CONCENTRATION AND TOXICITY LEVELS OF HEAVY METAL POLLUTANTS IN SOILS AND VEGETATION IN KITWE (COPPERBELT), ZAMBIA.

BY

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DECLARATION

I **MUBANGA STEPHEN LUPUPA,** do hereby declare that this dissertation represents my work and that, to the best of my knowledge, it has not been previously submitted for the award of a degree at this or any other University.

Signed ....

Date 19th February 1997

DEDICATION

To my father **KASEMBE LUPUPA** and mother **LOMBE LUPUPA**.

APPROVAL

This dissertation of **Mubanga Lupupa** is approved as fulfilling part of the requirements for the award of the degree of Masters of Science in Chemistry by the University of Zambia.

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ABSTRACT

In Zambia, mining of minerals is concentrated in the Copperbelt province. This and other industries of the area has brought about environmental degradation through release of possible unwanted toxic substances. The purpose of this study was to obtain the concentration of heavy metal pollutants, and determine the extent of pollution in the city of Kitwe, Zambia.

Cadmium, Cobalt, Copper, Lead and Zinc were investigated up to 20km away from the Nkana smelter in three directions; North-west, West and South-east. High concentrations of metals were detected in soils and plants near the smelter and show inverse relationship with distance from the smelter.

The results ranged between 0.7 to 43mg Co/kg, 6.6 to 5300mg Cu/kg, 1.4 to 30.5mg Pb/kg, 0.5 to 76.5mg Zn/kg in soils and 4.3 to 94.5mg Co/kg, 7.6 to 2330mg Cu/kg and 22.2 to 175mg Zn/kg dry matter in plants. The results were trace for lead in plant samples and trace for cadmium in both soil and plant samples.

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ABBREVIATIONS

AAS	Atomic Absorption Spectrometry
APDC	Ammonium Pyroline Dithiocarbamate
ASV	Anodic Stripping Voltametry
ECZ	Environmental Council of Zambia
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
INAA	Instrumental Neutron Activation Analysis
ISE	Ion-Selective Electrodes
NCEE	National Conservation Environment Education
NCZ	Nitrogen Chemicals of Zambia
PPM	Parts Per Million (mg/kg)
PIXE	Proton Induced X-Ray Emission
WCZ	Wildlife Conservation of Zambia
WWF	World Wildlife Fund
XRF	X-ray Fluorescence
ZCCM	Zambia Consolidated Copper Mines
ZEEP	Zambia Environmental Education Programme

CHAPTER ONE

INTRODUCTION

1.0 INTRODUCTION

Pollution can be defined in various ways. Miller [1] defines pollution as the introduction by man into the environment of substances that can adversely affect the health survival or activities of human and other living organisms. Pollutants are unwanted solid, liquid or gaseous chemicals produced as by-products or wastes when resource is extracted, processed, made into products or used. Pollution can also take the form of unwanted energy emissions such as excessive heat, noise or radiation. Alternatively, pollution has been expressed by Dix [2] as one type of matter in a wrong place [3, 4].

1.1 SOURCES OF ENVIRONMENTAL POLLUTION

Pollution can enter the environment by both natural and human activities. For instance volcanic activity and erosion by water are natural processes and therefore inevitable sources of environmental pollution. However, most natural pollution is dispersed over a large area and is often diluted or broken down to harmless levels by natural processes. In contrast most serious pollution from human occur in or near urban and industrial areas, where large amount of pollutants are concentrated in small volumes of air, water and soil [1, 4].

Some of the pollutants that are added to the atmosphere include carbon oxides (CO_2, CO) largely generated from complete and incomplete combustion of hydrocarbons in petrol engines, Volatile organic compounds or hydrocarbons (HC) arising from combustion of fossil fuels and the oxides of nitrogen and sulfur (NO_x, SO_x) are created by burning fossil fuels particularly those containing sulfur. We also add suspended particulate matter or solid particles like dust, soot, pesticides which include polychlorinated biphenyls (PCBs) and many others. Heat produced when any kind of energy is transformed from one form to another, noise produced by factories, mines, motor vehicles, air planes, cassette players and many others pose a source of environmental pollution [4, 5].

1.2 EFFECTS OF ENVIRONMENTAL POLLUTION

The general effect of pollution produce deteriorating of the quality of the environment. This means pollution is responsible for the dirty streams, rivers and atmospheric contamination. Contaminated environment can have a number of unwanted effects like damage to human health caused by some chemical substances present in the air, food and water. Damage to plants and aesthetic quality of the environment caused by smoke, chemical fumes, dust, dumping of waste and dereliction. All these deleterious factors are affecting our environment in which we reside, work and spend our leisure time [2].

Substances like carbon monoxide at high concentration, causes death in human by blocking oxygen system in blood. SO_x groups of pollutants are highly destructive and very common in metal smelting and coal mining. These also cause adverse chemical reactions to steel structures, power lines, some roofing materials, many natural stones, cement and paints [1, 5]. Long exposure to high noise levels can cause permanent hearing damage and similar exposure to dust can damage lung tissue and in extreme cases cause premature death [1, 5]. Pollution has many other effects on the environment some of which are irreversible.

1.3 HEAVY METAL POLLUTION

Heavy metals are natural components of the lithosphere and as such may be found throughout the ecosystem. It has been known for several decades that trace quantities of certain elements exert a positive or negative influence on plant, animal and human life [6, 7]. Some elements are essential to life and non-toxic, and hence non-polluting in certain formulations [1]. Heavy metals, recognised as highly toxic and dangerous pollutants, are placed only second to pesticides in environmental importance [8]. Metals are not biodegradable, as a result they accumulate in vital organs of man and exert progressively long term growing toxic actions. The metal concentration by body tissues of invertebrates, including insects, have been reported by several authors. Suzuki et al. [9] collected the larvae of mayflies in a metal contaminated river. The copper concentration was 18.4 times higher than in those from the non-contaminated river.

Stary and Kubiznakova [10] have determined content of heavy metals in several species of formica in two different polluted areas. Pihlajamaki et al. [11] analysed the levels of Cadmium, Copper, Zinc, Manganese, Aluminium and Lead in "Laothoe populi (L), Sphinx pnastri (L), Euproctic Chrysorihoea (L) and Malacosoma neustria (L)", by Atomic absorption Spectrophotometry. The level of copper was about twice as high as in their host plants. Below are some of the possible sources from which heavy metal of environment may originate:

1.3.1 **Spoil Heaps**

Heavy metal pollution resulting from spoil heaps is usually a consequence of insanitary habits. In urban areas, soil pollution is associated with dumping on land of domestic refuse and solid resulting from the treatment of sewage and industrial wastes. The soil is thus becoming increasingly polluted with chemicals including heavy metals and products of petroleum industries. These can reach surface and ground water beneath and ultimately get incorporated into food chain in the affected urban ecosystem. Water pollution usually severely damages aquatic communities and, can cause immediate and long term harmful effects to human life [6, 12, 13, 14, 15].

1.3.2 **Industrial Sources:**

Apart from smoke and fumes released from industries, the disposal of industrial solid wastes constitute a major source of environmental pollution by toxic chemicals. These wastes have given rise to severe problems of soil pollution either by poisoning the soil or crops or by eventual entry into surface and ground water sources [13]. Observation of farmland by Burkitt et al. [16] in the neighbourhood of chemical factories have indicated that this is a potential danger of fall out from plume emitted by the stoke-stacks of chemical works.

Mining of minerals involve removing of material from earth's crust and dumping on land of unwanted large masses of rock and waste material somewhere else, usually near mining site, resulting in slimes dams. Toxic substances leach out of such materials enter the soil and run off into streams and ground water. The processing of ores to recover economic mineral results in process effluent which contain suspended solids [17]. Mining, therefore, has severe local, and sometimes regional, environmental impact on land, air and water. Mining of base metals or heavy metals result in gradual release to natural environment of toxic substances of which the most important are metal ions and chemical reagents. It is unusual for lethal concentrations to be released from a mine, however the long term of exposure to sub-lethal doses are uncertain [1, 5, 13]. Spoil tips associated with non-ferrous mines contain anomolously high levels of heavy metals compared with other environments [18]. Table 1.1 shows some industrial and agricultural sources of heavy metals in the environment.

Table 1.1: Industrial and Agricultural Sources for Metals in the Environment

Use	**Metal**						
Batteries and other electricals	Cd	Hg	Pb	Zn	Mn	Ni	
Pigments and paints	Cd	Au	Pb	Zn	Ti	Hg	Mn
	Cr	Al	As	Fe	Sn		
Alloys and Solder Biocides (pesticides, Herbicides preservatives)	As	Hg	Pb	Cu	Sn	Zn	Mg
Glass	As	Sn	Mg	Ca	Na		
Fertilizers	Cd	Hg	Pb	Al	As	Cr	Cu
Plastics	Cd	Sn	Pb				
Textile	Cr	Fe	Al				
Fuel	Ni	Hg	Cu	Fe	Mn	Pb	Cd
Refineries	Ni	V	Pb	Fe	Mn	Zn	
Tannery	Cr	Al					

1.3.3 Atmospheric Sources

Natural and man-made processes have been shown to result in metal containing airborne particulates. Depending on the prevailing climatic conditions, these particulates may be blown by wind over long distances [6]. The trace metal elements present in the atmosphere are eventually removed by precipitation in rainfall or gravitational fall out. There is therefore a continual transfer of trace element contaminants from atmosphere into the water and soil. Therefore air provides a route for contamination by trace metal elements discharged in smoke and fumes. Trace elements contamination of soil from atmospheric pollution from an industrial source lead to accumulation of contaminant elements in the surface horizon, since the trace elements tend to remain near the top soil [19, 20] .

Atmospheric pollution occurs during smelting which results in slag. The dust and toxic metals in these wastes blow into air and water leaches toxic and radioactive substances into nearby surface and groundwater [4, 16].

1.3.4 Miscellaneous Sources of Contamination:

In any urban area incidental contamination include pollution from leaks and effluents, corroding metal objects such as galvanized roofs, tins, cans, objects plated with cadmium and objects made of copper, brass or bronze. Once metal objects become immersed in soil, they are subjected to corrosion and dispersion due to microbial activity. Other miscellaneous sources of environmental contamination include bonfires, discarded car batteries, water from lead cisterns or pipes, middens and general litter. Such sources probably account for the high viability of trace element levels characteristic of soils in urban and industrial areas. The use of chemicals in agriculture such as fertilizers and growth regulating agents results in environmental pollution [12, 19] see Table 1.1.

1.4 ENVIRONMENTAL POLLUTION IN ZAMBIA

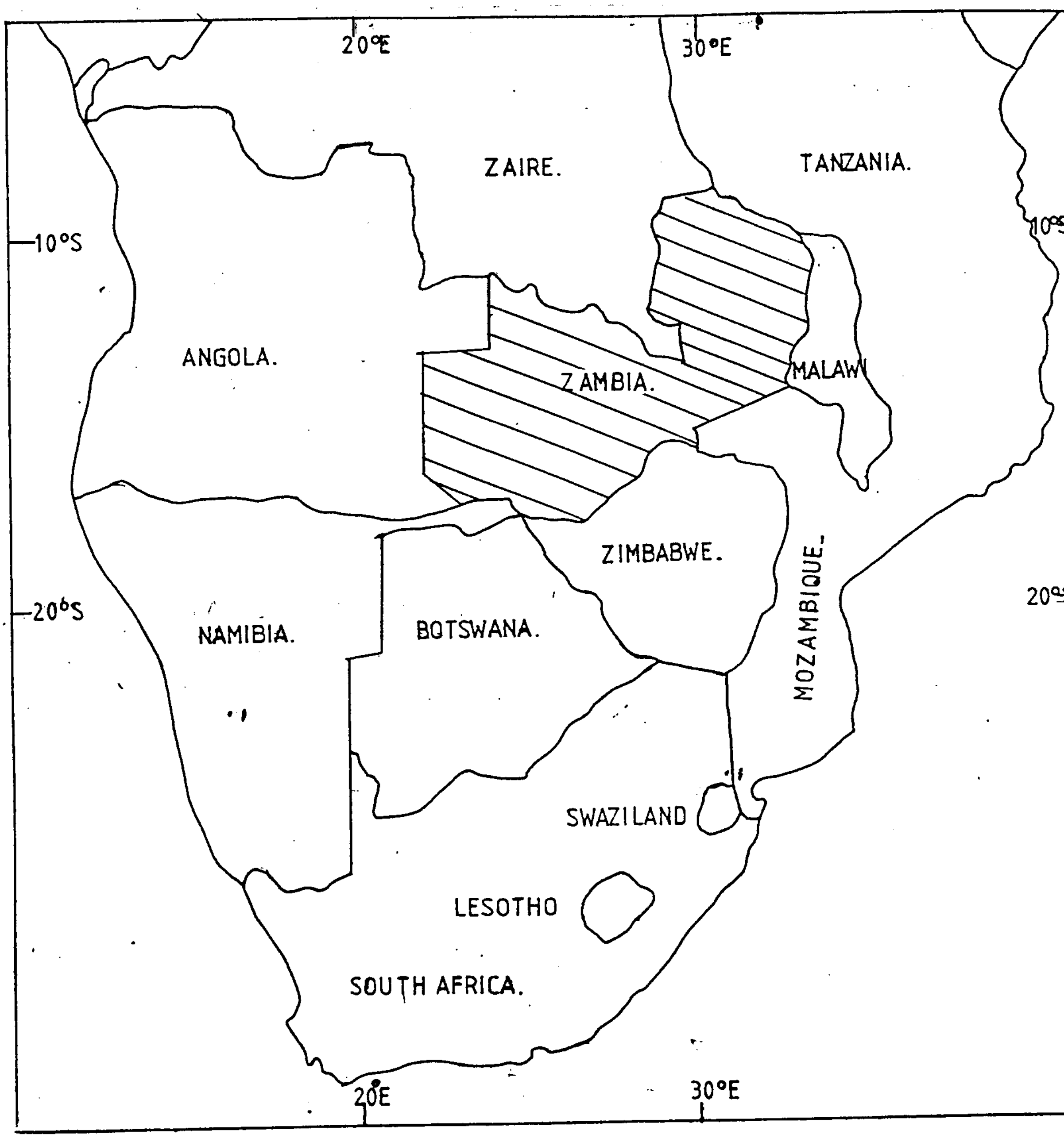
Africa has one of the fastest growing populations and the lowest standard of living. The increasing human population will affect the environment because more land will be needed for agriculture, shelter and recreation. The vast population must be fed, clothed and provided with basic needs. To do this governments in Africa have to adopt chemical technologies which have deleterious effects on the environment [21].

Zambia is a landlocked developing nation situated in Southern Africa (figure 1.1). It is located between latitudes 8 and 18 degrees south and longitudes

22 and 34 degrees east. It has a total surface area of about 752 600km^2 with a high population growth rate. The wildlife conservation society

has warned that the 3.2 percent annual population growth rate in Zambia was a threat to the environment because the natural resources were reduced by the same percentage. The ability of our environment to sustain us determines the future of our nation in social, economic and political spheres. Environmental pollution has become serious in Zambia with the development of modern industry in urban areas. The development of harmful materials in the atmosphere and water sources are increasing and people who are engaged in some special work are more likely to be hurt by pollutants [22, 23, 24]

Figure 1.1: Map showing the position of Zambia in southern Africa



1.5 SOURCES OF ENVIRONMENTAL POLLUTION IN ZAMBIA

Zambia's main sources of environmental pollution are the many industries in urban areas. *Industrial activity in Zambia is mainly confined to areas of Kafue* and Copperbelt towns. In heavily industrialised areas, soil, water and air have become polluted with deleterious effects on the biota [25].

