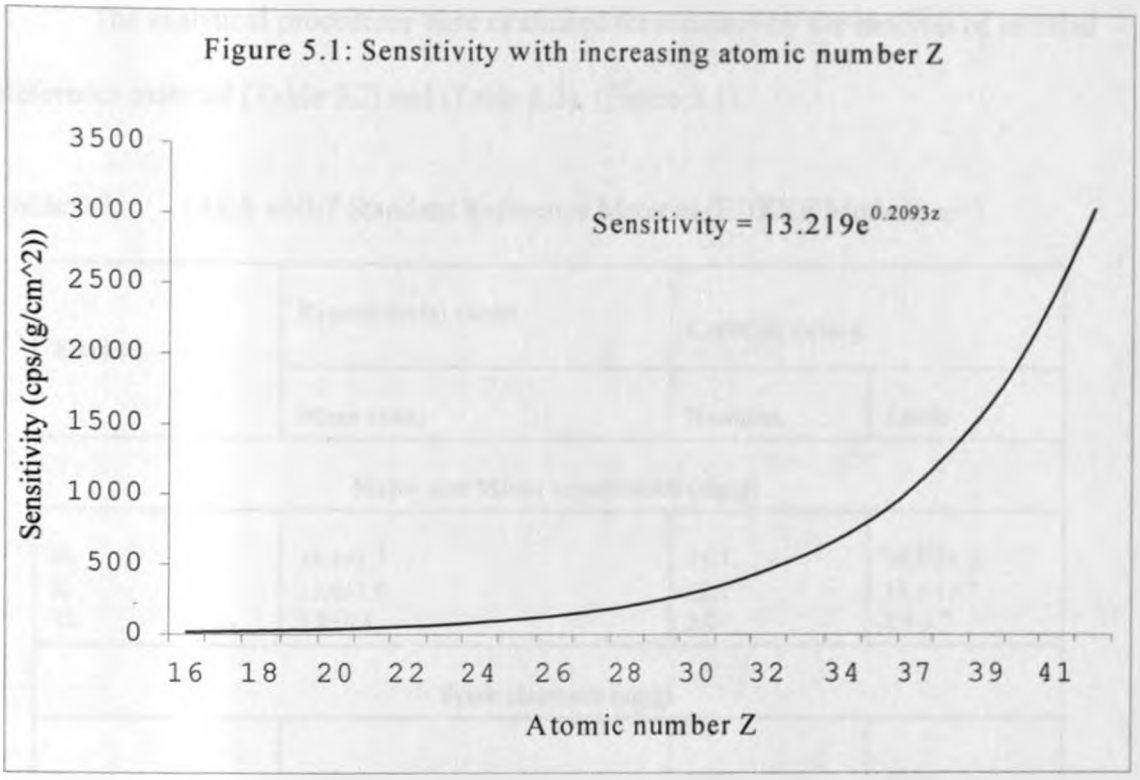
5.1 Calibration of the Si(Li) Detector for Efficiency Measurements Of Characteristic X-Ray Radiation

The following efficiency ratios were determined experimentally from measurements of spectral line intensities of thick pellets of pure compounds of KCl and K_2SO_4. Using ^{55}Fe radioisotope annular source: $\frac{\varepsilon(2.6)\,kev}{\varepsilon(3.3)\,kev} = 0.7236$ and $\frac{\varepsilon(2.3)\,kev}{\varepsilon(3.3)\,kev} = 0.5872$ values were determined for KCl and K_2SO_4 respectively, while using ^{109}Cd radioisotope source: $\frac{\varepsilon(2.6)\,kev}{\varepsilon(3.3)\,kev} = 0.6387$, $\frac{\varepsilon(3.3)\,kev}{\varepsilon(5.4)\,kev} = 0.6416$ and $\frac{\varepsilon(2.3)\,kev}{\varepsilon(3.3)\,kev} = 0.6381$ ratios were determined for KCl, K_2CrO_4 and K_2SO_4, respectively (*Kinyua, 1982)*. These results, compared with the respective calculated ratios of efficiencies (Table 5.1), show that the dead layer thickness of Si(Li) detector as 0.28 μm.

Table 5.1 Average intensities and calculated Si(Li) detector relative efficiency ratios

^{109}Cd-radioisotope source				
Salt	**Dead Layer (μm)**	**Intensity ratios**	**Proportionality constant (k)**	**Calculated relative efficiency ratios**
KCl	0.1 0.2 0.25 0.28	0.7681±0.070	0.84	0.3817 0.4627 0.5367 0.6452
K_2SO_4	0.1 0.2 0.25 0.28	0.0856±0.002	7.46	0.5293 0.6182 0.6259 0.6385
K_2CrO_4	0.1 0.2 0.25 0.28	0.3334±0.013	1.92	0.8407 0.689 0.6736 0.6412
^{55}Fe-radioisotope source				
KCl	0.1 0.2 0.25 0.28	0.6244±0.01	1.16	0.7451 0.7399 0.7297 0.7243
K_2SO_4	0.1 0.2 0.25 0.28	0.0883±0.001	6.69	0.4551 0.5735 0.5818 0.5904

Figure 5.1: Sensitivity with increasing atomic number Z



From figure 5.1 it is observed the sensitivity of this detector increases exponentially with increasing Z of the target element. Therefore the detector is more sensitive to high Z elements.

5.2 Evaluation of the analytical methods

The analytical procedures were evaluated for accuracy by the analyses of certified Reference material (Table 5.2) and (Table 5.3), (Figure 5.1).

Table 5.2: IAEA soil-7 Standard Reference Material (EDXRF Method) n=5

Element	Experimental values	Certified values	
	Mean conc.	Recomm.	Limits
Major and Minor constituents (mg/g)			
Fe	26.5±1.7	25.7	25.2-26.3
K	12.6±1.6	12.1	11.3-12.7
Ti	3.8±0.4	3.0	2.6-3.7
Trace elements (μg/g)			
Cr	67.7±0.3	60.0	49-74
Cu	48.4±11.7	11.0	9-13
Pb	67.8±6.7	60.0	55-71
Mn	732±99	631	604-650
Rb	47.2±4.3	51.0	47-56
Sr	101±7	108	103-114
Y	23.4±2.5	21.0	15-27
Zn	109±11	104	101-113
Zr	187±13	185	180-201
Trace constituents (μg/g)			
Br	7.4±1.4	7.0	3-10
Ga	9.2±0.8	10.0	9-13
Ni	28.7±1.5	26.0	21-37
Nb	9.3±1.7	12.0	7-17

From the results of analyses (Table 5.2) it is observed that for most elements of interest, the differences between the experimental values and certified values are within one standard deviation (<10%).

However the copper values obtained are much higher than certified reference values. The variations may be due to the unreliability of the Soil-7 SRM for copper values

The AAS Spectrometer used was evaluated for accuracy by analysis of standard materials, which were prepared according to the recommendation procedures by manufacturer (*Varian Techtron, 1979),* briefly described as follows:

Cadmium: 1 gram of cadmium granules (99.99%) was dissolved in a minimum volume of 1:1 Nitric acid and then diluted to give 1000 μg/ml cadmium.

Mercury: 1.354 g of mercuric chloride ($HgCl_2$ A.R. grade) were dissolved in 10ml Nitric acid. The solution was then diluted to 1 litre to give 1000 μg/ml Hg.

Lead: 1 gram of lead metal (99.9%) was dissolved in 1: 1 Nitric acid. The solution was then diluted to 1 litre to give 1000 μg/ml Pb.

Zinc: 1 gram of zinc metal granules (99.99%) was dissolved in 1:1 Nitric acid. The solution was then diluted to 1 litre to give 1000 μg/ml Zn.

Then an aliquot of 1ml of each solution was taken and diluted to 100 ml to give 10 ppm of the element that was analysed and the results obtained are given in table 5.3.

Table 5.3: Analysis of Standards by A.A.S technique

Element	Experimental value (μg/ml)	Expected value (μg/ml)
Pb	9.9±1.2	10
Cd	9.9±1.0	10
Zn	10.0±1.6	10
Hg	9.7±0.9	10

Table 5.3 shows that the accuracy of AAS for most elements of interest is high (>97%).

The detection limits for the of interest using XRF and AAS are presented in tables 5.4 and 5.5 respectively

Table 5.4: Detection limits for the Pb, Cd, Hg and Zn determined using Energy dispersive x-ray fluorescence technique.

Element	Soil pellets (μg/g)	Food crop pellets (μg/g)	Water (μg/l)
Lead	5.0±1.0	5.1±0.9	9.4±2.3
Zinc	7.2±1.8	6.8±0.5	6.1±0.7
Mercury	9.3±2.4	8.0±1.8	6.8±3.2
*Cadmium	-	-	-

* not determined because the EDXRF source was ^{109}Cd

Table 5.5 Detection limits for the Pb, Cd, Hg and Zn using A.A.S technique. (*Varian Techtron, 1989)*

Element	μg/ml
Lead	0.02±0.002
Zinc	0.002±0.0004
Mercury	0.2±0.03
Cadmium	0.0006±0.0001

- Table 5.5 shows that AAS a more sensitive analytical technique than EDXRF (Table 5.4) for the elements of interest. AAS therefore is more appropriate for analyses of water samples in which the concentrations are low.

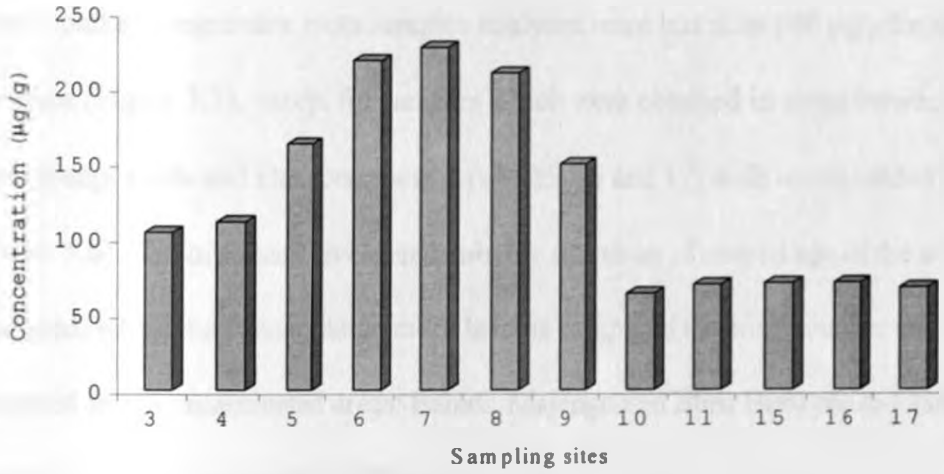
5.3 Results of analyses of soil and parts of Sugarcane Samples *(Saccharum Offinaram)* sampled from the Catchment of Nairobi River.

The results of analysis of soil and sugarcane parts samples are presented in table 5.6 and figures 5.2, 5.3 and 5.4

Table 5.6 Lead levels in sugarcane parts samples (µg/g) ±1 S.D, n=5 (EDXRF method)

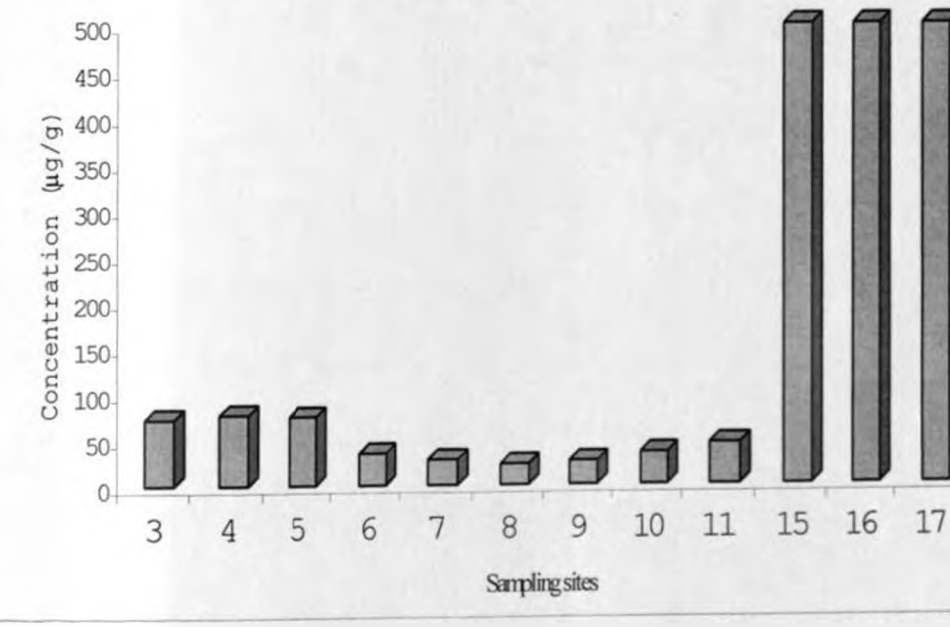
Site	Soil	Roots	Stem	Leaves
3	104±4	72.0±6.0	<5.0	10.0±2.0
4	111±4	77.0±2.0	11.2±2.5	11.7±2.1
5	163±14	74.8±9.0	7.6±2.6	12.9±1.2
6	219±20	34.9±2.7	13.2±3.6	25.6±3.1
7	228±10	27.9±2.3	<5.0	22.0±2.0
8	211±31	22.9±5.2	<5.0	14.6±2.6
9	150±28	25.7±2.1	12.5±0.9	20.8±2.8
10	64±5	34.8±4.2	10.2±1.1	27.5±3.1
11	70±4	45.0±4.0	11.3±1.7	30.8±4.7
15	71±4	867±57	18.0±0.4	206±14
16	71.3±4.0	877±57	17.5±4.8	195±13
17	68±5	865±50	17.8±0.5	182±8

