HEAVY METAL POLLUTION IN AND AROUND NAIROBI RIVER, AT NGARA AND GIKOMBA, DUE TO INFLUX OF METAL WASTES FROM COTTAGE INDUSTRIES IN THE MUNICIPALITY

BY

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ABSTRACT

Heavy metal pollution of a stretch of Nairobi river in the Ngara-Gikomba areas and their environs due to influx of wastes from cottage industries was studied. Surface (0-15 cm) soil samples were obtained from cottage industry locations between 0 and 1 000 m away from the centres of the installations. Plants were sampled at 5-320 m away, whereas sediment and water samples were drawn from the Nairobi river between Chiromo and the downstream end of Gikomba. Chromium, Pb, Cd, Cu and Zn were determined by Atomic Absorption Spectrophotometry following aqua regia digestion of soils and sediments and HNO_3-$HClO_4$ digestion of plant and water samples. Exchangeable heavy metals were extracted using 0.05M EDTA. Linear regression analyses of total and EDTA-extractable heavy metals on soils and sediments, pH, percent OC or percent clay were performed. Heavy metal contents of *Amaranthus* plants were regressed on soils' total and EDTA-extractable metals to establish the relationships. A remediation study was undertaken using EDTA solutions.

The results revealed that the cottage industries caused significantly (P = 0.05) higher levels of heavy metals in soils receiving wastes than in control soils. The heavy metal accumulations depended on the type, intensity and duration of activity of industry and distance from activity centre. There were significant (P = 0.05) correlations between EDTA-extractable Pb, Cu and Zn and percent OC and percent Clay of the soils.

Most metals in *Amaranthus* were significantly (P = 0.05) correlated with total soil metal levels, but very few with EDTA-extractable metals. There was increase in plant metal contents with increase of metal levels in soils.

Significantly (P = 0.05) higher metal levels of ~~in~~ sediments and waters from Nairobi river were contributed by the wastes from cottage industries.

The remediation study showed EDTA to extract substantial amounts of heavy metals from polluted soils, with maximum recovery of the metals accomplished using 0.1M or 0.25M EDTA.

DECLARATION

I, ODERO DISHON RAGA, do hereby declare to the Senate of the Sokoine University of Agriculture, Morogoro that this thesis is a result of my own original work and has not been submitted for a degree in any other University.

Signature:....................

Date:..7/12/1998........

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To my beloved parents, Festus Raga Ogwang' and Lorna Ayugi Raga, and brothers, George, the late James, Paul and Washingtone Omondi.

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LISTS OF ABREVIATIONS AND SYMBOLS

CL = clay loam

CWP = car washing and painting

DTPA = diethylenetriaminepentaacetic acid

EDTA = ethylenediaminetetraacetic acid

FAO = Food and Agriculture Organization

FE-AAS = Flame Emission Atomic Absorption Spectrophotometer

IDCRCL = Inter-Developmental Committee on Redevelopment of Contaminated Lands

IRPTC = International Register for Potentially Toxic Chemicals

kg = kilogram

l = litre

LKRG = Lower Kirinyaga Road Garage

m = metre

M = Molarity

MKRG = Middle Kirinyaga Road Garage

ml = millilitre

MW = Metal Welding

ns = not significant

NTA = nitrolotriacetic acid

OC = Organic Carbon

ppb = parts per billion

ppm = parts per million

PSES = Pergamon Series on Environmental Studies

SC = Sandy Clay

SCL = Sandy Clay Loam

SD = Standard Deviation

SL = Sandy Loam

UK = United Kingdom

USA = United States of America

USDA = United States Department of Agriculture

UKRG = Upper Kirinyaga Road Garage

UNEP = United Nations Environmental Programme

W = Welding

WHO = World Health Organization

µg = micro-gram

υ = Frequency

CHAPTER ONE

1.0 INTRODUCTION

Pollution of soil and aquatic ecosystems, over and above background levels, by such heavy metals as cadmium (Cd), copper (Cu), lead (Pb), zinc (Zn) and chromium (Cr) is a worldwide problem. At high concentrations in the environment, these toxic heavy metals may enter food chains and result in health hazards. Adverse effects due to consumption of contaminated foods have received much attention (Singh, 1991; 1994; Singh and Steinnes, 1994). But most of the information pertains to the industrialized world where pollution problems are serious, long-term and widespread. In developing countries, pollution problems occur largely in localised sites (Assey, 1995). The extent of pollution in these sites is probably as intense as in the developed world. As use of products containing these heavy metals which contribute to environmental hazards is on the increase in developing countries, there is an urgent need to monitor their accumulation.

Generally, these metals have a wide range of conventional industrial uses from which they find their way into soils and waters as industrial, domestic and other wastes. Use of these metals ranges from electroplating, textile, printing, chemical industries, electrical appliances and electronics, plastics, chemicals, paints, welding, soldering and battery industries (Nriagu, 1992). The metals used include Zn, Sn, Fe, Cd, Pb, Cu, Hg and Cr, among others. These same metals find use in non conventional industries, also called cottage industries, as can be found at the Ngara and Gikomba sites in Nairobi. When wastes from these industries are disposed of in rivers, such as the Nairobi river, pollution of the environment results in.

The Nairobi river flows through residential areas, slums and the cottage (jua kali) industry sites at Ngara and Gikomba in Nairobi, thus receiving large amounts of wastes from the cottage industries and the municipality. Some of the cottage industries which are disposing of their wastes into the river, as it flows through the Ngara and Gikomba sites, include fur finishing, car washing and painting, small scale chemical industries, laundry, pickling, dipping of metals, welding, soldering, dyeing, carpentry and joinery, and battery repair and recharging. These industries use chemicals and materials which contain heavy metals. Apart from these small scale industries, there are two large markets, Ngara and Gikomba, which are sources of food. Wastes from the two markets are channeled to the river. As a result of all these, the river water is likely to be a potential health hazard to the living organisms due to pollution, including that caused by the heavy metals.

Normally, the background levels of heavy metals in soils and waters in the absence of anthropogenic additions and enriched rocks are relatively low, and do not cause pollution problems (Nriagu, 1990). However, pollution arises when soils and waters receive high levels from anthropogenic additions and enriched natural sources. The main sources of heavy metal pollution are domestic sewage, industrial wastes, oil spills, combustion emissions, mining operations, metallurgical activities and garbage dumps (Bryan, 1976; Forstner and Wittman, 1979).

The major consequence of environmental contamination by these heavy metals is their toxicity to man, plants and animals. Cadmium poisoning, for instance, has been reported to have caused the *Itai-itai* disease in Northern

Japan (Kitagashi and Yamane, 1981). Clinical signs were characterised by osteomalasia, nephropathy, tiredness, loss of appetite, headache and hypertension in man, rabbits and dogs (Schroeder *et al.*, 1965; Perry and Elanger, 1974). Lead poisoning has also been reported to result in neurological defects, anaemia and damage to the central nervous system, especially in children (Cantorow and Trumper, 1944). In plants, Pb toxicity causes stunted growth (Assey, 1995), which may decrease crop yields in addition to accumulating in edible parts. Chromium and Cu are also toxic at high concentrations. For example, the hexavalent form of Cr causes toxicity through skin alceration, nasal perforation and lung cancer (Kagi and Nordberg, 1979). Copper, on the other hand, is known to result in a marked depression in feed intake and growth, especially in birds, and anaemia in mammals including man (Underwood, 1971; Kagi and Nodberg, 1978).

Todate, however, there is scanty information on environmental dynamics and public health implications of heavy metals within these areas of Nairobi city. So far, exhaustive investigations on the toxicity of such metals as Cd, Pb, Cu, Cr and Zn has been done in developed countries, but very little in developing countries such as Kenya. Furthermore, the contribution of cottage industries to heavy metal pollution is not well established in Kenya, yet they discharge toxic metals such as Cd, Pb, Cu, Zn and Cr which, as a consequence of polluting the environment, may affect the health of the operators and nearby residents (Nriagu, 1992).

The Nairobi river is agriculturally important as a source of water for irrigation of vegetable crops in the adjacent lands. The river receives the wastes from the industries and the municipality. Upon irrigation of crops, the heavy metals contained in the incoming wastes may contaminate the irrigated crops. This scenario needs to be evaluated. Information on the extent of heavy metal pollution in Kenya due to cottage industry activities has never been highlighted. With the expansion of the country's industrial (including cottage industry) sector, use of these heavy metals will also increase accordingly, thereby intensifying the pollution. This calls for attention and remedial measures in order to alleviate environmental hazards from these toxic metals.

The study reported herein was, therefore, aimed at assessing the degree of pollution of the Nairobi river and its environs by heavy metals from cottage industrial and municipal wastes.

The specific objectives were:

1. To document on the history and relative capacity of different cottage industries operating in the Ngara-Gikomba area for a period of 30 days

2. To determine the concentrations of heavy metals in water and sediment within the area influenced by the cottage industrial/market sites for 30 days

3. To determine the concentrations of the metals in soils within and around cottage industrial areas for 35 days

4. To evaluate the concentrations of metals in some plants growing within the sites for 25 days

5. To evaluate possible ways of remediation of polluted soils using a chelating agent for a period of 25 days.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Global concern of heavy metals

In recent years, there has been a growing awareness of the problem of pollution of the environment by heavy metals. The levels of heavy metals in the general environment are on the increase and, consequently, this has resulted in much global concern (Nriagu, 1992). The concern for these metals is based on their toxicity when levels in the environment are higher than established tolerable levels (Nriagu, 1992).

Such metals as mercury, cadmium and lead are biologically non essential elements, whose toxicity is of environmental concern. Hay (1984), for instance, reported that approximately 200 000 tons of lead were deposited on the earth's surface annually, as a result of use of tetra-ethyl lead in fuels. This has resulted in pathological effects in man (Kitamura, 1976). Cadmium poisoning has also increased as the world consumption of the metal increased (Hay, 1984).

Oehme (1978) reported that exposure to lead has occurred in circumscribed areas of the world for 3 000 years or more and was high among the Roman upper class population. Sporadic episodes of lead poisoning occurred in persons drinking water from lead pipes in soft water areas. When alkyl lead was added to gasoline as antiknock agent, further exposure to lead toxicity occurred (Oehme, 1978).

Cadmium was an industrial curiosity in the year 1900, but its use has sharply increased with resultant contamination of air, water and food (Hay, 1984). World production of refined Cd began in 1969, reaching to a peak of 17 000 tons. Since then, world production figures have fluctuated between 15 000 and 18 000 tons per year (Metallgesellschaft, 1978). Atmospheric emissions of Cd from man-made sources, estimated at 7 000 tons per year, exceeded those of natural sources by an order of magnitude (UNEP, 1986). The marked increase of Cd use during the last three decades has caused a corresponding increase in environmental contamination and toxicity problems (UNEP, 1986).

In 1971, world production of Cu stood at 3.1×10^8 tons (PSES, 1982). Excessive levels have also been observed due to its use in alloys of brass, in chemical catalysts, algicides, antifouling paints, insecticides and fungicides (Oehme, 1978). Hexavalent Cr is used in electroplating, tanning, paint and wood preservatives (PSES, 1982; Oehme, 1978). Thus, wastes from these activities contribute much to the environmental burden of Cr. Nriagu and Pacyna (1988), for instance, estimated the worldwide fallout of Cr from the atmosphere to soil to be between 5.1 x 10^3 kg/year. The majority of the total inputs come from disposal of wastes of various types on land. Kabata-Pendias and Pendias (1986) showed a steady global increase of Zn in the air in different locations. They recorded values ranging from 0.002-0.05, 10, 15, 14-6 800 and 55-1 600 ng/m^3 for the South pole, Norway, Shetland Islands, Japan and Germany, respectively. These high values were attributed to Zn mineral smelting, thereby releasing exhaust fumes. Natural sources such as volcanic eruptions and aeolian dusts were also reported to contribute significantly to environmental Zn pollution (Alloway, 1990).

2.2 Heavy metals in soils

Within the soil profile Cd, Zn, Pb and Cu were found to be in high concentration in the surface horizons as a result of recycling through vegetation, atmospheric deposition and adsorption by the soil organic matter (Alloway, 1990). The elements found concentrated in the lower horizons of the soil profile were mainly Al, Fe, Mg and Ni, which tended to be associated with accumulations of translocated clays and hydrous oxides (Bowen, 1979). However, recently polluted soils often had higher concentrations of pollutant metals in the top soils because the pedogenic processes had not been operating long enough to effect a redistribution within the profile.

In general, the total metal content in soil is the result of inputs of a metal from several sources such as parent materials, atmospheric deposition, fertilizers, agro-chemicals, organic wastes and other organic pollutants, minus losses in minerals removed by crop materials, leaching and volatilisation. Bowen (1979) and Webber (1984) reported the ranges of metal concentrations encountered in agricultural soils in various parts of the world. The natural concentration of metals in the normal soils was usually lower than the concentration in the earth's crust. For instance, the average concentration of Cd in the earth's crust was reported to be 0.2 ppm (mg/kg) (Bennett, 1981). The natural soil Cd concentration normally ranged from 0.01-0.7 ppm (Bennett, 1981). Average values of 0.2 to 0.4 ppm in uncontaminated soils have been found, with 0.9 ppm in the organic fraction (Bennett, 1981). Bennett (1981) further reported that the average concentration of 91 soil samples from farming areas in the USA was 0.57 ppm. However, Cd concentrations in contaminated soil may reach 800 ppm (Bennett, 1981). According to Kabata-Pendias and Pendias (1986), the average content of Cd ranged from 0.07 to 1.1 ppm and higher values usually reflected the anthropogenic impact on the Cd status in the top soils.

Piotrowski and Coleman (1980) recorded the range of Pb in uncontaminated soils to be 20 to 200 mg Pb/kg. In agricultural soils, the levels of Pb are typically in the range of 20 to 30 mg Pb/kg (Bennett, 1981). The distribution of Pb in uncontaminated surface soil was in the range of 48 to 160 mg Pb/kg in England, 20 to 80 mg Pb/kg in Scotland, 60 to 155 mg Pb/kg in the USA, 21 to 108 mg Pb/kg in Canada and 20 to 114 mg Pb/kg in some tropical soils from Cameroon. The Pb content in some agricultural soils in England and Wales was found to vary quite widely, the mean being 57 mg Pb/kg (Khan, 1980). The common Pb concentration range in argillaceous soils was from 0.1 to 10 mg/kg (Kabata-Pendias and Pendias, 1986). High Pb levels were reported in Denmark, Japan, Great Britain and Ireland, at above 100 mg/kg (Kabata-Pendias and Pendias, 1986).

Soil Cu has been discussed by several authors. Aubert and Pinta (1977), for instance, has given the Cu abundance in parent rocks and soils. They reported that the C horizon of soils derived from garnet and granulite contained up to 100 mg Cu/kg. Kabata-Pendias and Pendias (1986) reported the range of Cu in soils to be 2 to 100 mg/kg, with an average of 20 mg/kg. Davies (1980) reported an average value of 20 mg Cu/kg for soils.

A survey by McGrath (1987) of 6 000 soils in England and Wales resulted in the geometric mean concentrations Cr being 34 mg/kg. Williams (1988) gave the upper limits of Cr concentrations in soils receiving sewage sludge as 150-250 mg/kg. In the UK, trigger values for the concentrations of metals in soils have been adopted (Inter Departmental Committee on the Redevelopment of Contaminated Lands, 1987). These are threshold values that are used when an area is scheduled for redevelopment. If the concentration of the metals in soils was less than trigger value, the land was regarded as uncontaminated. The threshold trigger value varied according to the proposed use of the land. For Cr, 70 mg

Cr/kg soil was the trigger value wherever crops were to be grown, and 600 mg Cr/kg soil for domestic gardens and allotments, increasing to 1 000 mg Cr/kg for less intensive uses such as parks, playfields and open spaces (IDCRCL, 1987). Recognising that Cr IV was more toxic, threshold value for this was set lower, at 25 mg Cr/kg soil for all end uses (IDCRCL, 1987).

The common Zn range for soils was 10 to 300 mg/kg, with an average content of 50 mg/kg (Lindsay, 1972). Kabata-Pendias and Pendias (1984) reported values of 17 to 125 mg Zn/kg as background content of a large number of surface soils of different countries. The highest values were found in some alluvial soils, solonchaks, while the lowest values were for light mineral and light organic soils. In Zn contaminated soils concentrations of 1 000 to 10 000 mg Zn/kg soil have been found (Alloway, 1990).

The significance of contamination of soils by heavy metals is that from soils the metals may be dispersed to other environmental segments such as plants and water.

2.3 Heavy metal levels in waters

The natural concentrations of heavy metals are extremely low in the hydrosphere, and insoluble species are considered to be the controlling mechanism (Burrell, 1974). The heavy metals in true solution are highly reactive, hence their "trace level" concentrations may be removed by a variety of physico-chemical and biochemical processes such as biotic and inorganic particulate phases (Burrell, 1974). It has been established that most of the heavy metal complexes existed as oxides, hydroxides or carbonate solid phases which were of major importance in maintaining their levels in water as aquo ions (Stumm and Morgan, 1970).

The natural pathways of recycling heavy metals are largely controlled by two major processes: incorporation on or into various solid phases, and chemical complexation in solution. These mechanisms act to restrict and promote stabilization of the metals, respectively. However, immobilisation onto various solid sinks predominated and trace metals in all natural waters tended to be less than might be calculated based on known geochemical parameters. A considerable fraction of the soluble or colloidal heavy metal content of fresh water bodies was in the form of organic complexes (Burrell, 1974).

In industrialised regions of the world, where heavy metal pollution of waters has been a major concern, legislative controls have been set with respect to water resources pollution (Burrell, 1974). The most stringent requirements are concerned with drinking water quality.

Levels of Pb in normal surface waters and potable waters, for instance, were usually below 10 µg/litre (Piotrowski and Coleman, 1980). In cases where lead pipes were still in use, Pb levels in ground waters were in the range of 1 to 500 ppb, while in hot springs, they sometimes exceeded 1 ppm (Piotrowski and Coleman, 1980). Lead concentrations in deep ocean waters were about 0.02 to 0.02 µg/ml and 0.3 µg/ml in surface waters (Bennett, 1981). Dissolved Pb in rivers in unpolluted areas was less than 0.1 µg/ml, while in rain water, concentration was normally in 10 to 30 ppb. However, Pb levels were 0.1 to 0.5 µg/ml in rain waters collected from areas of heavy traffic (Bennett, 1981). The World Health Organization recommended limits for Pb in municipal water supplies to be 0.1 mg/litre (ppb) (WHO, 1971; Hay, 1984).

In uncontaminated fresh waters, Cd levels were well below 0.001 µg/ml (Piotrowski and Coleman, 1981). Ocean water normally contained Cd levels of 0.1 µg/ml (Piotrowski and Coleman, 1984). Dissolved Cd levels in contaminated waters are mainly dependent on pH. Thus, high concentrations of Cd have been found on suspended particulate matter to levels as high as 700 µg/ml, especially at neutral and alkaline water (Piotrowski and Coleman, 1980). The permissible level of Cd in drinking water has been recommended by WHO to be 0.01 mg/litre (WHO, 1971). According to Alala (1981), the range of Cd concentrations in water samples from seven Kenyan Lakes was 0.002 to 0.116 µg/litre. This range conformed with the values of 0.075-0.088 µg Cd/litre obtained from Malewa river in Kenya (Muigai, 1992).

2.4 Heavy metal toxicity to humans and animals

One significance of environmental pollution by heavy metals is their toxicity to humans and animals via food chains. Both essential and non essential elements may exhibit toxic effects whenever their doses exceed a certain critical level (Muigai, 1992). Toxicity effects are now reviewed briefly as follows:

a) Copper

Chronic Cu poisoning may occur in animals through contamination of feeds from industrial sources of pollution (Underwood, 1971). Copper toxicosis has been observed in sheep, pigs and cattle fed on unbalanced basal diet (Walbott, 1978). In all animals, excessive consumption of Cu results in the accumulation of Cu in the tissues, especially in the liver and the blood. The capacity for hepatic Cu storage and the liver Cu levels that can be tolerated without signs of Cu toxicosis vary greatly among species. In sheep and cattle, hypercupremia resulted in haemolysis and juandice, whereas adult birds exposed to excessive Cu intake exhibited a marked loss of body weight and anaemia (Schroeder, 1976). In pigs, dietary Cu levels of 425, 450, 600 or 750 ppm caused a severe toxicosis, manifested by a marked depression in feed intake and growth rate, hypochronic microcytic anaemia and juandice, marked increase in serum and liver Cu levels, and in serum asphartate aminotransferase (AAT) activities, leading to general tissue damage (Underwood, 1977). Schroeder (1976) reported a generalised icterus, haemoglobinuria and haemoglobinaemia in a steer fed with 5g of Cu sulphate for 122 days. Haemoglobinuria and haemoglobinaemia were associated with widespread necrosis and juandice.

Copper poisoning in man mainly occurred as an industrial hazard in workers engaged in Cu mining or processing, but was unlikely to occur from ingestion of food or water, because these other sources did not supply amounts sufficient to cause toxicosis. However, industrial exposure has been reported to result in the Wilson's disease, which is characterised by excessive concentration of Cu in the tissues, arising from metabolic defects involving absorbed Cu but not from the ingestion of excessive amounts of Cu (Underwood, 1971).

b) Chromium

Chromium, especially trivalent Cr, has a low level of toxicity. A wide margin of safety exists between ordinarily ingested amounts and those likely to cause deleterious effects (Mertz, 1986). A study using rats established the lethal dose at about 1 mg Cr/100g body weight (Mertz *et al.*, 1969). This was many times greater than the 0.05 to 0.10 µg Cr/100g required to correct impairment of glucose metabolism *in vivo* (Mertz *et al.*, 1969).