It is well known fact that mining and smelting operations can be detrimental to the environment [26]. The mining industry in Zambia is highly developed and has been identified as the chief polluter on the copperbelt where mining activities are concentrated. Most of the pollution by Zambia Consolidated Copper Mines (ZCCM) arises from the mining and processing of copper and cobalt at the smelters. The smelters are located in Kitwe, Mufulira and Luanshya. The Luanshya smelter is closed. Mining in Zambia has created serious environmental problems in localised areas. It is the main culprit for the environmental pollution in Kabwe, as found by Tembo [27], and on the Copperbelt. It emits large quantities of sulphur dioxide and particulate matter during processing of sulphur-bearing copper ore. ZCCM Nkana division in Kitwe has an acid plant where some of the sulphur dioxide is converted into sulphuric acid. The excess is released into the atmosphere through the stacks. At Mufulira division there is no acid plant and all the sulphur dioxide is discharged into the atmosphere. Sulphur dioxide is also produced during the combustion of fossil fuels (petroleum and coal) as these contain sulphur. The water effluents from ZCCM concentrators contain suspended solids (mainly copper and cobalt) which result in silt being deposited on the river bank [23]. The amount of copper and cobalt in suspended phase in the Kafue river were found by Patterson [25] to be 0.3μg Co/L and 462μg Cu/L at the municipal pump station in Chililabombwe before the river enters the mining area. Downstream at the Kafue mission centre in Kitwe, the amounts were found to be 3340μg Co/L and 3840μg Cu/L. The probable source of the enrichment was the mining processes.

Occupational hazards are often encountered in mining and other working environment. The major hazards arise from dusts, fumes and others. In Chingola there is an open pit mine where workers are exposed to dust, Chilanga cement in Lusaka and Ndola manufactures cement and is one of the major emitter of particulate matter. Cement dust from cement kilns is released to the atmosphere. Ndola Lime Company emits lime (calcium oxide) dust from kilns. Ndola Lime and Chilanga cement are wrongly positioned in the eastern area of Ndola instead of the west. Quarrying operations results in dust emissions. These dusts are solid particles generated by handling, crushing, grinding and disintegrating inorganic materials such as rocks, ore, metal and coal. Coal is mined in Southern

Zambia at Maamba Coal mine by ZCCM. There are effects upon the lung tissue and lung function resulting from inhalation and deposition of dust. The exposure to man leads to respiratory diseases like silicosis from free crystalline silica, talcosis from talc and others described as pneumoconiosis with such dust as amorphous silica, coal dust and natural graphite involved [13].

Asbestos is widely used as a pipe and building material in Zambia. Inhalation of asbestos fibres by workers has been known to produce asbestosis with death from lung cancer as a sequel for many years. The sources of asbestos in the air include processing and manufacturing of asbestos-containing products. The people working in asbestos industries are at risk. Besides asbestos fibres have been demonstrated in lungs of persons not occupationally exposed but in the vicinity of the asbestos factory and asbestos mines. Micheal et al. [28] found that the family members exposed to asbestos fibres brought home on the work clothes of asbestos industry workers may accumulate lung fibre burdens similar to those seen with occupational exposures and may be at risk for mesothelioma. In Kitwe, one of the asbestos factory raised public concern over workers working without protective materials. In USA asbestos is banned for use as water pipe, roofing material etc.

Many other industries take part in environmental pollution in Zambia like Nitrogen Chemicals of Zambia (NCZ) in Kafue which produce sulphuric acid for use in manufacture of fertilizers. The process results in sulphur dioxide emissions. Nitrogen oxide (NO_x) is also emitted during the production of nitric acid and ammonia gas. These fertilizer nutrients are washed down the Kafue river where they enrich the river bed and feed the Kariba weed (a shrub) clogging up the river [29]. This has made the government spend a lot of money trying to clear up the weed which does not even take long to reappear. The Kafue electric gorge downstream is threatened by this weed. The farming areas along the Kafue river bank which uses chemical fertilizers and pesticides over and over again also contribute greatly to the pollution of the river. The Nakambala Sugar estate and Nanga estate also depend on the Kafue river for irrigation. Kafue river is the main source of water for Copperbelt, Lusaka and Kafue town. However the domestic water works in Kafue, which provides water to Lusaka, is wrongly positioned downstream just after the Kafue town. The untreated effluents from NCZ, Kafue tannery, Municipal refuse etc. are released upstream into the river. The domestic water is treated from biological point of view only, and not from the chemical point of view. The effluents are diluted on entering the river. The dilution is more during the rainy season and less in the dry season. Whatever the season, the distance between municipal pump station and effluent release point is very short, and the river does not have the capacity to clean the water to safe levels. The domestic water works therefore must be changed from down stream to a safe point up stream before the Kafue town.

Other potential polluters in Zambia may be dumping even more toxic wastes running into ground and river water, like the pharmaceutical companies. Textile industries like the Kafue textile which releases chemicals used during dyeing processes. Bata tannery releases vast amounts of chromium during tanning processes. Monarch Zambia Limited in Kitwe dumps zinc ash laden with lead from galvanizing process inside its premises. The petroleum sludge on the Copperbelt has not been treated before release. Oil effluents from Indeni Petroleum refinery in Ndola contaminates water in Kaloko and Munkulungwe streams. In 1994, the contamination resulted in an outbreak of a skin disease among pupils at Fatima Girls' Secondary School and residents in the surrounding areas. The fish and other aquatic organisms were killed down the two streams [30, 31, 32].

1.6 POLLUTION IMPACT ON THE ZAMBIAN ENVIRONMENT

The environmental consequences of chemical emissions is a subject of continuous debate. Some of the pollutants are a direct threat to the health of people living in this exposed area.

Mining brings about noise pollution in three categories, these are fixed plant, mobile plant (used internally) and external transport movement. Fixed plant include equipment like crushers or processing machinery, loading facilities and others. Mobile plant used on site is associated with drilling, blasting and service operations. The other source of noise in mining is external movements associated with all mining operations, the despatch of all valuable products and waste and the movement of personnel [13]. As stated earlier long term exposure to high noise levels can cause permanent hearing damage to people.

1.6.1 POLLUTION EFFECT ON AIR

Air pollution may be defined as the presence in the out door atmosphere of one or more contaminants, which can be injurious to human, plant or animal life or property. This unreasonably interfere with the comfortable enjoyment of life and property. The wastes we release into the air change the composition of the air we breath. Depending on the waste constituents and their concentration there is long-range transport of soot, fly-ash and particles which are typical of industrial high temperature processing, (figure 1.5). With varying susceptibility to particular ranges of concentrations, plants and animal are damaged around the area.

Mining is one of the major sources of air pollution in Zambia. This has been confirmed in the state of environment report by the ECZ [30, 31, 33]. The industry releases particulate matter together with sulphur dioxide from the smelters in Kitwe and Mufulira. The sulphur dioxide in Mufulira and Kitwe are rated as severe. The ZCCM standard for sulphur dioxide level is 500 microgram per cubic meter (annual average) which is more than six times higher than World Health Organization (WHO) standard value of 80 microgram per cubic meter. This in combination with other health hazards like particulate matter, has affected and reduced vegetation in the two areas. Nkana west and especially Kankoyo in Mufulira are the most affected areas. The buildings have also been affected and the same emissions are causing disease of respiratory system, diseases of skin and diseases of eyes [30]. These pollution effects are obviously weakening the immune system of the residents of Kitwe and therefore make them more vulnerable to other diseases. People in the Copperbelt area with Human-Immuno deficiency Virus (HIV) could have their immune system go down faster and

AIDS would be pronounced here. In June 1992 an outbreak of cholera hit the Copperbelt province (Kitwe) resulting in 500 deaths. This could be a reflection of poor baseline health and nutritional status of the population of this mining area [34].

Besides the emitted toxic sulphur dioxide causes acid rain or acidic precipitation. This is precipitation having pH less than 5.6, the pH of pure water in equilibrium with atmospheric carbondioxide. Acid precipitation contains normally also various heavy metals as well as elements and organic pollutants. The pollutants sulphur and nitric oxides undergo transformations in the atmosphere leading to sulphuric acid, sulphate aerosols, nitrogen dioxide, nitric acid, ozone and photo-chemical oxidants. Acid precipitation is primarily a result of man-made sulphur emissions and may change the acidity of the soil. The change in acidity will therefore in general change the acidity of the soil and/or pH in streams and rivers of the Copperbelt. Acidification of water has a profound impact on aquatic life affecting all trophic levels. Continued water acidification is a threat to streams, rivers and lakes habouring fish population [35].

The effects on soil of precipitation containing strong acids will depend on a number of fundamental soil properties. The effects may be what is called detrimental or beneficial. Beneficial effects arise, for example, because nitrate (from nitrogen oxide) and sulphate (from sulphur dioxide) are important plant nutrients and because strong acids may enhance the solubility of plant nutrients by increasing weathering of the soil. Since forest growth may also be affected far away from emission sources, the sulphur dioxide emissions from copperbelt smelters may be helping create the right acidic conditions for pineapple growing in Mwinilunga district, North-western Zambia (figure 1.2). Pineapple grow well in rich, well drained loam soils or fertile sandy loam. It is sweet, and it grows where it is too acidic for other crops. An average soil pH of about 5.5 is considered to be suitable for the growth of pineapple [36, 37]. Sulphur is a major plant nutrient. Low doses of sulphur dioxide from the copper mines may therefore have another beneficial effect under conditions where soil is deficient in sulphur. However the extent of emissions from Copperbelt is detrimental to the soil and the environment as a whole.

1.6.2 POLLUTION EFFECT ON LAND

The heavy metals together with sulphur dioxide released into the air from the smelters, are removed by precipitation or by gravitational fall out onto the soil and plants.

Trees and plants are withering because of toxic fumes which are released during processing of the cobalt and copper ore. A large portion has been destroyed and if the situation is not checked Kitwe and Mufulira would face severe deforestation. Deforestation brings about land degradation which is reduction or loss of land capacity to produce what dependent society expects. The increasing desert-like land scape causes decreasing production and productivity failing economies, impoverished biodiversity and perhaps waste of all decreasing ability to combat the scourge. The corrective measure is to start planting new plants in the areas affected in the Copperbelt. In South Africa spectacular success has been achieved in covering the enormous, unstable sand dumps resulting from gold mining operations [87]. In other countries, extremely polluted areas have also been revegetated by use of substances like organic sludge [39].

Land degradation results from the misuse and mismanagement by man and /or our livestock of renewable natural resources. It is our own human activities which causes the loss and degradation of soil. There are many activities we carryout which leave scars on land scape which in time become centres of fertile soil loss. There is no doubt that mining damages most lands. It produces dangerous land slides, and the contamination of surface and ground water when a zone becomes a dump area for mining slag, like the one we have in Kitwe (figure 1.4). Mining causes negative environmental impacts which demand restorative action, to prevent land from becoming irreversibly degraded.

The increasing rate of Zambian population has socio-economic consequences. The relationship between population and environment are reciprocal. The needs and demands of growing Zambian population will affect the environmental quality and resource base. The change in the environmental quality and resource base will affect the standard of life, health, fertility, mobility, income and overall activity of the Zambians. There is serious increase in woodland deforestation, soil erosion and mounting problems of particularly atmospheric and water pollution due to anthropogenic sources. An ever increasing number of Zambian people migrate and enlarge the poverty stricken shanty towns around larger cities like Kitwe in search of a way to survive. Such unchecked urbanization is a factor in economic and political destabilization. Already the streets of most Zambian towns, especially Lusaka, are filled with vendors. However, in Zambia, where demography grows faster than the economy, there can hardly be any solution. This means ways must be found to slow down demographic growth, while developing the economy, an extremely difficult challenge and slow process as it must be based on education.

Soil is not only vulnerable to pollution by the mines but also to several other industrial sources. Where commercial fertilizers have been used over and over contamination of soil has taken place. The use of pesticides does not solve pest problems but increases them by killing beneficial species and building resistance in pests. Farming depends on the quality and therefore the state of preservation of the soil. Our physical development as human beings depends on the quality of what we eat and therefore on the quality of farming. We need to find ways of obtaining food that does not damage or pollute earth's natural systems on which we depend. Of the major economic sectors, the most vulnerable to environmental pollution degradation is agriculture because it is so dependent on natural systems and resources.

1.7 POLLUTION CONTROL IN ZAMBIA

Zambia instituted the Environmental Protection and Pollution Control Act in 1990. The Environmental Council of Zambia (ECZ) was then established in June 1992 in the Ministry of Environment and Natural Resources. The ECZ is an institution charged with responsibility of implementing the environmental protection and pollution control Act of 1990. Since its inception the ECZ has collected data on the environmental degradation and baseline data on pollution [33].

Development has mainly been guided by economic considerations with little or no regard to environmental management. The raising of public awareness is an important element in the promotion of environmental management, unless people are aware of the problems affecting them and consequent results, they would not be encouraged to take action in redressing the situation. The levels of awareness on the environment as well as environmental quality rights among Zambians is low. This is manifested in the widespread negative attitude that prevails among Zambians towards environment. The ECZ is therefore undertaking environmental education and awareness campaigns aimed at creating and enlightening the general public on environmental issues. This is taken as an integral part of the ECZ activities. Although Zambia has no clear-cut environmental education policy, it is guided by education and environmental policies under the Ministry of Education, Environment and Natural Resources. Non-governmental Institutions are also involved in environmental education. Some of these include Wildlife Conservation Society (WCS), Zambia Environmental Education Programme (ZEEP), National Centre for Environmental Education (NCEE) and many others like Child to Child Programme for UNICEF; World Wildlife Fund (WWF) [30, 31, 33].

The ECZ has enacted a series of statutes aimed at protecting land, water, air and wildlife. Activities threatening the related human health and the related ecological concern are subjected to permitting requirements aimed at requiring specific performance standards to be acceptable. The ECZ has formulations of standards and regulations on water pollution and effluent discharge, wastes management and waste water discharge and, pesticides and toxic substances unit. Noise abatement and air pollution control are in place, but regulations to back them are not yet finalised due to lack of expertise in the field. Environmental Impact Statements (EIS) have also been formulated, and wetlands policy documents on natural resources have been drafted [30, 31, 32, 33].

Under the waste management the ECZ has designated certain areas as dumping grounds. Strict rules have been set for companies and institutions to follow in waste disposal, failure to which they will be prosecuted. A governing licence to operate waste disposal site, the licence to transport waste shall be subject to conditions that will avoid spillage during transportation. Vehicles transporting the waste should be such that they do not scatter, pour or emit bad smells from the waste and should follow approved routes to licensed disposal sites or plant [40]. One such disposal site has been designated in Kitwe at Uchi near the agricultural show grounds. A number of industries are taking measures to address the pollution problem. Many are attempting to change the technologies they are using to make them more environmental friendly with the regulation and standards set up by the ECZ. This change can be encouraged in Zambia if the law concerning environmental pollution was made stronger. At the moment the penalty of those companies and institutions polluting the environment is as low as K20.00.

1.8 **OBJECTIVES**

The city of Kitwe is the hub of the Copperbelt Province of Zambia (figure 1.2). It is a copper mining town like Chililabombwe, Chingola, Kalulushi, Luanshya and Mufulira. Copperbelt, Kitwe in particular, has highly developed mining industry. Copper and Cobalt processing is carried out at Nkana smelter in Kitwe. Another smelter is situated in Mufulira (figure 1.3). The smelting of ores has resulted in a "mountain of Kitwe" from the dumping of smelting wastes. The slag is dumped just near the smelter and is evident as one enters the town from Ndola, see figure 1.4. Other toxic substances including heavy metals are released into the atmosphere through chimneys from processing of minerals at the smelter (figure 1.5). Additional tailings waste dump cover vast tracts of land in Kitwe The aesthetic value of the land has been lost in these areas apart from the pollution effect that these have on the environment.