Figure 5.2: Lead levels in soil samples on which sugarcane is grown along Nairobi River



Two groups of lead levels in soil samples on which sugarcane is grown; (64-111) µg/g and (150-221) µg/g are identified (Figure 5.2). The high lead levels are probably as a result of activities that have grossly contaminated the soils in areas between the densely

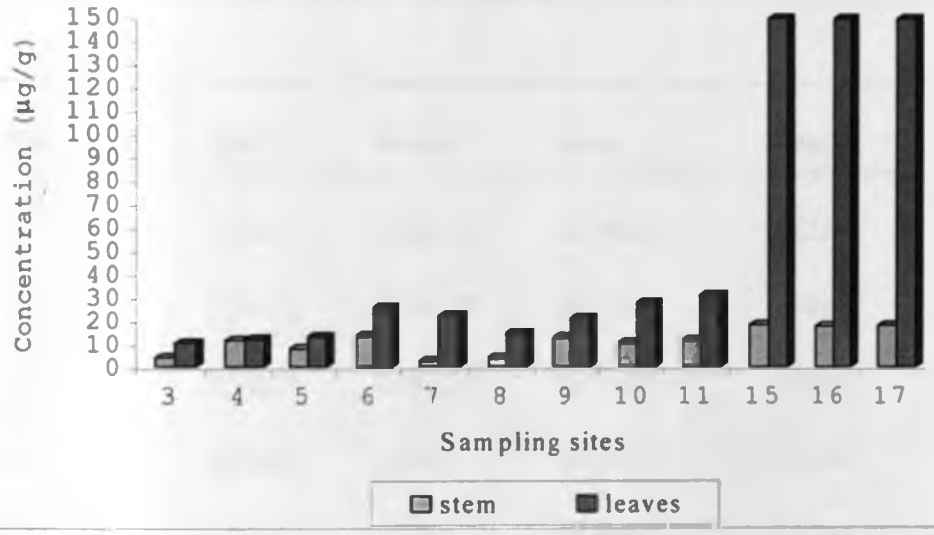
Figure 5.3: Lead levels in sugarcane roots samples obtained along Nairobi River.



populated Majengo slum and Buru Buru phase 1, adjacent to the Eastleigh air base (sites 6, 7, and 8).

- Lead uptake in sugarcane roots samples analysed were less than 100 μg/g for most samples (Figure 5.3), except for samples which were obtained in areas between Kariobangi south and Dandora phase 2 (site 15, 16 and 17) with levels (865-877) μg/g (Table 5.6). The high lead levels are probably due to an advanced age of the crop sampled, which has accumulated more lead as compared to those younger crops sampled from contaminated areas; Bahati. Majengo and Buru Buru phase 1 (site 6, 7 and 8), but with low levels (<100 μg/g).
- The high lead levels (>800 μg/g) in sugarcane roots samples may indicate that the phytotoxic levels of lead are high for sugarcane. The same trend has previously been shown for herbage (>1000 ppm) *Warren* and *Devault (1960).*
- It is observed that lead levels in sugarcane stem samples are less than 20 μg/g for most samples.

Figure 5.4 Lead levels in sugarcane stem and leaves samples.



- Figure 5.4 shows two groups of lead absorption in sugarcane leaves samples; <50 µg/g, and between 150-200 µg/g. The higher lead levels in leaves samples from Korogocho and Dandora (sites 15, 16 and 17).
- In general, it is noted that lead is significantly absorbed by sugarcane roots (upto 900 µg/g) and only a portion (5%) is translocated to the stems and approximately 25% to the leaves for the very aged crops. These findings agree with results from several studies on other non-cereal plants (*Burridge, 1969; Fleming, 1968; Dowdy, 1975; Warren and Devault, 1960; Page, 1972; Bazzaz, 1974; Rolfe, 1973*).
- The levels of lead in sugarcane stem samples are less than the corresponding levels in roots and leaves samples. In addition lead levels samples in roots, stem, and leaves correlate positively (r=0.77). However, the levels in stem samples are lower than the recommended dietary intake of less than 232 µg/day (*WHO, 1996*).

The levels of zinc in sugarcane parts samples are presented in table 5.7

Table 5.7: Zinc levels in sugarcane parts samples (μg/g) ±1S.D, n=5 (EDXRF method)

Site	Soil	Roots	Stem	Leaves
3	400±7	266±19	16.5±0.9	152±12
4	316±19	209±19	56.5±20	144±11
5	358±13	238±29	38.3±0.9	140±3
6	180±10	125±9	88.5±2.7	102±9
7	177±8	118±9	47.3±1.2	93.7±4.7
8	170±8	129±3	66.0±1.3	88.6±1.6
9	181±17	167±15	27.6±2.2	152±12
10	183±11	156±22	24.5±3.9	140±8
11	180±8	185±17	26.0±2.2	137±3
15	264±13	491±33	198±11	440±30
16	328±38	470±24	211±7	437±19
17	296±23	465±15	206±9	386±6

Figure 5.5: Zinc levels in soil samples on which sugarcane is grown along Nairobi River

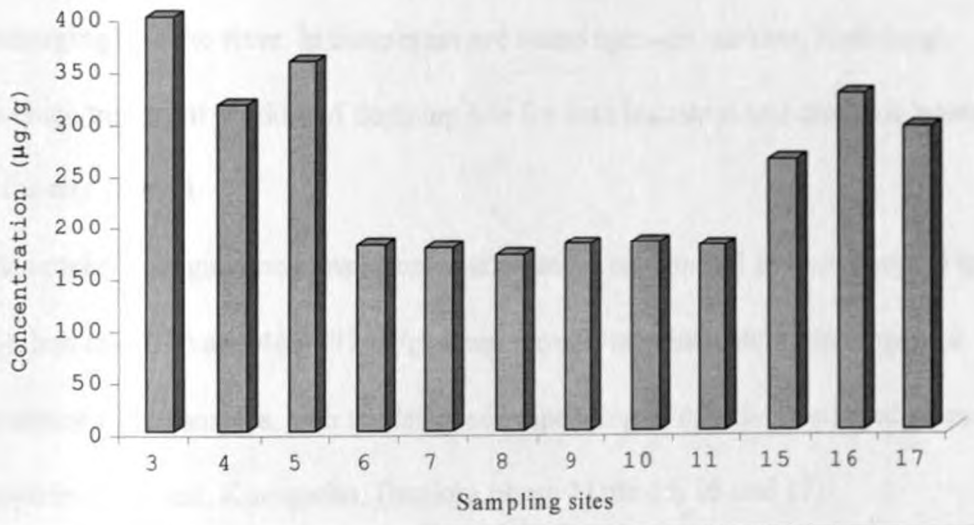
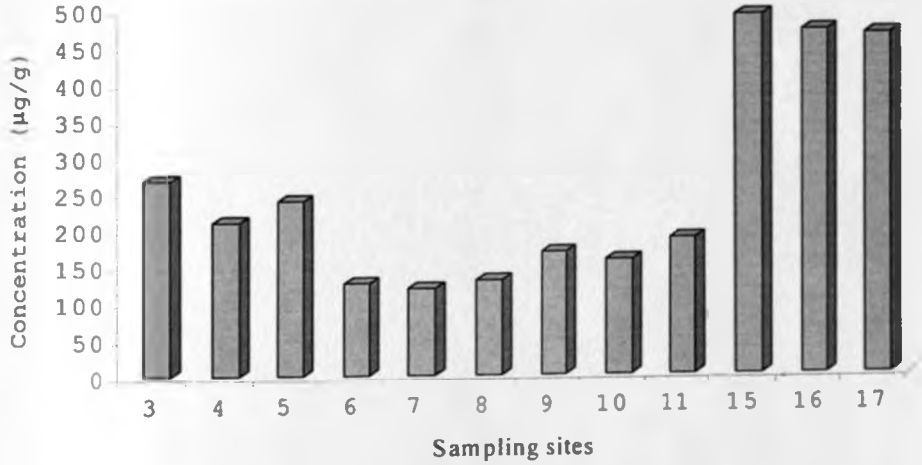


Figure 5.6: Zinc levels in sugarcane roots samples obtained along Nairobi River.



☐ Two groups for zinc levels in soil samples are identified (Figure 5.5); (i) 264-400 µg/g and 170-183 µg/g on which sugarcane is grown along Nairobi river. The high zinc levels (264-400) µg/g were determined in soil samples obtained from the densely populated areas of Pumwani, Makongeni, Shauri Moyo, Kariobangi South,

Korogocho and Dandora phase 2 (site 3, 4, 5, 15, 16 and 17), whereby there is evidence of high volumes of effluents from open-air garages and domestic effluents discharging into the river. In these areas are found open-air markets, Kariobangi sewerage treatment works and dumping site for both industrial and domestic wastes by the city council.

- Zinc uptake by sugarcane roots samples analysed is categorised in two groups (Figure 5.6); less than 270 and 465-491 μg/g. These groups may indicate various ages for sugarcane roots samples, with the latter corresponding to the advanced aged crops grown in Pumwani, Korogocho, Dandora phase 2 (site 15, 16 and 17).
- These are characterised by burst sewage, dumping site of metal scraps, domestic and industrial wastes (Pumwani, Korogocho and Dandora phase 2: sites 15, 16, 17).

Figure 5.7: Zinc levels in sugarcane stem samples obtained along Nairobi River.

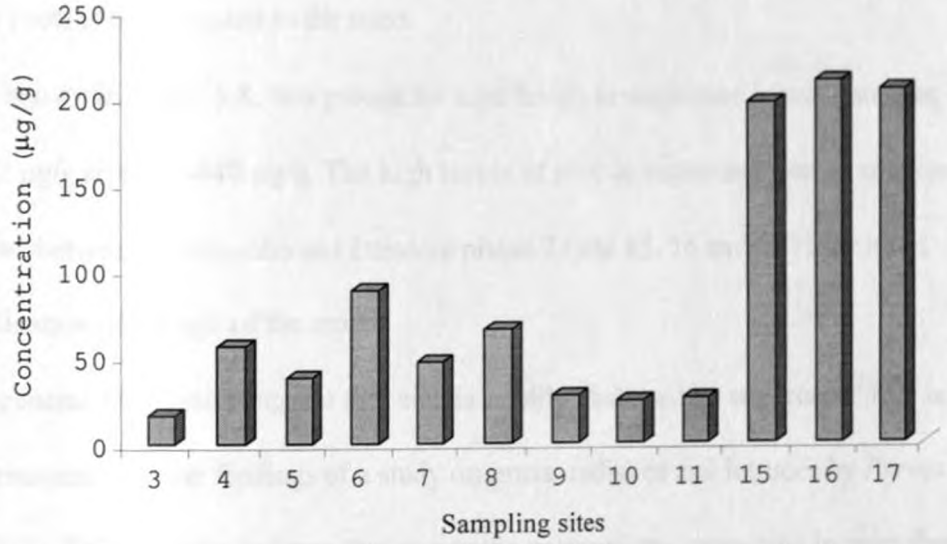
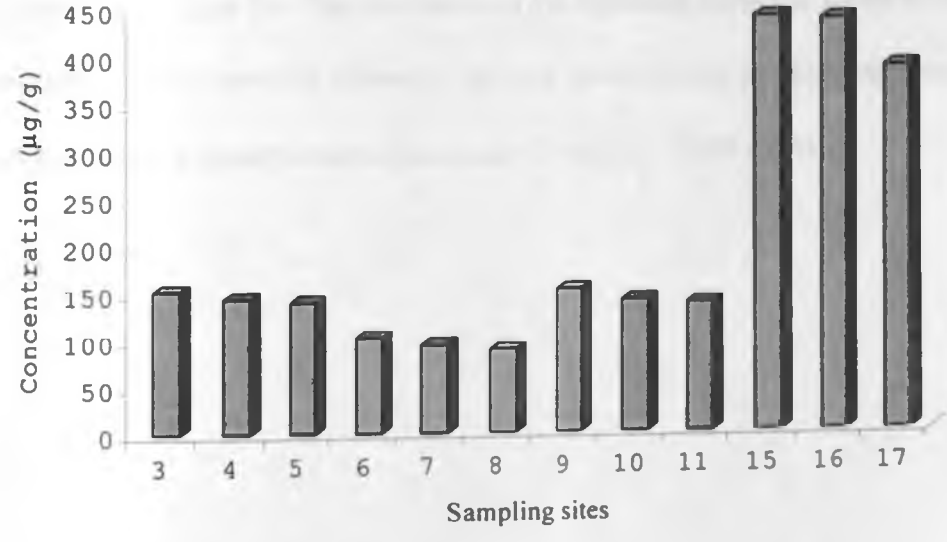


Figure 5.8: Zinc levels in sugarcane leaves samples obtained along Nairobi River.