Hexavalent Cr is much more toxic than trivalent Cr. Chronic exposure to chromate dust has been correlated with increased lung cancer in man and experimental animals. Oral administration of excessive levels (e.g. 50 ppm) has also been associated with growth depression and liver and kidney damage in experimental animals (Underwood, 1977). Chromium VI is also believed to be carcinogenic in cases of intense human exposure, such as that in the occupational setting (Levis and Bianchi, 1982).

c) Zinc

Zinc is also relatively less toxic to birds and mammals, with a wide range of safety margin between normal intake and toxicity levels (Underwood, 1971). Rats, pigs, poultry, sheep and cattle exhibit considerable tolerance to high intakes of Zn, depending on the composition of the basal diet. Rats, pigs and poultry, for instance, tolerated about 2 500, 1 000 and 1 200 to 1 400 ppm of Zn, respectively (Underwood, 1971). But, when a dietary intake of 5 000 ppm was given to rats as zinc chloride or zinc carbonate, growth was severely depressed, with heavy mortality (Underwood, 1971). Other symptoms which have been observed due to Zn toxicity were severe anaemia, anorexia and malformation of foetuses of pregnant rats. For weaning pigs, depressed growth and anorexia, arthritis and internal haemorrhages were observed at a dietary feed intakes of 4 000 or 8 000 ppm Zn (Prasad, 1976). Broilers and layer hens exhibited similar clinical signs when the Zn levels was increased to 3 000 ppm (Prasad, 1976).

Lambs and cattle are, somehow, less tolerant to high Zn intakes than rats, pigs or poultry. Consumption by lambs of diets containing more than 1 500 ppm of Zn, as oxide, caused depressed feed efficiency and mineral consumption (Underwood, 1977). Steers tolerated diets with less than 500 ppm Zn, but 900 ppm caused reduced weight gains and lowered feed efficiency. Levels of 1 700 ppm induced, in addition, depressed appetite characterised by excessive salt and other mineral consumption, and wood chewing (Underwood, 1977).

d) Cadmium

Biological interest in Cd is in its toxic properties, its possible relation to human hypertension, and its interaction with Zn and other essential metals. In human and animal nutrition, Cd is accumulative poison (Underwood, 1971). Some of the prominent effects associated with Cd toxicity included pulmonary and testicular lesions, renal dysfunction, poor bone mineralization, anaemia, liver and kidney damage, retarded growth, disturbed carbohydrate metabolism and inhibition of drug metabolising enzymes (Piotrowski and Coleman, 1980). Schroeder *et al.* (1965) showed that human hypertension patients had as much as 50 µg Cd/litre in the urine and a high Cd:Zn ratio in body tissues. This was reversed by injection of disodium zinc trans-cyclohexane-1,2-diaminetetraacetic acid (Na_2Zn-CDTA), which depleted renal and hepatic Cd, thus lowering the Cd:Zn ratio in tissues (Schroeder *et al.*, 1965). Rabbits fed on Cd developed hyperplastic bone marrow and hypochromic microcytic anaemia, whereas poultry developed a severe anaemia associated with markedly increased concentrations of plasma transferrin and elevated transferrin:albumin ratio (Nearthy and Miller, 1975).

High Cd levels in chicks' diet was reported to reduce live weight gains, increased mortality, reduction of red cell counts, haemoglobin levels and cytochrome oxidase activity in the heart (Nearthy and Miller, 1975). The syndrome was ameliorated by inclusion of Zn in the diet, since Zn reduced the toxicity effects of Cd by competing with Cd for the protein binding sites, thus increasing the excretion of Cd from the organism by kidneys, intestines or biliary tracts (Underwood, 1977). In the reproduction system, Cd was reported to cause sterility by inducing haemorrhagic necrosis in the experimental rats' testes and epididymis due to interference by Cd with testicular blood supply and the destruction of the seminiferous tubules (Underwood, 1971). This was prevented by administration of selenium as sodium selenate or selenite, which acted as protective agent against Cd toxicity (Underwood, 1971). In man acute Cd poisoning, at 10 mg administration, was reported by Hay (1984) to cause nausea, salivation, vomiting, diarrhoea and abdominal pain. Chronic Cd poisoning due to long term low dosage has also been observed in Cd industry workers. The most serious case of health hazards due to chronic Cd was observed in Japan, after world war II. Exposure to Cd occurred through ingestion of rice grown in the fields irrigated by polluted industrial waste water (UNEP, 1980;

Hay, 1984). The disease, then called *itai-itai kyo*, occurred most commonly among post menopausal women above 45 years of age. The affected subjects developed a syndrome that began with renal dysfunction and eventually resulted in painful bone changes (Friberg *et al*., 1974).

Normally, Cd ions absorbed from the intestine became bound to metallothionein or other transport proteins (Nearthy and Miller, 1975). Chicks, sheep, cattle, pigs, horses and man have all been shown to produce metallothionein in response to excessive intakes of Cd (Nearthy and Miller, 1975). The body burden of Cd in humans was shown to range from 10 to 60 mg Cd, with 0.5 to 2.0 µg/ml in urine (Piotrowski and Coleman, 1980). Nutritional deficiencies of elements like Zn, Fe and Ca predisposed individuals to adverse effects of dietary Cd levels of 250 to 350 µg/day, estimated to give renal Cd levels of 200 µg/g, the critical Cd concentration that caused kidney damage (Piotrowski and Coleman, 1980).

e) Lead

Food was the main source of Pb intake for humans living in rural areas unless specific exposures existed (Wanjie, 1992). Dietary intakes ranged from 100 to 500 µg/day (WHO, 1977). Processed and canned foods can contribute significantly to the intake, since food products such as processed milk and fruit juices in soldered cans have been shown to contain high Pb levels (WHO, 1977, 1979; IRRTC/UNEP, 1978). The distribution of Pb in the body has been reported by Lucas (1975) to range between 7.0 and 11.0 ppm in the bone, 2.0 ppm in the liver, 1.0 in the kidney, with the brain, heart and muscle tissue having 0.01 ppm. Underwood (1977) reported that the soft tissue of the adult human body contained Pb concentrations ranging from 1.3 to 1.7 ppm in fresh liver. Skeletal tissue is the long term storage site for Pb and contains most of the body burden of the metal (Wanjie, 1992). Lead deposited in bone replaced calcium, and more than 95% of the body burden was stored in bones as tripolyphosphates. Lead in the blood is biologically active and may result in health effects (UNEP, 1986). Blood Pb levels of less than 80 µg/100 ml usually indicates very low Pb exposure. Levels between 80 and 100 µg/100 ml indicate moderate Pb exposure, and levels greater than 100 µg/100 ml indicate more chronic Pb exposure (UNEP, 1986).

Experiments on animals have shown that even minute quantities of Pb interfered with respiratory pigments, energy production and membrane function. Other manifestations of Pb exposure occurred in adults occupationally exposed to high levels of Pb, thereby resulting in abdominal colic, anaemia, renal damage, nephroparthy and, occasionally, encephalopathy. Lucas (1975) further reported that Pb poisoning affected the formation of blood by retarding normal maturation of red blood cells in the bone marrow and also by inhibiting the synthesis of haemoglobin. Thus, Pb poisoning effects mainly involve blood forming mechanism, gastro-intestinal tract and, in advanced stage, the nervous system. After prolonged excessive Pb absorption, paralysis of eye muscles and the extensor muscles occurred (UNEP, 1984). Walbott (1978) reported that, the minimum lethal dose of inorganic Pb for man was between 300 and 700 mg/kg, resulting in blood levels of 0.8 mg/litre. Because of the effects discussed above, there is need to institute measures to reduce or prevent heavy metal pollution of the environment.

2.5 Industrial and municipal wastes as sources of heavy metals in soils and waters

Toxic heavy metals may be introduced into soils through disposal of industrial wastes from conventional and cottage industries (Mmbaga, 1997). Cottage industries, in this sense, include such small scale activities as soldering, welding, rubber burning, repair of lead battery accumulators, car washing and painting, metal smiths, pottery, etc. The types and concentrations of metals in the wastes depend on the nature of the industrial waste (Greenland and Hayes, 1981). Metals are normally used for making various industrial products from which the wastes find their way into soils and waters. Cadmium, for instance, is used in electroplating, where it is deposited either electrolytically or mechanically on objects to provide bright appearance and resistance to corrosion. Other uses of Cd include making of pigments from Cd sulphides, which gives yellow to orange colours. These pigments are used in the plastic industry, ceramics, paints and coatings, high quality industrial finishes, and in glass and enamel. Cadmium can also be used for making Cd phosphors as tubes in television sets, fluorescent lamps, X-ray screens and in making electrical and electronic appliances such as heavy duty relays, switches, automobile distributor contacts, and solar and photo cells (Oehme, 1978).

The earliest use of Cr was in the making of paint pigments in Germany, France and England. Recently, metallurgical grade chromite has been used in the production of ferroalloys. Presence of Cr in iron casting improves its resistance to corrosion and oxidation, and also increases the ability to withstand stress at elevated temperatures. The ferrochrome alloys are widely employed in the production of stainless steel and heat resisting steels which are used in corrosive environments, in petrochemical processing, turbine and furnace parts, cutlery and decorative trim, mechanical tools and jet engines. Chromite is also employed in the manufacture of refractory bricks, mortars, ramming gun mixes and high temperature furnace repair materials. Another important use of Cr is the making of chemicals. Most Cr chemicals are manufactured from pure sodium dichromate, obtained from chemical grade chromate. Chromium compounds are used as pigments, mordants and dyes, in textile industry, tanning agents in leather industry, and for chrome electroplating, anodising and dipping (Oehme, 1978). All these results in wastes which may contaminate the environment if improperly disposed of.

The largest user of Cu is the electrical industry. Usage under this category includes power transmission cables, electronics and electrical equipment. Copper is also used in construction and plumbing. Thus, Cu is incorporated into roofing and plumbing products, whereas alloys are used in bearings, fastenings and fittings in marine hardware.

Lead is one of the oldest metals known to man and, since medieval times, has been used in piping, building materials, solders, paints, type metal, ammunition and castings (Nriagu *et al.*, 1988). In more recent times, Pb has been used mainly in storage batteries, metal products, chemicals and pigments (Nriagu *et al.*, 1988). Because of its unique sound control characteristics, consumption of Pb has also increased in the manufacture of sound attenuation materials, both as sheets and composition paneling. Lead-casted steel sheeting (terne steel), which combines anti-corrosion and sound barrier properties with the strength of steel, has found several applications in building. Lead asbestos and anti-vibration pads are employed in foundation for buildings

(Nriagu *et al.*, 1988). It is also used in the mounting of various equipment, including air-conditioning systems, industrial equipment and commercial laundry machines (Oehme, 1978). Additional applications include cable sheathing, collapsible tubes, caulking materials and corrosive liquid containers. Tetramethyl lead constitute an antiknock agent in gasoline. Lead stearate is used in the production of synthetic polymers (Oehme, 1978).

A large proportion of the world production of Zn finds its way into industry in the metallic form, as in various types of brass, roland Zn sheets, decasting alloys and as a protective coating on iron and steel. Important quantities of the metal are also used in the production of white pigments such as zinc oxide and lithophone (Phillips, 1976; Oehme, 1978).

In general, the wastes produced from the various industries using these metals as raw materials contribute high amounts of the heavy metals into the environment. Secondary uses of the final products from the manufacturing industry, as in the case of cottage industries, also produces wastes containing high levels of these metals into the environment (Nriagu, 1992).

Municipal wastes integrate all sorts of wastes and discarded consumer items which contains varying levels of heavy metals. This can be a major source of metal pollution depending on the concentrations of the metal in the wastes (Greenland and Hayes, 1981). The careless or unauthorised dumping or disposal of metal containing items, ranging from miniature dry-cell batteries (Cd) to abandoned cars and car components (e.g. lead-acid batteries) can give rise to isolated areas of very high concentrations of metals in the soil (Alloway, 1990). The disposal of some domestic wastes by burning on garden bonfires or burial in the garden can also result in localised, but anomalously high concentrations of metals such as Pb in soils used for growing vegetables (Alloway, 1990). All these may pose serious human health hazards.

2.6 Adsorption of heavy metals by soils and sediments

The most important chemical processes affecting the bioavailability of heavy metals in soils and sediments are those concerned with the adsorption of the metals from the liquid phase onto the solid phase. These processes control the concentrations of metal ions and complexes in the soil solution and, thus exert a major influence on their uptake by plants' roots (Alloway, 1990). Several different mechanisms can be involved in the adsorption of metals, including cation exchange (or non-specific adsorption), specific adsorption, organic complexation and co-precipitation.

Cation exchange is the process whereby metal cations are attracted by and are adsorbed to the negative charge of soil colloids. Thus, electroneutrality is maintained where the negative charges are balanced by equal quantity of the oppositely charged counter-ions (Alloway, 1990). Alloway (1990), however, described ion exchange as the exchange between the counter ions balancing the surface charge on the colloids and the ions in the soil solution. During cation exchange, there was a high sensitivity at the exchange site, giving rise to a replacing order amongst the cations as determined by the valency and degree of hydration (Alloway, 1990). The higher the valency of an ion, the greater its replacing power and the greater the degree of hydration, and the vice versa (Alloway, 1990).

Specific adsorption involves the exchange of heavy metal cations and most anions with surface ligands to form partly covalent bonds with lattice ions (Greenland and Hayes, 1981). It results in metal ions being adsorbed to a far greater extent than would be expected from the cation exchange capacity of a soil. Brummer (1986), for instance, showed that the sorptive capacities of amorphous Fe and Al oxides for Zn were 7 and 26 time, respectively, greater than their cation exchange capacities at pH 7.6. Specific adsorption is strongly pH dependent and is related to the hydrolysis of the heavy metal ions (Brummer, 1986). The metals likely to form hydroxy complexes are specifically adsorbed to the greatest extent (Alloway, 1990). Specific adsorption increased with decreasing pK (equilibrium constant) values, but in case of Cu and Pb, which have the same pk value, Pb which has the greater ionic size was more strongly adsorbed (Alloway, 1990). Brummer (1986) gave the order for increasing specific adsorption as Cd (pK = 10.1)< Zn (pK = 9.0)<< Cu (pK = 7.7) < Pb (pK = 7.7). Hydrous oxides of Fe, Al and Mn were the main constituents involved in specific adsorption reactions (Alloway, 1990).

Co-precipitation is defined as the simultaneous precipitation of a chemical agent in conjunction with other elements by any mechanism and at any rate (Sposito, 1984).

Organic complexation involves solid-phase humic substances adsorbing metals by forming chelate complexes and low molecular weight organic ligands. Humic compounds with soluble reactive groups, such as hydroxyl, phenoxyl and carboxyl, form co-ordination complexes with metallic ions. Carboxyl groups play a predominant role in metal binding in both humic and fulvic acids. The maximum amount of any given metal that can be bound was found to be approximately equal to the number of carboxyl groups (Chen *et al.*, 1986).

It has, however, been found that at trace levels, where precipitation was not a factor, exchange adsorption and specific adsorption by the solid components of the soil were dominant (Chen *et al.*, 1986). The solid component of the soil responsible for adsorbing these metals are clay minerals, organic matter and oxides and hydroxides of Fe and Mn (Greenland and Hayes, 1981). In general, adsorption of metals in soils by organic and inorganic colloids depended on pH (Huang *et al.*, 1977). As the pH increased above 5.5, adsorption of metals like Cd and Pb increased and, with many of the metals, the reaction became partly irreversible (Greenland and Hayes, 1981). Adsorption of heavy metals including Cd^{2+}, Pb^{2+}, Cu^{2+}, Zn^{2+} and Cr^{3+}, conformed to the Langmuir or Freundlich isotherms over a wide range of concentrations (Soldatini *et al.*, 1976). The stability of the complexes formed as a result of adsorption tended to increase as pH increased, and depended on the type of the metal. The stability of the complexes has been reported to increase in the order of $Cu^{2+} > Pb^{2+} > Cr^{3+} > > Cd^{2+}$ (Greenland and Hayes, 1981). This stability is important in determining the amount of metal fixed by the colloidal surface.

2.7 Absorption of heavy metals by plants

Plant uptake of metals is generally influenced by soil characteristics. These include total quantity and total speciation of the metal present in the soil, soil pH, cation exchange capacity, clay mineralogy and organic matter content of the soil, as well as plant physiological factors (Xhung fung and Ghalamhoss, 1989). Many workers have reported that the absorption and the concentration of heavy metals in plants increase with increasing pH, organic carbon, cation exchange capacity and clay content of a soil. Dowdy and Larson (1975), for example, observed that when pH was increased from 5.3 to 6.5, the concentrations of Cd, Pb and Hg in some vegetable leaves increased by 7.3, 1.2 and 0.1 µg/g of dry matter, respectively.

Absorption mechanisms can vary for different metal ions, but ions which are absorbed into the root by the same mechanisms are likely to compete with each other (Alloway, 1990). For example, Zn absorption was inhibited by Cu and H^+, whereas Cu absorption was inhibited by Zn, NH_4^+ and Ca^{2+} (Kabata-Pendias and Pendias, 1986).

Since plants are the primary source of nutrient supply to man and other animals, absorption of heavy metals by plants is an important aspect in determining the amounts of metals circulating in food chains.

2.8 Remediation of soils polluted by heavy metals

Remediation involves the processes aimed at removing heavy metals from polluted soils. Removal of heavy metals from soil depend on clay content of the soil, pH, organic matter content, concentrations of the heavy metals involved and reaction time of the metals with extractant (Asami, 1988). Soil remediation may involve one or both of two major approaches: Ex-situ and in-situ remediation

(Moffat, 1995). Ex-situ remediation requires the excavation of the soil followed by its washing, whereas in-situ remediation involves applying remediating extractant to the soil without excavating it (Matschullat *et al.*, 1992).

Some workers have reported different ways of removing or reducing the concentration of heavy metals from contaminated soils. Benschoten (1994), for example, reported on the use of chelating agents, organic and/or mineral acid solutions to remove the heavy metals. The soil can as well be remediated by capping or covering it with an uncontaminated soil cover (Tokunaga, 1996). The polluted soil can also be diluted (or mixed) with unpolluted soil to bring down the concentrations of the heavy metals to an acceptable limit (Tokunaga, 1996).
Soil washing is one of the most suitable process of removing heavy metals from polluted soils. It uses a solution which contains either acids, bases or chelating agents (Benschoten, 1994). Generally a soil washing process consist of four basic parts: i) pre-treatment of the contaminated soil by sieving and hydrocylonation, ii) extraction of heavy metals from the soil, iii) separation of the cleaned soil particles from the liquid phase, iv) cleaning and/or recycling of the extracting agent (Tels,

1987). The contaminants in the extracting solution can be treated by conventional methods for reuse (Cushnie, 1985; Tels, 1987). The problem with the washing process, especially with mineral acids, is that the physical, chemical and biological properties of the soil are normally disturbed. This, therefore, requires preliminary bench-scale study to select the best extractant (Davis and Singh, 1995). Some of the solutions used in remediating polluted soils are summarised below:

a) Mineral acids

In many cases, the interaction between soil and the heavy metals is pH dependent (Arnfalk *et al.*, 1996). Except for Cr (VI), uptake of heavy metals increases with increasing pH. More than 60% of Cr(VI), for instance, was removed in the pH range of 2 and 3, and this may include those forms retained by aluminum oxide, a major soil component (Lo *et al.*, 1992). In general, heavy metals are hardly retained in soils in the low pH region, suggesting that soil-bound metals may be mobilized by decreasing the pH (Lo *et al.*, 1992). This, then, opened the possibilities of using mineral acids for remediation. For washing polluted soils, HCl and HNO_3 have been used extensively. A 0.1M

HCl solution, for instance, was effective in removing 77 to 97% Cu, Ni, Pb and Zn, and by increasing the concentration of HNO_3 from 0.01M to 0.1M, 70% of Zn, Pb, Cu, and Cd was removed (Tokunanga, 1996). The acid washing process is advantageous also in the subsequent treatment of the leachate containing heavy metals, which can be accomplished by some simple precipitation methods. But, adverse effects may occur to the soil's physical and chemical properties when strong acids are used which dissolve significant amounts of silica, aluminum and iron (Tokunaga, 1996). Concentration of acid should, therefore, be optimised by prior experimentation.

b) Inorganic cleaning agents

Other than mineral acids, there are inorganic cleaning agents such as mercuric sulphide, potassium iodide solution, sodium hypochlorite solution and calcium chloride. An acidic 0.1M KI solution, for instance, was reported to show a very high percentage removal of mercury, whereas 70 to 85% of Cr in soil was extracted with a hot 0.46M sodium hypochlorite solution at pH 8.5 (Tels, 1990). Calcium chloride remove Zn, Pb and Cd (Fischer *et al.*, 1993). The mechanism of removal was believed to be desorption cation exchange reactions, in which heavy metals were desorbed by the added secondary exchange cations of higher affinity to the soil than the heavy metals in question (Tokunaga, 1996).

c) Organic acids

Some naturally occurring organic acids are used for soil washing because of their ability to lower the pH of soil and to form soluble metal complexes. These include acetic acid, oxalic acid, glycine, and other aliphatic acids. Reed *et al.* (1995), for instance, reported that 0.1M acetic acid was effective in removing more than 50% Pb, Cu, Cd and Zn. Oxalic acid had higher ability to remove Pb, Cd, Cu and Zn than acetic acid (Leidmann *et al.*, 1994). Fischer *et al.*, (1993) reported that a 5% glycine solution removed 94.7% of the Cu, 84.9% of Ni, 69.9% of Zn and 61.3% of Cd contained in a soil.

d) Biosurfactants

Some biosurfactants produced by organisms form stable complexes with heavy metals, and hence can be used to remove heavy metals from soils (Miller, 1995).