The processing of ores further results in metal effluents containing suspended solids. The suspended solids may range from colloidal (non-settleable) to settleable. Similarly, mine water and surface drainage in contact with ore, tailings and waste rock usually contain suspended solids. Effluents from processing ore contain at least traces of many of these chemical elements associated with ore body [17], in this case Copper and Cobalt. Besides Kitwe stream is one of the highly polluted streams in Zambia by industries. Part of the pollution is caused by the Kitwe City Council for blocked sewers which run along the Kitwe stream. These pollutants eventually find themselves in food chain. The purpose of this study was two fold:

(i). to determine the levels of five heavy metal pollutants, that is cadmium, cobalt, copper, lead and zinc in soils and vegetation near the Nkana Smelter in Kitwe, and

(ii). to determine the extent of heavy metal pollution in the area with reference to internationally accepted safe values.

Figure 1.2: Map of Zambia showing the position of Kitwe in the Copperbelt province

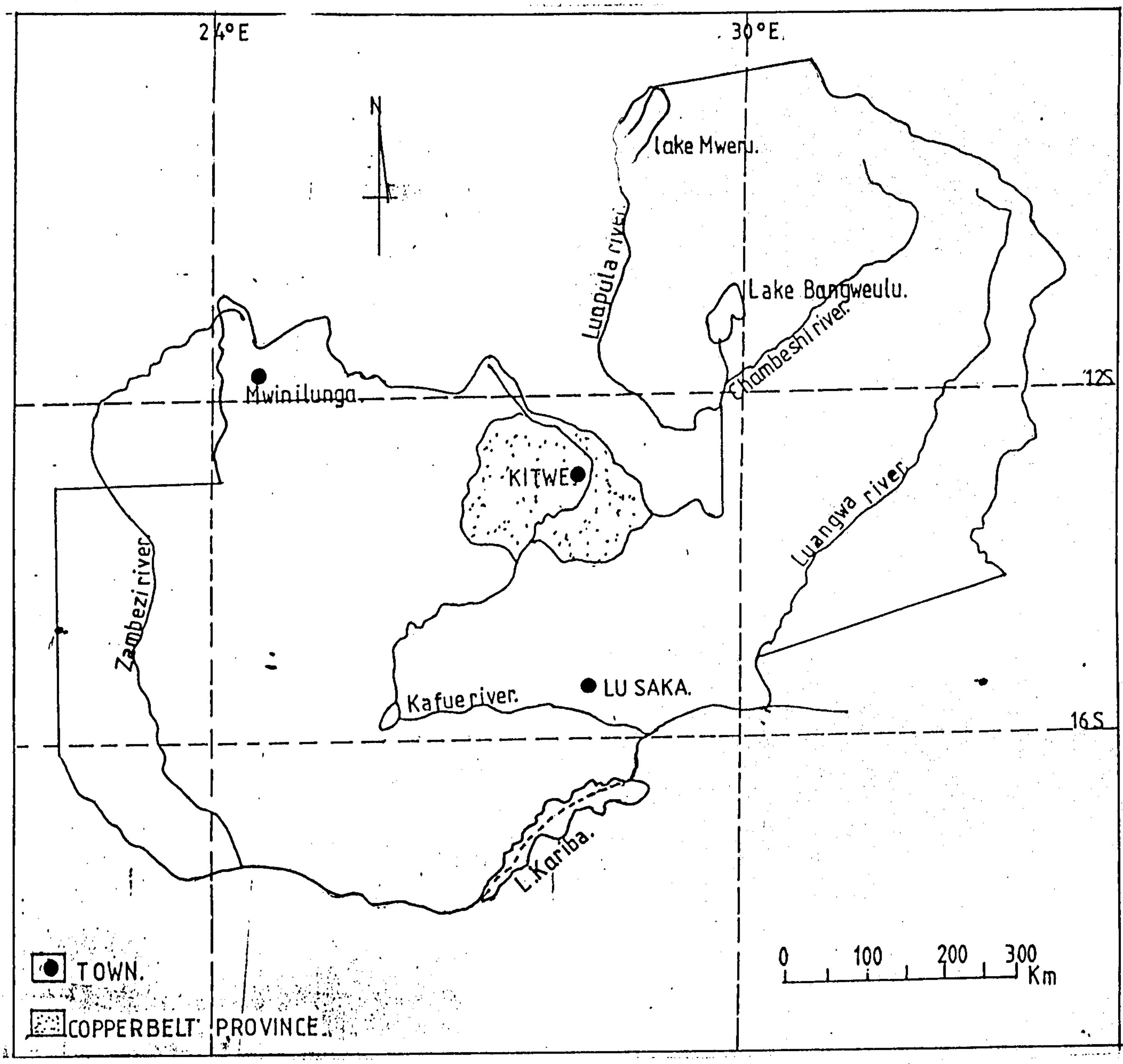


Figure 1.3: Copperbelt towns and minerals mined in the area

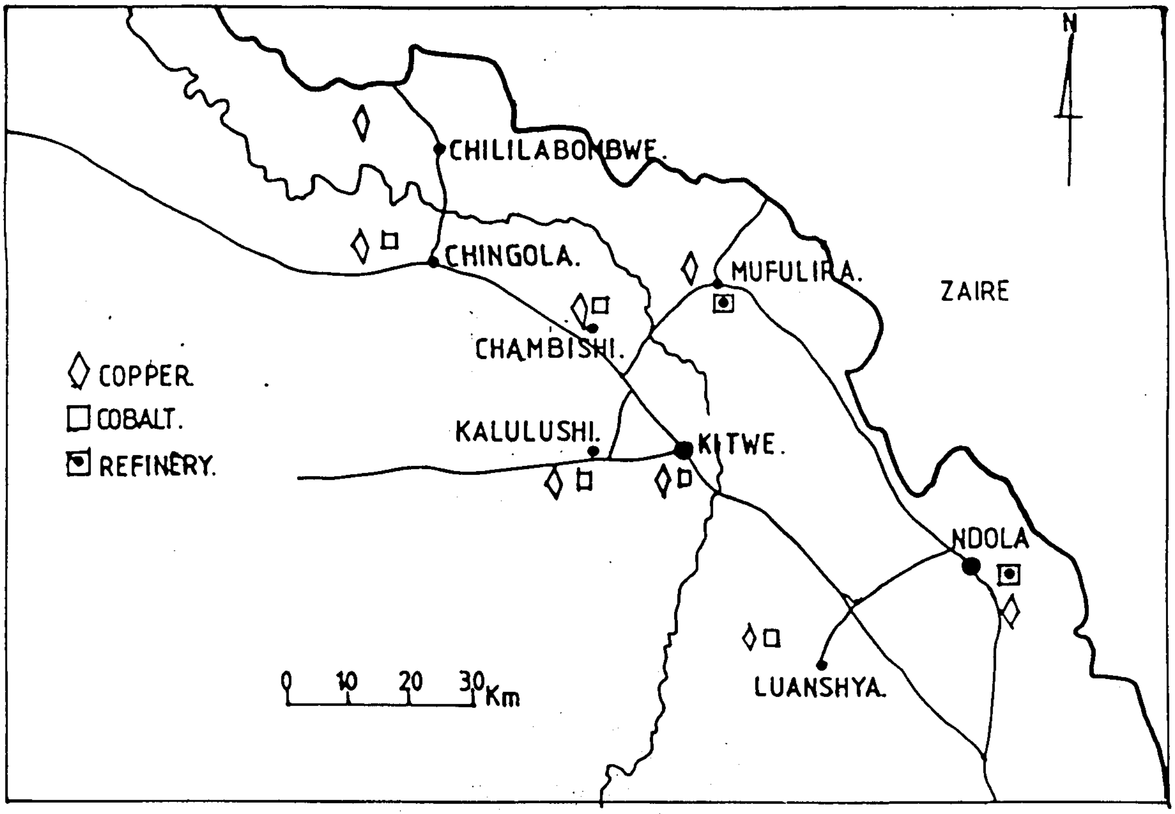


Figure 1.4: Photograph showing slag being dumped on the "hill of Kitwe". The "hill" is formed from the dumping of slag near Nkana smelter

Figure 1.5: Typical picture showing some tall stacks from which particulate emissions are released at Kitwe's Nkana smelter

CHAPTER TWO

THE EFFECTS OF SELECTED HEAVY METALS

2.0 THE EFFECTS OF SELECTED HEAVY METALS

2.1 CADMIUM (Cd)

2.1.1 NATURAL OCCURRENCE OF CADMIUM

Cadmium containing minerals are found in specific parts of the world, although the metal is widely distributed in trace amounts in earth's crust. Primarily *cadmium is closely associated with the natural occurrence of zinc ores.* However higher levels of cadmium are present in sedimentary rocks. Although rare, the predominant ore of cadmium is greenockite (Cadmium sulphide); often associated with deposits of sphalerite (Zinc sulphide) [6, 41, 42]. Cadmium occurs in Zambia and was found to be in excess in both plants and soils in Kabwe area [27].

2.1.2 SOURCES OF CADMIUM

Cadmium is one of the non-essential elements found in the body. Cadmium enters the human environment as a contaminant from mining and metallurgical chemical industries. It is also encountered industrially in the galvanizing industries often as an impurity in zinc used as a starting material [21]. Very high concentration of zinc, cadmium and lead are found near smelting works due to airborne pollution [16]. Municipal refuse contains cadmium from discarded nickel-cadmium batteries and plastics containing pigment and stabilizers [41].

Volcanic activity is a major natural source of atmospheric cadmium. Other sources of cadmium in the environment include scrap metal treatment and manure. Cadmium can also be present in phosphates, which are used as fertilizers, especially in phosphates from Morocco. Old abandoned mines can still be responsible for the continuing contamination of adjacent water courses [43]. An additional source is smoking. Twenty cigarettes cause inhalation of 2-4 micrograms of cadmium [42].

2.1.3 GENERAL EFFECTS OF CADMIUM ON THE ENVIRONMENT

The principal source of cadmium appears to be food rather than water and air [44]. However drinking water normally contains very low concentration of cadmium while most food stuffs contain traces of cadmium. Crops grown in polluted soil (from industrial contamination and from sewage sludge used as fertilizer) or irrigated with polluted water may contain increased concentration of cadmium just as meat from animals grazing on contaminated pastures. The transmission of cadmium through food chain to animals and man can not be avoided.

Cadmium affects the growth of plants in experimental studies. According to Strnad et al. [45], at high concentration of cadmium in soil, the uptake by plants increases with concomitant decrease in yields. Leaf litter decomposition is greatly reduced by heavy metal pollution and cadmium has been identified as the most potent causative agent for this effect.

2.1.4 HEALTH EFFECTS OF CADMIUM

Cadmium is not essential for a human body. It is a major environmental pollutant potentially harmful to health. What makes the cadmium contamination of environment a particularly serious hazard is its pronounced tendency to accumulate in the body. Both plants and animals have been found to accumulate cadmium. Terrestrial invertebrates are relatively insensitive to cadmium induced toxic effects, probably due to the effective sequestration mechanisms in specific organs. When cadmium toxic effects occur, they consist of reduced growth, reduced reproduction and anaemia. Russell et al. [46] fed subadult garden snails "Helix aspersa" on diets containing different levels of cadmium. Food consumption, shell growth and reproductive activity were strongly depressed. In studies by Van Straalen et al. [47], the collembolan "Orchesella cincta" and oribatid mite "Platynothrus peltifer" were exposed to cadmium food. The most sensitive parameters were female growth for "O. Cincta" and reproduction in "P. peltifer".

Acute cadmium poisoning is lethal. Death mainly results from cardio-pulmonary and renal damage [21]. Cadmium poisoning produces proteinurea and affects the proximal tubules of the kidney, causing the formation of kidney stones. Hunter and Johnson [48] monitored small mammals near to an industrial works complex and found that cadmium levels accumulated particularly in the liver and kidney.

Cases of *itai-tai* disease have been found in areas of Japan. In these areas, farmers were using water from Jintsu river to irrigate rice fields. The river was polluted with cadmium metal from a zinc mine situated upstream the affected villages [6]. The toxic effects of cadmium on mammalian testis has been well established [11]. Cadmium is virtually toxic to every system in the body.

2.2 **COBALT (Co)**

2.2.1 **NATURAL OCCURRENCE OF COBALT**

Cobalt is relatively scarce in the earth's crust [6]. It is found in meteorites as either the metal or metal oxide. Common mineral are CoS_2 and CoAs, usually associated with Copper [49]. Cobalt occurs in Zambia and is mined in the Copperbelt area shown in figure 1.3.

2.2.2 SOURCES OF COBALT

The main source of cobalt to human is water and food chain [13]. The element is distributed to soils, plants, animals, humans, micro-organisms, water and others from man-made substances containing cobalt. For instance most fertilizing materials and soil additives have low cobalt. Some however are applied at high rates per hectare making the concentration of cobalt appreciable. Other sources of trace quantities of cobalt are contaminants and dust from industrial products such as extra-hard steel, cement carbides, high temperature carbides and nickel electroplating. Human sources also include cobalt production and handling [13, 50].

2.2.3 HEALTH EFFECTS OF COBALT

The essential elements such as cobalt, copper and zinc are required for the normal growth and maintenance of health of plants and animals [19]. The known nutrient human function of cobalt is as a constituent of vitamin B_{12} (Cyanocobalamine) molecule. This element is bound to protein in foods of animal origin. But there are other forms of cobalt in other species. So it may be bioactive in other forms in humans as well.

Vitamin B_{12} is a large molecule with one atom of cobalt in the centre of its structure. This structure is necessary for the normal functioning of all body cells, particularly those of the bone marrow, the nervous system and gastrointestinal tract. Cobalt plays a part in the prevention of pernicious anemia by its association with Vitamin B_{12}. Pernicious anemia is characterised by disturbances in the gastrointestinal tract, nervous and blood forming systems. Symptoms include megaloblastic anemia, glossitis and neurological signs such as numbness and tingling of the hands and feet, poor coordination, agitation depression and dim vision. The chief cause of pernicious anemia is the absence of the intrinsic factor which has the effect of withholding vitamin B_{12} from the body [6, 44, 51, 52].

Liver, muscle meats, eggs and milk provide enough vitamin B_{12} to prevent deficiency under normal circumstances. Strict vegetarians who restrain from using milk and eggs as well as flesh foods may be at risk of developing vitamin B_{12} deficiency. They are advised to include vitamin B_{12} in their diets [51].

Ingestion of toxic levels of cobalt affects haemoglobin content and produces polycythaemia and hyperlipaemia. Cobalt is considered to be a goitrogenic agent. The symptoms of poisoning are cardiac insufficiency, mycardial failure and chloritic in bean decrease yield of cabbage etc.

2.3 COPPER (Cu)

2.3.1 NATURAL OCCURRENCE OF COPPER

Copper is found in nature in trace amounts in a variety of minerals that make up the common rocks. Copper ores occur principally as a mixed iron-copper-sulphate (chalcopyrite). Chalcopyrite is by far the most abundant being found widely dispersed in rocks and concentrated in largest copper deposit. In nature copper forms sulphides, sulphosalts, sulphates, carbonates and other compounds. Copper also occurs as a native metal in small flakes and particles. Common minerals found in Zambia include Azurite [$Cu_3(OH)_2(CO_3)_2$], Covelite (CuS), Bornite (Cu_5FeS), Chalcocite (Cu_2S), Chalcopyrite ($CuFeS_2$), cuprite (Cu_2O), Chrysocolla ($CuSiO_3 \cdot 2H_2O$), malachite ($Cu_2(OH)_2CO_3$) and others [42, 53, 54]. The ores are mined by open cast and deep shafts. Copper is by far the most important mineral mined in Zambia and is the main foreign exchange earner.

2.3.2 SOURCES OF COPPER

The primary route of copper entry into the environment is the weathering of rocks and the associated processes of soil formation. Copper in the atmosphere comes from a wide variety of natural and anthropogenic sources. Natural sources include wind blown dusts, volcanic particles, forest fires and others. The human sources of pollutant copper in the atmosphere are copper production and handling, *iron and steel production and fossil combustion. Copper emissions comes from* point sources such as smelters, utility plants and incinerator. Copper in the atmosphere is incorporated into rainfall and washed down to the soil, streams and rivers. Copper is also contained in a variety of foods and can be transferred to food from copper cooking dishes if the food actually comes into contact with the copper. Copper occurs in many of the same foods as does iron. Meats particularly liver and kidneys, nuts and dried legumes are excellent sources of copper [51, 55].