☐ The results in figure 5.7 suggest similar pattern for zinc levels in sugarcane stems samples as for roots samples; (16.5-88.5) µg/g and (198-211) µg/g. The high zinc

levels in stem samples were determined in samples from areas between Korogocho slum and Dandora phase 2(site 15, 16, 17) which may indicate that zinc absorbed by the roots is translocated to the stem.

- As shown in figure 5.8, two groups for zinc levels in sugarcane leaves samples; 88.6-152 µg/g and 386-440 µg/g. The high levels of zinc in sugarcane leaves samples from areas between Korogocho and Dandora phase 2 (site 15, 16 and 17) may be an indication of the age of the crop.
- In general, the results suggest that zinc is readily absorbed by sugarcane. This is in agreement with the findings of a study on grass, radishes and lettuces by *Purves (1977).* These results indicate that sugarcane accumulates more zinc in roots than in the leaves and the stem. This also indicates that the phytotoxic level of zinc in sugarcane is high, considering the levels in the leaves and roots samples from Dandora phase 1 (site 16). The zinc levels in the sugarcane roots and leaves samples correlate positively (r=0.75). However, the zinc levels in stem samples are lower than the recommended dietary intake of less than 45 mg/day *(WHO 1996).*

Table 5.8 presents the results of cadmium levels in sugarcane parts samples.

Table 5.8: Cadmium levels in sugarcane part samples (μg/g) ± 1 S.D. n=5 (AAS method)

Site	Soil	Roots	Stem	Leaves
3	1.50±0.10	0.20±0.04	0.30±0.04	0.40±0.02
4	1.18±0.20	0.10±0.01	0.20±0.01	0.40±0.03
5	1.50±0.50	0.10±0.02	0.30±0.01	0.30±0.01
6	1.70±0.70	0.40±0.01	0.20±0.04	0.40±0.05
7	1.60±0.10	0.20±0.03	0.30±0.01	0.30±0.01
8	1.70±0.25	0.30±0.01	0.20±0.01	0.40±0.01
9	1.80±0.20	0.30±0.02	0.20±0.01	0.40±0.02
10	1.77±0.12	0.30±0.01	0.30±0.05	0.40±0.03
11	1.82±0.30	0.20±0.03	0.20±0.01	0.40±0.02
15	1.36±0.10	0.30±0.01	0.30±0.02	0.30±0.01
16	1.32±0.20	0.20±0.01	0.20±0.01	0.40±0.02
17	1.28±0.20	0.20±0.03	0.30±0.05	0.50±0.03

Figure 5.9: Cadmium levels in soil samples on which sugarcane is grown along Nairobi River

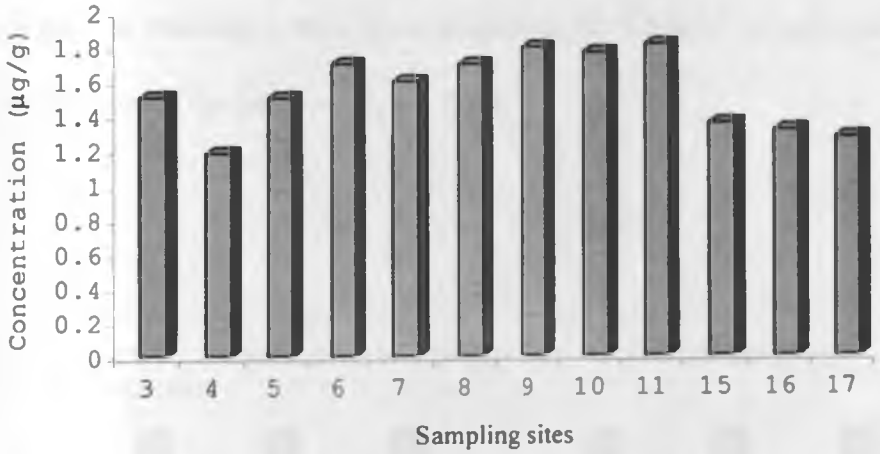
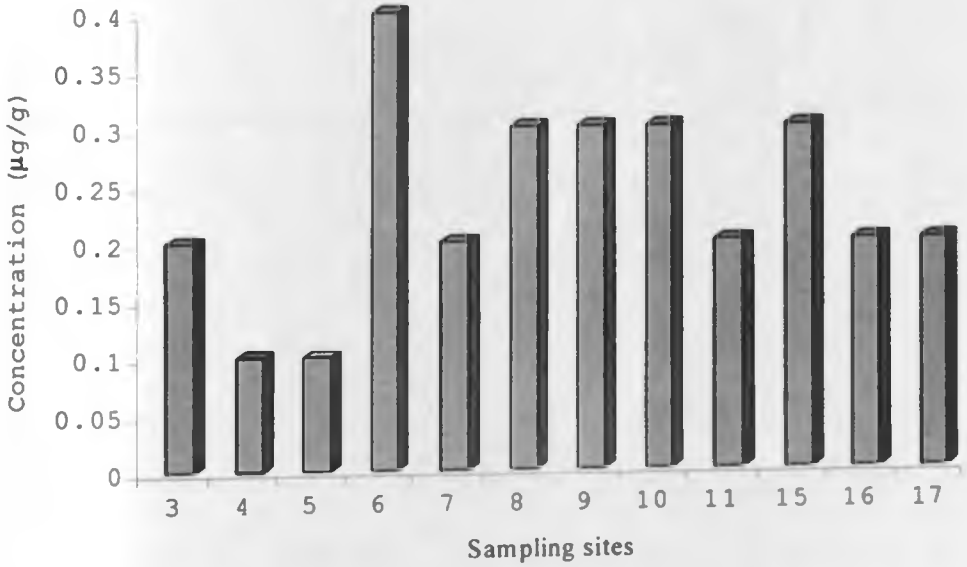


Figure 5.10: Cadmium levels in sugarcane roots samples obtained along Nairobi River.



- There is no wide ariation in cadmium levels in the analysed (1.28-1.8) μg/g soil samples (Figure 5.9).
- There is no wide variation in the levels of cadmium (0.2-0.3 μg/g) in the sugarcane roots samples for most of the samples (Figure 5.10).

Figure 5.11: Cadmium levels in sugarcane stem samples obtained along Nairobi River.

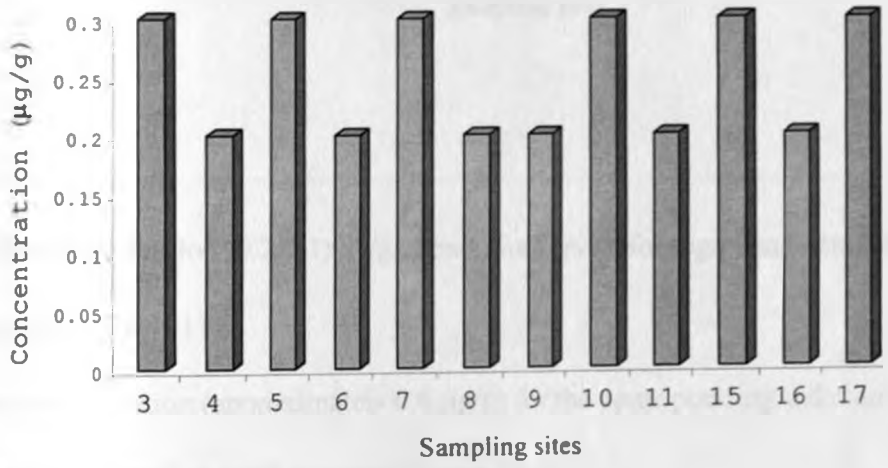
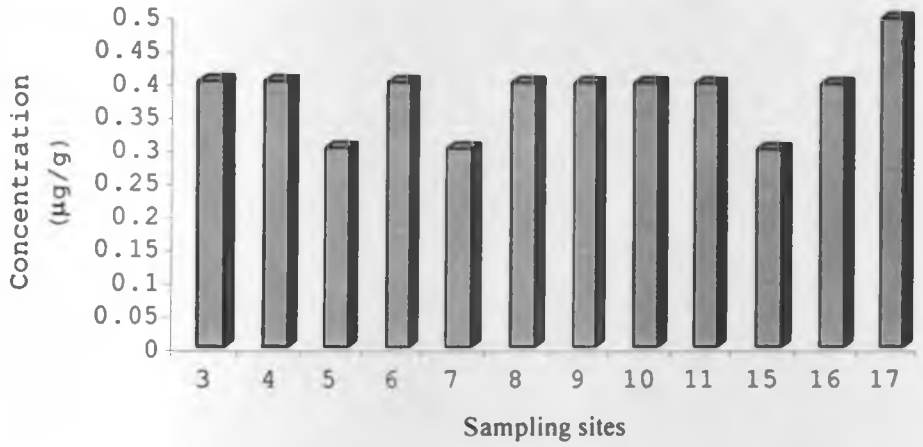


Figure 5.12: Cadmium levels in sugarcane leaves samples obtained along Nairobi River.



- A uniform distribution (0.2-0.3) µg/g of cadmium levels for sugarcane stem sample was observed (Figure 5.11).
- There is no variation (approximately 0.4 µg/g) for the corresponding cadmium levels in most of the sugarcane leave samples (Figure 5.12).
- In general it is observed that there is no significant variation (1.2-1.8) µg/g in the levels of cadmium for soil samples. The cadmium levels in sugarcane stem and sugarcane leaves samples vary (0.3-0.4 µg/g) for most of the samples analysed. These values are in agreement with the findings of a study by *Huffman* and *Hodgson (1973)* on wheat and perennial grass (< 0.3 ppm).
- The results indicate that sugarcane readily absorbs cadmium, which is later translocated differentially to the leaves and stems. These findings are in agreement with the findings of *John* and *Van Laerhoven (1976)* – that cadmium is translocated to the foliage parts.

The cadmium levels in sugarcane stem samples are within safe limits (46 µg/g) for consumption *(WHO, 1996)*.

5.4 Results of analyses of Arrowroots *(Colocasia Esculenta)* parts samples from the Catchment of Nairobi River

The results of analysis of arrow root parts samples are presented in table 5.9 and figures 5.13, 5.14 and 5.15

Table 5.9: Result of lead levels in arrow roots parts samples (µg/g)± 1 S.D, n=5 (EDXRF method)

Site	Soil	Tuber	Leaves
5	163±14	15.3±3.4	<5.0
6	219±20	7.0±2.0	<5.0
7	228±10	11.2±5.8	5.6±1.1
8	211±31	9.9±3.1	<5.0
9	150±28	8.8±1.7	<5.0
10	64±5	11.2±2.0	6.0±1.4
11	70±4	8.1±0.6	7.6±2.1
12	53.6±0.3	12.8±1.2	6.0±1.4
13	55.4±2.6	8.8±0.5	8.3±1.5
14	71.1±3.2	9.2±2.5	<5.0
15	71±4	6.7±1.8	<5.0
16	71.2±4.1	8.0±1.3	<5.0
17	68±5	8.8±2.3	19.2±2.0
18	62±3	8.3±2.4	16.4±1.8
19	61.2±3.4	8.5±0.4	20.2±0.1

Figure 5.13: Lead levels in soil samples on which arrow root is grown along Nairobi River