Biosurfactants are colloidal in nature, with molecular weight of less than 1500. An example of these biosurfactants are rhamnolipid, produced by *Pseudomonas aeruginosa*. It was effective in removing Pb, Cd and Zn (Herman *et al.*, 1995). Rhamnolipid had heavy metal selectivity in the order of Pb = Cd > Zn (Herman *et al.*, 1995).

e) Chelating agents

These normally form stable metal complexes and, hence, are used to extract soil-bound metals. Ethylenediaminetetraacetic acid (EDTA), nitrolotriacetic acid (NTA) and diethylenetriaminepentaacetic acid (DTPA) are some of the chelating agents which have extensively studied. EDTA, for instance, extracted up to 90% of heavy metals such as Cu, Zn, Cd and Cr (Leidman, 1994). Reed *et al.* (1995) further reported that a 0.01M EDTA solution was effective in extracting 100% of Pb in the form of Pb(II), $PbSO_4$ or $PbCO_3$. The Pb removal from soils containing 10 000 mg/kg were 64.2% and 19.1% for EDTA and NTA, respectively (Peters and Shem, 1992). Extraction with EDTA was rapid and pH insensitive, whereas that with NTA was slow and pH dependent (Davis and Singh, 1995). Davis and Singh (1995) also reported that a 3 x 10^{-3}M EDTA or DTPA (at pH 6), was effective in completely removing Zn from soil containing 4 450 mg Zn/kg. By using chelating agents, heavy metals can, therefore be removed, with high percentage removal achieved. However, there are problems with use of chelating agents. These are: i) high cost of chelating agents, ii) difficulty of leachate treatment because some leachate complexes are highly stable, and iii) environmental safety (Sorvari and Sillanpaa, 1996).

NTA is biodegradable without producing undesirable metabolites. Therefore, it has been utilized as detergent. DTPA is degradable, whereas EDTA is non degradable (Stumpf *et al.*, 1996).

Due to the comparatively confined nature of pollution in the cottage industry setting, excavation, gathering and remediation of such soils by washing processes could be a practical proposition in pollution abatement.

2.9 Review of the theory of atomic absorption spectroscopy using a flame

The atomic Absorption Spectrophotometer (AAS) was the analytical instrument used in the present study. It is a common tool used in metal analysis due to its high sensitivity, accuracy and reproducibility, ease of sample preparation, applicability to a large number of metals and comparatively low cost (Hamilton, 1986).

The determination of metallic elements by atomic absorption spectrophotometer is based on the principle of absorption or emission of radiation by free atoms, thus resulting in transition of these atoms from one steady state to another (Welz, 1976). The type of transition between the steady states depended on the magnitude of the energies involved (Welz, 1976). The basic reaction underlying AAS, following the excitation of a ground state atom from R to R* were stated as follows:

$$R + h\upsilon = R^*$$

where R is the ground state atom, R* is the excited state atom, h is the Planck's constant and υ is the frequency of radiation (Welz, 1976). An atom is said to be in the ground state when its electrons are in their lowest energy levels (Welz, 1976). When energy is transferred to such atoms, by means of thermal or electrical excitation, a number of different excitation states results in throughout the population of the atoms (Welz, 1976). The ground state atom, therefore, absorbs energy to yield the excited state, which in turn emits radiation following the de-excitation process. Absorption or emission of light is, therefore, associated with the process of transition of atoms from one steady state to the other (Welz, 1976).

Welz (1976) reported that for the steady states m and n with energies E_m and E_n, respectively, absorption of light was taking place when $E_n > E_m$ following the transition from m to n, while the transition from n to m resulted in the emission of light with frequency υ_{mn} inversely proportional to Planck's constant and given as:

$$\upsilon_{mn} = (E_n - E_m)/h$$

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

a) Emission of radiation from an excited state to (n) a lower energy state (m), due to external radiation of the same frequency υ_{mn},

b) Spontaneous emission (transition from excited state to lower energy state), converting n to m and

c) Absorption of energy from a lower energy state to a higher one due to external radiation with frequency υ_{mn}, converting m to n.

These transitions form basis of AAS. Absorption involving ground state atoms resulted in the production of resonance lines characteristic of the element (Welz, 1976). Emission of the absorbed energy when n is converted back to m again produces the same resonance lines characteristic of the element. These lines (emitted energy) are used analytically in AAS to determine the concentrations of the atoms involved.

The essential components of an AAS are shown in Figure 1. These include i) a light source (hollow cathode lamp) which emits radiation characteristic of the element under study, ii) a flame which produces atoms, iii) a wavelength selector (monochromator) which isolates the desired resonance line and iv) electronic system comprising a detector (photomultiplier), amplifier and read-out (recorder).

The hollow cathode lamp has a cathode which incorporates the element being determined. The radiation is passed through the flame (burner) and the resonance radiations are partially absorbed by the ground state atoms of the same element, if they are present in the sample. Atomization takes place at the burner (nebulizer) stage. The monochromator isolates the desired resonance line and allows this radiation to fall on the photomultiplier where an electrical signal is generated. The electronics of the unit are designed to respond selectively to the pulsed radiation emanating from the radiation source. Signal processing occurs, which results in electronic output proportional to the absorption by the analyte atoms (Price, 1972).

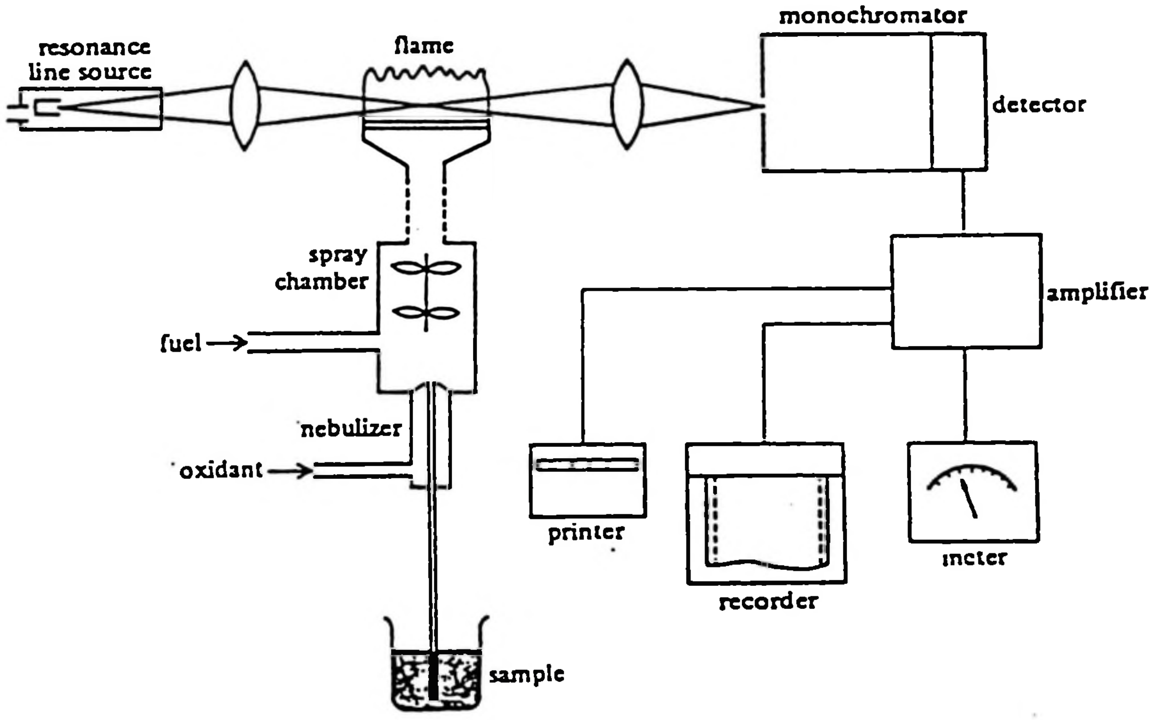


Figure 1. Practical system for atomic absorption spectrophotometer

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Investigation on the history and capacity of cottage industries

Twelve cottage industry locations were selected for the present study. These locations were in Ngara and Gikomba sites along the Nairobi river, as follows:

a) Middle Kirinyaga Road Garage Car Washing and Painting(MKRG CWP),
b) Middle Kirinyaga Road Garage Motor Welding (MKRG MW),
c) Lower Kirinyaga Road Metal Welding (LKRG MW),
d) Upper Kirinyaga Road Garage Car Washing and Painting (UKRG CWP),
e) Jilinda Soldering,
f) Ngara Garage Car Washing and Painting + Motor Welding,
g) Machakos Garage Battery Charging + Welding,
h) Country Bus Garage Motor Welding (C.B.G. MW),
i) Kamkunji Rubber Burning (K.R.B.),

j) Kamkunji Soldering (K.S.),

k) Kamkunji Metal Beating and Painting (K. MB + P),

l) Kamkunji Metal Beating + Painting + Welding (K. MB+P+W).

The general information concerning the approximate dates of their establishment and the raw materials used by each industry are given in Table 1.

According to industry owners, it was noted that most of the industries were installed where other activities, not known to these owners, had been undertaken. There was also a general trend of shifting from one activity to another, depending on how lucrative the business was. It was further observed that the activities of some of these industries were so integrated that it was difficult to quantify the contribution of a specific installation towards high levels of heavy metals in the soil. Thus, locating the point source of metal contamination, especially in the Ngara industries, was a difficult task. In recognition of this latter fact, sampling in some locations, such as Ngara Garage MW+CWP, Kamkunji MB+P+W and Kamkunji MB+P, was generally carried out in order to assess the combined contribution of the integrated

Table 1. Specific industries surveyed with dates of establishment, relative capacity rating, raw materials used and trends of operation of each industry

Industry location and activity	Date	Activity	Raw materials	Capacity	Trend of operation
MKRG CWP1	1990	car washing, painting, mechanics	Sadolac, sadocril & Higlose paint, Detergent	medium	fluctuating
MKRG MW2	1990	welding, panelling	gas + electric welder, welding rod (Cu & Pb), paints	medium	fluctuating
LKRG MW1	1993	welding, panelling, mechanics	gas + electric welder, welding rods (Cu & Pb), paints	large	consistent
UKRG CWP2	1983	washing, painting,	sadolac, primer,filler sadocril,higlose, paints, detergent	medium	consistent
Jilinda Soldering	1997	soldering	soldering wire (Pb, Cu)	small	fluctuating
Ngara Garage MW+CWP	1996	welding washing painting	gas + electric welder, welding rods (Pb +Cu), sadolac,sadocril paints, detergent	large	consistent
Machakos Garage Batt. Charg.+ Weld.	1988	battery charging, welding	Lead sulphate, welding rod (Pb, Cu), gas and electric welder	small	fluctuating
C.B. Garage Weld.	1978	welding, mechanics	gas + electric welder, welding rods (Pb, Cu)	large	consistent
Kamkunji Rubber Burn.	1984	rubber burning heating and reshaping metal sheet	vehicle tyres petrol, paints	large	consistent
Kamkunji Soldering	1980	soldering metal scraping	soldering wire, brass	large	consistent
Kamkunji MB + P	1982	metal beating, painting, plating	galvanized sheets, iron sheets, various paints	small	fluctuating
Kamkunji MB + P + W	1980	metal beating, painting, welding plating	galvanized metal sheets, various paints welding rods (Pb, Cu), gas welder	medium	consistent

industries towards high metal levels. Finally, there was little specialization within the cottage industry sector.

3.2 Sampling

3.2.1 Soil sampling, processing and routine analysis

This was undertaken during long rainy *El nino* period in January, 1998. For each cottage industry, a 200 g soil sample was drawn to a depth of 0-15 cm, within 0-5 m away from the centre of the industry activity, in four replicates.

Moving further away from the centre, and following the direction of prevailing winds, more soil samples were similarly collected at distances of 100, 200, 300, 500 and 1 000 m away from each of the two sites (Ngara and Gikomba). This was done in order to establish the extent of metal pollution away from the centre of each industry's activity. Four replications were maintained. Appendix 3 is a sketch map of the locations where sampling was undertaken.

However, it is worth noting that due to high rainfall during sampling period, some of the heavy metals may have been leached off or washed away by run-off, thus causing the determined metal levels in the soil samples lower than the expected values.

The moist soil samples were taken to the laboratory and air-dried. They were ground using mortar and pestle and sieved through a 2 mm sieve. The soils' routine physical and chemical properties were analysed. The pH was determined electrometrically using the UNICAM Model 292 MK2 pH Meter, at a 1:2.5 soil:water ratio (Maclean, 1982). Organic carbon was determined by the wet digestion method of Walkey and Black (Nelson and Sommers, 1982). Particle size distribution was determined by the Bouyoucos hydrometer method (Anderson and Ingram, 1993), while textural classes were obtained using the USDA textural class triangle. The soils' properties are shown in Table 2a.

The soils were generally on the alkaline range. However, the organic carbon content of soil samples were relatively low, although the Kamkunji Soldering location had a high value of 11.42%. The soils were heavy (clay) to light textured (sandy loam) with clay contents ranging from 11% to 44%.

The high pH observed may result in precipitation of most heavy metals into insoluble compounds. However, the high organic carbon and clay contents may lead to adsorption of the metals onto the soil colloids, thereby preventing them from leaching or washing off by run-off. Thus, most metals from these soils are likely to be retained due to high soil pH and clay content, with little influence from the low organic matter content.

3.2.2 Plant sampling and processing

Plant samples were collected at distances of 5-10, 40, 80, 120, 160, 200, 240, 280 and 320 m away from each of the two sites, again following the direction of prevailing winds. The edible species of *Amaranthus* was sampled. This species was chosen because it was the most abundant, widely distributed and edible plant found within the vicinity of the industry sites. The whole aerial portion of the *Amaranthus* plant was cut above the soil surface at each sampling spot. For each of the spots where a plant sample was collected, a 200 g soil sample

Table 2a. Physico-chemical properties of soils from Ngara and Gikomba cottage industry sites

Sampling locations	pH ± SD	% OC ± SD	% Sand	% Silt	% Clay	Textural. Class
Jilinda Soldering (0-5m)	8.3±0.21	2.89	62	17	21	SCL
MKRG CWP1 (0-5m)	8.1±0.13	4.64	78	8	14	SL
MKRG MW2 (0-5m)	7.9±0.09	6.19±0.04	62	19	19	SL
MKRG 100-150m from MW2 and WP1	7.8±0.28	1.57±0.08	36	20	44	Clay
LKRG MW1 (0-5m)	7.9±0.19	6.05	48	14	38	SC
LKRG MW1 (50-100m)	8.2±0.13	3.13	65	16	19	SL
LKRG MW1 (100-150m)	8.0±0.14	1.62±0.03	36	22	42	Clay
UKRG CWP1 (0-5m)	8.1±0.11	3.34	62	16	22	SCL
UKRG CWP1 (50-100m)	7.9±0.05	2.85	40	16	44	Clay
Ngara Garage MW+CWP (0-5m)	8.3±0.21	3.18±0.02	43	17	40	Clay
Ngara site (300m away)	7.1±022	2.24	40	18	42	Clay
Ngara site (500m away)	7.8	1.41±0.09	44	15	41	Clay
Ngara site (1,000m away)	6.6	5.75±0.05	46	20	34	SC
Machakos Ga. Bat. Ch.+ W. (0-5m)	7.7±0.09	7.99	64	23	13	SL
C.B. Gar. Weld.(0-5 m)	7.5±0.14	9.81	70	19	11	SL
C.B. Gar. Weld.(100-150)	7.9±0.06	0.60±0.03	45	16	39	CL
Kamkunji Rubber Burn. (0-5m)	7.2±0.24	4.85±0.04	66	18	16	SL
Kamkunji Soldering (0-5m)	7.9±0.14	11.42	74	14	12	SL
Kamkunji MB+P (0-5m)	7.3±0.38	2.42±0.03	50	18	32	CL
Kamkunji MB+P+W(0-5m)	8.0±0.09	4.77±0.04	60	24	16	SL
Gikomba Site (300m) away	7.5±0.28	3.78	56	25	19	SL
Gikomba Site (500m) away	7.4±0.3	2.20	63	18	19	SL
Gikomba Site (1 000) away	7.3±0.16	3.62±0.02	43	24	33	SC

SD = standard deviation, OC = organic carbon, SCL = sandy clay loam, SC = sandy clay, SL = sandy loam, CL = clay loam was also drawn for subsequent heavy metal analysis. The objective of this was to correlate the amounts of heavy metals in the soils with those in the associated plant samples. The samples were transported to the laboratory for further preparation. The soils were treated as described in section 3.2.1 above. The plants were washed with tap water and rinsed well with distilled water to remove any adhering soil particles. They were dried at 60° C and ground using a plant sample grinder.

3.2.3. Sediment sampling, processing and routine analysis

This was also done during long rainy season when the river was flooded. Sediment sampling was restricted to the river bank up to a depth of 100 cm below the water surface. This was due to lack of sophisticated equipment for deep water sampling. The sediments were collected using a stainless steel scoop, which was washed between samplings. The samples were drawn at various locations along the Nairobi river. These were Chiromo, Chiromo-Ngara midpoint, Ngara upstream, Ngara midstream, Ngara downstream, Ngara-Gikomba midpoint, Gikomba upstream, Gikomba midstream and Gikomba downstream. Three replications were maintained at each point. The samples were packed in polyethylene bags and transported to the laboratory, dried and ground as described for soils. Routine sediment analysis was carried out as for soils and the results of analysis are shown in Table 2b.

The river sediments were predominantly clay textured with pH above 7.0, and with low contents of organic carbon. As in the case of soils, this implies that most of the metals are likely to be retained in the sediments through precipitation and adsorption onto clay colloids, but little influence from organic matter.

3.2.4 Water sampling

Water samples were collected in one-litre, high density polyethylene bottles using a stainless steel scoop. Sampling was done to a width of 2m across the river using simple tools due to limitations caused by constant flooding of the river and lack of sophisticated water samplers. The sample containers were washed prior to sampling as described in section 3.3 below, and rinsed several times with the water from the point of collection. The pH of the water samples were recorded at every sampling site using portable pH meter. The pH of

Table 2b. Some selected properties of sediments obtained from Nairobi river (between Chiromo and Gikomba downstream)

Sampling location	Ph ± SD	% OC ± SD	% Sand	% Silt	% Clay	Textural class
Chiromo	7.1±0.12	1.39±0.01	56	15	29	SCL
Chiromo-Ngara mid-point	7.4±0.21	1.06±0.03	46	16	38	SC
Ngara upstream	7.4±0.07	1.85±0.01	26	7	67	Clay
Ngara mid-stream	7.5±0.15	1.57±0.08	22	20	58	Clay
Ngara downstream	7.0±0.07	1.88±0.06	28	18	54	Clay
Ngara-Gikomba mid-point	7.4±0.02	1.23±0.03	31	19	50	Clay
Gikomba upstream	7.8±0.15	1.05±0.01	24	11	65	Clay
Gikomba mid-stream	7.0±0.02	1.59±0.05	28	8	64	Clay
Gikomba downstream	7.5±0.06	1.41±0.02	44	22	34	CL

SD = standard deviation

OC = organic carbon

SCL = sandy clay loam

SC = sandy clay

CL = clay loam

the samples were later adjusted to about 2.0 or less, using concentrated nitric acid. The addition of acid was to prevent metabolic processes of micro organisms which could cause biochemical changes in the samples. Furthermore, it helped prevent flocculation and precipitation of metal compounds and reduced adsorption of the metals onto the surfaces of the containers (Muigai, 1992). The pH data is shown in Table 2c.

Table 2c. pH of the Nairobi river water samples

Sampling location	pH ± SD
Chiromo upstream	7.1±0.03
Chiromo - Ngara point	7.2±0.01
Ngara upstream	7.3±0.05
Ngara midstream	7.1±0.02
Ngara downstream	7.2±0.01
Ngara - Gikomba point	7.1±0.01
Gikomba upstream	7.1±0.03
Gikomba midstream	7.0±0.03
Gikomba downstream	7.3±0.01

SD = standard deviation

The pH of the Nairobi river water samples was slightly alkaline, with a range of 7.0-7.3. This implies that metal solubility in water environment may be reduced due to high pH.

3.3 Washing and preconditioning of laboratory ware

All the laboratory ware including digestion beakers and flasks, pipettes, volumetric flasks, sampling containers and watch glasses were rinsed with tap water, then soaked for 24 hours in detergent solution. They were then rinsed again with tap water and soaked in 1:25 hydrochloric acid:water for 24 hours. Washing was completed by rinsing with deionised water before use.

3.4 Digestion of samples for total metal analysis

3.4.1 Digestion of soil and sediment samples

From the 2 mm sieved samples, 10 g was drawn and further ground into fine powder. Exactly 2.0000 ± 0.0005 g of the soil was weighed and transferred into a 100 ml beaker. To the samples in the dry beakers 15 ml concentrated hydrochloric acid and 5 ml nitric acid (aqua regia) were added (Jeng and Bergseth, 1992). The samples were swirled and left to stand overnight. The following day the beakers were placed on a hot plate and boiled at 90-100° C under reflux conditions for two hours. Refluxing was stopped and boiling continued until the solutions almost dried, but without caking. The samples were cooled and the residues dissolved in 5 ml concentrated HNO_3. After cooling, the contents were transferred quantitatively into 50 ml volumetric flasks and made to volume using deionized water. They were filtered through Whatman no. 42 filter paper and transferred to washed (preconditioned) 100 ml polypropylene bottles. Heavy metals in the digests were determined using Flame Emission Atomic Absorption Spectrophotometry Model 680 (FE-AAS), with appropriate standards prepared in a similar matrix (i.e. 10% HNO_3).