2.3.3 GENERAL EFFECTS OF COPPER ON THE ENVIRONMENT

The accumulation of copper in the soil and on foliage of crops and native plants has caused serious effects. It has resulted in decrease in plant yields, deaths of livestock, poisoning of soils and water bodies [45]. The effects may occur to biota above or below the soil at considerable distances from the source, as a result of either long distance plume dispersal or drainage from soil into water bodies. Copper in solution imparts a colour and undesirable taste to drinking water [42, 53].

2.3.4 HEALTH EFFECTS OF COPPER

Copper is an essential nutrient to the healthy life of many plants and animals. In plants it is necessary for respiration. It is present in all body tissues with the highest concentrations in liver, kidney, brain and heart. A number of copper containing enzymes have been identified. The mineral is also involved in many ways with the functioning of iron in the body. It appears to be necessary for the normal absorption of iron from the gastrointestinal tract, for its transport, and for its incorporation into haemoglobin. Normal use of iron in the body is therefore dependent on adequate intake and utilization of copper. A copper containing protein, ceruloplasmin, is necessary for the release of iron from storage in the body. Thus copper deficiency may result in iron deficiency even when the body has adequate iron stores. Copper is also essential for the normal development of bone, the central nervous system, connective tissue and melanin formation [19, 42, 51, 52].

Deficiency of copper in plants like tomato manifests itself in very stunted growth of shoots, exceedingly poor root development, curling leaves and absence of flower formation [54]. Deficiency of copper is rare in human beings. However copper deficiency causes alterations in immune system due to altered activity of cuproenzymes [55]. If copper intake is low on a continuing basis, then anemia and decreased rate of cellular oxidation in liver, muscle and nervous tissue lead to lassitude. In adults if copper intake is marginal on a continuing basis, then the risk of coronary heart disease is increased. Copper deficiency has been seen in children with iron-deficiency anemia and with Kwashiorkor. About 1-3mg daily will apparently maintain the copper balance in an adult [51, 56]. Some pastures may lack copper, so grazing cattle on the herbage may develop anemia due to lack of copper.

Although copper is an essential element, excessive intake of the metal can have serious toxic effects in mammals. Excess copper causes Wilson's disease in which the quantity of ceruloplasmin is limited and results in excessive storage of copper in the liver and brain which may lead to mental illness and death. Large doses of copper by man also leads to severe mucosal irritation and corrosion, capillary damage, hepatic and renal damage, and central nervous system irritation followed by depression [42, 44, 56].

2.4 LEAD (Pb)

2.4.1 NATURAL OCCURRENCE OF LEAD

Lead is a natural constituent of the earth's crust. It occurs naturally in plants and in soils throughout the world. It has always been present in man's environment. Lead is present in a number of minerals, the principle one being galena (lead sulphide, PbS), lead carbonate ($PbCO_3$) and lead sulphate ($PbSO_4$). In Zambia galena is mined in Kabwe area by ZCCM from the zinc-lead mine.

2.4.2 **SOURCES OF LEAD**

Lead has been widely used for various purposes in many places and some contamination of the environment has occurred. It is released into the environment from natural sources as well as human industrial activities [57]. The major source of lead in the environment of significance to living organisms, arise from lead mining and the refining and smelting of lead and other metals. The metal is distributed widely by atmospheric transport of aerosols, dust and smokes.

The major source of contamination of the soil from atmospheric pollution is undoubtedly the exhaust of motor vehicles using petrol to which tetraethyllead has been added [19, 58]. Tetraethyllead is added to the fuel as an "anti-knock" to improve engine performance [4]. Lead is released in exhaust fumes largely as minute particles of inorganic lead compounds. This has resulted in lead concentration being highest in soils, vegetation and organisms close to the roads where traffic is high [20, 50, 59, 61]. Khalid et al. [62] analysed soil samples from different areas of Baghdad and found that lead concentrations were highest in areas of high traffic volume and city centre. Chow [63] established, that lead detected in soil and dried grass derived exclusively from alkyllead compounds added to petrol. For obvious toxic reasons, developed countries avoid using leaded petrol instead unleaded petrol is increasing world wide. In 1972 the use of Tetraethyllead and Tetramethyllead was over 440 x 10^6 kg, but by 1982 it had fallen to 143 x 10^6 kg and it was projected to 91 x 10^6 kg by 1986. The US centre for environmental health estimated there would have been 80% fewer cases of lead toxicity among children if lead had been eliminated from gasoline entirely between 1977 and 1981. In 1985 the US environmental protection agency moved the date after which lead could no longer be put into gasoline up to 1988 [64]. In Israel the lead content of petrol has been steadily decreasing over the past few years from 0.42 grams per litre to 0.15 grams per litre. Unleaded petrol has also been introduced [65].

Other man made sources of lead contamination of the environment include: Copper and Zinc smelting, production and repair of leaded batteries, manufacture of brass and leaded paints, agricultural chemicals, sewage sludge, the burning of lead painted surfaces, the burning of coal and the incineration of lead plastics and others. Lead glazed earthen ware and flaking paints from buildings are possible sources of lead exposure in a domestic environment. The type of housing to which the child is discharged has a major influence on blood lead levels because of the accidental chewing of objects [12, 13, 21, 42, 44]. The metallic lead deriving from short-gun cartridges or used as fishing weights is lost in the environment and often remain available to organisms [58, 59].

2.4.3 GENERAL EFFECTS OF LEAD ON THE ENVIRONMENT

Lead has been recognized as an industrial hazard for many years and its long term effects as an environmental hazard has become important [66]. Humans absorb lead from air they breath, from water and from food they eat. Food is the major source of intake of lead in adults who are not occupationally exposed [12, 13, 42]. In Zambia we are still using mostly leaded gasoline. Leaded gasoline is the main source of atmospheric lead because nearly all the lead added to gasoline gets back to the environment through air. The people living in Zambian cities are therefore exposed to air contaminated with lead, especially Lusaka which has a large volume of traffic moving in a relatively small area. Though most lead starts as airborne pollution and is dispersed by atmospheric transport, it eventually settles on land, water and buildings. Food crops grown in lead contaminated soil contain small quantities of lead as a result of some absorption of the metal from soil and because of deposition on the surfaces from lead in the air [67]. Acute level in plants causes decrease in yields [45]. The land spreading of Municipal sewage contains elevated concentration of heavy metals.

2.4.4 **HEALTH EFFECTS OF LEAD**

Lead is not known to be essential for functioning biological systems and the general view is that where possible the exposure to lead should be kept as low as possible [6]. Lead in high doses is highly toxic and it has been recognised as a cumulative general metabolic poison [68]. Lead is toxic because it mimics many aspects of the metabolic behaviour of calcium and inhibits many enzyme systems. Lead poisoning can cause severe mental retardation or death. Lead toxicity in animals and humans is attributed to its action on neuromuscular system [44, 69]. Lead interferes with the kidney function and blood forming processes. Lead has been associated with hypertension in adults and even low levels of lead has been shown to cause mental retardation [12, 21, 42]. Thus lead has an obvious potential to disturb learning ability, adaptive responses and other aspects of behaviour. Interaction of lead and the brain, particularly developing brain, takes the form of mental retardation, lower intelligence quotient and behavioural abnormalities.

2.5 ZINC (Zn)

2.5.1 NATURAL OCCURRENCE OF ZINC

Zinc is one of the most abundant metals. The common zinc containing minerals include Zinc blende or Sphalerite ZnS; Marmatite (ZnFe)S, Calamine or Smithsonite $ZnCO_3$ and many others. Zinc blende is often associated with the sulphides of other metals like lead, cadmium, copper and iron [42, 70]. In Zambia Zinc blende is mined in Kabwe area. Tembo [27] found excess zinc in soils, and plants near the zinc-lead mining area in Kabwe.

2.5.2 SOURCES OF ZINC

Zinc is present in small or trace amounts in all living matter. In humans, a total of 2 to 3 grams of zinc is distributed throughout the body with the highest concentrations found in tissues of the eye and male sex organs [51]. Food is by far the largest source of zinc to humans. Meats and dairy products are richest in zinc. A gross of excess may be ingested from acidic foods that are stored in galvanised containers [42]. Man made sources of zinc into the environment is due to zinc mining and processing operations. Other industries using zinc also contribute to the environmental contamination.

2.5.3 HEALTH EFFECTS OF ZINC

Zinc is an essential nutrient for both animals and man. The nutrient function of zinc is primarily as a constituent of numerous enzymes such as thymidin kinase, which is necessary for nucleic acid synthesis; carbonic anhydrase, which is involved in carbondioxide transport; lactic dehydrogenase, which is involved in the interconversion of pyruvic to lactic acid; and alkaline phosphate which liberates inorganic phosphates [42, 44, 45]. Important in the formation of protein, zinc is necessary for growth and for normal sexual development in children.

Zinc deficiency syndromes have developed in farm animals in areas of the USA where soils were lacking in available zinc. Deficient intake of zinc results in observable effects; growth retardation or dwarfism and sexual infantilism results from decreased thymidine kinase activity which reduces DNA synthesis and cell division; decreased appetite; decreased sense of taste and smell; skeletal abnormalities, zinc deficiency also causes skin lesions, poor healing of burns and other wounds where high zinc losses occur. However most of the effects of zinc deficiency are improved by increasing the daily intake of zinc.

Zinc toxicity is known to occur. If an excess is ingested all at one time, then vomiting, dehydration, electrolyte imbalance, nausea, lethargy, dizziness, abdominal pain, drousiness and lack of muscular coordination results [42, 44, 56].

CHAPTER THREE

METHODS OF CHEMICAL ANALYSIS

3.0 METHODS OF CHEMICAL ANALYSIS

Several methods have been used to determine trace elements in environmental matrices. In early years gravimetric, colorimetric and volumetric techniques were employed. The more common colorimetric involved formation of soluble metal complexes chealates with such organic compounds as dithizone, O-phenanthroline and Ammonium pyroline dithiocarbamate (APDC). Modern methods such as pulse polarography, differential pulse polarography, Anodic stripping voltametry (ASV) and the use of ion-selective electrodes (ISE) are based on electrochemical principles.

Other methods employ nuclear related techniques. These include proton-induced x-ray emission (PIXE), instrumental neutron activation analysis (INAA), X-ray fluorescence (XRF) and inductively coupled plasma mass spectrometry (ICP-MS) [71]. However most of these are expensive and not available at the University of Zambia. In this study Atomic absorption spectrometry (AAS) was used.

3.0.1 GENERAL PRINCIPAL OF ATOMIC ABSORPTION SPECTROMETRY

Atomic Absorption Spectrometry (AAS) uses the basic principle of Kirchoff's law. The atoms absorb spectral lines at exactly the same energy as they emit. It is a highly specific means of elemental analysis based on the selective absorption of line radiation by atomic species in the vapour phase. To observe the atomic absorption signal it is necessary to generate a population of free, neutral atoms of the element of interest [72].

3.0.2 Absorption process:

Since a photon behaves rather like an alternating electric field, it can interact with negatively charged electrons in an atom. Under certain conditions this interaction can lead to a photon being absorbed by an atom. The energy levels are quantized, that is, they can have certain well defined energy levels. An important consequence of this is that the photon, hν, must be exactly equal to the energy separation between a filled energy level (ground state, E_0) and an unoccupied energy level (excited state, E_1).

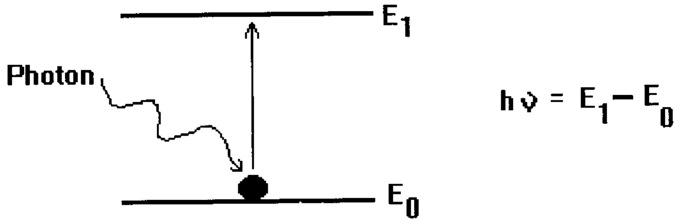


Figure 3.1: **Representation of an absorption process.**

The wave in figure 3.1 represents a photon colliding and being absorbed by an atom in ground state E_0. The straight arrow represents the excitation of the atom from E_0 to excited state E_1. The photon atom interaction forms the basis of Atomic absorption spectroscopy [73].

The absorption follows the Beer's Lambert law. That is the absorbance is directly proportional to the path length in the flame and to the concentration of atomic vapour in the flame. The pathlength is kept constant and the concentration of atomic vapour is directly proportional to the concentration of the analyte in the solution being aspirated. A calibration curve of concentration versus absorbance is prepared [74].

3.0.3 INSTRUMENTATION

Atomic absorption spectrometers can be thought to consist of three parts:

1. light source
2. cell (flame)
3. light detection system (monochromator, detector and readout).

3.0.4 SOURCE

The source used in Atomic Absorption Spectrometry is exclusively a hollow-cathode lamp (figure 3.4). It is a sharp line source that emit spectral lines exactly the same energy as the absorbing atoms in the cell (flame). It consists of a tungsten anode and a cathode made of the element to be determined. An alloy of several elements is used in a cathode lamp. Some of the emitted characteristic spectral lines of the element, which are passed through the flame, become absorbed because they contain just the right energy and the right wavelength to result in the discrete electronic transitions [73, 74, 75, 76].

3.0,5 **BURNER**

The burner is the part in which the neutral atoms and ions are formed in the gaseous state. Combustion flames are widely used in the atomization of samples (conversion of the sample into atomic vapour). The sensitivity of Atomic Absorption technique is very dependent on the flame to vapourize the solution. In the flame atomization, the aqueous solution of the sample is dispersed (nebulized) and then mixed with gaseous fuel and oxidant that carry it into the burner where combustion takes place at the tip [72, 74, 75, 77, 78].

3.0.6 **DETECTOR:**

The light emitted from the source undergoes absorption and the resulting light intensity is measured by the detector. The detector normally used is the photomultiplier since this is very sensitive and has fairly uniform response to light over the visible-UV region [68, 69].

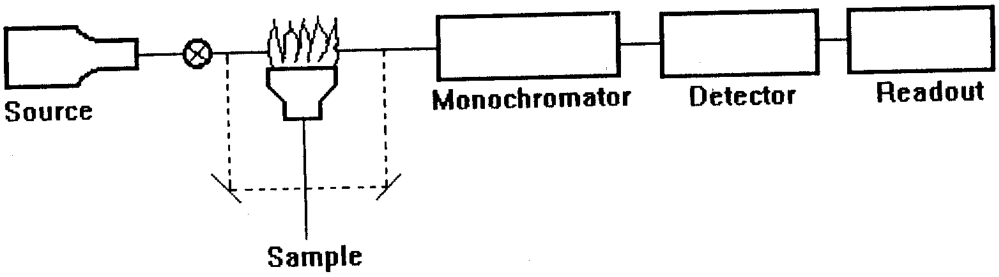


Figure 3.2: Schematic diagram of an Atomic Absorption Spectrometry

3.0.7 ADVANTAGES OF ATOMIC ABSORPTION SPECTROMETRY (AAS)

AAS is useful for determination of trace metals and is almost independent of the molecular form of the metal in the sample. The sensitivity and selectivity of the AAS method is quite high for most elements and thus is the most frequently used method for trace metal analysis in aqueous solutions. Flame atomic absorption spectrometry has a sensitivity of 0.5μg/ml for cadmium, 2μg/ml for cobalt, lμg/ml for copper and 10μg/ml for lead. One of its principal advantages is that determination can be carried out in the presence of many other elements without interference. It is most widely used of all the atomic methods because of its simplicity, reproducibility, effectiveness and relatively low cost [21, 71, 73, 76, 79].