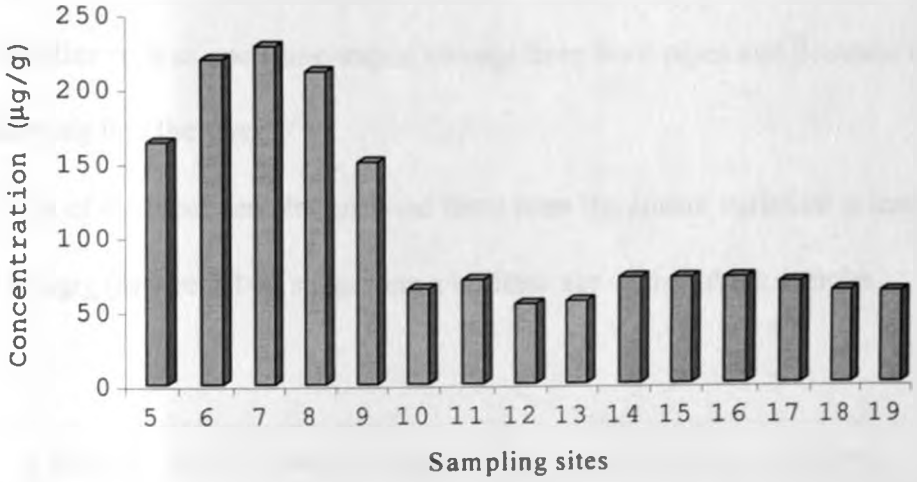
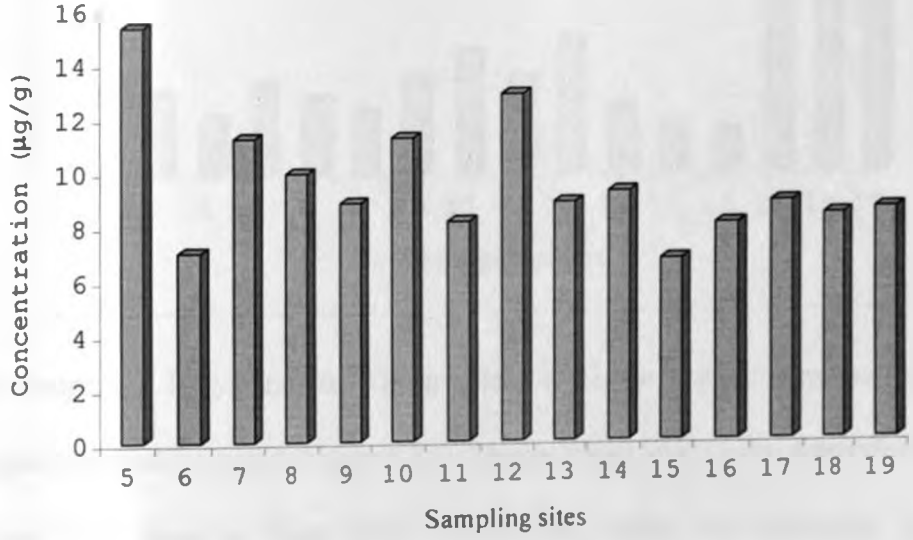
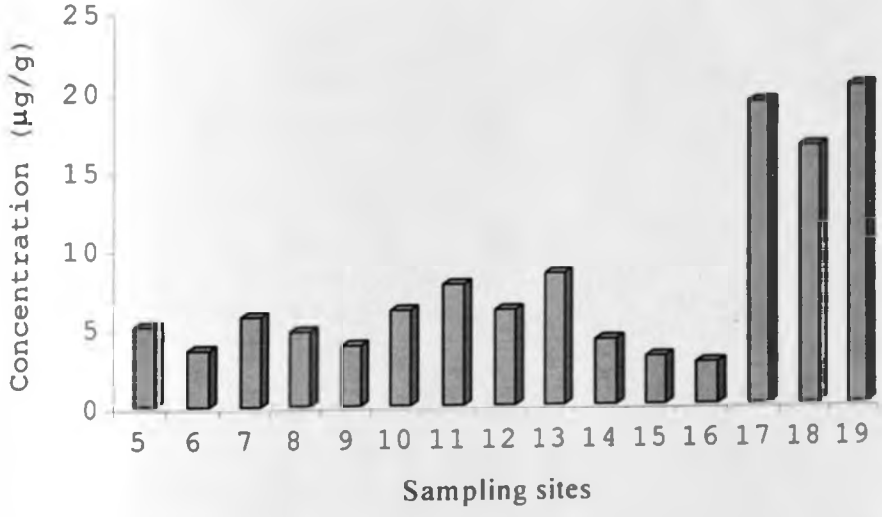


Figure 5.14 Lead levels in arrow roots tuber samples grown along Nairobi River.



- Two groups for lead levels in soil samples are identified (Figure 5.13); 150-228 µg/g and 53-71 µg/g.
- The high lead levels were observed in samples which were obtained from the densely populated areas between Shauri Moyo, Bahati and Eastleigh (site 5-9) characterised by activities such as open air-garages, sewage from burst pipes and domestic effluents discharging into the river.
- For most of the tuber samples analysed there is no significant variation in lead levels (7-9.9) µg/g (Figure 5.140, suggesting a uniform age of the tubers samples.

Figure 5.15 Lead levels in arrowroots leaves samples



- Two groups; 3-8.3 µg/g and 16-20 µg/g of lead levels for most of corresponding leave samples analysed are noted (Figure 5.15). The high lead levels were determined for the samples from Dandora phase 2(site 17, 18, 19), which were advanced in age in comparison to other samples analysed. The high lead levels in arrowroots leaves samples

from site 17, 18, 19 may also be ascribed to foliar contamination by motor vehicle lead *(Warren and Devault, 1960)* and from the burning of domestic and industrial wastes by the Nairobi city council.

- In general, arrowroots accumulate more lead in their tubers than in leaves. a finding that is in agreement with the results of *Page (1972)*. However, the lead levels in tubers are lower than the recommended dietary intake of less than 232 µg/day *(WHO, 1996)*.

Table 5.10 presents the results of zinc levels in arrow roots sample parts.

Table 5.10: Zinc levels in arrow roots parts samples (μg/g) ±1 S.D. n=5 (XRFA method)

Site	Soil	Tuber	Leaves
5	358±13	270±19	329±22
6	180±10	340±24	340±11
7	177±8	305±50	371±8
8	170±8	292±17	325±5
9	181±17	252±92	364±6
10	183±11	264±11	386±4
11	180±8	260±54	241±9
12	188±4	273±13	229±12
13	255±5	145±22	119±3
14	290±22	134±11	136±10
15	264±13	166±13	141±10
16	328±38	145±23	175±4
17	296±23	386±26	327±22
18	342±20	420±27	307±19
19	390±11	405±24	296±20

- Zinc levels in the soil samples increase downstream (Figure 5.16). The zinc levels increases progressively from 170-358 μg/g. The high zinc levels were analysed in soil samples which were obtained from areas between Huruma and Dandora phase 2 (site 13-

19) whereby dumping sites are located for both domestic and industrial wastes by the city council.

- Three groups; 252-340 μg/g, 134-166 μg/g and 386-420 μg/g are identified for zinc levels in tuber samples (Figure 5.17). The higher levels of zinc were determined in samples, which were obtained from densely populated areas of Dandora phase 2 and Lucky Summer estate (sites 17, 18 and 19).
- The variations of zinc levels in arrowroot leaves samples are similar in pattern as tuber samples (Figure 5.18).
- In general, the results indicate that zinc is readily taken up by arrowroots (*Purves, 1977*) with most of the proportion translocated to the leaves than in the tubers. There is a strong positive correlation for zinc levels in the tubers and leaves samples (r=0.713). However, the levels of zinc in arrowroots tuber samples are lower than the recommended dietary intake of less than 45 mg/day *(WHO, 1996)*.

Figure 5.16 Zinc levels in soil samples on which arrowroot is grown along nairobi River

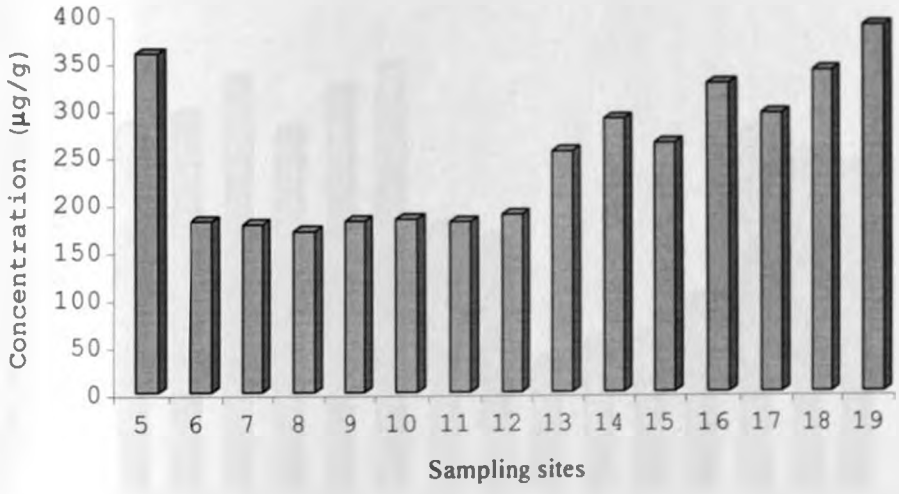


Figure 5.17 Zinc levels in arrow roots tuber Samples.

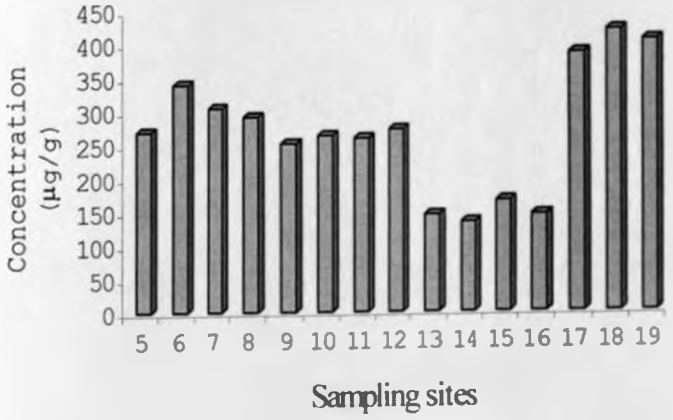


Figure 5.18 Zinc levels in arrowroot leaves samples

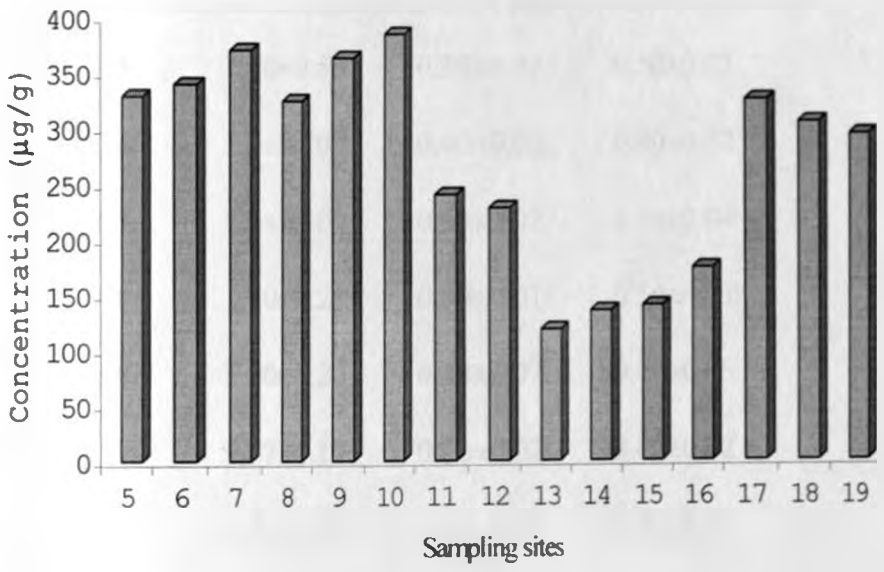


Table 5.11: Results of Cadmium level in arrow roots parts samples (μg/g) ±1 S.D, n=5 (AAS method)

Site	Soil	Tuber	Leaves
5	1.50±0.50	0.30±0.03	0.50±0.02
6	1.7±0.70	0.40±0.02	0.80±0.02
7	1.6±0.30	0.30±0.02	0.30±0.04
8	1.70±0.25	0.30±0.01	0.50±0.03
9	1.80±0.20	0.10±0.07	0.70±0.05
10	1.77±0.12	0.20±0.02	0.40±0.02
11	1.82±0.30	0.30±0.02	0.30±0.01
12	1.88±0.70	0.20±0.03	0.60±0.07
13	1.84±0.90	0.30±0.04	0.30±0.03
14	1.20±0.10	0.20±0.01	0.40±0.05
15	1.36±0.10	0.10±0.04	0.30±0.03
16	1.32±0.20	0.20±0.01	0.40±0.04
17	2.00±0.60	0.30±0.02	0.20±0.02
18	1.74±0.20	0.30±0.05	0.20±0.01
19	1.87±0.30	0.40±0.02	0.50±0.02

Figure 5.19: Cadmium levels in soil samples on which arrowroots is grown along Nairobi River