3.4.2 Digestion of plant samples

For plant samples, wet digestion using the HNO_3-$HClO_4$ method of Baker and Amacher (1982) was used. Exactly 1.0000 ± 0.0005 g finely ground plant sample was weighed into a 100 ml beaker. To the weighed sample 5 ml concentrated HNO_3 and 2 ml concentrated perchloric acid ($HClO_4$) were added and the contents covered with a watch glass and incubated for 24 hours.

The samples were then digested on a hot plate at a temperature range of between 90 and 100° C to a final volume of 3 to 5 ml. The digest was allowed to cool for 20 minutes after which 15 ml of deionized water was added. The digest was quantitatively transferred into a 50 ml volumetric flask and made to volume with deionized water. It was filtered using Whatman no. 42 filter paper. This was then transferred to a preconditioned 100 ml polypropylene bottle. Heavy metals were determined by FE-AAS, with appropriate standards used.

3.4.3 Digestion of water samples

The water samples were thoroughly shaken to mix, and 50 ml samples transferred into 100 ml beakers. They were evaporated at a temperature of 100° C until about 5 ml remained. To the remaining volume of water, 8 ml of a 3:1 volume/volume mixture of nitric acid and perchloric acid was added. The digestion beakers were covered with watch glasses, incubated for 12 hours and then transferred to a hot plate and heated to about 130-140° C until all the brown fumes of nitrogen dioxide gas were completely expelled. Digestion was continued for 20 more minutes until dense white fumes appeared. The solutions were cooled at room temperature. The sides of the beakers and watch glasses were washed down with 15-20 ml of warm deionized water. The pH of the final solution was adjusted to below 2 using HNO_3. The digests were quantitatively transferred into 50 ml volumetric flasks and made to volume using deionized water. They were filtered using Whatman no. 1 filter paper into 100 ml polyethylene bottles. Heavy metals were determined using FE-AAS, with appropriate standards. This procedure for digestion of water has been recommended and adopted by many workers, including Hesse (1971), Griffiths and Wordsworth (1977), Rees and Hilton (1978), Thompson and Wagstaff (1980), Alala (1981), Maina (1982) and Muigai (1992).

However, during AAS analysis of heavy metals in water, the levels of most metals were below detection limit (non-detected) of the instrument due to limitation of the sensitivity of instrument to a certain concentration. Therefore, a more sensitive instrument would have been necessary in order to detect the very low metal concentrations in water. For the case of the present study, only FE-AAS was available for the analysis.

3.5 Extraction of heavy metals from soils and sediments using EDTA solution

The objective of this experiment was to determine the amounts of extractable Cr, Pb, Cd, Cu and Zn released into the soil solution since this may correlate with the forms taken up by plants, which may subsequently circulate in food chains.

A 0.05M ethylenediaminetetraacetic acid (EDTA) solution was prepared from disodium-EDTA ($C_{10}H_{14}N_2Na_2O_8.2H_2O$) salt by dissolving 18.612g of the salt into a one-litre volumetric flask and adding deionized water to the mark.

To 20g of the 2 mm sieved soil samples in 100 ml plastic bottles, 40 ml of 0.05M EDTA solution was added and the bottle screw capped tightly. The mixture was then shaken on a mechanical shaker at 120 revolutions per minute(rpm) for two hours. The suspension was filtered using Whatman No.42 filter paper. Heavy metals were determined using FE-AAS, with appropriate standards.

3.6 Studies on remediation of polluted soils

The objective of this experiment was to explore possible ways of removing heavy metal contamination of the most polluted soils by using EDTA. The concentrations of EDTA solution that could give maximum recovery of the heavy metals were explored. The ratio of soil:EDTA volume used was 1:10.

Different concentrations (0.005M, 0.01M, 0.05M, 0.1M, 0.25M and 0.5M) of EDTA solutions were prepared. The most polluted soil sample for each of the studied metals (Cr, Pb, Cd, Cu and Zn) were selected for the study. Thus, the four most polluted samples selected included Kamkunji Soldering (Pb = 3796.25 mg/kg), Kamkunji Rubber Burning (Cd = 7.26 mg/kg and Zn = 349.81 mg/kg), Kamkunji MB+P+W (Cr = 81.43 mg/kg) and Kamkunji Soldering (Cu = 1159.75 mg/kg). Six washed plastic bottles were prepared for each of the selected soil samples. To each of the six bottles, 4g of 2mm sieved soil sample was weighed and 40 ml of EDTA solution added, each bottle containing a different concentration of EDTA solution. The suspension was shaken on a mechanical shaker at 120 rpm for two hours and filtered using Whatman No. 42 filter paper into plastic bottles. Three replicates were used. The heavy metals were determined using FE-AAS.

3.7 Stock solutions, standards and standard curves used for determination of concentrations of the metals in the samples

For each metal, analytical grade reagents ($Pb(NO_3)_2.4H_2O$, $Cd(NO_{3,})2.4H_2O$, $CuSO_4.5H_2O$, $Zn(NO_3)_2$ and $K_2Cr_4O_7$) were used to prepare 1 000ppm stock solutions. Working standard solutions of concentrations 1, 2, 3, 4, 5 and 6ppm were prepared by diluting respective stock solutions of the metals using the equation:

$$C_0V_0 = C_1V_1$$

where V_0 is the initial volume (ml) required in order to make C_1, C_0 is the concentration of the metal (ppm) in the stock solution, C_1 is the metal concentration (ppm) required in V_1 and V_1 is the volume (ml) as determined by the volumetric flask. The corresponding absorbance for each concentration was read from the AAS instrument and used to draw standard curve for each metal as shown in Figures 2-6. The concentrations of the metals in the unknown samples were then read from these curves, and calculations made to obtain the metal concentrations in the soil, sediment, plant and water samples.

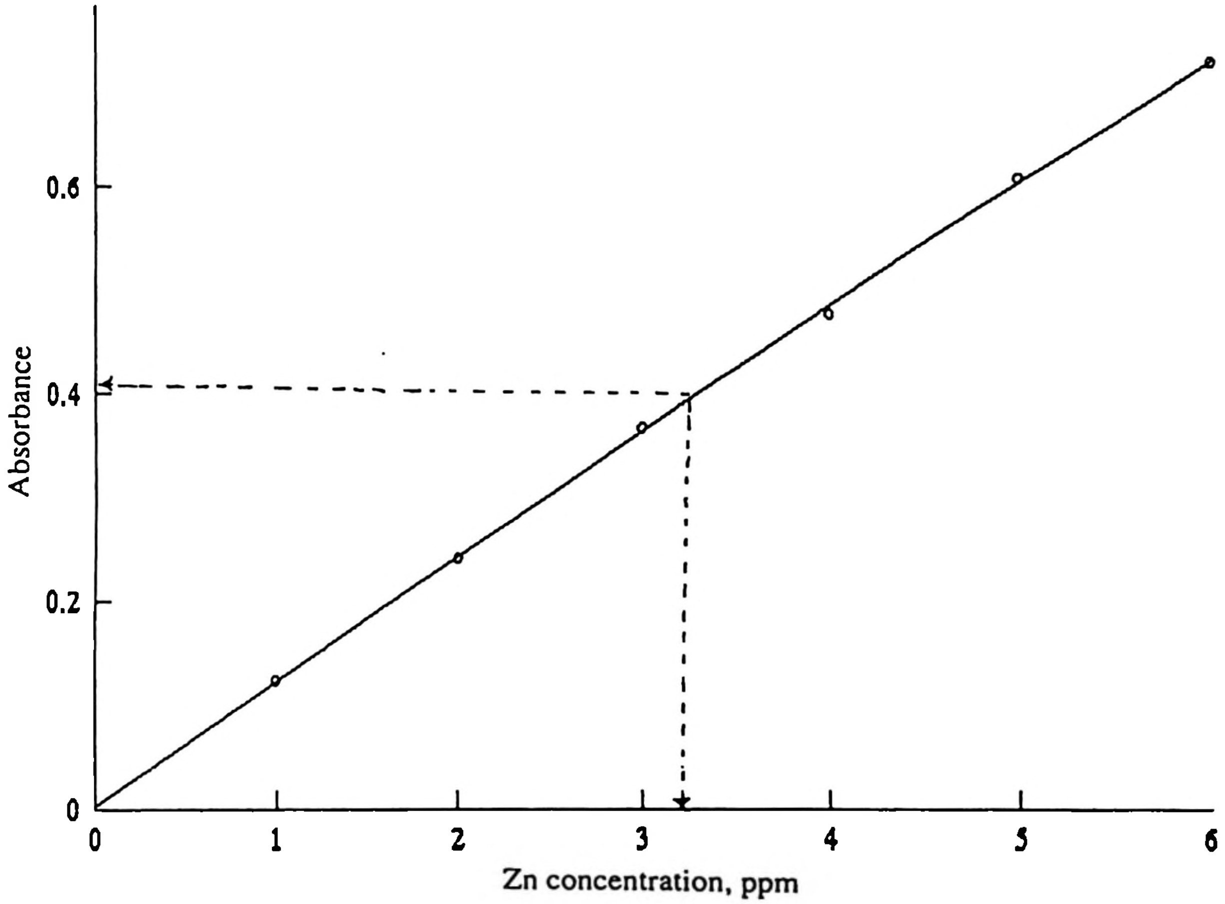


Figure 2. The zinc standard curve

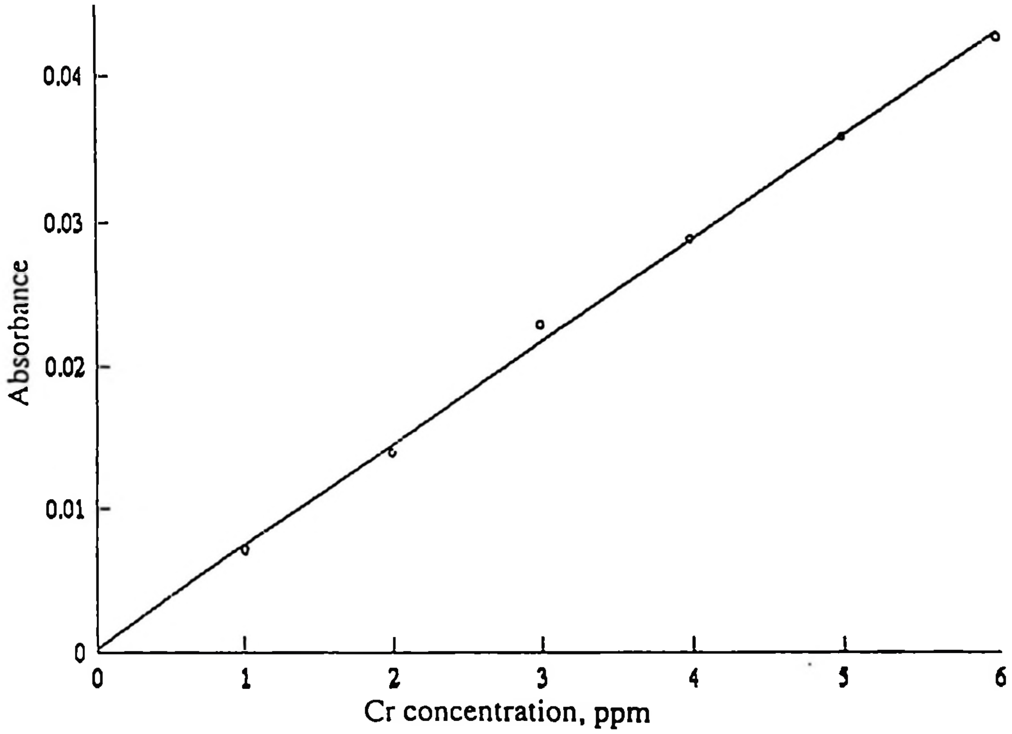


Figure 3. The chromium standard curve

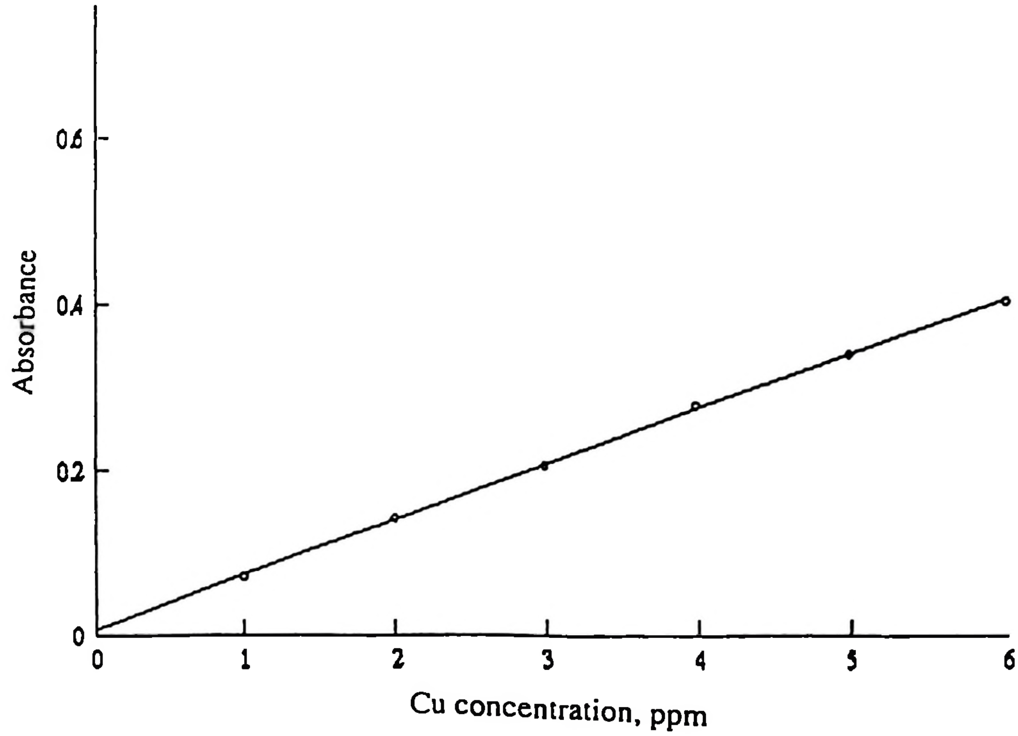


Figure 4. The copper standard curve

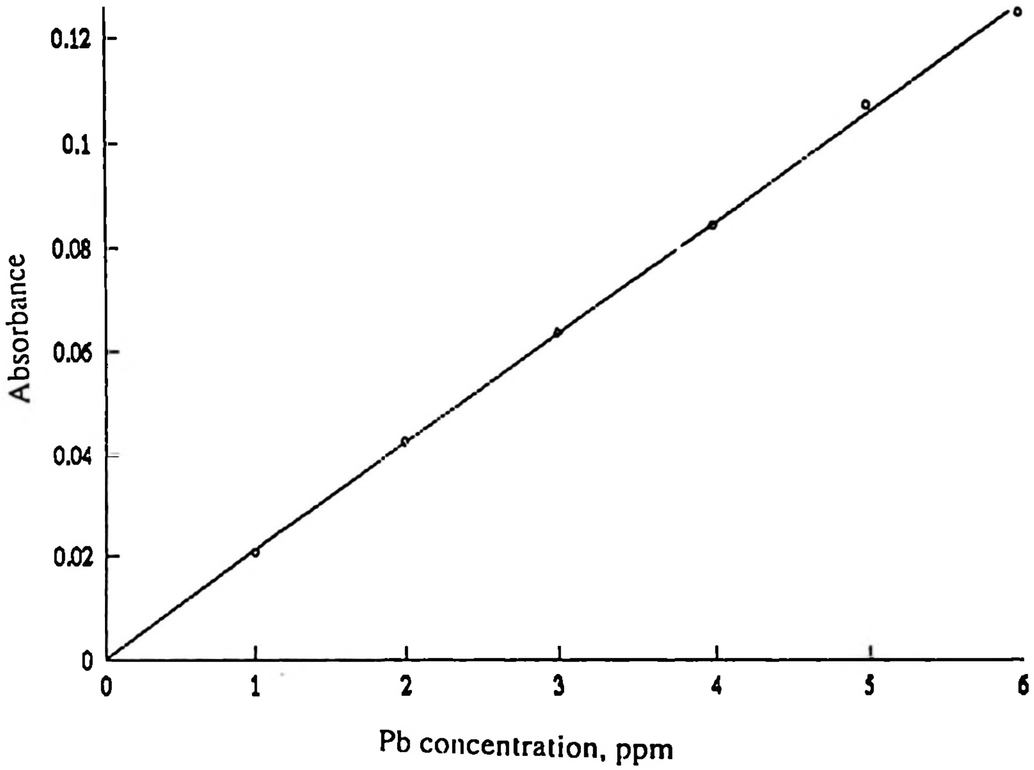


Figure 5. The lead standard curve

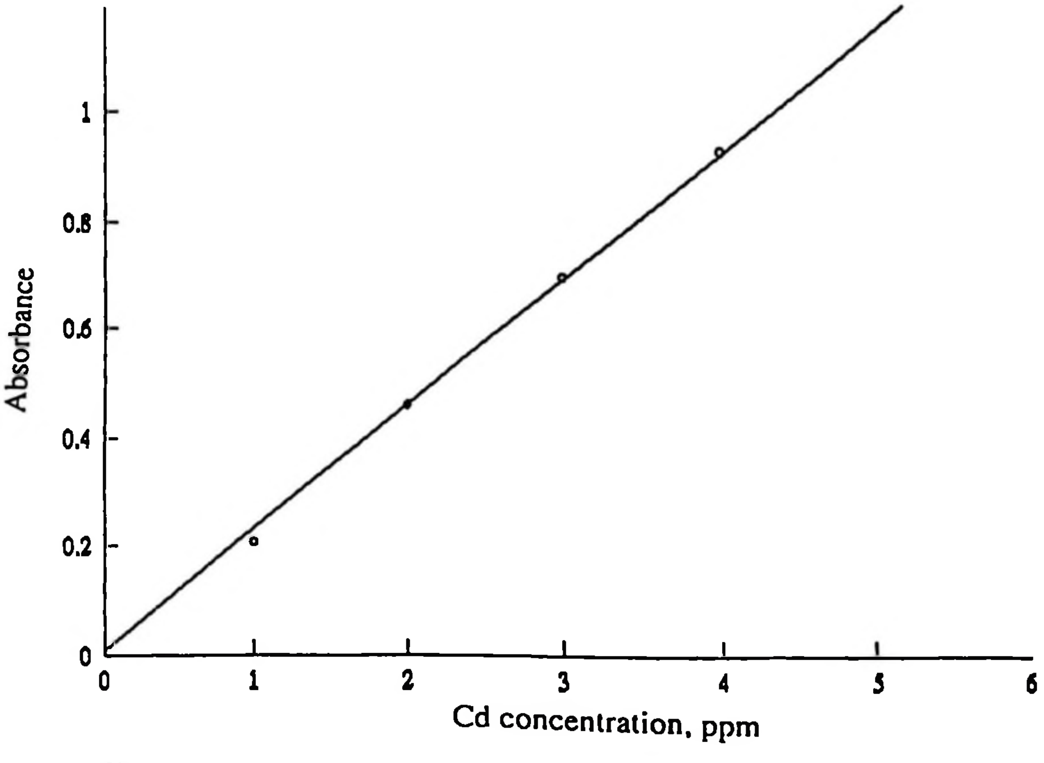


Figure 6. The cadmium standard curve

3.8 Statistical Analysis

Total and EDTA-extractable heavy metals were statistically analysed by analysis of variance using the MSTAT programme. The Completely Randomised Block Design was used to assess the influence of cottage industry activities and distance away from the centre of activity on total and EDTA-extractable Cr, Pb, Cd, Cu and Zn. The Duncan's Multiple Range Test (at probability level, $P = 0.05$) was used to rank the means.

Simple linear regressions of EDTA-extractable heavy metals on selected physico-chemical properties of the soils (pH, organic carbon and clay content) were run in order to assess (using coefficient of determination, R^2) the influence of these factors on the extractable heavy metals. Heavy metal contents of *Amaranthus spp* were also regressed on total and EDTA-extractable metals using simple linear regression in order to establish the relationship between plant's contents and soil's total and extractable heavy metal contents. The Statgraphics PLUS programme was used in running linear regression analysis.

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

4.1 Total heavy metal contents in the soils of cottage industry areas

The total heavy metal (Cr, Pb, Cd, Cu and Zn) contents in soils of cottage industries in the Ngara site are shown in Table 3.

Total metal levels in soil were generally highest within the centres of activity (0-5 m). Within the 0-5 m zones in Ngara, UKRG CWP2 (0-5) and LKRG MWI (0-5 m) locations had the highest quantities of most metals. However, the metal levels generally differed among all the 0-5 m locations. These levels were significantly ($P = 0.05$) higher than those in samples collected at 300 m, 500 m or 1 000 m away. The metal contents in soils obtained between 300 and 1 000 m were not significantly ($P = 0.05$) different within that interval.