3.0.8 EXPERIMENTAL

Soil samples were shaken on an MK V mechanical shaker (L.H engineering Co. stoke pages, England) and filtered by using Whatman No.42 ashless filter paper. Vegetation (grass and vegetable) samples were dried in HIRASAWA, TEHER CONSTANT TEMPERATURE OVEN (JAPAN) before grinding using RETCH. GNBH 5657 HAAN (GERMANY) hammer mill. The CARBOLITE SHEFFIELD FURNACE (ENGLAND) was used to dry-ash the samples. All the heavy metals were estimated by Atomic Absorption spectrometry using Varian techtron 1000. All solutions were prepared from analytical grade reagents and distilled deionized water obtained from AQUARIUS 65-50 (JAPAN). Measurements were done in the air-acetylene oxidizing flame under conditions given in table 3.1.

Table 3.1 Parameters under which the instrument was set when determining the five heavy metal elements

Parameter	Cadmium	Cobalt	Copper	Lead	Zinc
Current, I (mA)	5	5	5	5	5
Wavelength, (nm)	228.8	240.7	324.7	217.5	213.9
slit-width	0.5	1.0	0.2	1.0	0.2
Flame	air-ace*	air-ace*	air-ace*	air-ace*	air-ace*
Source:	cadmium Cathode Lamp	Multi-element Lamp	Copper cathode Lamp	Lead cathode Lamp	Zinc cathode Lamp
Manufacturer:	Varian techtron	Varian techtron	Varian techtron	Varian techtron	Varian techtron

Air-ac*: Air acetylene oxidizing flame

3.1 STUDY AREA

The study area is the copper mining town of Kitwe around the Nkana Copper Smelter. The area's potential polluters are described in the introduction.

3.2 SAMPLING

Three types of samples were collected for experimentation. These are soil, grass and edible vegetable samples. Taking the Nkana smelter as the centre, samples were collected from three accessible directions. Representative samples of soil and grass were collected from each point shown on the sketch map by the mark "X" (figure 3.3). The three directions sampled are generally:

(i) West of the Nkana smelter

(ii) North-west of the Nkana smelter

(iii) South-east of the Nkana smelter

The three directions were considered because the winds in the area mainly blow from east to west (easterly winds).

3 2 1 **SOIL SAMPLES**

Representative soil samples were collected from each of the points indicated on the sketch map (figure 3.3) at about 0, 5, 10, 15 and 20km from the smelter. Samples at zero distance were collected near the mine (smelter). The samples were collected up to 20cm depth using a soil sampler (Auger). All samples were collected in polyethylene plastics ready for treatment and preparations at the laboratory.

3.2.2 **GRASS SAMPLES**

The giant grass was chosen for sampling because it is very common in the area and was readily available at most of the sampling points. Representative grass samples were collected at or near each site where soil samples were collected. These too were packed in polyethylene plastics ready for treatment and preparations at the laboratory.

3.2.3 **VEGETABLE SAMPLES**

Vegetable samples were collected in two categories. First, the vegetable samples were collected from the nearest point to where soils and grass samples were collected in the three directions indicated above. The vegetables were collected from about five kilometres from the smelter onwards. There was nothing grown nearest the smelter at or near points indicated as zero kilometres in case of soil and grass. Pumpkin leaves were preferred for sampling as pumpkins are widely grown and were in season at the time of sampling (January).

The second category of edible vegetable samples were collected at random from some residential areas of Kitwe. Vegetable samples from backyard gardens were collected in polyethylene plastics just like soil and grass for transportation for analysis. The following are the residential areas shown in figure 3.4 from which vegetable samples were collected: Buchi, Chimwemwe, Kwacha, Mindolo-Miseshi, Ndeke village, Nkana east, Nkana west, Twibukishe and Wusakile.

3.3 SAMPLE PREPARATIONS

3.3.1 SOIL SAMPLES

The soil samples were air-dried, ground in a porcelain mortar with a porcelain pistle. The ground soil was then passed through a 2mm plastic sieve. 20.0g of air dried and sieved soil was weighed in a 250ml Erlenmeyer flask. 100ml of 0.5M nitric acid was added and then shaken for thirty minutes on a mechanical shaker. The suspension was then filtered, using Whatman No. 42 ashless filter paper. The filtrate was collected in polyethylene bottles ready for determination of cadmium, cobalt, copper, lead and zinc. Duplicate blanks were carried out through same parallel steps of the sample preparation procedure [16, 18, 80].

3.3.2 **GRASS SAMPLES**

Grass samples were first cut into smaller pieces using stainless steel scissors and dried in an oven at 110^0C to constant weight. The dried material was ground in a hammer mill. The hammer mill was thoroughly cleaned before the next sample was ground.

2.000 grams of each of the ground sample were dry-ashed in a furnace at 450^0C for three hours in porcelain crucibles. The ash was transferred quantitatively into a 100ml beaker by means of 20ml of lM nitric acid (AnalaR). The sample was digested by boiling on a heating mantle for thirty minutes. The suspension was then filtered on an ash free filter paper (Whatman No. 42) into a 100ml volumetric flask. The washings were decanted through the same filter paper and solution made up to the mark with distilled deionized water. Determination for cadmium, cobalt, copper, lead and zinc were carried out on this solution.

3.3.3 VEGETABLE SAMPLES

Vegetable samples were dried at 110^0C to constant weight, ground and then prepared for analysis following the same procedure as for grass samples. Duplicate blanks were carried out through the same parallel steps of the sample preparation procedure [59, 68, 80].

3.4 PREPARATION OF STANDARDS

Preparation of all working standards were done using distilled deionised water.

3.4.1 Standard Cadmium Solution

1000 ppm Cadmium stock solution was prepared by dissolving 2.1032g Cadmium (II) nitrate, $Cd(NO_3)_2$, AnalaR in a minimum amount of distilled deionised water and diluted to 1000ml. 10.0ml of stock solution was diluted to 100ml to form a 100ppm solution. Calibration standards containing 0, 0.1, 0.4, 0.8ppm Cadmium were prepared.

3.4.2 **Standard Cobalt Solution**

1000ppm Cobalt stock solution was prepared by dissolving 1.000g of cobalt metal in a minimum 1:1 nitric acid (AnalaR) and diluted to 1000ml. 10.0 ml of stock solution was diluted to 100ml to form 100ppm solution. Calibration standards containing 0, 0.2, 0.5, 0.6, 0.8 and 1.0 ppm Cobalt were then prepared.

3.4.3 **Standard Copper Solution**

1000ppm Copper stock solution was prepared by dissolving 1.000g copper metal in a minimum of 1:1 nitric acid (AnalaR) and diluted to 1000ml. 10.0ml of stock solution was diluted to 100ml to form a standard solution containing 100ppm copper. Calibration standards containing 0, 0.2, 0.5, 0.8, 1.0, 2.0ppm Copper were prepared.

3.4.4 **Standard Lead Solution**

1000ppm of lead stock solution was prepared by dissolving 1.5985g lead (II) nitrate, $Pb(NO_3)_2$, (AnalaR) in distilled deionised water and diluted to 1000ml. 10.0ml of this stock solution was diluted to 100ml to form a 100ppm lead solution. Calibration standards containing 0, 0.5, 1.0, 1.5, 2.5, and 4.0ppm Lead were prepared.

3.4.5 **Standard Zinc Solution**

Zinc atomic absorption standard solution (1ml ≅ 1.00mg Zinc ≅ 15.3mmol./L) was used to prepare working standards. 10.0ml of this stock solution (≅ 1000ppm) was diluted to 100ml to form a 100ppm Zinc solution. Calibration standards containing 0, 0.2, 0.3, 0.4, 0.6, 0.8 and 1.0ppm Zinc were prepared [80, 81].

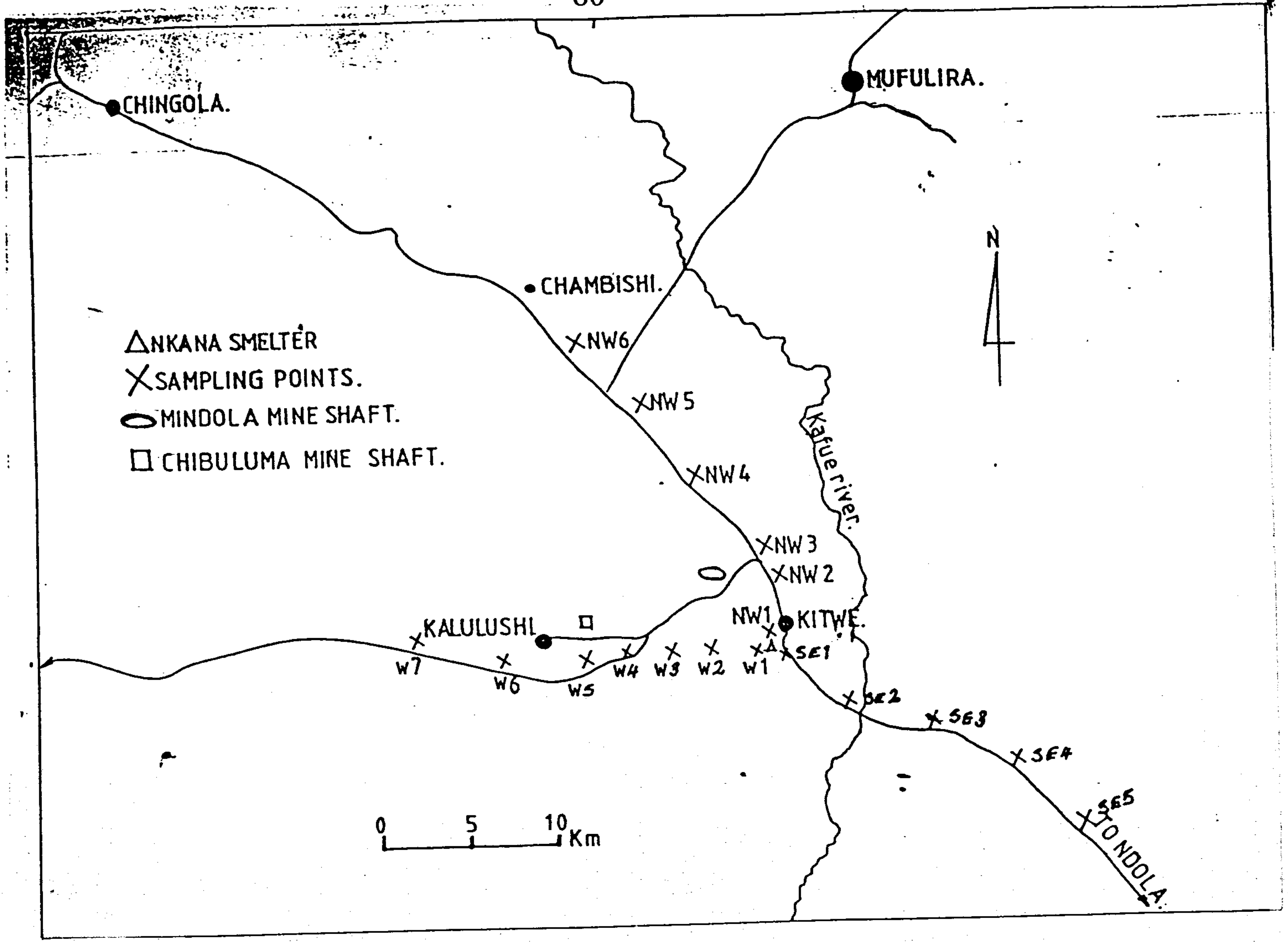
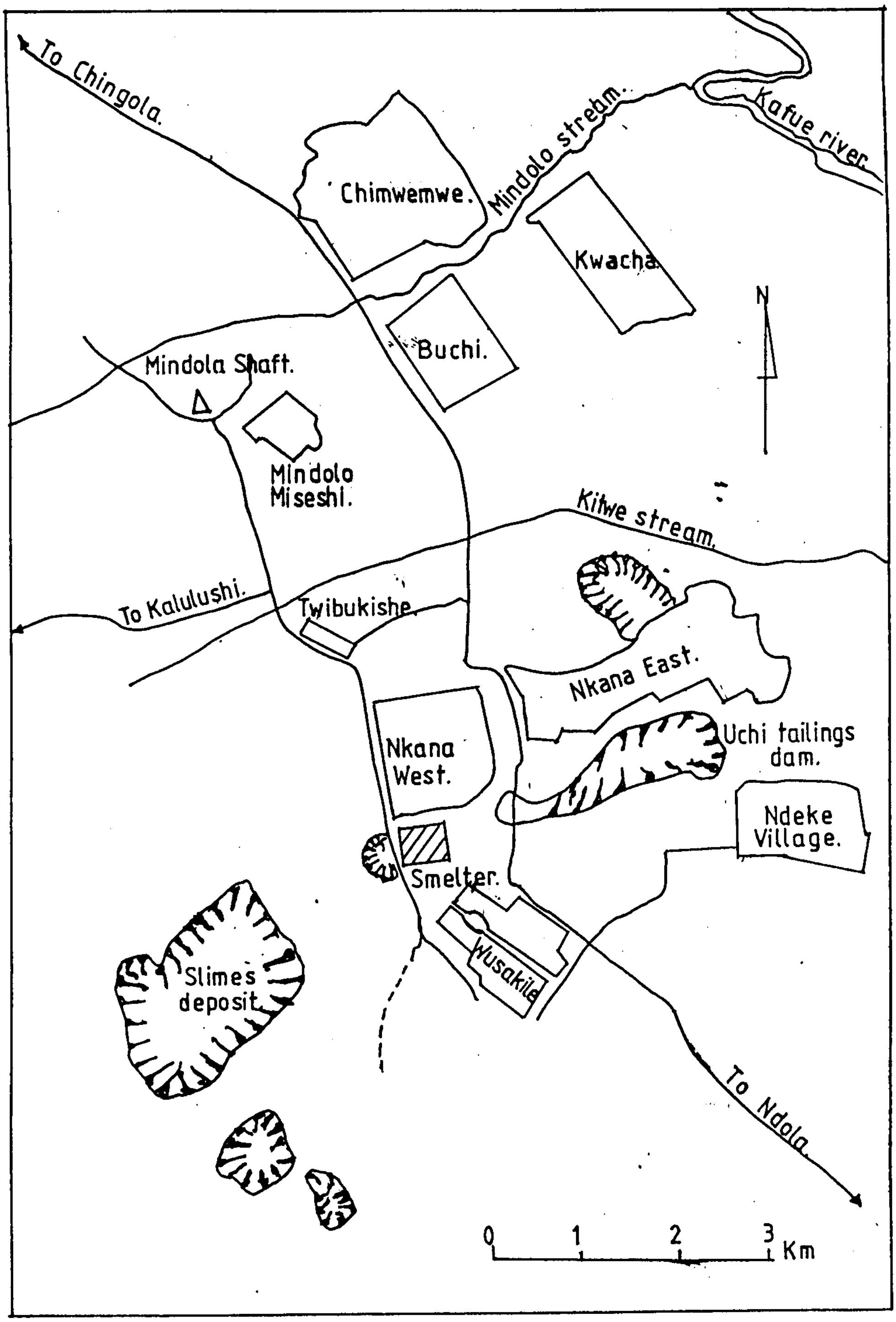


Figure 3.3: Sketch map showing the sampling points in relation to the smelter

Figure 3.4: Sketch map of Kitwe showing residential areas from which edible vegetable samples were collected



CHAPTER FOUR

RESULTS

4.0 **RESULTS**

The results for the analyses of the soils and grass samples obtained from the three directions are given in tables 4.1 to 4.6. The results of the edible vegetable samples from backyard gardens are given in table 4.7. Figures 4.1 to 4.9 shows the average concentrations of metal elements in soils, grass and edible vegetable samples from the three directions.

Correlation coefficients (r) are given in tables 4.8 to 4.14. The percentage recovery of the metals are shown in the tables 4.15 to 4.24 and standard deviation of the mean is given in tables 4.25 and 4.26.

Table 4.1: The concentration of metal elements in soils, obtained from North-west of the Nkana smelter in mg/kg.