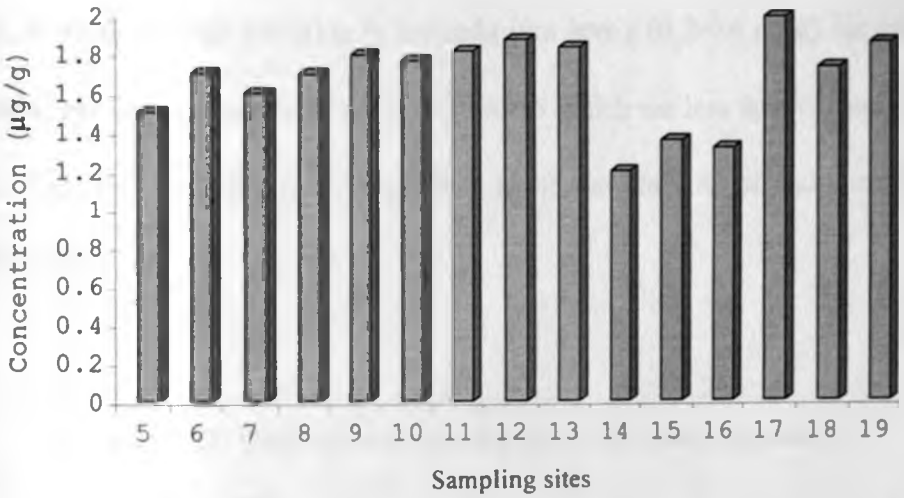
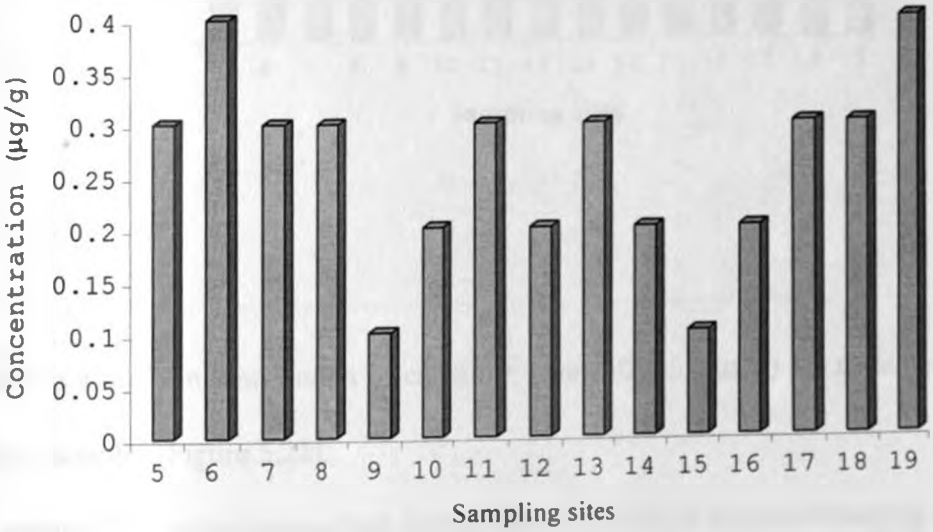
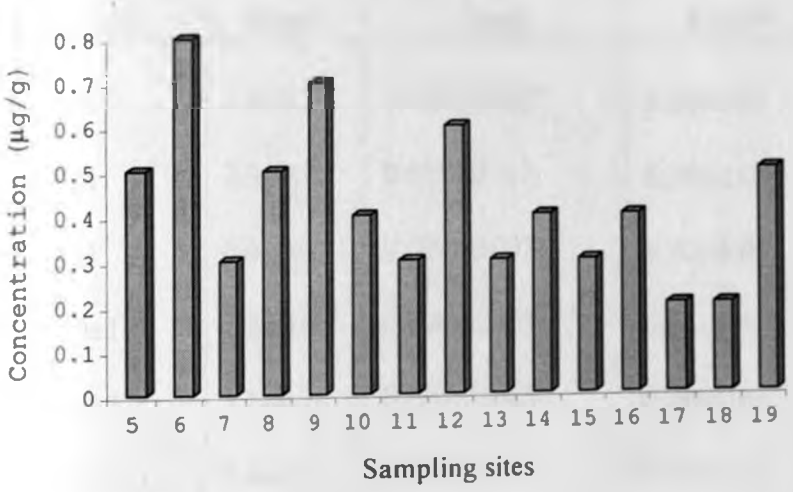


Figure 5.20: Cadmium levels in arrowroot tuber Samples.



- There is no significant variation in the cadmium levels for most soil samples analysed (Figure 5.19), (1.2-1.88) μg/g.
- There is no significant variation in the cadmium levels (0.2-0.4 μg/g) for most tuber samples, except for those from site 9 and site 15 which are less than 0.1 μg/g) (Figure 5.20). This low variation may be ascribed to non-availability of cadmium for plant absorption.

Figure 5.21: Cadmium levels in the arrowroot leaves samples.



- There is a uniform distribution of cadmium levels (0.2-0.5 μg/g) for most arrowroot leaves samples (Figure 5.21).
- In general, the results indicate that arrowroots slowly absorb cadmium from the soil and accumulate it more in leaves than tubers, an observation agreeable with findings of a

study by *John* and *Van Laerhoven* (1976). The levels of cadmium in tubers are lower than the recommended dietary intake of less than 46 µg/day *(WHO, 1996)*.

5.5 Results Of analyses of Kale Samples (*Brassica Olevacea*) Parts Samples from the Catchment of Nairobi River.

Results of analyses of lead, zinc and cadmium levels in kale saples are presented in tables 5.12; 5.13 and table 5.14

Table 5.12: Results of lead levels in Kale parts samples (µg/g) ±1 S.D, n=5 (AAS method)

Site	Soil	Roots	Stem	Leaves
10	64±5	2.6±0.2	0.060±0.002	0.20±0.01
11	70±4	2.3±0.7	0.030±0.002	0.20±0.02
12	54±3	0.4±0.1	0.070±0.002	0.20±0.05
13	55.0±1.5	2.2±0.6	0.090±0.005	0.14±0.01
14	71.0±3.2	1.1±0.7	0.090±0.005	0.20±0.03
15	71.0±4.0	0.4±0.1	0.100±0.002	0.13±0.01
16	71.2±4.0	1.8±0.6	0.050±0.002	0.20±0.01
17	68±5	1.7±0.3	0.070±0.002	0.14±0.01
18	62±3	2.7±0.9	0.160±0.050	0.20±0.03
19	61.2±3.4	1.9±0.5	0.190±0.070	0.20±0.01

Figure 5.22: Lead levels in soil samples on which kale is grown along Nairobi River

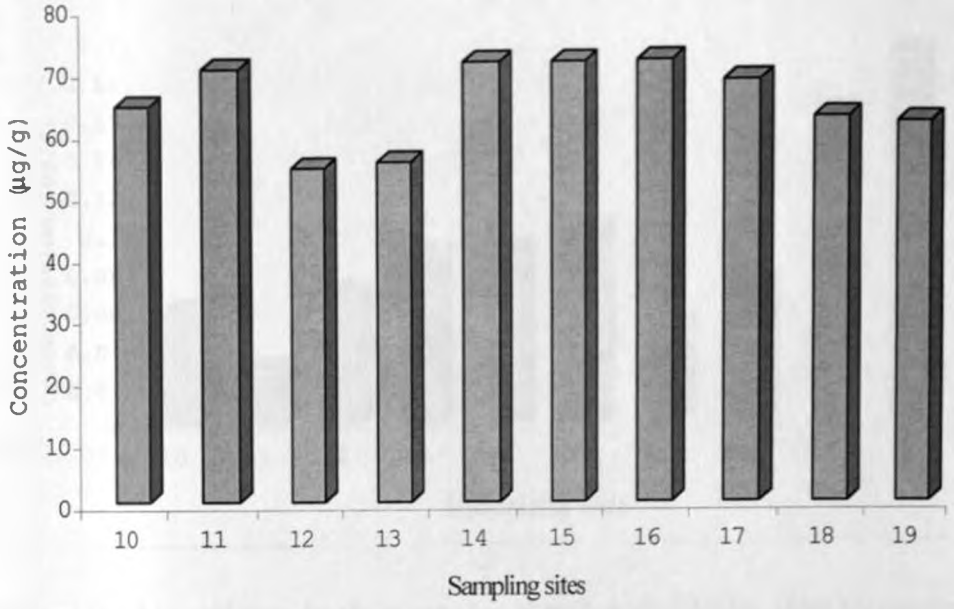


Figure 5.23: Lead levels in kale roots Samples obtained along Nairobi River.

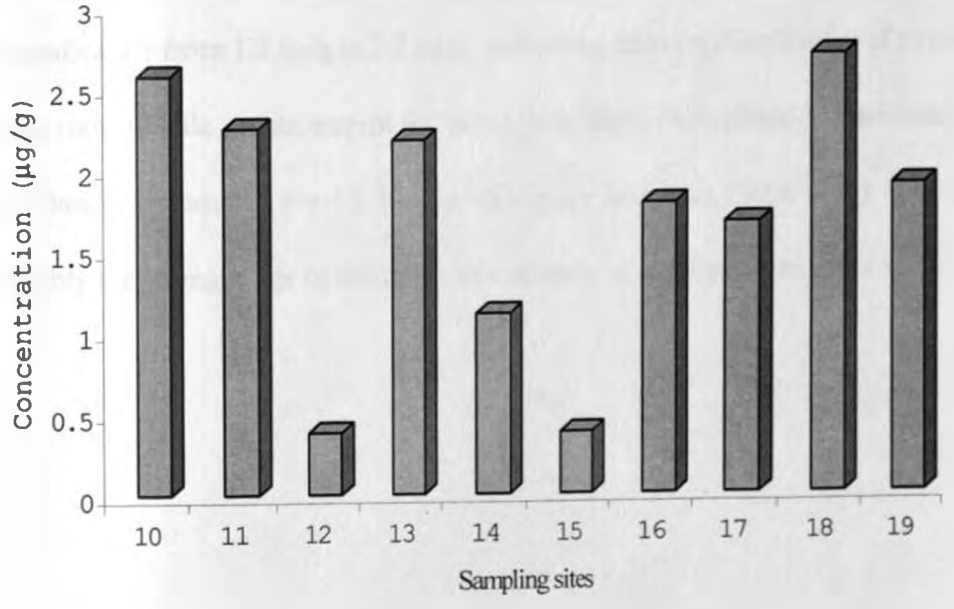
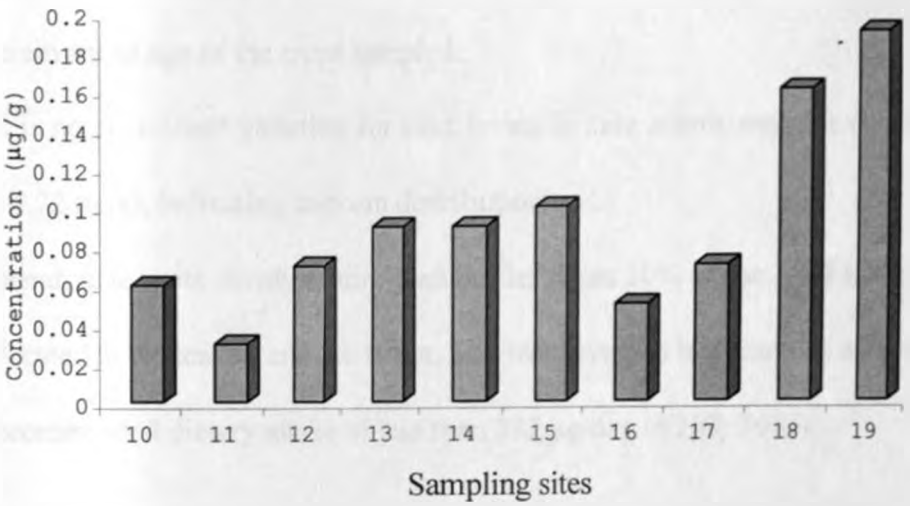


Figure 5.24: Lead levels in kale stem Samples.



- The lead level in soil samples does not vary significantly (20-36 µg/g) for most samples analysed. The high lead levels may be due to contamination by the effluents from nearby industries and from the quarries (Figure 5.22).
- For most of the kale roots samples analysed (Figure 5.23), the levels of lead vary insignificantly from 1.7 µg/g to 2.7 µg/g, indicating uniform distribution of this element in the roots of kale plants, except for those from Buru Buru phase 1, Kariobangi south and Dandora phase 1 (site 12 14 15) which are less than (<0.4 µg/g). This implies probably the younger age of the crops in comparison to those from other areas.

- A progressive increase of lead level in kale stem samples (Figure 5.24) is noted. However Samples from Dandora phase 1 and 2 (site 18, 19) have higher levels of lead probably due to advanced age of the crops sampled.
- There is no significant variation for lead levels in kale leaves samples (Figure 5.25) (0.13-0.22 µg/g), indicating uniform distribution.
- In general, kale roots slowly absorb lead but less than 10% of the level in the roots is translocated to the leaves, and the stems. The lead levels in leaf samples are lower than the recommended dietary intake of less than 232 µg/day *(WHO, 1996)*.

Figure 5.25: Lead levels in kale leaves Samples.