Table 3. Total heavy metal contents of cottage industry soils of the Ngara site

Sampling location (± Activity)	Mean metal concentration				
	Cr	Pb	Cd	Cu	Zn
	……………………mg/kg……………………				
MKRG CWP1 (0-5 m)	17.97 b	372.75 d	0.70 cd	62.87 bc	246.71 ab
MKRG MW2 (0-5 m)	11.00 cd	784.88 b	0.89 c	171.81 b	262.63 a
MKRG 100-150 m from MW2 and CWP1	8.83 de	87.25 e	0.15 g	15.61 c	141.42 d
Jilinda Soldering (0-5 m)	10.00 d	347.00 d	0.57 d	131.9 b	245.45 ab
LKRG MW1 (0-5 m)	29.83 a	572.59 c	1.52 a	412.05 a	273.76 a
LKRG MW1 (50-100 m)	11.78 c	124.61 e	1.07 b	45.34 bc	215.00 b
LKRG MW1 (100-150 m)	7.26 e	46.88 e	0.44 e	11.68 c	100.15 e
UKRG CWP2 (0-5 m)	32.67 a	1 156.94 a	1.11 b	327.58 a	248.99 ab
UKRG CWP2 (50-100 m)	8.13 de	371.31 d	0.54 de	47.57 bc	179.71 cd
Ngara Garage MW + CWP (0-5 m)	11.57 c	161.37 e	0.13 gh	76.04 bc	200.90 c
Ngara Site (300 m away)	6.20 ef	118.66 e	0.34 ef	11.48 c	102.71 e
Ngara Site (500 m away)	5.21 ef	79.06 e	0.21 f	11.06 c	134.30 de
Ngara Site (1 000 m away)	3.14 f	23.37 e	0.09 h	7.22 c	103.35 e

Means within a column followed by the same letter were not significantly ($P = 0.05$) different according to the Duncan's New Multiple Range Test.

Table 4. Total heavy metal contents in cottage industry soils of Gikomba site

Sampling location (± activity)	Mean metal concentrations				
	Cr	Pb	Cd	Cu	Zn
	..........................mg/kg..........................				
Machakos Gar. Batt. Char. and Weld. (0-5 m)	44.65 b	1 468.25 c	1.81 d	440.25 b	262.10 c
C.B. Gar. Weld. (0-5 m)	36.91 bc	2 333.81 b	0.57 ef	379.94 bc	254.18 cd
C.B. Gar. Weld.(100-150m)	8.23 cd	189.85 de	0.54 ef	28.36 e	219.91 de
Kamkunji Rubber Burn (0-5 m)	69.97 ab	3 595.50 a	7.26 a	171.23 d	349.81 a
Kamkunji Soldering (0-5 m)	26.94 c	3 796.25 a	1.67 d	1 159.75 a	307.94 b
Kamkunji MB+P (0-5 m)	22.28 c	457.44 d	6.12 b	329.66 c	293.06 bc
Kamkunji MB+P+W (0-5 m)	81.43 a	2 345.75 b	3.54 c	389.11 bc	314.19 b
Gikomba site 300 m away	9.82 cd	181.93 de	1.02 e	38.29 e	244.12 d
Gikomba site 500 m away	8.84 cd	69.79 e	0.49 ef	30.80 e	247.13 d
Gikomba site 1 000 m away	3.61 d	30.88 e	0.19 f	5.80 e	108.49 e

Means within a column followed by the same letter were not significantly (P = 0.05) different according to the Duncan's New Multiple Range Test.

For the Gikomba site, the total heavy metal contents are shown in Table 4. The trend was similar to that observed in Ngara.

The total heavy metal levels in soils of Gikomba were also generally highest within the centre of activity (0-5 m) and differed significantly (P = 0.05) from those in soils collected further away. Furthermore, the total metal levels differed within the 0-5 m zones away from the centres of activities. However, samples obtained between 100 m and 1000 m did not differ significantly (P = 0.05) in total heavy metal levels.

From the observations above, the high concentrations of the heavy metals obtained in both Ngara and Gikomba sites resulted from disposal of the wastes of the cottage industries installed there. Those cottage industries were using raw materials which contained high levels of the heavy metals. Therefore, disposal of wastes in the vicinity resulted in high levels of the metals in soils, especially within 0-5 m of the centre of activity.

However, the differences in heavy metal contents amongst the locations within the centres of activity may be attributed to three factors. The first is the type of activity taking place within the individual industry. For instance, areas where car washing and painting were undertaken in Ngara, like UKRG CWP (0-5 m) and MKRG CWP (0-5 m), showed high levels of all the metals. Thus, the levels of Cr, Pb, Cd, Cu and Zn were 32.67, 1 156.94, 1.11, 327.58 and 248.99 mg/kg, respectively, for the former location and 17.95, 372.75, 0.7, 62.87 and 246.71 mg/kg, respectively, for the latter (Table 3). These significantly ($P = 0.05$) high levels may be attributed to the fact that some of these metals were used in formulation of paints and stabilizers during manufacturing of paints e.g. Cr and Cd, while others were chemical constituents of paints, pigments or lubricants e.g. Pb and Zn (Nriagu, 1978; 1980; 1988). Therefore, apart from the spillage of the paint in the process of car painting, the original paint would normally be scraped off before a new paint was added or during metal beating operations. As a result of this, the metals contained in the old paint were discharged into the soil environment, leading to high soil metal contents due to these paint wastes. Likewise, the high levels of Pb and Cu around Kamkunji Soldering (3 796.25 mg Pb/kg and 1 159.75 mg Cu/kg) and Machakos Garage Batt. Char.+ Weld (1 468.25 mg Pb/kg and 440.25 mg Cu/kg) in Gikomba were due to soldering and battery charging activities. These high levels of Pb and Cu were realised owing to the fact that Pb and Cu formed integral components of the raw materials used in soldering wires and in Pb accumulators (PSE, 1982; Oehme, 1978). Therefore, during soldering and battery charging operations splinters or fragments from the soldering rods and battery contents resulted in accumulation of these metals in the recipient soils. Also, rubber burning operations, such as that at Kamkunji Rubber Burning (0-5m), contributed to significantly ($P = 0.05$) high levels of Cd (7.26 mg/kg). This may be due to the fact that Cd is normally incorporated during manufacturing of rubber materials, such as vehicle tyres and plastics (Hiscock, 1979, cited by Wanjie, 1992), which were burned at that location.

Integration of cottage industry activities was also a factor which contributed to significantly ($P = 0.05$) high levels of the metals involved in those activities. An example is in the case of Kamkunji MB+P+W (0-5 m) (81.43 mg Cr/kg, 2 345.75 mg Pb/kg, 3.54 mg Cd/kg, 389.29 mg Cu/kg and 314.19 mg Zn/kg) where metal beating, painting and welding activities were undertaken within the same enterprise. Thus, painting could have resulted in high levels of Cr, Cd and Zn whereas welding probably contributed to high levels of Pb and Cu. Similar influences of cottage industries on heavy metal levels in soils were reported by Assey (1995) and Mmbaga (1997).

The second factor that may have contributed to differences in heavy metal concentrations within 0-5 m zones was the volume of work handled by each industry. Some industries handled larger volumes of work while others had smaller capacity, thereby resulting in differences in the amounts of wastes disposed of by an individual industry. For example, the activities of MKRG MW (0-5 m) and LKRG MW (0-5 m) were similar and started at almost the same time (1990 and 1993, respectively). However, because of differences in the intensities of operation between the two, metal contents were relatively higher in LKRG MW than in MKRG MW. LKRG MW must have been disposing of large volume of wastes due to its large scale operations. Furthermore, the large-scale operation of Kamkunji Soldering (0-5 m) over Jilinda Soldering (0-5 m) may have led to the former disposing of more wastes which resulted in high levels of Pb (3 796.25 mg/kg) and Cu (1 159.75 mg/kg), while the latter discharged smaller amounts (347.00 mg Pb/kg and 131.90 mg Pb/kg) into the soil. Mmbaga (1997) also reported on variations of heavy metal concentrations with intensity of operation of cottage industries.

Thirdly, the duration over which an industry has been operating also influenced the differential metal contents at the 0-5 m zones. Thus, industries which have been operating for longer duration of time had higher metal levels than their short-term operated counterparts. For instance, the two locations UKRG CWP2 and MKRG CWP1 had similar activity and almost the same capacity of operation, but the metal contents were different. The high concentrations of heavy metals observed in UKRG CWP2 (32.64 mg Cr/kg, 1 156.94 mg Pb/kg, 1.11 mg Cd/kg, 327.58, mg Cu/kg and 248.99 mg Zn/kg) may have been due to the fact that the industry started working earlier (1983), as compared with MKRG CWP1 (17.95 mg Cr/kg, 372.75 mg Pb/kg, 0.70 mg Cd/kg, 62.87 mg Cu/kg and 246.71 mg Zn/kg) which started much later (1990). Similar evidence may be drawn from Kamkunji Soldering and jilinda Soldering which handled the same type of activity. Although both were operating on a large scale, Kamkunji Soldering had been operating since 1980, while Jilinda Soldering was started in 1997. Differential metal levels within locations due to different duration of operation was also reported by Mmbaga (1997). The distances away from the centres of activity of the industries played a significant role in causing the differences in heavy metal levels further way from the centre of activity. The sharp decrease in soil heavy metal contents at 50-150 m away from the centre of activity to approach nearly constant background levels in samples collected between 300 m and 1 000 m away may haven been contributed by three factors. First, the wastes were usually dumped not far away from the centre of operation of an individual industry. Thus, higher levels of heavy metals were found mainly within the area receiving most of the wastes dumped, especially the 0-5 m zones.

The second factor which confined high metal levels near the industries may have been minimal influence of winds and water in distributing these metals in these environments. The inability of winds to transport metal dusts to far off distances was probably as a result of obstructions such as tall buildings within the areas studied. Furthermore, the metals must have been released in non-volatile forms which could not be transported easily by winds from the site of contamination.

Thirdly, the soil's physico-chemical properties such as pH, organic carbon and clay content may have contributed to heavy metal retention in the soils resulting in low mobility of the metals in the soils (Alloway, 1990). The high (alkaline) pH must have precipitated the metals, whereas clay and organic carbon probably adsorbed the metals, thereby preventing them from being leached out or washed away by run-off. Adsorption by soil constituents in these soils is implied by the data presented in section 4.2 and 4.3. A similar decrease in heavy metal concentrations with distance was also reported by Oduor (1992) and Assey (1995).

The levels of the heavy metals in soils obtained from 1 000 m away were the lowest, probably reflecting the background levels. The values for 1 000 m reported in Tables 3 and 4 are consistent with background levels for soil Pb, reported to be between 15 and 25 mg/kg (Aubert and Pinta, 1977, cited by Assey, 1995), and soil Cd of less than 0.5 mg/kg (Oduor, 1992).

4.2 EDTA-extractable heavy metals in soils of cottage industry areas

The concentrations of EDTA-extractable heavy metals in soils of Ngara cottage industry areas are presented in Table 5.

The highest levels of EDTA-extractable heavy metals were observed in samples obtained within 0-5 m away from the centre of industry activities, as was the case for total metal contents. These levels differed significantly (P = 0.05) from those of samples collected 1 000 m away. Generally, soil samples collected between 150 m and 1 000 m away did not show significant (P = 0.05) difference in EDTA-extractable metals. Similar trends obtained in Ngara (Table 5) were also observed for the Gikomba site (Table 6).

In general, the significant (P = 0.05) difference in EDTA- extractable metals between the 0-5 m zones and the other locations further away from the centre of activities may be attributed to two factors. First is probably the high total metal concentrations in the soil as a result of dumping of wastes in the vicinity as discussed in section 4.1. The higher the concentration of total metals in the soil, the higher the levels of the metal extracted. An example is shown in the case of UKRG CWP2 (0-5m) in Ngara, whose extractable Pb level ranked highest (343.9 mg Pb/kg), consistent with highest total level (1 156.94 mg Pb/kg). Similarly, in the Kamkunji Rubber Burning (0-5 m) location of Gikomba site, the high

Table 5. EDTA-extractable heavy metals in soils of cottage industries within Ngara site (mg/kg)

Sampling locations	Mean metal concentration				
(± activity)	Cr	Pb	Cd	Cu	Zn
	....................................mg/kg....................................				
MKRG CWP1 (0-5 m)	0.31 b	164.32 b	0.27 c	17.22 d	28.22 ab
MKRG MW2 (0-5 m)	0.25 bc	335.45 a	0.46 b	45.67 b	29.55 a
MKRG 100-150 m from MW2 + CWP1	0.21 c	44.4 0de	0.06 e	14.09 e	22.72 c
Jilinda Soldering (0-5 m)	0.05 d	137.76 bc	0.19 cd	33.91 c	28.42 ab
LKRG MW1 (0-5 m)	0.20 c	179.00 b	0.72 a	78.07 a	30.36 a
LKRG MW1 (50-100)	0.24 bc	55.97 d	0.17 d	27.05 cd	24.00 b
LKRG MW1 (100-150)	0.29 b	11.45 e	0.06 e	6.33 ef	17.92 d
UKRG CWP1 (0-5 m)	0.18 c	343.90 a	0.43 b	53.33 b	27.26 ab
UKRG CWP1 (50-100)	0.11 d	47.16 de	0.12 de	10.72 e	20.84 cd
Ngara Gara. MW+CWP (0-5 m)	0.54 a	96.38 c	0.08 de	13.27 e	25.95 b
Ngara site 300 m	0.09 d	9.01 e	0.05 e	5.06 ef	20.03 cd
Ngara site 500 m	0.07 d	26.51 e	0.05 e	5.55 ef	18.48 d
Ngara site 1 000 m	0.06 d	8.06 e	0.06 e	1.32 f	18.49 d

Means within a column followed by the same letter were not significantly (P = 0.05) different according to Duncans's New multiple Range Test.

Table 6. EDTA-extractable heavy metals in soils of cottage industries in Gikomba

Sampling locations	Mean metal concentration				
(± activty)	Cr	Pb	Cd	Cu	Zn
	....................................mg/kg....................................				
Machakos Ga. Batt. Ch.+Weld (0-5 m)	0.27 bc	389.35 a	0.53 b	47.68 b	29.43 bc
C.B.Garage Weld. (0-5 m)	0.22 bc	324.05 b	0.16 b	36.17 b	28.16 c
C.B.Garage Weld. (100-150 m)	0.15 bc	111.01 c	0.09 b	11.67 c	26.77 d
Kamkunji Rubber burn. (0-5 m)	0.76 a	296.60 b	1.85 a	18.95 c	34.57 a
Kamkunji Soldering (0-5 m)	0.08 c	391.80 a	0.34 b	79.17 a	32.24 ab
Kamkunji MB+P (0-5 m)	0.37 bc	143.18 c	0.18 b	47.66 b	31.85 b
Kamkunji MB+P+W (0-5 m)	0.31 bc	305.60 b	1.38 a	65.95 a	32.44 ab
Gikomba site 300 m	0.45 b	46.90 d	0.29 b	9.78 c	29.96 bc
Gikomba site 500 m	0.18 bc	40.65 d	0.11 b	9.51 c	27.70 cd
Gikomba site 1 000 m	0.07 c	9.93 d	0.07	2.26 c	18.16 e

Means within a column followed by the same letter were not significantly (P = 0.05) different according to Duncan's New Multiple Range Test.

total metal levels (69.97 mg Cr/kg, 3 595.50 mg Pb/kg, 7.26 Mg Cd/kg and 349.81 mg Zn/kg) subsequently resulted in high levels of EDTA-extractable metals (0.76 mg Cr/kg, 296.60 mg Pb/kg, 1.85 mg Cd/kg and 34.57 mg Zn/kg). These relatively high EDTA-extractable metal levels were probably due to the fact that as more metals were added into the soil, the exchange/adsorption sites of the various soil's organic and inorganic components got saturated, leaving some cations loosely attached/adsorbed onto the colloidal surfaces of the soil. Those loosely bound heavy metal cations may have been easily extracted by EDTA solution. The relatively low levels of EDTA-extractable metals in locations between 300 and 1 000 m away was probably due to initially low total metal contents of those soils. Similar results were reported by Assey (1995) and Mmbaga (1997).

The second factor which may have caused variation in the EDTA-extractable metal concentrations between soil samples obtained from the industry locations was probably the physico-chemical properties of the soils, such as pH, organic matter and Clay content. For example, LKRG MW (0-5m) and UKRG CWP (0-5 m), whose pH, %OC and clay contents were relatively high (7.9, 6.05 and 37.6, respectively, for the former, and 8.1, 3.24 and 21.60, respectively, for the latter), it was observed that the ratio of the EDTA-extractable metals to total metals were relatively low. This may be attributed to the precipitation of the metal cations to form insoluble compounds at the high soil pH, leading to low extraction by EDTA. Organic matter must have also complexed these metals, thereby making them difficult to extract. For instance, out of the high total Pb level (3796.25 mg/kg) obtained from Kamkunji Soldering (0-5 m), only a small fraction (391.80 mg Pb/kg) was extracted by EDTA. This was probably due to high organic matter content (11.42 %OC) of Kamkunji Soldering soil, which perhaps contributed to increased retention of the metal in soil colloids. In locations with high contents of clay, more metal cations may have been held up firmly, thus making them difficult to be extracted. For example, the Ngara site between 300 and 1 000 m, and Kamkunji MB+P (0-5 m), had low EDTA-extractable metals, but high clay contents. Therefore, clay may have contributed to low metal extracted by EDTA. Similar observations were reported by Assey (1995). The trends observed for the EDTA-extractable heavy metals agree well with the results of regression analysis, as outlined in section 4.3.

4.3 Relationships between EDTA-extractable heavy metals and some physico-chemical properties of the soils of Ngara and Gikomba.

Regression equations for EDTA-extractable heavy metals on pH, %OC and %Clay of soils of the cottage industries in Ngara area are shown in Table 7. Those for the Gikomba site are given in Table 8.

In Ngara, EDTA-extractable Pb and Cu were significantly (P=0.05) correlated with %Clay and %OC, respectively, whereas Zn was significantly (P = 0.05) correlated with both %OC and %Clay. However, EDTA-extractable Cd and Cr were not significantly (P = 0.05) correlated with %OC or %Clay. The rest of the metals were not correlated with any of the soil parameters. Copper and Zn were positively correlated with %OC, while Pb and Zn showed negative relationships with %Clay. The chemistry of the respective metals may have contributed to the selective correlation observed.

In Gikomba, only Pb and Cu were significantly (P = 0.05) correlated with %OC, and the relationships were positive.

The significant (P = 0.05) positive regressions of EDTA-extractable Pb, Zn or Cu with %OC in Ngara and Gikomba as observed in Tables 7 and 8, respectively, may be an indication that a substantial proportion of these metals were held by the organic matter in easily exchangeable forms. This may imply that the bonding energy was not high to retain the metals against the force of extraction by EDTA. Such metals may be easily taken up by plants, since large proportions are likely to be released into the soil solution and, thus, made available for absorption by plant roots. Similar findings were reported by Jeng and Bergseth (1992) and He and Singh (1993). The negative correlation between clay and exchangeable Pb and Zn in Ngara was probably due to strong binding energy of clay for these heavy metals, thus preventing them from being released into soil in large quantities. These metals, therefore, may not be easily available for plant absorption because of the strong binding energy by clay colloids. Jeng and Bergseth (1992) and He and Singh (1993) made similar observations.

Table 7. Regression equations for EDTA-extractable metals on pH, %OC and %Clay for Ngara soils

Metals	Regression equation	R^2
Cr	Extractable Cr = -0.907+0.141(pH)	0.255 ns
	Extractable Cr = 0.197+0.001(OC)	0.000 ns
	Extractable Cr = 0.226-0.001(Clay)	0.004 ns
Pb	Extractable Pb = -632.77+94.95(pH)	0.156 ns
	Extractable Pb = -10.03+35.81(OC)	0.275 ns
	Extractable Pb = 327.02-(6.62(Cay)	0.414 *
Cd	Extractable Cd = -1.50+0.224(pH)	0.184 ns
	Extractable Cd = 0.020+0.071(OC)	0.227 ns
	Extractable Cd = 0.394-0.004(Clay)	0.037 ns
Cu	Extractable Cu = -117.70+18.0(pH)	0.145 ns
	Extractable Cu = 1.27+7.40(OC)	0.501 *
	Extractable Cu = 50.46-0.817(Clay)	0.162 ns
Zn	Extractable Zn = -16.34+18.0(pH)	0.300 ns
	Extractable Zn = 19.00+1.47(OC)	0.504 *
	Extractable Zn = 32.30-0.26(Clay)	0.483 *

OC = percent organic carbon

ns = no significant correlation at P = 0.5

* = significant at P = 0.05

Table 8. Regression equations for EDTA extractable heavy metals on pH, %OC and %Clay of soils of Gikomba

Metal	Regression equation	R^2
Cr	Extractable Cr = 2.28-0.263(pH)	0.146 ns
	Extractable Cr = 0.314-0.006(OC)	0.009 ns
	Extractable Cr = 0.340-0.003(Clay)	0.014 ns
Pb	Extractable Pb = -1520.39+228.35(pH)	0.205 ns
	Extractable Pb = 32.21+34.82(OC)	0.697 **
	Extractable Pb = 406.93-10.02(Clay)	0.366 ns
Cd	Extractable Cd = 0.077+0.056(pH)	0.007 ns
	Extractable Cd = 0.404+0.019(OC)	0.013 ns
	Extractable Cd = 0.992-0.025(Clay)	0.132 ns
Cu	Extractable Cu = -364.61+52.57(pH)	0.350 ns
	Extractable Cu = 70.77+5.03(OC)	0.469 *
	Extractable Cu = 56.85-1.194(Clay)	0.167 ns
Zn	Extractable Zn = -1.66+4.07(pH)	0.071 ns
	Extractable Zn = -26.86+0.454(OC)	0.130 ns
	Extractable Zn = 31.75-0.131(Clay)	0.068 ns

OC = percent organic carbon

ns = not significant at P = 0.05

* = significant at P = 0.05

4.4 Influence of cottage industries on heavy metal contents of *Amaranthus* plants growing within the Ngara and Gikomba areas

The heavy metal contents of *Amaranthus* plants growing within Ngara and Gikomba areas are shown in the Tables 9 and 10, respectively.

In both Ngara and Gikomba, the concentrations of heavy metals in the plants were generally higher in the 5-10 m zone than at 320 m away.