Distance from smelter in km	Sampling Area	Number of samples	Cadmium (Cd)	Cobalt (Co)	Copper (Cu)	Lead (Pb)	Zinc (Zn)
0	Opposite starlite night club (NW_1)	4	–	16.2 ± 0.4	1450 ± 50	26.0 ± 1.4	58.0 ± 3.5
3	Freedom park (NW_2)	3	–	11.0 ± 2	269 ± 15	24.0 ± 3.3	16.2 ± 1
5	CAMS (NW_3)	3	–	8.0 ± 0.9	416 ± 57	8.0 ± 1.4	15.3 ± 1.8
10	Twatasha area (NW_4)	3	–	5.9 ± 0.4	175 ± 8.6	12.0 ± 0.5	8.6 ± 0.9
15	COSETCO (NW_5)	3	–	0.7 ± 0.2	34.2 ± 5	2.6 ± 0.9	0.9 ± 0.3
20	Chambishi mine Farm (NW_6)	3	–	1.7 ± 0.3	42.4 ± 6.1	3.5 ± 1.0	2.8 ± 0.5

– Not detected

Table 4.2: The concentration of metal elements in soils, obtained from West of the Nkana smelter in mg/kg.

Distance from smelter in km	Sampling Area	Number of samples	Cadmium (Cd)	Cobalt (Co)	Copper (Cu)	Lead (Pb)	Zinc (Zn)
0	Nkana west (W_1)	3	–	43.0±3.2	3780±300	23.3±2.1	63.0±2.3
3	Slimes dam area (W_2)	3	–	33.6±7.3	2500±215	8.0±0.2	10.7±1.2
5	Slimes dam area (W_3)	3	–	7.2±0.8	1770±81	7.3±0.6	9.2±1.6
8	Off slimes dam (W_4)	4	–	4.5±0.5	763±15	6.3±0.4	6.5±1.5
10	Chibuluma mine farm (W_5)	3	–	8.2±1.8	375±2.3	2.3±0.3	5.6±0.8
15	St. Joseph turn off (W_6)	3	–	1.3±0.2	26.6±2.0	2.2±0.3	0.8±0.3
20	Chimpinde farm (W_7)	4	–	0.9±0.2	55.9±2.5	1.4±0.2	0.9±0.3

Table 4.3: The concentration of metal elements in soils, obtained from South-east of the Nkana smelter in mg/kg.

Distance from smelter in km	Sampling Area	Number of samples	Cadmium (Cd)	Cobalt (Co)	Copper (Cu)	Lead (Pb)	Zinc (Zn)
0	Wusakile market (SE_1)	3	–	22.6 ± 2.1	5300 ± 120	30.5 ± 1.0	76.5 ± 1.5
5	Mulenga Compound (SE_2)	3	–	1.3 ± 0.2	262 ± 4.2	2.9 ± 0.8	36.4 ± 0.7
10	Zam-Tan Compound (SE_3)	3	–	0.8 ± 0.3	18.5 ± 1.2	2.3 ± 1.1	4.3 ± 0.9
15	Kamfinsa Mission (SE_4)	4	–	2.3 ± 0.2	18.6 ± 1.0	1.8 ± 0.4	0.5 ± 0.2
20	Maposa area (SE_5)	4	–	0.9 ± 0.3	6.6 ± 0.6	2.3 ± 0.6	1.0 ± 0.2

Table 4.4: The concentration of metal elements in grass, obtained from North-west of the Nkana smelter in mg/kg. Dry matter.

Distance from smelter in km	Sampling Area	Number of samples	Cadmium (Cd)	Cobalt (Co)	Copper (Cu)	Lead (Pb)	Zinc (Zn)
0	Opposite starlite night club (NW_1)	3	–	30.6 ± 2	1800 ± 78	–	71 ± 3
3	Freedom park (NW_2)	3	–	21.0 ± 1.2	185 ± 60	–	66 ± 6.3
5	CAMS (NW_3)	4	–	27.8 ± 1.5	200 ± 33	–	55.4 ± 8.2
10	Twatasha area (NW_4)	4	–	8.3 ± 2.5	15 ± 2	–	56 ± 10
15	COSETCO (NW_5)	3	–	6.0 ± 0.5	11 ± 0.6	–	34 ± 5.6
20	Chambishi mine Farm (NW_6)	3	–	6.0 ± 0.5	11 ± 0.8	–	27 ± 4

Table 4.5: The concentration of metal elements in grass, obtained from West of the Nkana smelter in mg/kg.

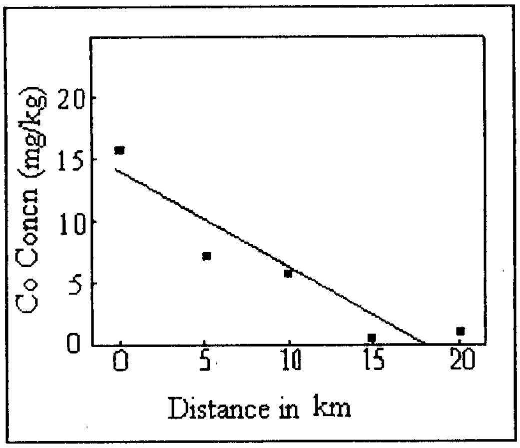
Distance from smelter in km	Sampling Area	Number of samples	Cadmium (Cd)	Cobalt (Co)	Copper (Cu)	Lead (Pb)	Zinc (Zn)
0	Nkana west (W_1)	3	–	22.6 ± 1.8	2330 ± 140	–	30.0 ± 1.2
3	Slimes dam area (W_2)	3	–	22.8 ± 2.1	2020 ± 220	–	30.9 ± 0.6
5	Slimes dam area (W_3)	3	–	17.8 ± 2.4	536 ± 17.9	–	28.7 ± 1.3
8	Off slimes dam (W_4)	4	–	23.8 ± 1.5	246 ± 8.4	–	22.0 ± 1.3
10	Chibuluma mine farm (W_5)	3	–	6.0 ± 0.4	34 ± 7.1	–	26.4 ± 1.6
15	St. Joseph turn off (W_6)	3	–	6.0 ± 0.8	26.6 ± 3.2	–	22.8 ± 1.3
20	Chimpinde farm (W_7)	4	–	6.0 ± 0.6	26.0 ± 2.5	–	24.0 ± 0.4

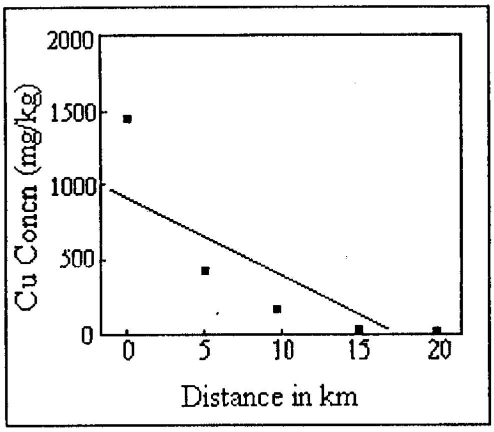
Table 4.6: The concentration of metal elements in grass, obtained from South-east of the Nkana smelter in mg/kg. Dry matter

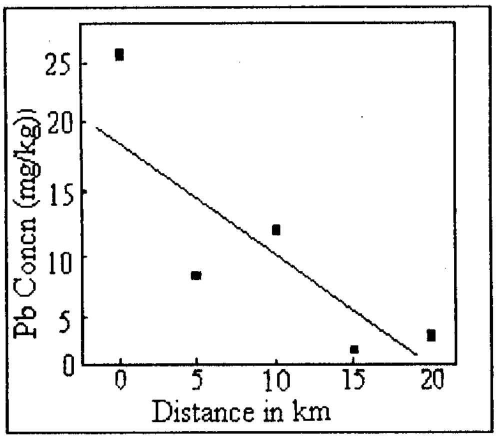
Distance from smelter in km	Sampling Area	Number of samples	Cadmium (Cd)	Cobalt (Co)	Copper (Cu)	Lead (Pb)	Zinc (Zn)
0	Wusakile market (SE_1)	3	–	55.4 ± 5.7	2220 ± 18.5	–	167 ± 8.2
5	Mulenga Compound (SE_2)	3	–	9.0 ± 1.3	77.5 ± 7.6	–	76.3 ± 4.2
10	Zam-Tan Compound (SE_3)	3	–	4.3 ± 0.5	26.9 ± 0.4	–	118 ± 5.7
15	Kamfinsa Mission (SE_4)	4	–	4.3 ± 0.8	17.2 ± 1.1	–	57.2 ± 0.5
20	Maposa area (SE_5)	4	–	4.3 ± 1.2	7.6 ± 2.0	–	32.5 ± 1.8

FIGURE 4.1: The Average concentration of metal elements in soils obtained from north-west of the Nkana smelter in mg/kg

DISTANCE FROM SMELTER IN KM	CADMIUM	COBALT	COPPER	LEAD	ZINC
0	–	16.2	1450	26	58
5	–	8.0	416	8	15.3
10	–	5.9	175	12	8.6
15	–	0.7	34.2	2.6	0.9
20	–	1.7	42.4	3.5	2.8







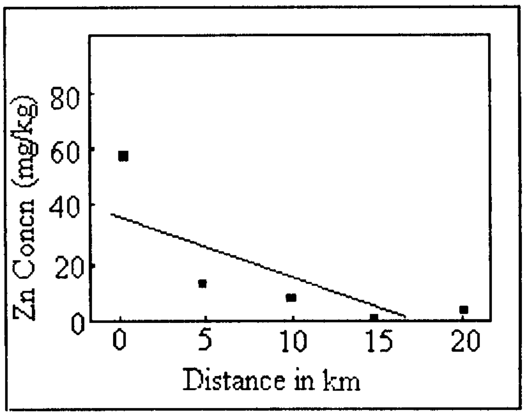


Figure 4.2: The Average concentration of metal elements in soils obtained from west of the Nkana smelter in mg/kg

DISTANCE FROM SMELTER IN KM	CADMIUM	COBALT	COPPER	LEAD	ZINC
0	–	43	3780	23.3	63
5	–	7.2	1770	7.3	9.2
10	–	8.2	375	2.3	5.6
15	–	1.3	26.6	2.2	0.8
20	–	0.9	55.9	1.4	0.9

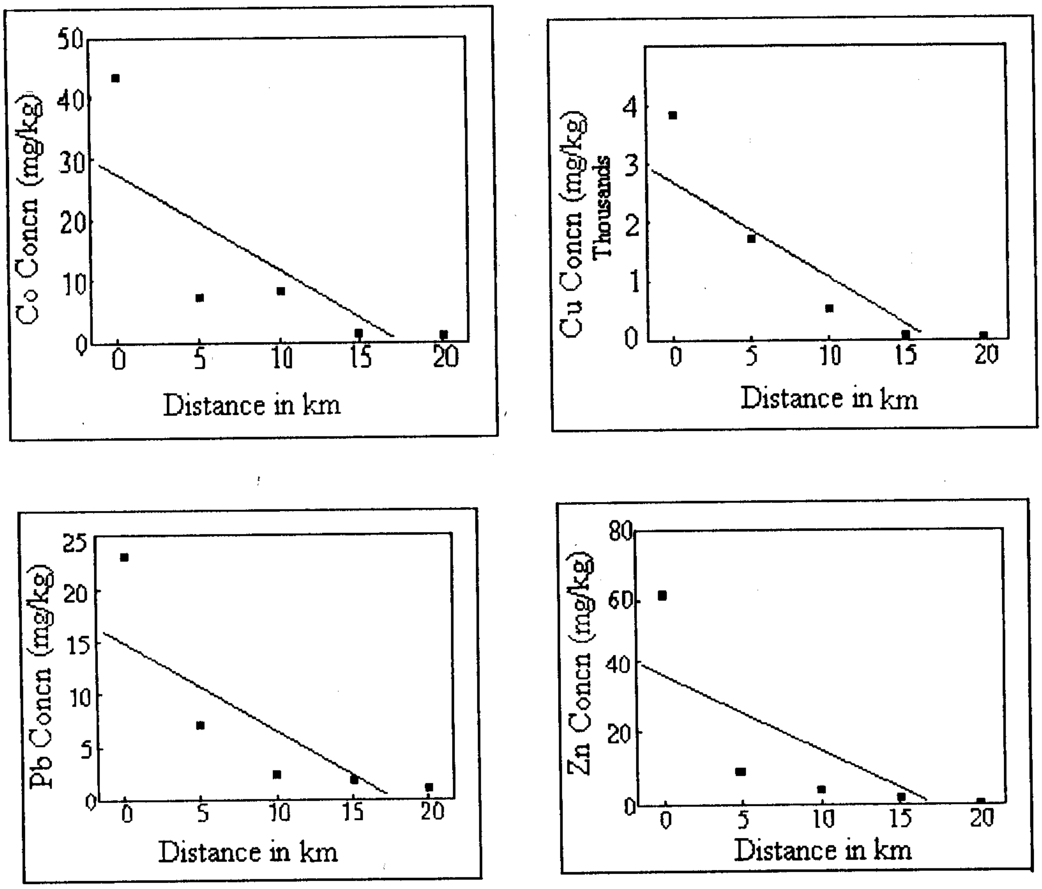


Figure 4.3: The Average concentration of metal elements in soils obtained from south-east of the Nkana smelter in mg/kg

DISTANCE FROM SMELTER IN KM	CADMIUM	COBALT	COPPER	LEAD	ZINC
0	–	22.6	5300	30.5	76.5
5	–	1.3	262	2.9	36.4
10	–	0.8	18.5	2.3	4.3
15	–	2.3	18.6	1.8	0.5
20	–	0.9	6.6	2.3	1

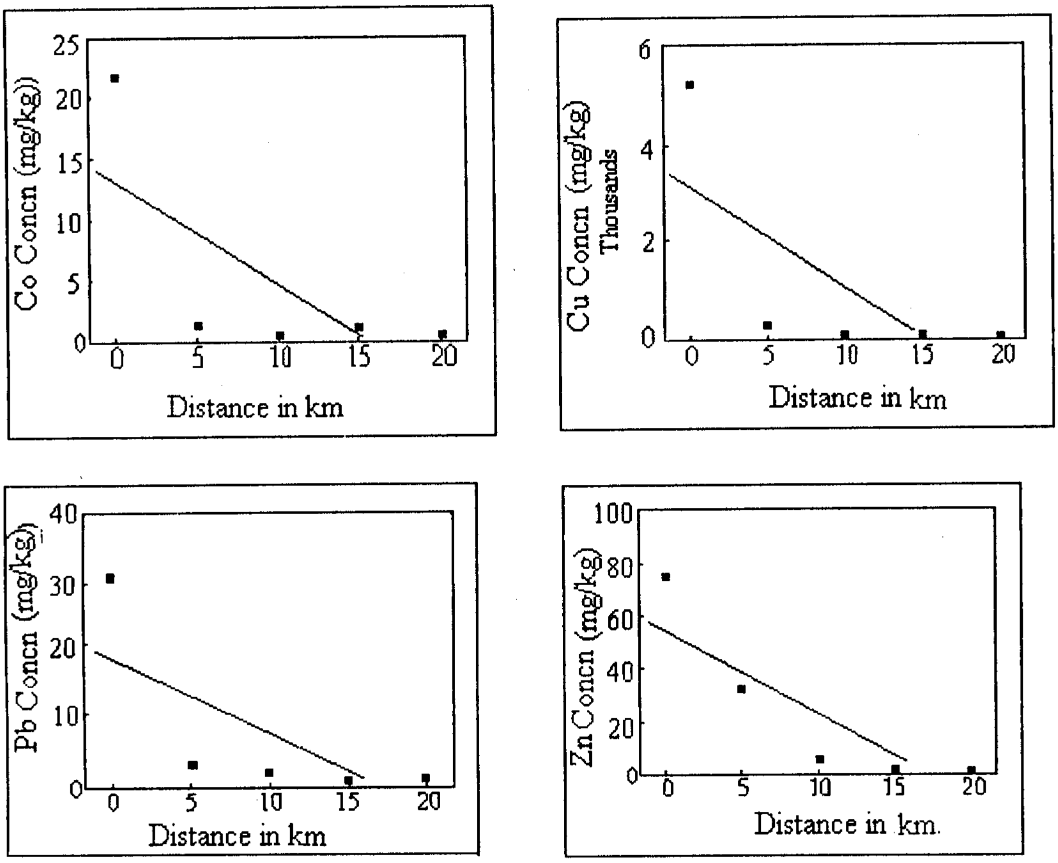
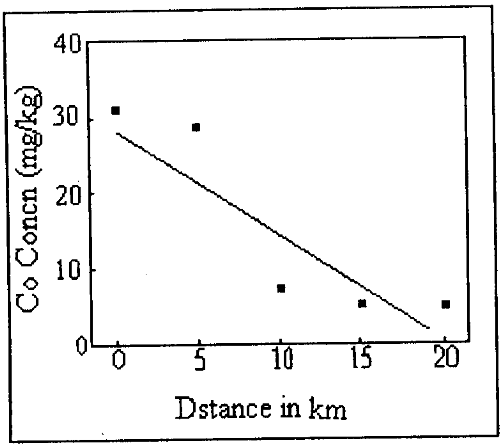
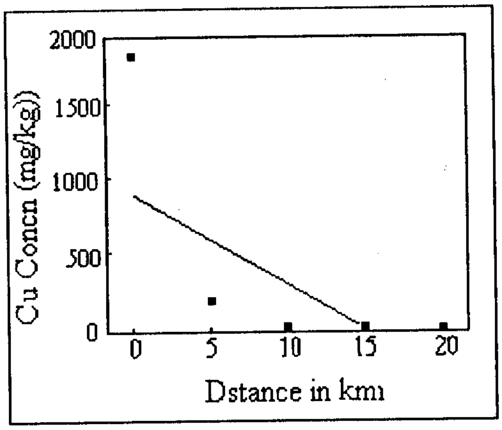