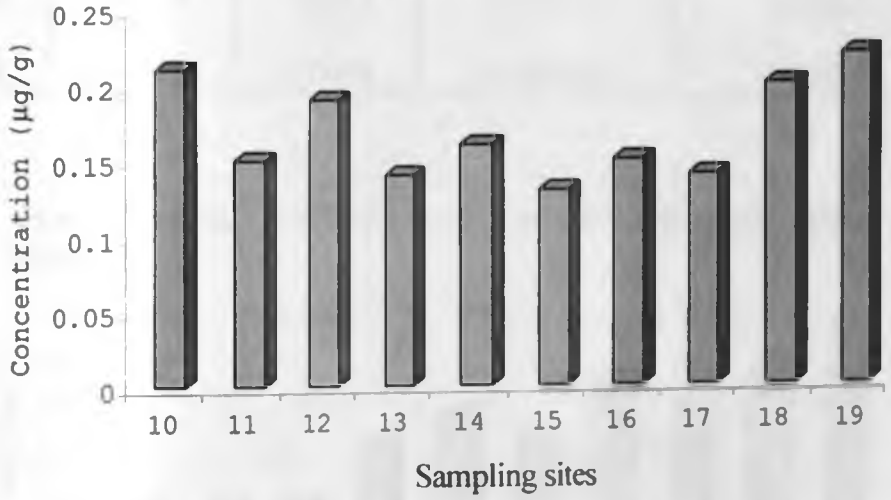


Table 5.13: Results of zinc levels in Kale parts samples (µg/g) ±1 S.D, n=5 (AAS method)

Site	Soil	Roots	Stem	Leaves
10	183±11	2.6±0.9	0.78±0.05	2.2±0.5
11	180±8	4.0±1.3	0.31±0.02	1.1±1.4
12	188±4	1.6±0.7	0.69±0.04	3.0±0.4
13	255±5	4.5±1.4	0.21±0.02	1.1±0.2
14	290±22	1.5±0.6	0.40±0.01	2.7±0.4
15	264±13	2.4±0.7	0.23±0.03	1.9±0.3
16	328±38	1.5±0.8	0.17±0.05	1.9±0.5
17	296±23	7.1±1.2	0.29±0.01	1.4±0.2
18	342±20	1.5±0.5	0.54±0.01	2.1±0.3
19	390±11	2.7±0.9	0.26±0.03	2.0±0.4

Figure 5.26: Zinc levels in soil samples on which kale is grown along Nairobi River

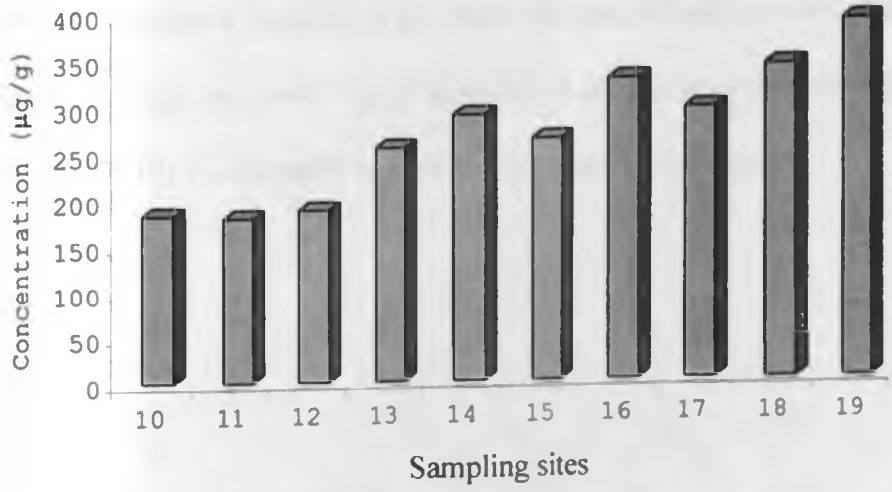
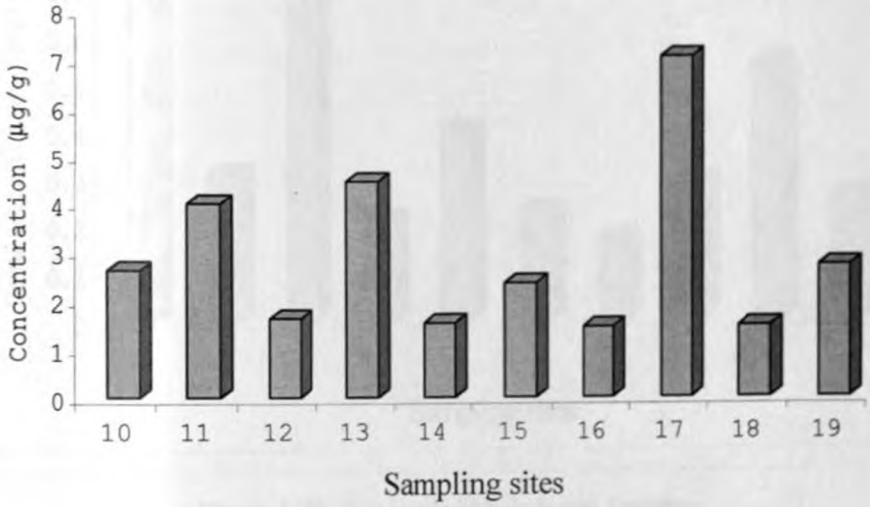


Figure 5.27: Zinc levels in kale roots samples obtained along Nairobi River.



- The level of zinc in soil samples on which kale is grown progressively increases downstream (Figure 5.26). The high zinc levels, (290-390 µg/g), were noted for soil samples which were obtained from Buru Buru phase 1, Kariobangi south and Dandora phase 2(site 14, 19), whereby there is abundant disposal of metal scraps and domestic and industrial.
- There is no significant variation of zinc levels in most of kale roots samples analysed (Figure 5.27). High zinc level (7 µg/g) was noted in samples from Dandora phase 2 (sites 16, 17, 18 and 19) where nearby is a massive garbage-dumping site.

Figure 5.28: Zinc levels in kale stem Samples.

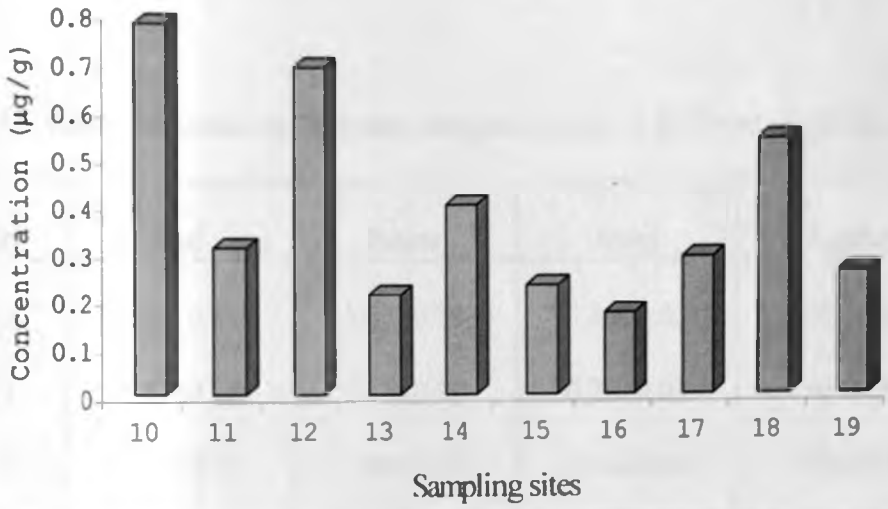
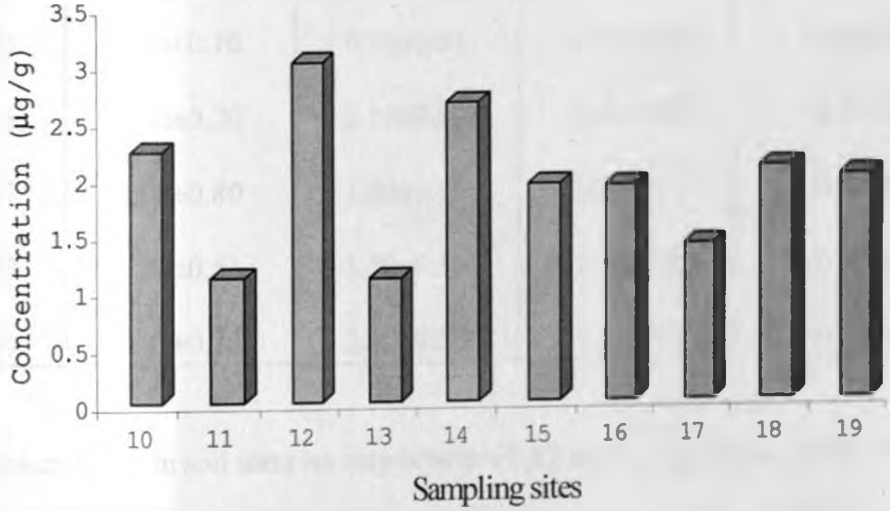


Figure 5.29: Zinc levels in kale leaves Samples.



- Likewise, there is no significant variation for zinc levels for most kale stems samples (Figure 5.28).
- A similar variation of zinc levels for kale leaves samples is noted (Figure 5.29).
- In general, the results indicate that kale slowly absorb zinc from the soil, accumulating more zinc in the roots than in the leaves and stems. The result agrees with findings by

Purves (1977) on oats and clovers. Zinc levels in kale leaves samples are lower than the recommended dietary intake of less than 45 mg/day *(WHO, 1996)*.

Table 5.14: Cadmium levels in Kale parts samples (µg/g) ±1 S.D, n=5 (AAS method)

Site	Soil	Roots	Stem	Leaves
10	1.77±0.12	3.00±0.20	0.45±0.02	<0.0006
11	0.82±0.32	2.30±0.30	0.25±0.01	<0.0006
12	1.88±0.70	1.60±0.10	0.34±0.02	<0.0006
13	1.84±0.90	2.30±0.30	0.58±0.02	0.02±0.003
14	1.20±0.10	1.00±0.20	0.01±0.001	0.01±0.002
15	1.36±0.10	0.10±0.01	0.06±0.01	<0.0006
16	1.32±0.20	2.10±0.50	0.95±0.03	<0.0006
17	2.00±0.80	1.80±0.40	0.03±0.01	<0.0006
18	1.74±0.51	3.10±0.30	1.95±0.2	<0.0006
19	1.87±0.32	2.20±0.50	1.06±0.3	<0.0006

- Cadmium levels in soil samples vary between 0.82 and 2 µg/g (Figure 5.30). The highest levels belong to soil samples that were obtained from Dandora phase 2 (site 17 18), whereby there is massive disposal site for domestic and industrial wastes.

Figure 5.30 Cadmium levels in soil samples on which kale is grown along Nairobi River

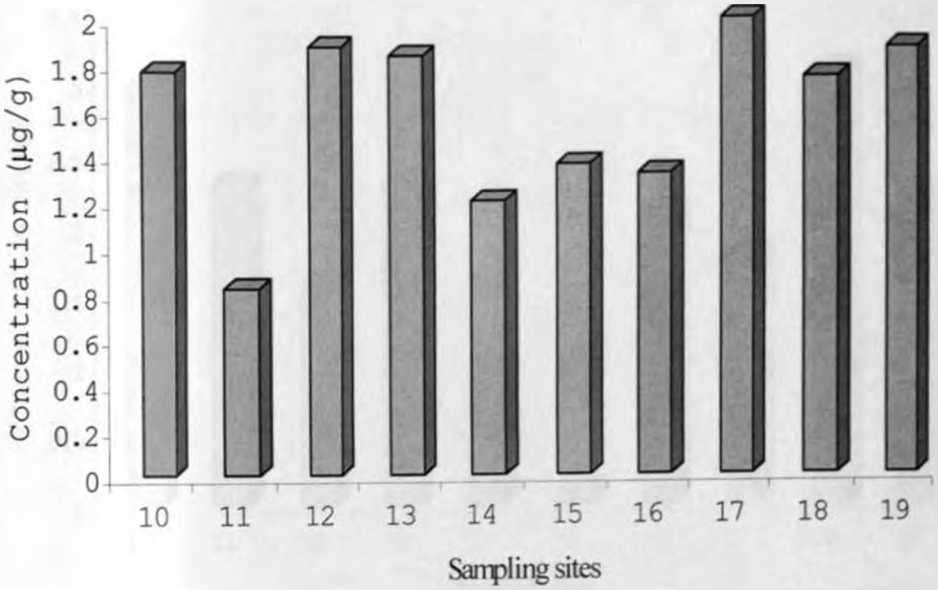


Figure 5.31: Cadmium in kale roots samples obtained grown along Nairobi River.