The difference in heavy metal contents of *Amaranthus* sampled within 5-10 m zone compared with those from 320 m away may have been contributed by differences in both total and EDTA-extractable metals in the soils as influenced by differential accumulation of the wastes from the cottage industries within those distances. Within the 5-10 m zone the total and EDTA-extractable levels of heavy metals were generally high as a result of dumping of wastes from the cottage industries. Due to this, plants growing within these locations may tend to absorb high levels of heavy metals owing to exposure to large quantities in the soil. The low total and EDTA-extractable heavy metal levels in soils collected from 320 m away may have contributed to low levels in *Amaranthus* plants growing there. Kabata-Pendias and Pendias (1986) reported a linear relationship between Cd, Zn, Pb, and Cu contents in edible portions of cabbage or lettuce and total contents of these metals in the soil, implying that as the soil contents of heavy metals increased, the uptake by plants also increased linearly. The high heavy metal contents of *Amaranthus* at 5-10 m away from the centre of activities of industries compared with the rest, which are consistent with this reasoning.

In general, the high heavy metal levels in *Amaranthus* plants growing within the 5-10 m away may be a health risk to man and other animals since it can results in

Table 9. Heavy metal contents of *Amaranthus* plants growing within Ngara area, and corresponding soil metal contents

Distance away from industries	Cr			Pb			Cd			Cu			Zn		
	Total	EDTA Ext	Amar	Total	EDTA Ext	Amar	Total	EDTA Ext.	Amar	Total	EDTA Ext.	Amar	Total	EDTA Ext	Amar
								mg/kg							
5-10 m	19.53	0.289	3.95	577.00	73.90	3.60	1.70	0.668	0.650	65.03	20.01	3.55	274.50	33.68	92.80
40 m	12.27	0.181	2.55	236.15	41.68	1.25	1.30	0.534	0.200	36.53	22.30	3.25	226.30	28.46	97.95
80 m	12.00	0.336	3.30	133.00	28.04	2.10	1.03	0.486	0.300	27.55	12.37	3.75	256.75	31.10	77.55
120 m	11.90	0.164	1.15	116.55	59.50	1.71	0.70	0.524	0.350	161.43	48.04	2.75	243.18	28.52	53.15
160 m	8.33	0.296	0.57	68.53	54.62	1.11	0.42	0.332	0.100	39.75	27.20	2.70	196.38	28.76	89.70
200 m	10.65	0.212	1.25	146.70	12.38	2.25	0.45	0.360	0.015	23.35	16.91	3.85	247.60	32.02	60.15
240 m	14.65	0.322	6.00	192.10	74.34	2.65	0.48	0.282	0.150	47.28	27.92	6.35	236.00	28.65	60.10
280 m	11.85	0.158	2.20	239.00	92.70	2.15	0.38	0.156	0.013	30.88	19.85	0.50	239.25	28.38	34.25
320 m	9.55	0.112	0.97	98.65	53.68	1.83	0.43	0.234	0.013	52.45	22.10	0.35	251.50	29.06	38.65

EDTA Ext. = EDTA-extractable

Amar. = *Amaranthus* plant

Table 10. Heavy metal contents of Amaranthus growing within Gikomba area, and corresponding soil metal contents

Distance from industries	Cr			Pb			Cd			Cu			Zn		
	Total	EDTA Ext.	Amar.	Total	EDTA Ext.	Amar.	Total	EDTA Ext.	Amar.	Total	EDTA Ext.	Amar.	Total	EDTA Ext.	Amar.
									mg/kg						
5-10 m	21.77	0.485	6.50	1033.0	147.1	2.80	2.08	0.29	0.45	148.6	51.96	4.70	298.0	31.34	79.35
40 m	20.40	0.488	3.55	855.3	61.10	2.60	1.10	0.23	0.16	66.68	8.74	3.35	286.0	32.54	82.05
80 m	10.45	0.132	3.45	214.1	125.6	1.51	0.88	0.56	0.29	44.98	29.52	6.25	281.5	27.36	100.3
120 m	9.13	0.206	4.60	311.7	33.22	1.75	0.35	0.11	0.10	12.65	4.84	2.00	212.0	28.26	50.70
160 m	10.95	0.508	3.00	147.0	92.50	2.85	0.48	0.34	0.15	20.90	12.66	2.25	259.3	30.74	92.85
200 m	7.75	0.310	2.80	139.8	83.46	1.49	0.60	0.45	0.10	20.35	16.37	3.00	275.8	32.42	127.4
240 m	12.83	0.428	3.85	109.9	15.18	1.34	0.70	0.25	0.12	39.40	10.88	1.15	262.3	29.36	36.75
280 m	11.28	0.056	3.60	64.9	27.50	1.20	1.38	1.06	0.30	12.25	5.70	1.50	274.5	31.40	92.10
320 m	13.13	0.156	0.12	70.6	24.10	1.08	1.18	0.39	0.19	14.63	8.12	2.85	265.5	31.92	74.95

EDTA Ext. = EDTA-extractable

Amar. = *Amaranthus* plant

toxicity upon consumption of the contaminated *Amaranthus* plants. Toxicity hazards due to long-term consumption of Cd contaminated rice in Japan were reported by Kitagashi and Yamane (1981).

4.5 Relationships between heavy metal contents of *Amaranthus* plant and soils' total and EDTA-extractable heavy metal contents within Ngara-Gikomba areas

Regressions of plant heavy metal contents on total and EDTA-extractable heavy metals in soils of Ngara and Gikomba are given in Tables 11 and 12. These regressions were obtained from the raw data recorded in Tables 9 and 10.

In Ngara, significant ($P = 0.05$) positive correlations between plant heavy metals and total soil heavy metals, except for Cu (Table 11) was observed. Zinc was negatively correlated with total Zn in soil. Only plant Pb and Cd had positive and significant ($P = 0.05$) correlations with EDTA-extractable Pb and Cd in soil.

In Gikomba, plant Pb was positively and significantly

(P= 0.05) correlated with EDTA-extractable Pb. Plant Cd was also positively and significantly (P = 0.05) correlated with both total and EDTA-extractable Cd (Table 12).

The positive and significant (P = 0.05) correlations between plant heavy metal contents and total soil metal levels indicates that as the concentrations of soil heavy metals increased, plant uptake of these metals also increased proportionally. The uptake of heavy metals from the soil largely depended on the total concentrations in the soil, speciation of the metal in the soil solution, the efficiency of transport of that metal from the root surface into the root and translocation of the metal from the root to the aerial parts of the plant (Alloway, 1990). In the soils of the present studies, total contents of the heavy metals, especially Pb, Cu and Cd were sometimes high Table 3 and 4). This led to high EDTA-extractable levels for these metals (Table 5 and 6), implying a high level of availability to plant absorption. These observations are consistent with the significant regressions of the metals in *Amaranthus* plants on the metal levels in soils as depicted in Tables 11 and 12. In greenhouse pot experiments, Singh and Jeng (1993) and Assey (1995) found similar increases in plants' uptake of heavy

Table 11. Regression equations for heavy metal contents of *Amaranthus* on soils' total and EDTA-extractable heavy metals in Ngara.

Metal	Regression equation	R^2
Cr	Plant Cr = -2.39+0.392(TotalCr)	0.530 *
	Plant Cr = -.0457+12.59(EDTACr)	0.347 ns
Pb	Plant Pb = 1.30+0.004(TotalPb)	0.610 *
	Plant Pb = 1.57+0.009(EDTAPb)	0.090 ns
Cd	Plant Cd = -0.09+0.378(TotalCd)	0.732 **
	Plant Cd = -0.243+1.113(EDTACd)	0.774 **
Cu	Plant Cu = 2.78+0.000(TotalCu)	0.0001 ns
	Plant Cu = 2.84-0.003(EDTACu)	0.0002 ns
Zn	Plant Zn = 158.15-0.40(TotalZn)	0.408 *
	Plant Zn = -0.249+2.08(EDTAZn)	0.023 ns

ns = not significantly (P = 0.05) correlated

* = significant at P = 0.05

** = significant at P = 0.01

Table 12. Regression equations for heavy metal contents of *Amaranthus* on soils' total and EDTA-extractable heavy metals in Gikomba

Metal	Regression equation	R^2
Cr	Plant Cr = 0.577+0.198(TotalCr)	0.236 ns
	Plant Cr = 1.75+4.78(EDTACr)	0.262 ns
Pb	Plant Pb = 1.38+0.001(TotalPb)	0.355 ns
	Plant Pb = 1.25+0.009(EDTAPb)	0.522 *
Cd	Plant Cd = 0.089+0.098(TotaLcD)	0.495 *
	Plant Cd = 0.104+0.196(EDTACd)	0.464 *
Cu	Plant Cu = 2.73+0.004(TotalCu)	0.160 ns
	Plant Cu = 2.05+0.048(EDTACu)	0.009 ns
Zn	Plant Zn = -59.53+0.527(TotalZn)	0.150 ns
	Plant Zn = -86.24+5.49(EDTAZn)	0.233 ns

ns = not significantly (P = 0.05) correlated

* = significant at P = 0.05

metals as soil metal contents increased. When these heavy metals taken up by *Amaranthus* enter food chain due to consumption of contaminated *Amaranthus* by man and/or other animals, the ultimate consequence is toxicity.

4.6 Heavy metal contents in sediments from Nairobi river

The total heavy metal contents in sediments drawn from the Nairobi river between Chiromo and the downstream end of Gikomba are shown in Table 13.

The total contents of heavy metals were comparatively lower in sediment samples drawn from locations between Chiromo (control) and Ngara upstream than those obtained from the midstreams and upstreams of Ngara and Gikomba stretch of the river. The concentration of the metals increased significantly ($P = 0.05$) between Ngara upstream and Ngara downstream and also between Gikomba upstream and Gikomba downstream, with the midstream points having the highest ($P = 0.05$) of most of the metals. For example, the highest levels of all heavy metals were obtained from Gikomba midstream (11.54 mg Cr/kg, 161.07 mg Pb/kg, 32.23 mg Cu/kg and 189.53 mg

Zn/kg), while Ngara midstream had the highest level of Cd (0.34 mg/kg).

The low levels of heavy metals in the sediments obtained between Chiromo and Ngara upstream, which may represent background or control levels, was probably due to little or no influence of metal wastes because there were no cottage industries on the upstream side of these locations. The significantly ($P = 0.05$) higher levels of metals obtained from Ngara upstream sediments (5.80 mg Cr/kg, 29.35 mg Pb/kg, 0.09 mg Cd/kg, 4.04 mg Cu/kg and 105.98 mg Zn/kg) compared with the contents in the control (4.49 mg Cr/kg, 20.39 mg Pb/kg, 0.05 mg Cd/kg, 3.50 mg Cu/kg and 75.10 mg Zn/kg) was probably due to the combined contributions of metal-rich exhaust fumes from heavy traffic in the city, municipal wastes and, to some extent, wastes from Chiromo (University) Campus located about 500 m away from the river. However, the much higher metal levels observed in sediments collected from the midstreams and downstreams of Ngara and Gikomba parts of the river may have been contributed by two factors. First, the metal wastes released from the cottage industries within Ngara and Gikomba sites were either directly dumped or washed away by run-off into the river at these points.

Table 13. Total heavy metal contents in sediments drawn from the Nairobi river

Sampling locations	Mean metal concentration				
	Cr	Pb	Cd	Cu	Zn
	...mg/kg...				
Chiromo	4.49 ef	20.39 e	0.05 d	3.50 d	75.10 c
Chiromo-Ngara midpoint	4.17 f	26.26 de	0.04 d	3.37 d	68.79 c
Ngara upstream	5.80 de	29.35 de	0.09 c	4.04 cd	105.98 bc
Ngara midstream	6.94 d	156.21 a	0.34 a	31.53 ab	170.65 a
Ngara downstream	7.37 c	82.92 b	0.30 ab	23.15 b	170.98 a
Ngara-Gikomba midpoint	5.59 e	41.55 d	0.18 b	12.70 c	123.15 b
Gikomba upstream	4.84 ef	20.39 e	0.04 d	7.78 cd	97.49 bc
Gikomba midstream	11.54 a	161.07 a	0.23 ab	32.23 a	189.53 a
Gikomba downstream	9.74 b	63.59 c	0.08 cd	26.56 ab	170.66 a

Means within a column followed by the same letter were not significantly (P = 0.05) different according to Duncan's New Multiple Range Test.

These industries were installed very close to the river and, therefore, wastes may be discharged directly into the river. Secondly, two large city markets (Ngara and Gikomba markets) were also disposing of food and associated wastes into the river at these spots. These wastes probably contained some levels of these heavy metals. However, at the time of sampling the wastes were continuously washed away by the flooded river due to heavy rains. Thus I recommend that more work be done during the dry season for comparison purposes.

The highest metal contents in Gikomba midstream (11.54 mg Cr/kg, 161.07 mg Pb/kg, 0.23 mg Cd/kg, 32.23 mg Cu/kg and 189.53 mg Zn/kg) and Ngara midstream (6.94 mg Cr/kg, 156.21 mg Pb/kg, 0.34 mg Cd/kg, 21.53 mg Cu/kg and 170.65 mg Zn/kg) may have been due to the fact that these were the immediate spots where industry and market wastes were directly discharged since they were the closest to the Gikomba and Ngara cottage industry installations. Elevated heavy metal contents of sediments have also been reported by other workers. Muigai (1992), for instance, reported values of Pb and Cd in sediments obtained from Malewa river in Kenya to range between 13.710-28.084 mg Pb/kg and 1.418-2.129 mg Cd/kg, respectively. Alala (1981) also reported values between 6.7-210 mg Pb/kg and 1.0-3.0 mg Cd/kg in sediments from seven Kenyan lakes. These values for Pb were comparable with ranges of 20.39-161.07 mg Pb/kg obtained from the Nairobi river sediments. For Cd, the values for the Nairobi river sediments (0.04-0.34 mg Cd/kg) were relatively lower probably due to heavy rains which had washed away the wastes and, in the process, diluted the metal levels in the sediments. Also Cd contents in the industry wastes were generally low, hence low amounts released into the river.

4.7 Relationships between heavy metal contents in the sediments and selected physico-chemical properties of the sediments

The regressions of heavy metal contents in sediments' pH, %OC and %Clay are shown in Table 14.

Copper was positively and significantly (P = 0.05) correlated with soil clay content. However, there were insignificant (P = 0.05) correlations between total metals and pH, %OC or %Clay, for other metals.

The positive and significant (P = 0.05) correlation between total Cu and %Clay indicates that high clay content in the sediments probably increased the retention of Cu at the colloidal surface of the sediments. This was probably due to the fact that clay may have adsorbed the metal, thereby preventing it from leaching (Alloway, 1990).

The insignificant (P = 0.05) correlations of other metals with pH, %OC and %Clay implied that these parameters had little or no influence on total heavy metal retention in the sediments. This was probably

Table 14. Regressions of heavy metals in sediments on pH, %OC and %Clay

Metals	Regression equation	R^2
Cr	Total Cr = 35.15 - 3.46(pH)	0.135 ns
	Total Cr = 1.62 + 3.52(OC)	0.185 ns
	Total Cr = 4.92 + 0.035(Clay)	0.040 ns
Pb	Total Pb = 591.32 - 71.41(pH)	0.114 ns
	Total Pb = -47.33 + 78.87(OC)	0.184 ns
	Total Pb = -4.79 + 1.40(Clay)	0.127 ns
Cd	Total Cd = 1.38 - 0.167(pH)	0.145 ns
	Total Cd = -0.168 +0.220(OC)	0.331 ns
	Total Cd = -0.010 + 0.003(Clay)	0.148 ns
Cu	Total Cu = 97.52 - 11.08(pH)	0.057 ns
	Total Cu = -6.65 + 15.71(OC)	0.153 ns
	Total Cu = 6.74 + 0.184(Clay)	0.454 *
Zn	Total Zn = 502.27 - 50.65(pH)	0.085 ns
	Total Zn = 11.10 + 82.31(OC)	0.297 ns
	Total Zn = 7.19 + 0.003(Clay)	0.253 ns

OC = percent organic carbon

ns = not significant at P = 0.05

* = significant at P = 0.05

caused by altered physico-chemical conditions within the water environment.

4.8 Heavy metal contents in the Nairobi river

The heavy metal levels of waters of the Nairobi river are shown in Table 15.

The levels of metals were generally low in water samples drawn from the upstream control location (Chiromo). However, the midstreams and downstreams of Ngara and Gikomba had higher levels which differed significantly ($P = 0.05$) from the control in all the metals. The other locations showed significantly ($P = 0.05$) higher levels of only Cr, Cu and Zn relative to those in the control site.

The low levels of the heavy metals in Chiromo (control) water samples may have resulted from its location far away and upstream from the discharge points of the wastes from cottage industries and/or municipality. Alala (1981) also observed that sampling sites located far away from the metal-rich effluents from industry had relatively low levels of heavy metals. However, the significantly ($P = 0.05$) high levels of heavy metals in

Table 15. Total heavy metal concentrations in water samples drawn from Nairobi river between Chiromo and Gikomba downstream

Sampling location	Water pH	Mean metal concentration				
		Cr	Pb	Cd	Cu	Zn
		....µg/l........................				
Chiromo	7.1±0.03	27.33 f	0.00 c	0.00 d	3.67 c	14.00 d
Chiromo-Ngara midpoint	7.2±0.01	47.67 def	0.00 c	0.00 d	8.00 de	27.33 cd
Ngara upstream	7.3±0.05	78.33 c	0.03	0.00 d	9.67 d	45.67 bc
Ngara midstream	7.1±0.02	111.67 b	1.47 a	0.01 c	27.33 b	73.67 a
Ngara downstream	7.2±0.01	89.67 bc	0.81 ab	0.02 b	51.67 a	38.33 c
Ngara-Gikomba midpoint	7.1±0.01	63.33 d	0.07 c	0.00 d	29.67 b	30.33 cd
Gikomba upstream	7.1±0.03	66.33 cd	0.04 c	0.00 d	23.67 c	28.00 cd
Gikomba midstream	7.0±0.03	126.33 ab	0.087 ab	0.03 a	26.33 b	84.00 a
Gikomba downstream	7.3±0.02	181.33 a	0.28 b	0.01 c	24.00 bc	59.67 b

Means within a column followed by the same letter were not significantly ($P = 0.05$) different according to the Duncan's New Multiple Range Test water samples drawn from the midstreams and downstreams of Ngara and Gikomba were possibly attributed to metal-rich wastes discharged into the river from the Ngara and Gikomba cottage industries and also from the two markets (Ngara and Gikomba markets), as was discussed for sediments (section 4.6). It was observed that sampling locations closest to the cottage industries like Gikomba midstream showed relatively high contents of these metals (126.33 µg Cr/1, 0.87 µg Pb/1, 0.03 µg Cd/1, 26.33 µg Cu/1 and 84.00 µg Zn/1). Muigai (1992) also reported high levels of Pb (1.117-1.342 µg/1) and Cd (0.075-0.088 µg/1) in water samples drawn from river Malewa close to industries in Naivasha, Kenya. The comparatively lower ranges of Pb (0.00-1.47 µg/1), Cd (0.00-0.03 µg/1) and other metals (27.33-181.33 µg Cr/1, 3.67-51.67 µg Cu/1 and 1.00-84 µg Zn/1) obtained from Nairobi river was probably due to heavy rains which had diluted out the wastes that accumulated in the river prior to the rains, thereby reducing metal concentrations in the river water.

The locations such as Ngara upstream, which had relatively high levels of Cr, Cu and Zn (78.33 µg/1, 9.67 µg/1 and 45.67 µg/1, respectively), and yet had not received wastes from the cottage industries may have been contaminated by assorted metal-containing wastes from the municipality.

4.9 Evaluation of EDTA for remediation of heavy metal polluted soils of the cottage industries

The results of the remediation study using EDTA are shown in Table 16.

Extremely small quantities of heavy metals were removed from soil samples when deionised water (no EDTA) was used. When different concentrations of EDTA solutions were added, significantly ($P = 0.05$) higher extents of metal recovery were realised. However, the different concentrations of EDTA applied recovered significantly ($P = 0.05$) different levels of each of the heavy metals. The highest levels of most heavy metals were recovered when 0.1 or 0.25M EDTA was applied.

The lower concentrations of heavy metals removed when no EDTA was applied revealed that without a chelating agent, there was no complexation of the heavy metals; thus they were not extracted from the soil colloids (Reed et al., 1995). This may indicate the need for a complexing substance, for example EDTA, to maximize recovery of heavy metals from soils polluted by such types of pollutants. This is important as far as heavy metal pollution abatement is concerned because a complexing agent may lead to maximum recovery of heavy metals, thereby reducing the chances of these metals circulating in food chains and causing toxicity hazards (Tokunaga, 1996).