Figure 4.4: The Average concentration of metal elements in grass obtained from North-west of the Nkana smelter in mg/kg dry matter

DISTANCE FROM SMELTER IN KM	CADMIUM	COBALT	COPPER	LEAD	ZINC
0	–	30.6	1800	–	71
5	–	27.8	200	–	55.4
10	–	8.3	15	–	56
15	–	6	11	–	34
20	–	6	11	–	27





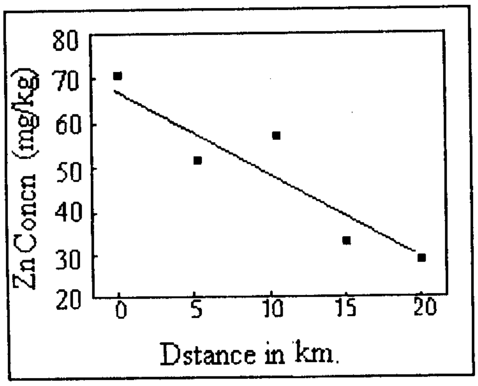


Figure 4.5: The Average concentration of metal elements in grass obtained from west of the Nkana smelter in mg/kg dry matter

DISTANCE FROM SMELTER IN KM	CADMIUM	COBALT	COPPER	LEAD	ZINC
0	–	22.6	2330	–	30
5	–	17.8	536	–	28.7
10	–	6.0	34	–	26.4
15	–	6	26.6	–	22.8
20	–	6	26	–	24

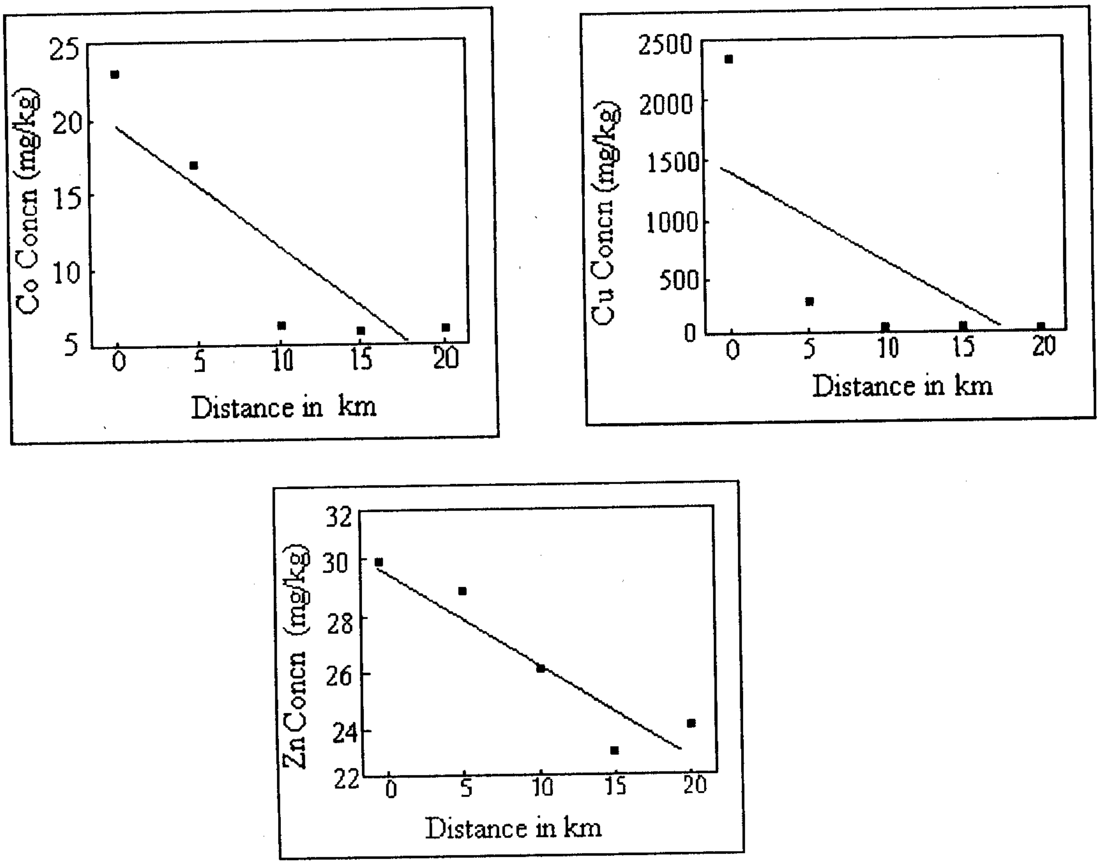


Figure 4.6: The Average concentration of metal elements in grass obtained from South-east of the Nkana smelter in mg/kg dry matter

DISTANCE FROM SMELTER IN KM	CADMIUM	COBALT	COPPER	LEAD	ZINC
0	–	55.4	2220	–	167
5	–	9.0	77.5	–	76.3
10	–	4.3	26.9	–	118
15	–	4.3	17.2	–	57.2
20	–	4.3	7.6	–	32.5

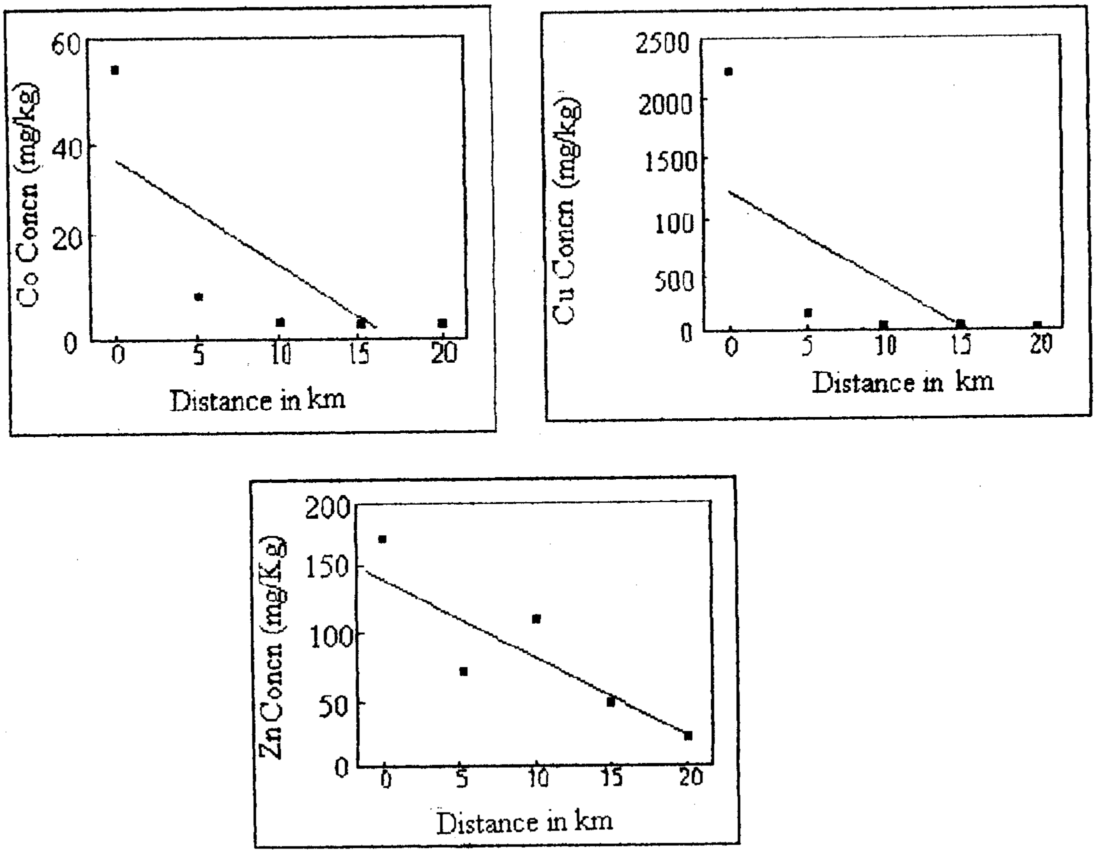
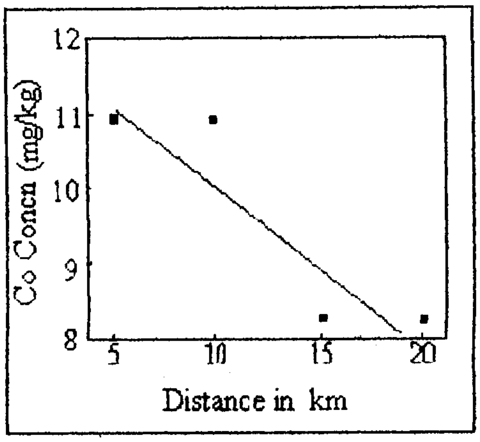
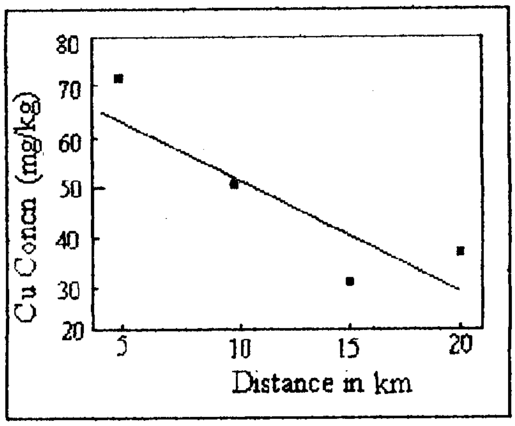


Figure 4.7: The Average concentration of metal elements in edible vegetables obtained from North-west of the Nkana smelter in mg/kg dry matter

DISTANCE FROM SMELTER IN KM	VEGETABLE	CADMIUM	COBALT	COPPER	LEAD	ZINC
5	Bean leaves	–	11.0	71	–	105
10	Pumpkin leaves	–	11.0	51	–	47.9
15	Rape	–	8.3	41	–	56.9
20	Rape	–	8.3	38	–	57





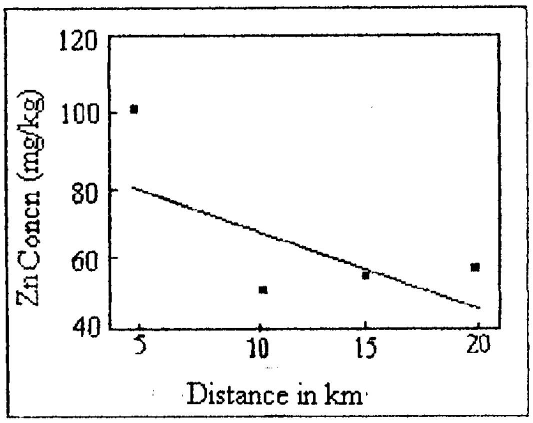


Figure 4.8: The Average concentration of metal elements in edible vegetables obtained from west of the Nkana smelter in mg/kg dry matter

DISTANCE FROM SMELTER IN KM	VEGETABLE	CADMIUM	COBALT	COPPER	LEAD	ZINC
5	Pumpkin leaves	–	11.5	173	–	104
10	Pumpkin leaves	–	6.7	64.5	–	88.4
15	Pumpkin leaves	–	9	39.8	–	58.4
20	Bean leaves	–	6.7	59	–	48.8

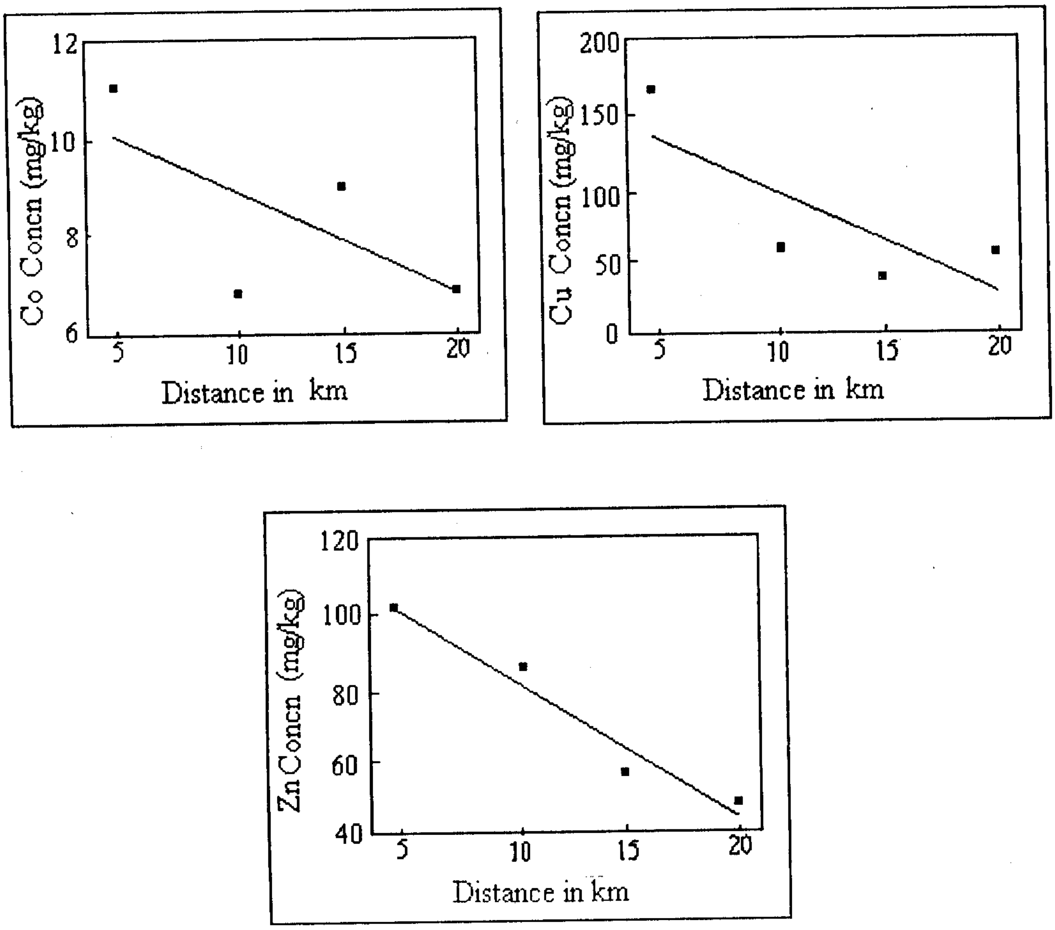
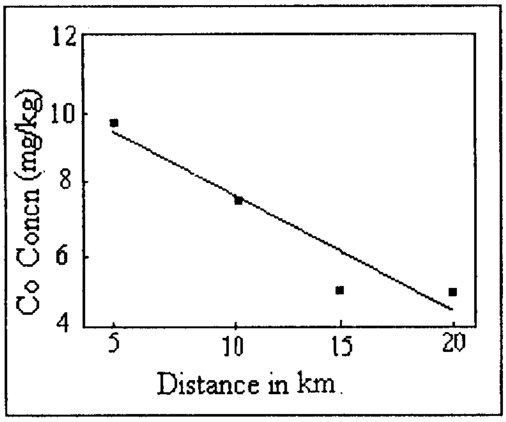
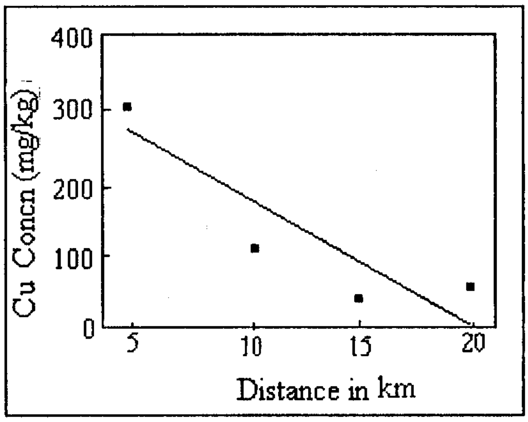