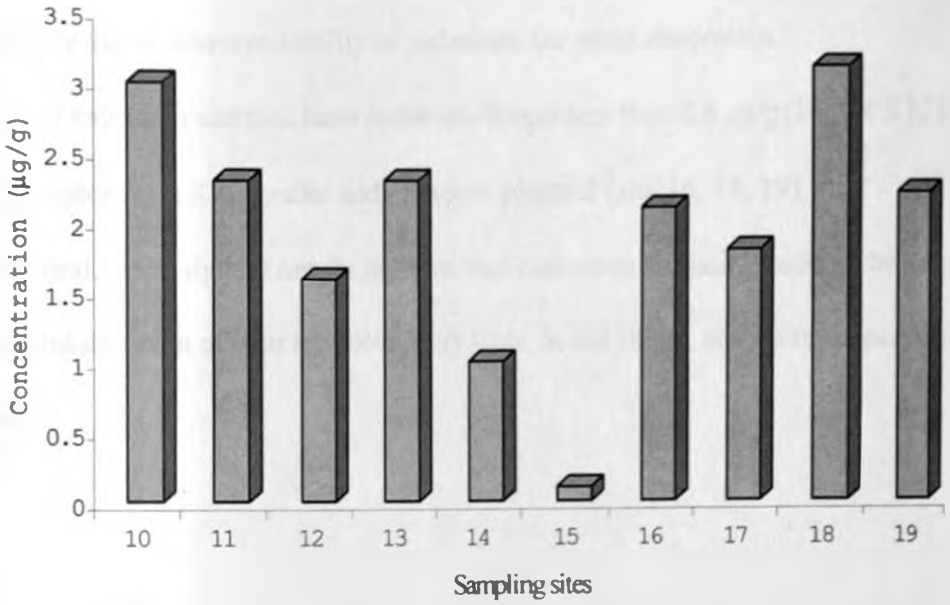
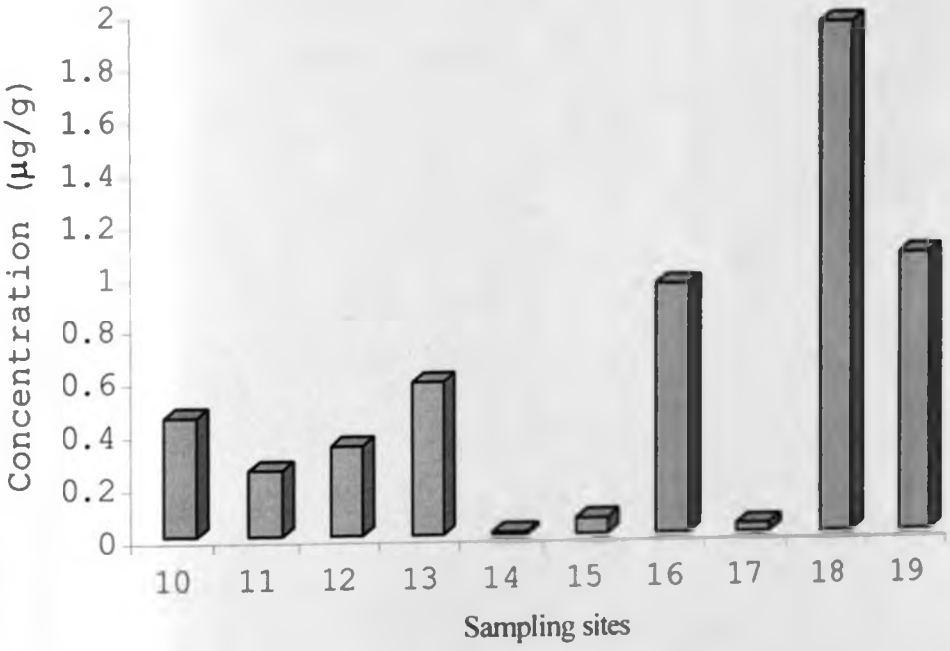


Figure 5.32: Cadmium in Kale stem Samples.



- For most kale roots samples analysed the cadmium levels are between 1 and 3 µg/g (Figure 5.31), except for samples from Korogocho (site 15). The low variation is probably due to non-availability of cadmium for plant absorption.
- Most of kale stem samples have cadmium levels less than 0.6 µg/g (Figure 5.32), except for samples from Korogocho and Dandora phase 2 (site 16, 18, 19).
- In general, the analytical results indicate that cadmium is readily absorbed by kale, which accumulates most of it in the roots, very little in the stems, and no translocations to the leaves.

5.6 Results of analysis of water samples obtained from Nairobi river.

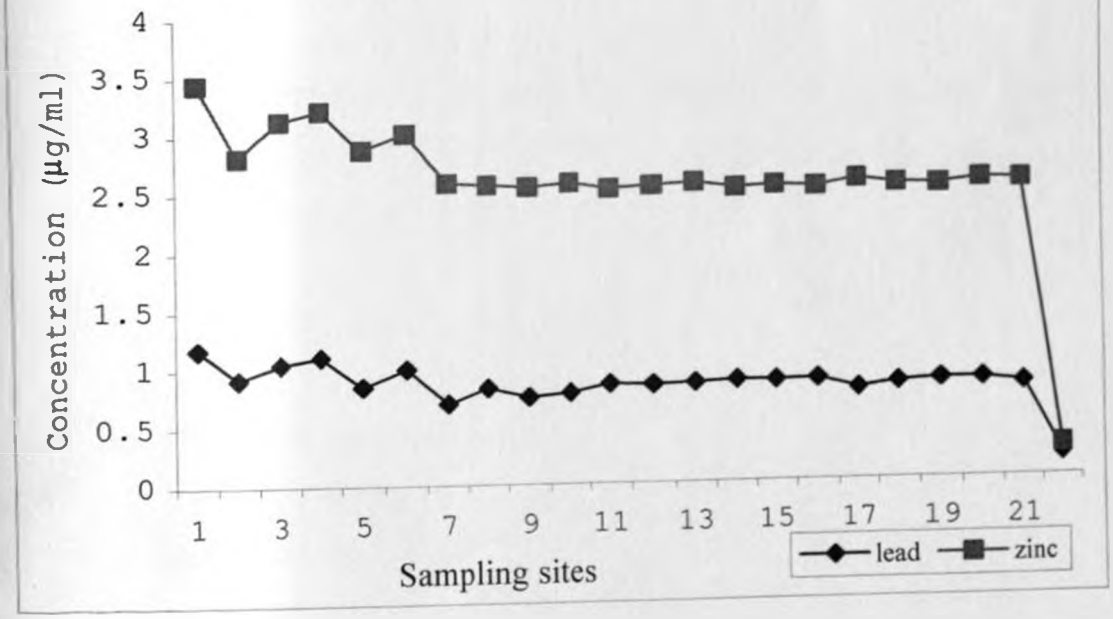
The results of analyses for lead, zinc, cadmium and mercury levels in water samples are presented in table 5.15.

Table 5.15: Results of lead, zinc, cadmium and mercury levels in water samples (μg/ml) ± 1 S.D, n=3 (AAS method)

Site	Lead	Zinc	Cadmium	Mercury
1	1.18±0.01	3.45±0.06	<0.0006	<0.2
2	0.92±0.01	2.82±0.04	<0.0006	<0.2
3	1.05±0.09	3.13±0.01	<0.0006	<0.2
4	1.11±0.02	3.22±0.05	<0.0006	<0.2
5	0.85±0.06	2.88±0.02	<0.0006	<0.2
6	1.00±0.03	3.02±0.01	<0.0006	<0.2
7	0.71±0.02	2.59±0.04	<0.0006	<0.2
8	0.83±0.04	2.57±0.01	<0.0006	<0.2
9	0.75±0.06	2.55±0.03	<0.0006	<0.2
10	0.78±0.03	2.58±0.09	<0.0006	<0.2
11	0.85±0.05	2.53±0.02	<0.0006	<0.2
12	0.84±0.07	2.55±0.05	<0.0006	<0.2
13	0.85±0.03	2.57±0.03	<0.0006	<0.2
14	0.87±0.09	2.52±0.06	<0.0006	<0.2
15	0.86±0.02	2.54±0.02	<0.0006	<0.2
16	0.87±0.01	2.52±0.01	<0.0006	<0.2

Site	Lead	Zinc	Cadmium	Mercury
17	0.78±0.04	2.58±0.05	<0.0006	<0.2
18	0.83±0.06	2.54±0.02	<0.0006	<0.2
19	0.85±0.01	2.53±0.07	<0.0006	<0.2
20	0.85±0.03	2.57±0.05	<0.0006	<0.2
21	0.81±0.01	2.56±0.03	<0.0006	<0.2
22	0.19±0.07	0.27±0.01	<0.0006	<0.2

Figure 5.33: Lead and zinc levels in water samples obtained from Nairobi river



- The levels of zinc in most water samples vary between 2.5 and 3.5 µg/ml, with the highest level of 3.5 µg/ml being from samples obtained at a bridge 200 metres west of Chiromo campus hostels (site 1).

- Lead levels in water samples vary between 1.18 and 0.75 µg/ml, and it was also observed that the highest levels were from samples obtained from about 200 m west of Chiromo campus hostels, site 1.
- The high levels of lead and zinc observed in water samples from site 1 could be due to contamination of river waters by construction activities just about 200 metres upstream of the site.
- On average, the levels of zinc in water samples are about three times higher than lead levels (Figure 5.33).
- The levels of lead and zinc in water samples exceed the recommended *WHO* limits which are 0.05 µg/litre and <0.5 µg/litre, respectively (*WHO, 1984*), which is an indication of cross pollution of the river waters by these metals.

5.7 Results of analysis for available elements in the soil samples.s

Table 5.16 presents the results of analyses of soil samples for the 'available' levels of lead, zinc, cadmium and mercury.

Table 5.16: Results of analysis of soil samples for available element (μg/g), ±1 S.D., n=5 (AAS method)

Site	Lead	Zinc	Cadmium	Mercury
1	0.060±0.001	0.345±0.002	<0.0006	<0.2
2	0.037±0.004	0.282±0.005	<0.0006	<0.2
3	0.030±0.001	<0.002	<0.0006	<0.2
4	0.060±0.002	0.039±0.001	<0.0006	<0.2
5	0.083±0.004	0.046±0.002	<0.0006	<0.2
6	0.052±0.001	<0.002	<0.0006	<0.2
7	0.031±0.001	0.259±0.04	<0.0006	<0.2
8	0.030±0.004	0.019±0.001	<0.0006	<0.2
9	0.023±0.006	0.255±0.03	<0.0006	<0.2
10	0.028±0.002	0.013±0.002	<0.0006	<0.2
11	0.030±0.002	<0.002	<0.0006	<0.2
12	0.023±0.001	<0.002	<0.0006	<0.2
13	0.064±0.002	0.580±0.06	<0.0006	<0.2
14	0.059±0.005	<0.002	<0.0006	<0.2
15	0.062±0.002	<0.002	<0.0006	<0.2
16	0.030±0.001	0.030±0.003	<0.0006	<0.2
17	0.028±0.003	<0.002	<0.0006	<0.2
18	0.023±0.001	0.014±0.001	<0.0006	<0.2
19	0.062±0.001	0.255±0.02	<0.0006	<0.2
20	0.030±0.004	<0.002	<0.0006	<0.2

- The available soil lead level for plant absorption varies (0.02-0.08) μg/g), while that for zinc varies (0.013-0.345) μg/g. Zinc is readily more available than lead in most of these samples by factor of 8.

5.8 Results of measurement of soil pH

Table 5.17: Results of measurement of soil pH

Site	pH	Site	pH
1	7.5±0.03	11	6.5±0.01
2	7.5±0.01	12	7.8±0.01
3	6.8±0.02	13	7.8±0.01
4	7.4±0.01	14	7.8±0.01
5	7.4±0.03	15	7.8±0.01
6	7.3±0.02	16	7.8±0.01
7	7.3±0.01	17	7.8±0.01
8	7.4±0.01	18	7.3±0.03
9	6.4±0.03	19	6.7±0.01
10	7.2±0.01	20	6.2±0.01

- The levels of soil pH vary between 6.2-7.8. implying that most of the soil samples analysed are basic.

5.9 Comparison of EDXRF and AAS analytical results

Table 5.18: Comparison of EDXRF and AAS analytical results

Element	Site	EDXRF (ppm))			AAS (ppm)			
		Soil	roots	leaves	Soil	Roots	stem	leav
Pb (sugarcane)	7	228±10	27.0±2.3	22.0±2.0	393±21	36.8±6.0	29.4±4	30±8
	8	211±31	22.9±5.2	14.6±2.6	249±12	24±2	12.1±2	15.4
Zn (Arrow roots)	5	358±13	270±19	329±22	401±9	356±41	427±19.0	
	16	328±38	145±23	175±4	370±25	164±6	201±32	

- Sugarcane and arrowroot plant samples were selected for comparison of the analytical results by AAS and EDXRF techniques, from sites (7 & 8 and 5 & 16), which had shown higher levels of lead and zinc in the soil samples. Good agreement was obtained for the values of lead and zinc determined by the two techniques.

5.10: CONCLUSIONS AND RECOMMENDATIONS

5.10.1 CONCLUSIONS

The objectives of this research were realised in a big measure, with particular regard to the uptake characteristics of Pb, Zn and Cd by food crops. However, any relationship between these elements in food crops and the soils on which they are grown could not be reached because in the field variables were many; soil type, soil pH, age of crops, concentration levels of elements. Therefore, due to the time limit, the relationship between all of them could not be studied.

In summary, this study has shown that heavy metal concentrations in different food crops species often show large variations even at the same locations in the field. This is probably due to variations in plant uptake characteristics and growth rates. Generally, most elements were found at concentrations normally observed in vegetables grown in uncontaminated areas while increased levels of lead and zinc were determined particularly in arrowroots and kale leaves. Lead levels in soil samples were lower than those reported elsewhere (90-300 μg/g) for urban gardens *(Kabata-Pendias, 1984).* This means that the Nairobi River catchment agricultural soil is not that significantly contaminated by lead from domestic and industrial activities.

The following conclusions have been drawn from the findings of the study and are presented as per sample type.