The significantly ($P = 0.05$) higher proportions of the metals removed by EDTA compared with those of the control (no EDTA added) attested to the power of EDTA, and possibly other chelating agents, in recovering heavy metals from heavy metal polluted soils. The inclusion of the control (0.000 M EDTA) was significant in comparing the amounts of heavy metals released before and after addition of a remediating agent. For example, when 0.005M EDTA solutions were added to the soil samples, the proportions of Pb, Cd, Cu, Zn and Cr (26.2%, 16.6%, 33.1%, 44%, and 32%, respectively) removed were significantly ($P = 0.05$) higher compared with the 0.02%Pb, 0.03%Cd, 0.05% Cu, 0.10% Zn and 0.03% Cr removed from the control samples. The same was true with all other concentrations of EDTA used. The various EDTA solutions added probably resulted in formation of soluble EDTA-metal complexes in soil solutions, thus

Table 16. Proportions of heavy metals recovered using different concentrations of EDTA

Sampling location	Metal	Conc. of EDTA (M)	Total soil metal (mg/kg)	Amount extracted (mg/kg)	% extraction
Kamkunji Soldering (0 - 5 m)	Pb	0.000	3 796.3	88.9 f	0.02
		0.005	3 796.3	992.6 e	26.2
		0.01	3 796.3	1 189.3 d	31.3
		0.05	3 796.3	1 997.6 c	52.6
		0.1	3 796.3	2 530.0 a	66.6
		0.25	3 796.3	2 300.7 b	60.6
		0.5	3 796.3	1 971.0 c	52.0
Kamkunji Rubber Burning (0 - 5 m)	Cd	0.000	7.26	0.219 f	0.03
		0.005	7.26	1.193 e	16.6
		0.01	7.26	1.29 e	18.0
		0.05	7.26	2.93 c	40.6
		0.1	7.26	5.17 a	71.8
		0.25	7.26	4.58 b	63.6
		0.5	7.26	2.59 d	36.0
Kamkunji Soldering (0 - 5 m)	Cu	0.000	1159.8	53.8 e	0.05
		0.005	1159.8	383.6 d	33.1
		0.01	1159.8	471.5 c	40.7
		0.05	1159.8	514.4 b	44.4
		0.1	1159.8	524.9 ab	45.3
		0.25	1159.8	529.9 a	45.7
		0.5	1159.8	508.7 bc	43.9
Kamkunji Rubber Burning (0 - 5 m)	Zn	0.000	349.8	36.1 e	0.10
		0.005	349.8	156.6 d	44.8
		0.01	349.8	168.7 c	48.2
		0.05	349.8	177.1 ab	50.6
		0.1	349.8	179.9 a	51.4
		0.25	349.8	173.8 b	49.7
		0.5	349.8	172.3 bc	49.3
Kamkunji MB.+P.+W. (0 - 5 m)	Cr	0.000	81.43	2.481 g	0.03
		0.005	81.43	26.67 f	32.8
		0.01	81.43	32.50 e	39.9
		0.05	81.43	38.13 d	46.8
		0.1	81.43	49.83 c	61.2
		0.25	81.43	76.60 a	94.1
		0.5	81.43	64.13 b	78.8

For each metal, means within a column followed by the same letter were not significantly (P = 0.05) different according to the Duncan's New Mulptiple Range Test.

recovering the heavy metals from the strong binding by soil colloids. Similar observations have been reported by other workers. Peters and Shem (1992), for instance, reported Pb recovery to be 64.2% from a total soil Pb content of 10 000 mg/kg when 0.1M EDTA solution was applied to the soil. Davis and Singh (1995) reported a 100% removal of Zn from soil with a total Zn content of 4 450 mg/kg when 0.03M EDTA was added to the soil.

The significant ($P = 0.05$) increase in the levels of the metals removed with increasing concentrations of EDTA solutions was probably due to increase in concentrations of the cations associated with EDTA which played a significant role in displacing heavy metal cations from the soil colloids. Basically the cations which are associated with Na-EDTA ($C_{10}H_{14}Na_2O_8.2H_2O$) are Na^+ and H^+. Once displaced from the soil colloids by Na^+ and H^+, the heavy metals are released into the soil solution where they form metal complexes with anions such as COO^- and OH^- resulting in from the dissociation of the Na-EDTA dissolved in water (Alloway, 1990). Therefore, increasing the EDTA concentration implied an increased level of each of these ions and, subsequently, enhanced displacement and complexation reactions, thus resulting in increased heavy metal removal from the contaminated soils. Thus, when EDTA concentration was increased from 0.005M to 0.05M, the proportions of heavy metals removed also increased from 26.2% Pb, 16.6% Cd, 33.1% Cu, 44.8% Zn and 32.8% Cr to 52.6% Pb, 40.7% Cd, 44.4% Cu, 50.6% Zn and 46.8% Cr. These proportions further increased to 66.6% Pb, 71.8% Cd, 45.3% Cu, 51.1% Zn and 61.2% Cr when the concentration of EDTA was increased to 0.1M. Similar observations have been reported by Farrah and Pickering (1978), Linn and Elliot (1988) and Davis and Singh (1995).

The highest proportions of the different heavy metals were recovered when 0.1M or 0.25M EDTA was added. This may have meant that the concentrations of EDTA that gave maximum recovery of each metal were probably attained in this study. For instance, the highest proportions of Pb (66.6%), Cd (71.8%) and Zn (51.4%) were removed when 0.1M EDTA was applied, whereas 45.7% Cu and 94.1% Cr were removed when 0.25M EDTA was applied. Perhaps higher recovery levels may have been obtained if the equilibrium (shaking) time was extended longer than the two hours used in the present study. Different times of shaking should subsequently be evaluated to maximize the extractability. For example, Davis and Singh (1995) reported 100% extraction of Zn from a soil Zn content of 4 450 mg/kg after shaking for more than six hours. However, the soil:EDTA solution ratio should also be optimized in order to obtain maximum recovery. Beyond 0.1 or 0.25M EDTA, the proportions of the heavy metals recovered decreased significantly (P = 0.05), probably due to saturation of the soil with the ions supplied during dissolution of EDTA in water. Those ions replaced the heavy metals in the EDTA-heavy metal complexes, leading to readsorption of the heavy metals onto the soil colloids (Alloway, 1990). This decreased the levels of heavy metals in the soil solution. This may be supported by the case of Cr whose recovery decreased proportionally from 94.07% to 78.75%, or of Cd (from 63.61% to 35.97%), when EDTA concentration was increased from 0.25M to 0.5M. Similar results were reported by Reed *et al.* (1995) as cited by Tokunaga (1996).

In general, EDTA remediation of heavy metal polluted soils may hold promise even for the cottage industry-contaminated soils since a high percentage of heavy metals can be extracted. However, it should be borne in mind that the EDTA costly and, therefore, may be difficult for large-scale application. Leachate treatment of EDTA-heavy metal complexes may be difficult because of the high stability of the complex formed. Therefore recovering the metals or EDTA from the complex for further remediation may be a problem. Furthermore, there is a problem of environmental safety due to use of EDTA since it is non-biodegradable (Stumpf *et al.*, 1996). These constraints may impede its field application and, therefore, careful investigation in order to find a feasible way of using EDTA is called for.

CHAPTER FIVE

5.0 CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The results of the present studies revealed that the total and EDTA-extractable Cr, Pb, Cd, Cu and Zn levels in both Ngara and Gikomba soils were generally highest within the centre of activity of cottage industries (0-5) and differed significantly (P = 0.05) from soils collected further away (between 100 and 1 000m). The highest levels observed were 81.43 mg Cr/kg, 3 796.25 mg Pb/kg, 7.26 mg Cd/kg, 1 159.79 mg Cu/kg and 349.81 mg Zn/kg. However, samples obtained between 150 and 1 000m did not differ significantly (P = 0.05) in the total heavy metal contents. The high levels of heavy metals obtained within the 0-5 m zones resulted in from disposal of metal-rich wastes from the cottage industries. The differential metal contents among the locations within the centres of activity were due to three factors: i) the type of activity taking place within the individual industry (e.g. car washing and painting, metal welding, battery charging and repair, rubber burning, soldering and metal plating); ii) the volume of work handled by each industry and iii) the duration over which an industry has been operating. The sharp decrease in heavy metal contents between 0-5 m zone to approach nearly constant background levels in samples collected between 300 m and 1 000 m were due to three factors: i) wastes were not dumped far from the centre of operation ii) minimal influence of wind and water in distributing these metals in these environments and iii) the possible retention of the heavy metals in the soil through precipitation due to high (alkaline) pH, and retention by soil clay and organic matter. It is concluded that cottage industry activities contributed to high levels of heavy metals in the soils.

Regressions of EDTA-extractable heavy metals on soil pH, percent OC and percent clay showed significant ($P = 0.05$) positive correlations of Pb, Cu and Zn with percent OC, and negative significant ($P = 0.05$) correlations of the same metals with percent clay. The positive correlations indicated that a substantial proportion of these metals were held by the organic matter in easily exchangeable forms. The negative correlations of the metals with clay indicated stronger retention of these metals by clay colloids.

The concentrations of heavy metals were high in *Amaranthus* collected from the 5-10 m zone than in those collected 320 m away because of high total metal levels in soils receiving metal-rich wastes from the cottage industries (5-10 m) and low levels at 320 m away from industries. Regression analysis revealed positive and significant (P = 0.05) correlation between most metals in *Amaranthus* and total soil metal contents, but insignificant relationships with EDTA-extractable metals, except for Pb and Cd.

Sediment samples collected from midstreams and downstreams of Ngara and Gikomba spots had significantly (P = 0.05) higher metal levels than those of the control at Chiromo. This was due to direct influx through dumping and/or washing in by run-off of metal-rich wastes released from Ngara and Gikomba cottage industries and wastes from Ngara and Gikomba markets which probably contained metals.

Similarly, highest levels of heavy metals were observed in samples drawn from the midstreams and upstreams of Ngara and Gikomba spots than those of the control (Chiromo) due to influence of metal wastes from cottage industries and, possibly, market wastes. However, the concentrations of heavy metals in waters were generally low, probably due to heavy rains which diluted out the wastes that accumulated in the river prior to the rains.

Remediation of the polluted soils indicated that 0.1M or 0.25 EDTA gave maximum recovery of the metals studied.

It can be concluded that cottage industry activities contributed to high levels of heavy metals in both the terrestrial and the aquatic environment in the vicinity of the industries.

5.2 Recommendations

In view of the results of this study, the following are recommended for future consideration.

1. Since wastes from cottage industries are potential sources of heavy metal pollution, a common dumping site should be constructed in which they can be disposed of instead of dumping them wantonly within the site of activity and the river where they cause heavy metal accumulation and contamination of the environment. Dumping sites should be carefully selected to ensure that

further spread of heavy metals to other sites does not occur.

2. Cottage industries should not be installed in locations which are close to agricultural lands, residential areas or livestock rearing sites, in order to avoid health risks associated with the heavy metals released from these industries.

3. Agricultural activities should not be undertaken within the areas where cottage industries are located, as is encountered in the Ngara and Gikomba sites. Edible plant species like *Amaranthus,* which grow within or close to cottage industry activities should not be consumed in order to avoid heavy metal accumulation in food chains.

4. Awareness should be created to the general population concerning the contribution of cottage industries to heavy metal pollution of the environment and the toxicity hazards associated with the heavy metals if they accumulated in food chains.

5. Heavy metal contaminated water of the Nairobi river should not be used for irrigating crops growing nearby or for drinking by the local residents. This is because these are the pathways through which heavy metals enter food chains and subsequently cause health risks to man and other animals.

6. Last, but not least, further research is required in order to come up with feasible methods of remediating heavy metal contaminated soils like those of Ngara and Gikomba. The use of a complexing agents like EDTA should be thoroughly evaluated because this is one method of recovering heavy metals from polluted soils. Equilibrium (shaking) time, concentrations of a complexing agent and soil:solution ratios should be evaluated when carrying out remediation studies because these factors affect the maximum recovery of a particular metal.

6.0 REFERENCES

Alala, L.N.N. (1981) Heavy Metals in Kenyan Lakes. *M.Sc. Thesis*, University of Nairobi, Nairobi, Kenya. pp 161.

Alloway, B.J. (1990) *Heavy Metals in Soils.* John Wiley and Sons Inc., New York. pp 339.

Anderson, J.M. and Ingram, J.S.I. (Editors) (1993) *Tropical Soil Biology and Fertility. A Handbook of Methods. 2nd Edition*. C.A.B. International, Wallingford, UK. pp 88-95.

Arnfalk, P., Wasay, S.A. and Tokunaga, S. (1996) A comparative study of Cd, Cr(III), Cr(VI), Hg and Pb uptake by minerals and soil minerals. *Water, Air and Soil Pollution* 87, 131-148.

Asami, T. (1988) Soil pollution by metals from mining and smelting activities. In: *Chemistry and Biology of Solid Wastes (Edited by Sakomons, W. and Forstner, U.)*. Springer-Verlag, New York. pp 91-111.

Assey, J.P. (1995) The Concentrations of Lead in Industrial Effluent, Soil, Lead Adsorption by Soil and its Uptake by Maize (*Zea mays*). *M.Sc. Thesis*, SUA, Morogoro. pp 73.

Aubert, H. and Pinta, M. (1977) *Trace Elements in Soils*. Elsevier Scientific Publishing Company, Amsterdam. pp 398.

Baker, D.E. and Amacher, M.C. (1982) Nickel, copper and cadmium. In: *Methods of Soil Analysis. Part 2. Agronomy Monograph No.9. (Edited by Page, A.L., Miller, R.H. and Keeney, D.R.)* American Society of Agronomy, Madison, Wisconsin. pp 323-336.

Bennett, B.G. (1981) *Exposure Commitment on Assessment of Environmental Pollutants*. A Technical Report 1 (2), 3-5. In: MARC Report No. 25.

Benschoten, J.E.V., Reed, B.E., Matsumoto, M.R. and McGarvey, P.J. (1994) Metal removal by soil washing for an iron-oxide coated Sandy soil. *Journal of Water Environment Research* 66, 168-174.

Bowen, H.J.M. (1979) *Environmental Chemistry of Elements.* Academic Press, London. pp 533.

Brummer, G.W. (1986) *The Importance of Chemical Speciation in Environmental Processes.* Springer-verlag, Berlin. pp 169-192.

Bryan, G. W. (1976) Heavy metal contamination in the sea. In: *Marine Pollution (Edited by Johnstone, R.).* Academic Press, London. pp 185-302.

Burrell, D.C. (1974) *Atomic Spectrophotometric Analysis of Heavy Metal Pollutants in Water.* Ann Arbor Science Publishers Inc., Michigan. pp 331.

Cantorow, A. and Trumper, M. (1944) *Lead Poisoning.* Williams and Wilkins, Baltimore, Maryland. pp 321.

Chen, Y. and Stevenson, F.J. (1986) *The Role of Organic Matter in Modern Agriculture.* Martinus Nijhoff, Dordrecht. pp 73-112.

Cushnie, G.C. (Editor) (1985) *Electroplating Waste Water. Pollution Control Technology*. Noyes Publication, Park Ridge, New York. pp 24.

Davies, B.E. (Editor) (1980) *Applied Soil Trace Elements*. John Wiley and Sons, Chichester. pp 482.

Davis, A. and Singh, I. (1995) Washing of zinc II from polluted soil column. *Journal of Environmental Engineering*. New York 121, 174-185.

Dowdy, R.H. and Larson, W.E. (1975) The availability of sludge-borne metals to various vegetable crops. *Journal of Environmental Quality* 4, 278-282.

Farrah, H. and Pickering, W.F. (1978) Extension of heavy metal ions sorbed on clays. *Water, Air and Soil Pollution Journal* 9, 491-498.

Fischer, K., Rainer, C., Bieniek, D. and Kettrup, A. (1993) Extraction of heavy metals from polluted materials by amino acids. *Journal of Polluted Soils* 93, 1157-1158.

Forstner, U. and Wittmann, G.T.W. (1979) *Metal Pollution in the Aquatic Environment*. Springer-Verlag, New York. pp 32-68.

Friberg, L., Piscator, M., Nordberg, G.F. and Kjellstrom, T. (1974) *Cadmium in the Environment II*. CRC Press, Cleveland, Ohio. pp 284.

Greenland, D.J. and Hayes, M.H.B. (Editors) (1981) *The Chemistry of Soil Processes*. A Wiley Inter-Science Publication, Chichester, New York, Brisbane and Toronto. pp 714.

Griffiths, J. and Wadsworth, G. (1977) Heavy metal pollution of farms near an industrial complex. In: *Inorganic Pollution and Agriculture (MAFF Ref. Book 326)*. HMSO, London. pp 70-76.

Hamilton, E.I. (1980) Analysis for trace elements II: Instrumental Analysis. In: *Applied Soil Trace Elements (Edited by Davies, B.E.)*. John Wiley and Sons Limited, London. pp 72-79.

Hay, R.W. (1984) *Bio-Inorganic Chemistry*. Ellis Horwood Limited, Chichester. pp 189-191.

He, Q.B. and Singh, B.R. (1993) Plant availability of Cd in soils. Extractabile Cd in newly and long-term cultivated soils. *Acta Agriculturae Scandinavica, Section B, Soil and Plant Science* 43, 134-141.

Herman, D.C., Artiola, J.F. and Miller, R.M. (1995) Removal of Cd, Pb and Zn from soil by a rhamnolipid biosurfactant. *Environmental Science and Technology 29*, 2280-2285.

Hesse, P.R. (1971) *A Text Book of Soil Chemical Analysis*. John Murray Ltd, London. pp 371-378.

Hiscock, S.A. (1979) *Production, Consumption and Uses of Cadmium in the European Community (1965-1976)*. Zinc Development Association/Cadmium Association, London. pp 791.

Huang, C.P., Elliot, H.A. and Ashmead, R.M. (1977) Interficial reactions and the fate of heavy metals in soil-water system. *Journal of the Water Pollution Control Federation* 49 (5), 745-756.

IDCRCL (1987) *Guidance on the Assessment and Redevelopment of Contaminated Lands, 59/83*. 2nd Edition. Department of the Environment, London. pp 126.

IRPTC/UNEP (1978) *Data Profiles for Chemicals for the Evaluation of their Hazards to the Environment of the Mediteranean Sea*. International Register for Potentially Toxic Chemicals, Geneva. pp 119.

Jeng, A.S. (1992) Weathering of some Norwegian alum shales, II. laboratory simulation to study the influence of Aging, acidification and liming on heavy metal release. *Acta Agriculturae Scandinavica, Section B*, 42:76-87.

Jeng, A.S. and Bergseth, H. (1992) Chemical and mineralogical properties of Norwegian alum shale soils, with special emphasis on heavy metal content and availability. *Acta Agriculturae Scandinavica, Section B, Soil and Plant Science* 42, 88-93.

Kabata-Pendias, A. and Pendias, H. (Eds) (1984) *Trace Elements in Soils and Plants*. CRC Press, Inc. Boca Raton, Florida, USA. pp 312.

Kabata-Pendias, A. and Pendias, H. (Eds)(1986) *Trace Elements in Soils and Plants*. CRC Press, Inc. Boca Raton, Florida. pp 315.

Kagi, J.H.R. and Nordberg, M. (1979) Metals and metallothionein. *Bulletin of Environmental Contamination and Toxicology* 36 (1), 168-172.

Khan, D.H. (1980) *Lead in the Soil Environment*. MARC Report No. 21. A Technical Report, MARC/UNEP, Geneva. pp 17-27.

Kitagashi, K. and Yamane, I. (Editors) (1981) *Heavy Metal Pollution in Soils of Japan*. Japan Science Society Press, Tokyo. pp 302.

Kitamura, S. (1976) *Effects and Dose Relationships of Toxic Metals*. Elsevier Scientific Publishers Co., Amsterdam. pp 88.

Leidmann, P., Fischer, K.,Bieniek, D., Nuflein, F. and Kettrup, A. (1994) Removal of heavy metals from polluted soil with grass silage juice. *Chemosphere* 28, 383-390.

Levis, A.G. and Bianchi, V. (1982) *Biological and Environmental Aspects of Chromium*. Elsevier, Amsterdam. pp 135-187.

Lindsay, W.L. (1972) Zinc in soils and plant nutrition. *Advances in Agronomy* 24, 147-148.

Linn, J.H. and Elliott, H.A. (1988) Mobilization of Cu and Zn in contaminated soil by nitrilotriacetic acid. *Water, Air and Soil Pollution* 37,449-458.

Lo, K.S.L., Yang, W.F. and Lin, Y.C. (1992) Effects of organic matter on the specific adsorption of heavy metals by soil. *Journal of Environmental Chemistry* 34, 139-153.

Lucas, J. (1975) *Our Polluted Food. A Survey of the Risk. 1st Edition*. Charles Knight Co., London. pp 250.

Maclean, E.O. (1982) Soil pH and lime requirement. In: *Methods of Soil Analysis, Part 2. (Edited by Page, A.L., Miller, R.H. and Keeney, D.R.)* American Society of Agronomy, Madison, Winsconsin. pp 199-224.

Maina, J.W. (1982) Ground water chemistry of the area to the immediate North of Nairobi Conservation area. *M.Sc. Thesis*, University of Nairobi, Nairobi. pp 101.

Matschullat, J., Andreae, H., Lessmann, D., Malessa, V. and Siewers, U. (1992) Catchment acidification from the top down. *Environmental Pollution* 77, 143-150.

McGrath, S.P. (1987) *Pollutant Transport and Fate in Ecosystems. Special Publication No. 6 of the British Ecology Society*. Blackwell Scientific, Oxford. pp 301-317.

Mertz, W. (1969) Chromium occurrence and functions in biological systems. *Journal of Physiological Evolution* 49, 163.

Mertz, W. (Editor) (1986) *Trace Elements in Human and Animal Nutrition*. 5th Edition. Academic Press Inc. San Diego, New York, London and Montreal. pp 499.

Metallgesellschaft, A.G. (1978) *Metal statistics*. 65th Edition. Frankfurt Am Main. P. 1967-1977.

Miller, R.M. (1995) Biosurfactant facilitated remediation of metal contaminated soils. *Environmental Perspective Supplementary Journal* 103 (1), 59-62.

Mmbaga, T.M. (1997) Contents of Heavy Metals in Some Soils of the Morogoro Municipality, Tanzania, as a result of Cottage-Scale Metal Working Operations. *Special Project*, Department of Soil Science, Sokoine University of Agriculture, Morogoro. pp 47.

Moffat, A.S (1995) Plants providing their worth in toxic metal clean-up. *Science Journal* 269, 302-303.

Muigai, P. G. (1992) Determination of Levels of Mercury, Cadmium and Lead in Fish, Water, Sediments, Soils and Plants from Naivasha Area, Kenya. *M.Sc. Thesis*, University of Nairobi, Nairobi. pp 247.