Figure 4.9: The Average concentration of metal elements in edible vegetables obtained from south east of the Nkana smelter in mg/kg dry matter

DISTANCE FROM SMELTER IN KM	VEGETABLE	CADMIUM	COBALT	COPPER	LEAD	ZINC
5	Pumpkin leaves	–	9.9	311	–	175
10	Pumpkin leaves	–	7.5	126	–	74.9
15	Rape	–	5	47.8	–	57.8
20	Pumpkin leaves	–	5	49.7	–	53.8





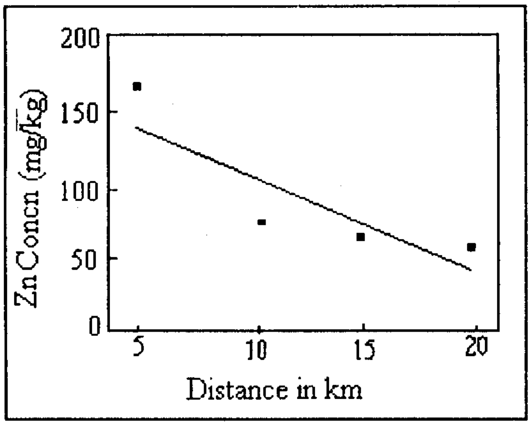


Table 4.7 Amounts of metallic elements in vegetable samples in mg/kg from backyard gardens. Samples were collected from different gardens in the same area

BUCHI AREA

Sample	Number of samples	Cd	Co	Cu	Pb	Zn
Rape	1	–	61.5	51.9	–	97.3
Rape	2	–	62.3	47.5	–	105
Chinese	2	–	50.0	97.6	–	80.5
Chinese	2	–	18.3	60.0	–	94.9
Spinach	1	–	60.4	71.1	–	373
Pumpkin leaves	2	–	46.2	85.7	–	97.8

CHIMWEMWE

Sample	Number of samples	Cd	Co	Cu	Pb	Zn
Rape	1	–	63	21.0	–	82.7
Rape	1	–	59.5	31.0	–	64.9
Chinese	2	–	38.5	97.6	–	
Chinese	2	–	15.7	26.1	–	49.3
Potato leaves	1	–	60	24.8	–	37.3
Potato leaves	1	–	64.5	40.0	–	47.9
Pumpkin leaves	2	–	62.5	40.0	–	151.4

KWACHA

Sample	Number of samples	Cd	Co	Cu	Pb	Zn
Rape	1	–	56.4	14.3	–	48.2
Rape	1	–	39.2	12.3	–	63.1
Potato leaves	2	–	47.5	229	–	38.9
Potato leaves	2	–	46.6	40.0	–	33.2
Bean leaves	3	–	32.8	40.8	–	43.1

NKANA EAST

Sample	Number of samples	Cd	Co	Cu	Pb	Zn
Rape	1	–	23.6	15.0	–	83.5
Rape	2	–	31.3	39.4	–	125
Chinese	2	–	26.2	54.8	–	81.5
Chinese	3	–	22.3	81.4	–	70.1
Chinese	3	–	18.3	60.0	–	99.0
Chinese	3	–	27.2	12.0	–	119
Cabbage	1	–	28.5	27.5	–	72.2
Couliflower	1	–	38.1	23.2	–	50.8

WUSAKILE

Sample	Number of samples	Cd	Co	Cu	Pb	Zn
Rape	1	–	23.6	69.6	–	62.6
Chinese	1	–	26.2	96.9	–	50.8
Chinese	1	–	19.6	63.0	–	98.2
Cabbage	1	–	31.0	44.5	–	137

MINDOLO - MISESHI

Sample	Number of samples	Cd	Co	Cu	Pb	Zn
Rape	1	–	42.2	84.4	–	110
Rape	1	–	13.1	54.9	–	51.8
Chinese	1	–	61.6	170	–	119
Cabbage	1	–	41.8	57.8	–	35.3
Couliflower	1	–	54.6	44.5	–	33.5

NDEKE - VILLAGE

Sample	Number of samples	Cd	Co	Cu	Pb	Zn
Rape	1	–	25.5	17.9	–	75.0
Potato leaves	1	–	31.0	150	–	57.1
Pumpkin leaves	1	–	29.1	122	–	16.0
Pumpkin leaves	2	–	31.0	223	–	62.6

TWIBUKISHE

Sample	Number of samples	Cd	Co	Cu	Pb	Zn
Rape	1	–	75.3	159	–	85.3
Pumpkin leaves	1	–	70.5	127	–	56.1
Pumpkin leaves	2	–	72.0	135	–	82.5
Potato leaves	2	–	69.4	56.7	–	26.2

NKANA - WEST

Sample	Number of samples	Cd	Co	Cu	Pb	Zn
Rape	1	–	59.5	107	–	71.3
Bean leaves	2	–	63	179	–	62.9
Bean leaves	1	–	60.5	104	–	69.1
Bean leaves	2	–	57.6	205	–	159
Groundnut leaves	1	–	53.2	97.1	–	82.6
Potato leaves	1	–	68.5	147	–	86.2
Potato leaves	1	–	64.5	219	–	115
Potato leaves	2	–	40.5	91.7	–	131.2
Pumpkin leaves	1	–	94.5	306	–	70.2
Pumpkin leaves	1	–	50.0	311	–	110
Pumpkin leaves	1	–	86.4	167	–	78.2

CORRELATION COEFFICIENT

The correlation coefficient is used to measure the correlation between two variables X and Y. The value of r is given by the following equation:

$$r = \frac{\sum(\mathrm{X}_i - \overline{\mathrm{X}})(\mathrm{Y}_i - \overline{\mathrm{Y}})}{\sqrt{\left[\sum(\mathrm{X}_i - \overline{\mathrm{X}})^2\right]\left[\sum(\mathrm{Y}_i - \overline{\mathrm{Y}})^2\right]}}$$

Where r = correlation coefficient.

X_i and Y_i are individual values of the variables X and Y.

$\overline{\mathrm{X}}$ is the mean of X

$\overline{\mathrm{Y}}$ is the mean of Y

r can take values in the range $-1 \leq \mathrm{r} \leq +1$

r value of -1 describes perfect negative correlation between X and Y.

r value of $+1$ describes perfect positive correlation between X and Y.

When there is no correlation between X and Y the value of r is zero.

PERCENTAGE RECOVERY

Some samples were spiked with known amount of metals then analysed for the same metals to establish the recovery rate of the metals.

Table 4.8: Correlation coefficients (r) between metal concentration in soil samples and distance from the Nkana smelter in the three directions

DIRECTION	CADMIUM	COBALT	COPPER	LEAD	ZINC
North-West	–	–0.93	–0.74	–0.86	–0.77
West	–	–0.80	–0.89	–0.78	–0.68
South-East	–	–0.70	–0.73	–0.72	–0.89

Table 4.9: Correlation coefficients (r) between metal concentration in grass samples and distance from the Nkana smelter in the three directions

DIRECTION	CADMIUM	COBALT	COPPER	LEAD	ZINC
North-West	–	–0.90	–0.65	–	–0.97
West	–	–0.82	–0.80	–	–0.75
South-East	–	–0.75	–0.72	–	–0.86

Table 4.10: Correlation coefficients (r) between metal concentration in vegetables and distance from the Nkana smelter in the three directions

DIRECTION	CADMIUM	COBALT	COPPER	LEAD	ZINC
North-West	–	–0.89	–0.87	–	–0.67
West	–	–0.68	–0.79	–	–0.98
South-East	–	–0.94	–0.90	–	–0.86

Table 4.11: Correlation coefficients (r) between metal concentration in soil and metal concentration in grass

DIRECTION	CADMIUM	COBALT	COPPER	LEAD	ZINC
North-West	–	0.88	0.99	–	0.91
West	–	0.86	0.95	–	0.96
South-East	–	0.99	1.0	–	0.77

Table 4.12: Correlation coefficients (r) between metal concentration in soil samples

DIRECTION	METALS					
	Co/Cu	Co/Pb	Co/Zn	Cu/Pb	Cu/Zn	Pb/Zn
West	0.93	0.85	0.82	0.92	0.85	0.98
North-West	0.86	0.95	0.91	0.72	0.99	0.79
South-East	1.00	1.00	0.89	1.00	0.91	0.90

Table 4.13: Correlation coefficients (r) between metal concentration in grass samples

DIRECTION	METALS					
	Co/Cu	Co/Pb	Co/Zn	Cu/Pb	Cu/Zn	Pb/Zn
West	0.70	–	0.46	–	0.82	–
North-West	0.70	–	0.80	–	0.62	–
South-East	1.00	–	0.81	–	0.81	–

Table 4.14: Correlation coefficients (r) between metals in edible vegetables

DIRECTION	METALS					
	Co/Cu	Co/Pb	Co/Zn	Cu/Pb	Cu/Zn	Pb/Zn
West	0.79	–	0.58	–	0.80	–
North-West	0.87	–	0.43	–	0.80	–
South-East	0.97	–	0.93	–	0.99	–

Table 4.15 Percentage recovery of Cadmium in soil in mg/kg

Soil sample	Initial amount present	Amount added	Total Amount detected	Amount recovered	% recovery
1	–	0.5	0.4	0.4	80
2	–	1.0	1.0	1.0	100
3	–	2.5	2.2	2.2	88
4	–	5.0	4.5	4.5	90
5	–	10	9.5	9.5	95

Table 4.16 Percentage recovery of Cadmium in plants in mg/kg

Plant sample	Initial amount present	Amount added	Total Amount detected	Amount recovered	% recovery
1	–	2.5	2.5	2.5	100
2	–	5.0	5.0	5.0	100
3	–	10.0	8.3	8.3	83
4	–	20.0	18.3	18.3	92
5	–	30.0	25	25	83

Table 4.17 Percentage recovery of Cobalt in soil samples in mg/kg

Soil sample	Initial amount present	Amount added	Total Amount detected	Amount recovered	% recovery
1	6.0	2.0	7.7	1.7	85
2	7.2	5.0	11.6	4.4	88
3	7.8	5.0	11.9	4.1	82
4	1.3	10.0	9.4	8.1	81
5	0.9	10.0	9.4	8.5	85

Table 4.18 Percentage recovery of Cobalt in plant samples in mg/kg Dry matter

Sample	Initial amount present	Amount added	Total Amount detected	Amount recovered	% recovery
1	3.8	2.0	5.4	1.6	80
2	–	4.0	3.0	3.0	75
3	–	6.0	4.0	4.0	67
4	–	8.0	5.6	5.6	70
5	–	8.0	5.8	5.8	73

Table 4.19 Percentage recovery of Copper in soil samples in mg/kg

Soil sample	Initial amount present	Amount added	Total Amount detected	Amount recovered	% recovery
1	18.5	2.0	20.4	1.9	95
2	6.6	5.0	11.0	4.8	96
3	18.6	15.0	33.3	14.7	98
4	26.6	20.0	45.2	18.6	93
5	1450	100.0	1550	100	100

Table 4.20 Percentage recovery of Copper in plant samples in mg/kg Dry matter

Plant sample	Initial amount present	Amount added	Total Amount detected	Amount recovered	% recovery
1	38.9	4.0	42.7	3.8	97
2	42.5	4.5	46.9	4.4	97
3	15.7	5.0	20.5	4.8	96
4	47.8	20.0	67.6	19.9	99
5	47.8	25.0	70.9	23.1	92

Table 4.21 Percentage recovery of Lead in soil in mg/kg

Soil sample	Initial amount present	Amount added	Total Amount detected	Amount recovered	% recovery
1	12.0	3.0	14.7	2.7	90
2	20.1	5.0	24.9	4.8	96
3	1.8	10.0	11.8	10.0	100
4	1.8	15.0	16.8	15.0	100
5	2.0	2.5	4.3	2.3	92

Table 4.22 Percentage recovery of Lead in plant samples in mg/kg

Plant sample	Initial amount present	Amount added	Total Amount detected	Amount recovered	% recovery
1	–	0.5	0.5	0.5	100
2	–	2.0	1.9	1.9	95
3	–	4.0	4.0	4.0	100
4	–	5.0	4.8	4.8	96
5	–	15	14.3	14.3	95

Table 4.23 Percentage recovery of Zinc in soil in mg/kg

Soil sample	Initial amount present	Amount added	Total Amount detected	Amount recovered	% recovery
1	0.5	2.0	2.5	2.0	100
2	15.7	2.0	17.6	1.9	95
3	4.9	2.0	6.8	1.9	95
4	4.7	5.0	9.5	4.8	96
5	14.3	25.0	39.1	24.8	99

Table 4.24 Percentage recovery of Zinc in plant samples in mg/kg

Plant sample	Initial amount present	Amount added	Total Amount detected	Amount recovered	% recovery
1	24.0	2.0	25.9	1.9	95
2	16.2	5.0	21.0	4.8	96
3	34.3	10.0	44.2	9.9	99
4	74.5	30.0	101	26.5	88
5	31.2	40.0	63.6	32.4	81

Table 4.25 Standard deviation of the mean (standard error) in soil samples

Sample		Cadmium	Cobalt	Copper	Lead	Zinc
Soil 1	$\overline{x}$	–	1.92	218	6.17	7.9
(6)	S	–	0.52	47.99	1.95	1.25
	SE	–	0.21	19.59	0.80	0.5
Soil 2	$\overline{x}$	–	1.78	93.73	5.88	1.98
(6)	S	–	0.29	17.21	0.64	0.38
	SE	–	0.12	7.02	0.22	0.15

Table 4.26 Standard error of elements in vegetation samples

Sample		Cadmium	Cobalt	Copper	Lead	Zinc
Sample 1	$\overline{X}$	–	28.2	35.8	–	65.7
(6)	S	–	2.5	3.6	–	5.48
	SE	–	1.0	1.5	–	2.2
Sample 2	$\overline{X}$	–	26.3	57.3	–	40.8
(6)	S	–	4.6	5.2	–	0.7
	SE	–	1.9	2.1	–	0.3

(6) = Number of samples

$\overline{X}$ = Avarage

S = Standard deviation, $S = \sqrt{\frac{\sum(X_i - \overline{X})^2}{N-1}}$

SE = Standard error, $SE = \frac{S}{\sqrt{N}}$