- The total mercury levels in soil samples are below detection limit (0.2 μg/g) and total cadmium content is within the range of uncontaminated soils (<2 μg/g). While the total lead and zinc levels in soil samples are as high as 228 μg/g and 400 μg/g respectively.

- The 'available' levels of mercury and cadmium in the soil for plant absorption are below detection limits (0.2 and 0.0006 μg/g, respectively), while the highest 'available' levels of lead and zinc (0.083 and 0.58) μg/g respectively, account for less than 1% of the total soil content.
- The soil samples of the study area are basic with pH value averaging 7.31±0.05.
- Mercury and cadmium levels in water samples were found below detection limits (<0.02μg/ml and <0.0006 μg/ml) respectively. Lead and zinc levels in water samples exceed *WHO* limits (0.05 and 0.5 μg/litre) respectively.

(a) Sugarcane (*saccharum offinaram)*

- In general, lead is absorbed in significant proportions by the cane roots (up to 900 μg/g) and only a portion, less than 20 μg/g (5%) is translocated to the stalk/stem and approximately 210 μg/g (25%) to the leaves for the very aged crops. Levels of lead in roots, stem and leaves samples correlate positively (r>0.89). The lead levels in sugarcane stem samples are less than 20 μg/g, which is lower than the *WHO* recommended dietary intake of 232 μg/day (*WHO, 1996)*.
- The levels of zinc in sugarcane samples are high which is an indication of its high absorption (up to 200 μg/g) for areas further downstream in Kariobangi South, Dandora and Komarock, but less than 50 μg/g in other areas. These findings concur with those done by *Purves (1977)* on grass, radishes and lettuce. The levels of zinc in sugarcane roots, stem and leaves samples correlate positively (r>0.75). The recommended dietary daily intake limits for zinc is less than 45 μg/day.

- There is no significant variation (1.2-1.8 μg/g) in the levels of total cadmium present in the soil samples analysed from which cane is grown.
- Results of analysis indicate that sugarcane slowly absorbs cadmium, which is translocated differentially to the leaves and stem in varying proportions between (0.3-0.4 μg/g) for most samples. These findings are in agreement with those of *John* and *Van Laerhoven (1976).* The levels of cadmium in sugarcane stem samples are within save limits (less than 46 μg/g) for consumption (*WHO, 1996).*

(b) **Arrowroots *(colocasia esculenta)***

- The total lead content is higher (150-200 μg/g) by a factor of 5 in soil samples from places near the city centre which are characterised by activities such as open-air garages, sewage from burst pipes and domestic effluents from residential areas (Shauri Moyo, Bahati and Eastleigh).
- There is no significant variation in lead levels (<15 μg/g) for most of the tuber samples analysed- suggesting an even distribution and similar age of the plant sampled. In general, arrowroots tend to accumulate more lead in their tubers than in the leaves, but these levels are within the recommended dietary intake of less than 232 μg/day for human consumption (*WHO, 1996).*
- Arrowroots readily absorb zinc, with most of it translocated in the leaves than in the tubers.
- In general, the results indicate that arrowroots slowly absorb cadmium from the soil and accumulate it more in leaves than in the tubers-results whose findings are in agreement with those by *John* and *van Laerhoven* (1976).

- Zinc levels in tuber samples are within recommended dietary intake of less than 45 mg/day (*(WHO, 1996).*
- The results also indicate that arrowroots slowly absorb cadmium from the soil and accumulate more in the leaves than tubers. However, the levels of cadmium in tubers are within the recommended dietary intake of less than 46 μg/g (*WHO, 1996).*

(C) **Kale (*brassica olevacea)***

- Less than 10% of the lead which is absorbed by the roots is translocated to the leaves in levels within the *WHO* recommended daily dietary intakes (<232 μg/g).
- Kales slowly absorb zinc from the soil, accumulating more in roots then leaves and stems. Zinc levels in kale leaves samples are within the *WHO* recommended dietary intakes (of less than 45 mg/day).
- Cadmium is readily absorbed by kale where almost (20%) of the total soil content is accumulated in roots but with no significant translocation to the leaves and stems.

(d) **Water samples**

- Zinc levels are higher (2.5-3.5 μg/ml) than lead levels (0.8-1.2 μg/ml) in water samples, by factor of 3, for most of the samples analysed in this study. These levels exceed the *WHO* recommended limits (<0.05 μg/l and <0.5 μg/l) respectively for raw water use in domestic and industrial use, a clear indication of gross pollution of the river waters by these metals.

5.10.2 RECOMMENDATIONS

- Under the field conditions it was not possible to achieve all the objectives of this study. There was no conclusive relationship to be drawn with regard to the levels of lead, zinc, cadmium and mercury in the food crops and the soil on which the food crops are grown, due to a multiplicity of variables; soil type, soil pH, age of food crops, concentration levels of the elements and plant species varieties. Therefore, further studies should be done by varying only one factor at a time and holding the rest a constant, in order to evaluate their relationships.

- The following recommendations are necessary on the monitoring of the Nairobi River waters on long-term goal, in order to increase awareness for environmental issues and also to improve the condition of river waters. Another goal is to provide high quality data to any interested private, government, or citizens organisation. To achieve this goal, a strict quality assurance/quality control programme is recommended for the monitoring of the following parameters:-

  - **Bacterial analyses**:

The major sources of high bacteria are from road runoff and sewage. By tracking changes in bacteria counts from year to year, it may be possible to identify sources of pollution and predict changes in river water quality in future years.

  - **Chloride Analyses**

Sources include industrial waste and sewage from residential areas. From runoff or from storm drains emptying directly into our rivers, the chlorides are put into our environment. In

addition to being corrosive, chlorides can harm vegetation in concentrations over 1000 ppm.

- **Testing for Dissolved Oxygen**

Biological monitoring supplements chemical testing by giving a long-term picture of water quality. By using indicator organisms that must exist in a certain section of the stream and that are sensitive to DO, a better idea of oxygen concentrations on a day-to-day basis may be obtained.

- **Oil and Grease Measurement**

When these compounds are in large quantities, a sheen or slick may be visible on the water surface. Even when these compounds are not in high quantity, enough oil and grease will dissolve and/or be churned up and suspended by the movement of the water to cause significant damage to the ecosystem.

- **Micro-invertebrate Investigation**

Micro-invertebrates are not likely to move from their habitat during the aquatic stage of their life. Because of this, they are subject to any drop in oxygen or pollutant. If the pollution or oxygen is persistent, certain invertebrate will not be able to live in water.

- **Nitrate/Nitrite analyses**

The source of nitrate could be runoff from fertilised lawns and parks along the river catchment, rainwater (nitric acid is produced in rainwater from pollution or electrical storms), and industry.

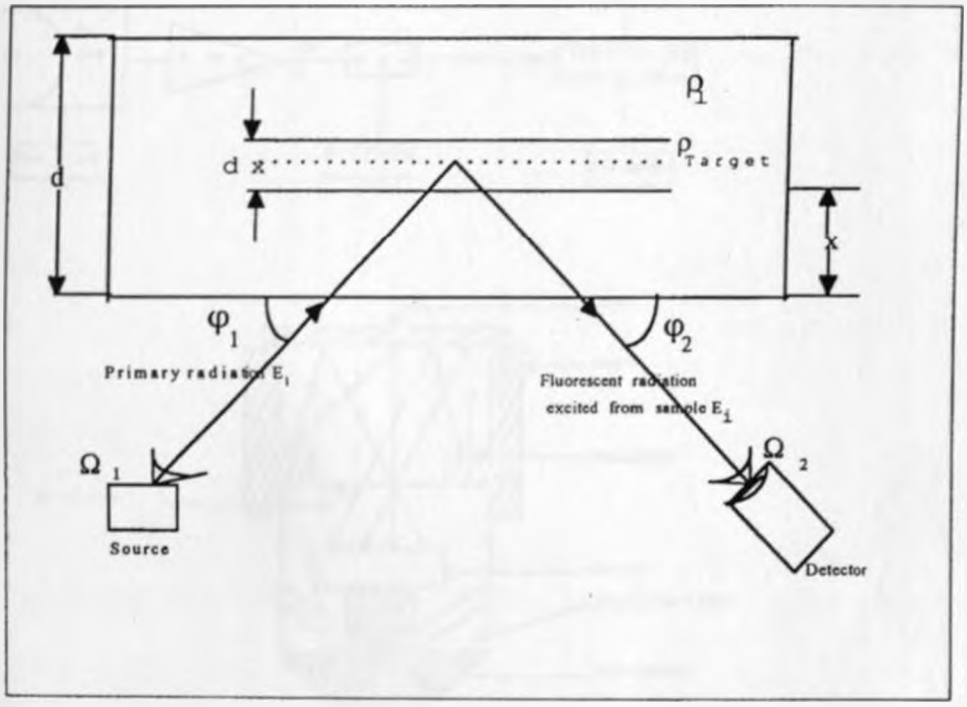
❑ Physical Measurements

▪ Iron and Zinc Ion Concentration

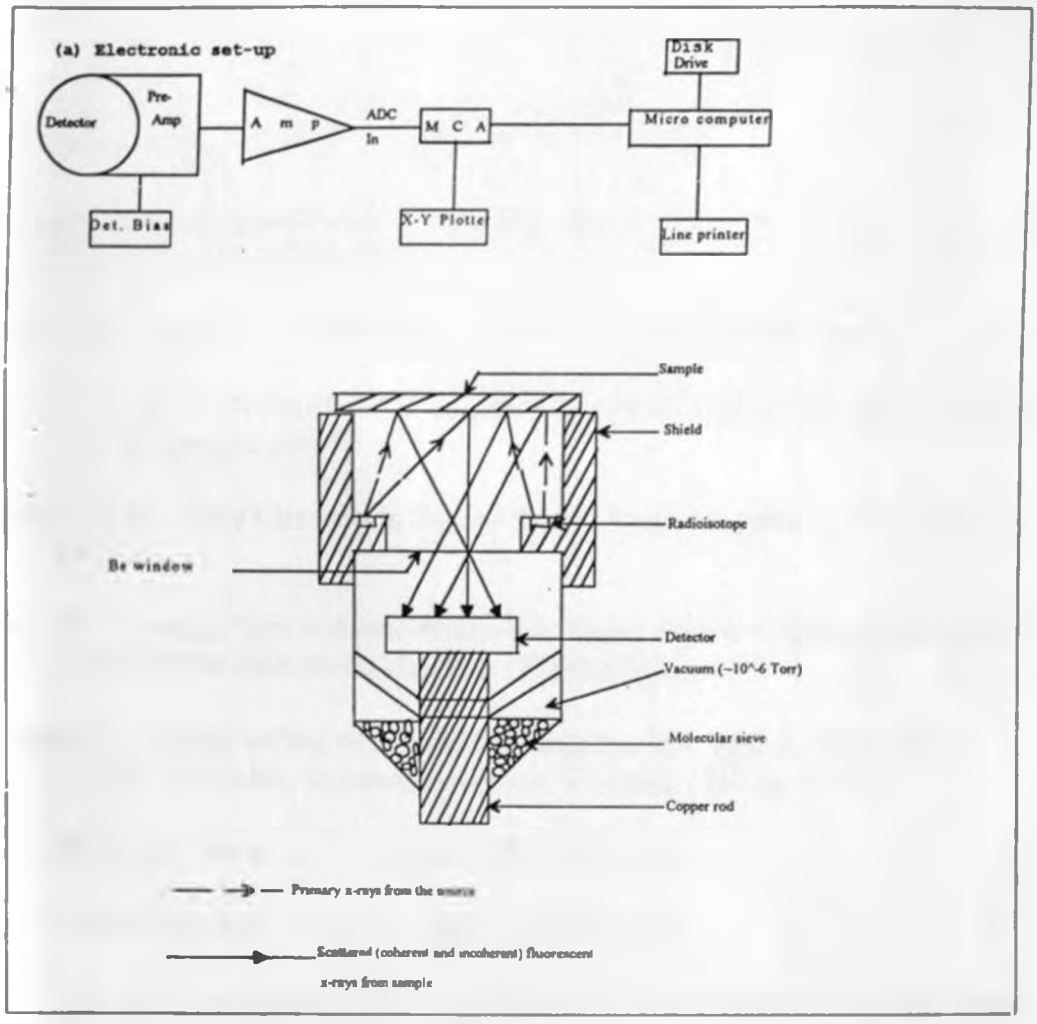
Ionised iron in water is not considered to be a health hazard to humans. In fact, drinking iron rich waters might provide only 15% of the recommended allowance for iron. In higher concentrations, iron has been shown to be toxic to some aquatic organisms and also, indicates the presence of other, more toxic metal ions such as Cd^{+2}, Pb^{+2}, and Cu^{+2}. industrial discharge, and the weathering, rusting, and erosion of metal containing products (steel parts, synthetics, and grease and oil from the machinery and cars) are some of the point and non-point sources for iron ion. Zinc is more toxic than iron. It is also an indicator ion, usually associated with toxic heavy metal such as lead, cadmium and other ions.

APPENDICES

Appendix 1: Schematic representation of the XRF experiment



Appendix 2: Schematic representation of source-detector assembly geometry



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