Nearthy, M.W. and Miller, W.J. (1975) Metabolism and toxicity of cadmium, mercury and lead in animals. *A Review on Dairy Science* 58, 1767-1780.

Nelson, D.W. and Sommers, L.E. (1982) Organic carbon in soils. In: *Methods of Soil Analysis Part 2. (Edited by Page, A.L., Miller, R.H. and Keeney, D.R.)* American Society of Agronomy, Madison, Winsconsin. pp 570-571.

Nriagu, J.O. (Editor) (1978) *The Biochemistry of Lead in the Environment*. Elsevier/North Holland, Amsterdam. pp 121.

Nriagu, J.O. (Editor) (1980) *Cadmium in the Environment. Part 1. Ecological cycling* . John Wiley, New York. pp 119.

Nriagu, J.O. (1990) Global metal pollution. *Journal of Environment* 32, 7-11; 28-33.

Nriagu, J.O. (1992) Toxic metal pollution in Africa. *The Science of Total Environment* 121, 1-37.

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

Nriagu, J.O., Pacyna, J.M., Milford, J.B.and Davidson, C.I. (Eds) (1988) *Chromium in the Natural and Human Environment*. John Wiley, New York.

Oehme, F.W. (Editor) (1978) *Toxicity of heavy metals in the environment*. Comparative Toxicology Laboratory, Kansas State University. Vol. 1, pp 1-19 and Vol. 2 P. 568-597.

Oduor, O.F.D. (1992) A study on the extent to which lead and cadmium from vehicles have contaminated roadside soils and vegetation in Nairobi and Kiambu, Kenya. *M.Sc. Thesis*, University of Nairobi, Nairobi. pp 117.

Page, A.L., Bingham, F.T. and Chang, A.C. (1981) Effects of heavy metal pollution on plants. *Journal of Applied Science* 1, 72-109.

Pergamon Series on Environmental Science, (1982) *Inorganic chemistry and the earth, chemical resources, their extraction, use and environmental impact*. Vol. 6.

Perry, H.M. and Erlanger, M.V. (1974) Laboratory clinical medicine. *Bulletin of Environmental Contamination and Toxicology* 23, 445-450.

Peters, R.W. and Shem, L. (1992) Use of chelating agents for remediation of heavy metal polluted soil. In: *Environmental Remediation (Edited by American Chemical Society)*. pp 70-84.

Phillips, D.A. (1976) *Metals and Metabolism*. Oxford University Press, London. pp 324.

Piotrowski, J.K. and Coleman, D.O. (1980) *Environmental Hazards of Heavy Metals: Summary Evaluation of Lead, Cadmium and Mercury*. A General Report of MARC/UNEP, No. 20, Nairobi (1980).

Prasad, A.S. (Editor) (1976) *Trace Elements in Human Health and Diseases*: *Zinc and Copper*. Academic Press, New York, San Fransisco, London. pp 470.

Price, W.J. (Editor) (1972) *Analytical Atomic Absorption Spectroscopy*. Heyden and Sons Limited, London. pp 139.

Reed, B.E., Moore, R.E. and Cline, S.R. (1995) Soil flushing of a sandy loam polluted with Pb(II), $PbSO_4$(s), $PbCO_3$(s) or Pb-naphthalene column results. *Soil Contamination* 4(3), 243-267.

Schroeder, H.A., Balassa, J.J. and Vinton, W.H. (1965) Chromium, cadmium and lead in rats: Effects on lifespan, tumours and tissue levels. *Journal of Nutrition* 56, 51-55.

Schroeder, H.A. (1976) *The Trace Elements and Nutrition. Some Positive and Negative Aspects.* Faber and Faber, 3 Qeensquare, London. pp 151.

Singh, B.R. (1991) Unwanted Components of Commercial Fertilizers and Their Agricultural Effects. *The Fertilizer Society of London, UK.* pp 28.

Singh, B.R. (1994) Trace element availability to plants in agricultural soils, with special emphasis on fertilizer Inputs. *Environmental Reviews* 2, 133-136.

Singh, B.R. and Jeng, A.S. (1993) Uptake of zinc cadmium, mercury, lead, chromium and nickel by rye grass grown in a sandy soil. *Norwegian Journal of Agricultural Sciences* 7, 147-157.

Singh, B.R. and Steinnes E. (1994) Soil and Water Contamination by Heavy Metals. In: *Soil Processes and Water Quality* (Edited by Lal, R. and Stewart, B.). Lewis Publishers, Boca Raton, USA. pp 233-271.

Soldatini, G.F., Riffaldi, R. and Levi-Minzi, R. (1976) Lead adsorption by soils 1. Adsorption as measured by Langmuir and Freundlich isotherms. *Water, Air and Water Pollution* 6 (1), 111-118.

Sorvari, J. and Sillanpaa, M. (1996) Influence of metal complex formation on heavy metals and free EDTA and DTPA acute toxicity determined by *Daphnia magna*. *Chemosphere* 33 (6), 1119-1127.

Sposito, G. (1984) *The Surface Chemistry of Soils*. Oxford University Press, New York. pp 340.

Stumm, W. and Morgan, J.J. (1970) *Aquatic Chemistry: An Introduction Emphasizing Chemical Equilibria in Natural Waters*. Wiley-Interscience (A Division of John Wiley and Sons, Inc.), New York, London and Sidney. pp 583.

Stumpf, M., Ternes, T.A., Schuppert, B., Haberer, K., Hoffmann, P. and Ortner, H.M. (1996) Sorption and degradation of NTA, EDTA and DTPA during underground passage. *Vom Wasser* 86, 157-171.

Tels, M. (1987) Advances in treating heavy metals containing wastes. *Resource Conservation Journal* 14, 71-86.

Thompson, K.C. and Wagstaff, K. (1980) *Analyst*. John Murray Ltd, London. pp 105.

Tokunaga, S. (1996) Remediation of Soils Polluted by Heavy Metals. *Proceedings of the International Symposium on Cleaning Technology*. September 13, Seoul, Korea. pp 199-205.

Underwood, E.J. (Editor) (1971) *Trace Elements in Human and Animal Nutrition*. Third Edition. Academic Press, London. pp 543.

Underwood, E.J. (Editor)(1977) *Trace Elements in Human and Animal Nutrition*. 4th Edition. Academy Press, New York. pp 545.

UNEP (1980) *The State of World Environment; Heavy Metals.* Annual Report. UNEP, Geneva. pp 250.

UNEP (1984) *Governing Council, 12th Session*, Item 7B. UNEP/GC, 12/16. 7TH February 1984.

UNEP, (1986) *Third meeting of experts to update the lists of environmentally dangerous chemical substances and processes of global significance*. Geneva. pp 8-12.

Walbott, G.L. (1978) *Health Effects of Environmental Pollutants*. 2nd Edition. C.V. Mosby Co. London. pp 449.

Wanjie, G.C. (1992) Evaluation of Lead and Cadmium in Kenyan Population and Sources including Determination of Trace Elements in Consumable Clays. *M.Sc. Thesis*, University of Nairobi, Nairobi. pp 72.

Webber, M.D., Kloke, A. and Tjell, J.C. (Eds) (1984) Processing and Use of Sewage Sludge. In: *Heavy Metals in Soils. (Edited by Alloway, B.J. 1990)*. John Wiley and Sons, Inc. New York. pp 29-38.

Welz, B. (Editor) (1976) *Atomic Absorption Spectroscopy*. 2nd Edition. Verlag Chemie, Weinheim, New York. pp 64-71; 158-159.

World Health Organization (WHO), (1971) *International Standards for Drinking Water*. World Health Organization, Geneva, Third Edition.

WHO (1977) *Environmental Health Criteria 3. Lead*. World Health Organization, Geneva.

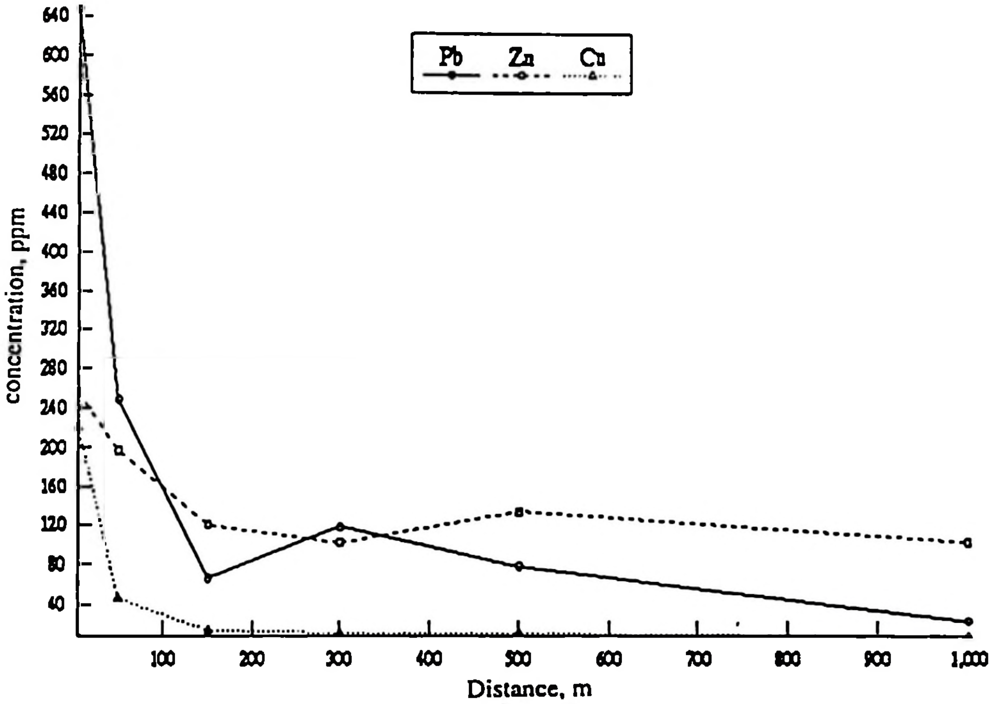
WHO (1979) *Joint FAO/WHO Food and Animal Feed Contamination Monitoring Programme*. Summary Report Stage. World Health Organization, Geneva. pp 1-197.

Williams, J.H. (1988) *Chromium in Sewage Sludge Applied to Agricultural Land.* Commission of the European Communities, Brussels. pp 237.

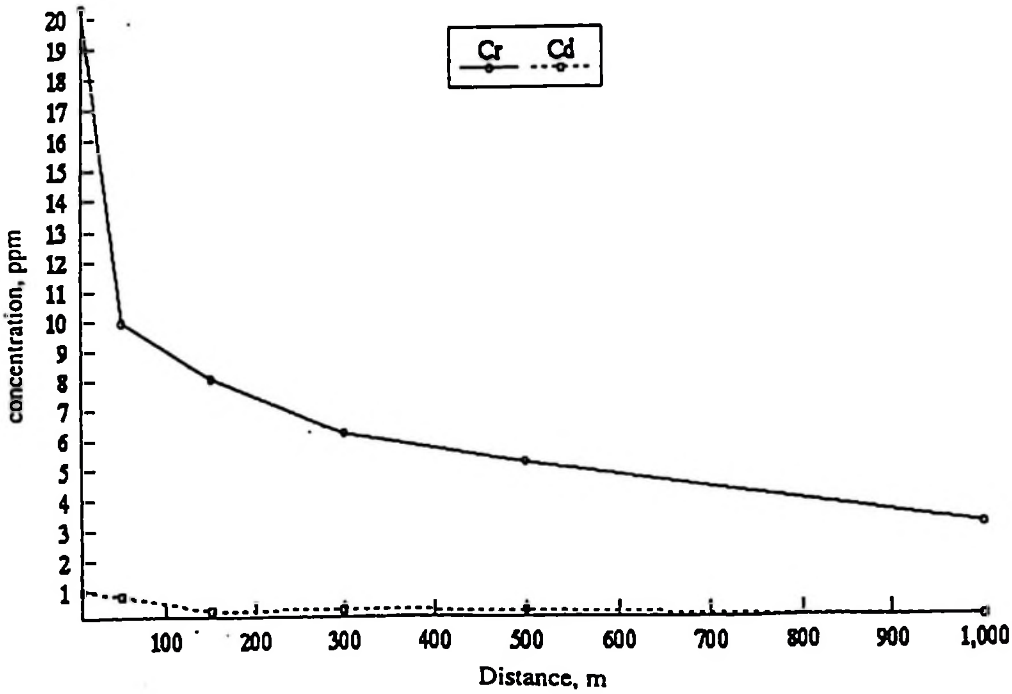
Xhung Fung, X. and Ghalamhoss, S. (1989) Effects of pH on chemical forms of and plant availability of cadmium, zinc and lead in polluted soils. *Water, Air and Soil Pollution* 45, 265-273.

APPENDICES

Appendix 1. Distance profiles of the metals in the Ngara cottage industries

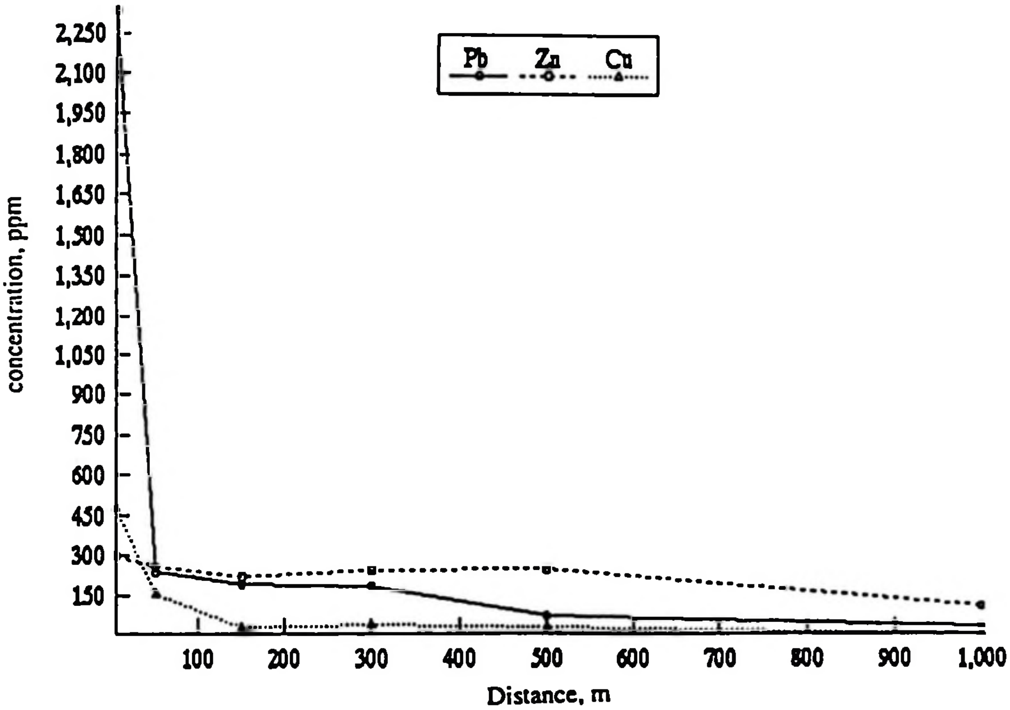


a. Distance profiles of Pb, Zn and Cu in the Ngara site

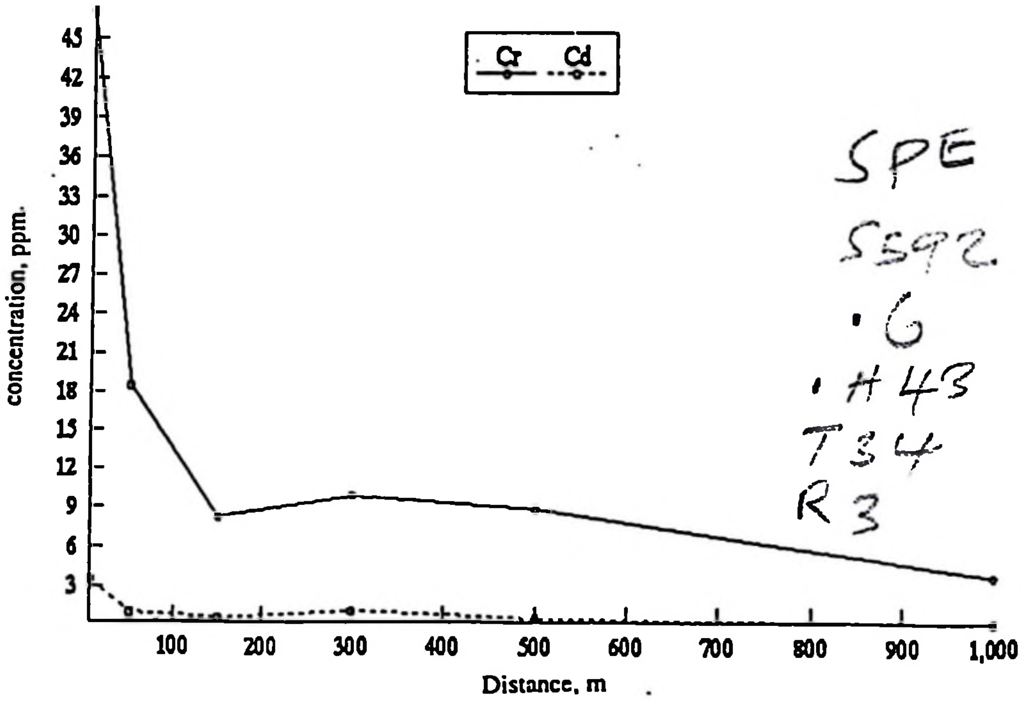


b. Distance profiles of Cr and Cd in the Ngara site

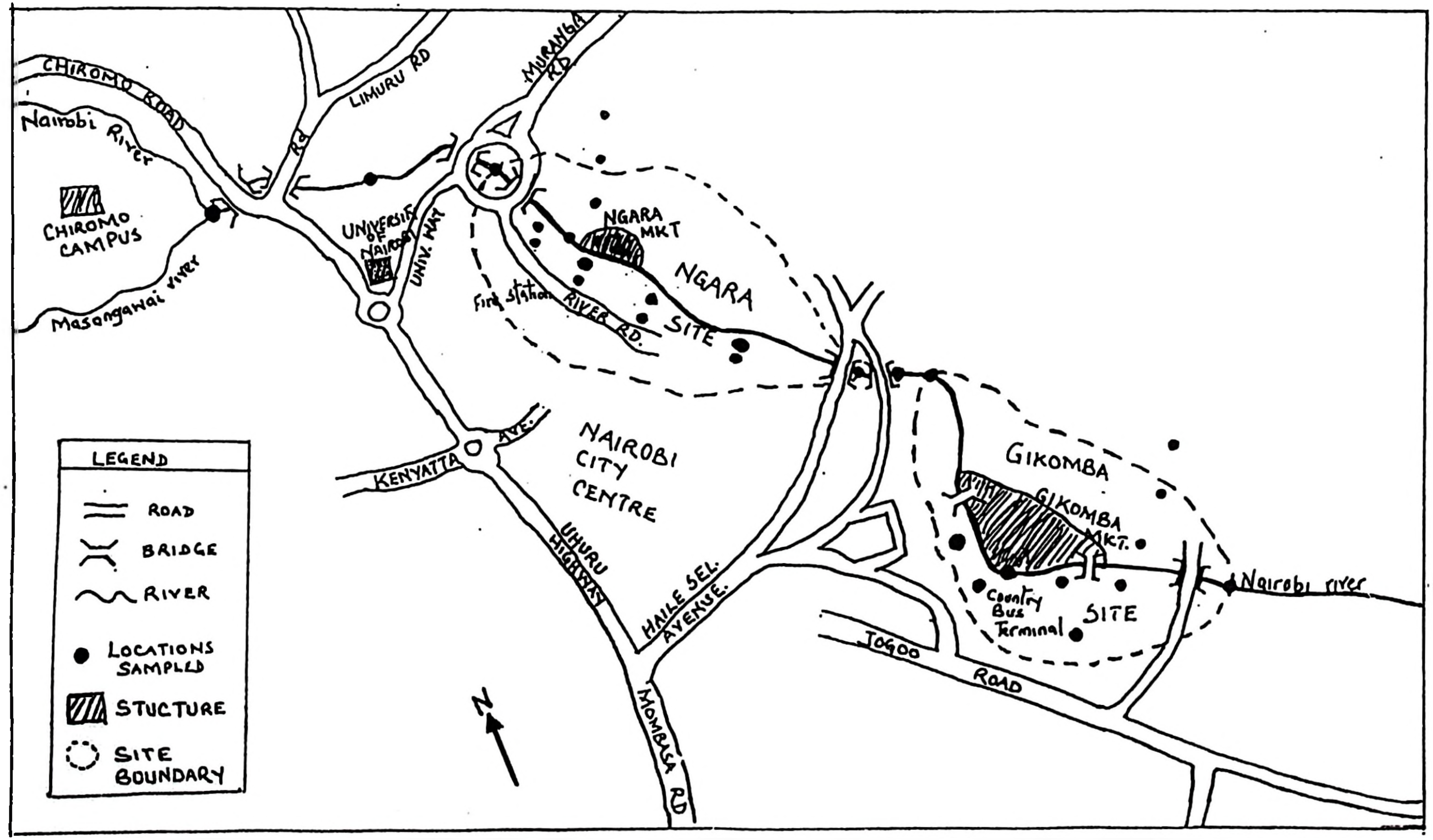
Appendix 2. Distance profiles of the metals in the Gikomba site.



a. Distance profiles of Pb, Zn and Cd in the Gikomba site



b. Distance profiles of Cr and Cd in the Gikomba site



Appendix 3. Sketch map showing locations sampled in and around Nairobi river