ANALYSIS OF THE LEVELS OF HEAVY METALS IN SOIL, PLANT, WATER, SEDIMENT AND URINE SAMPLES AROUND THE ATHI RIVER REGION.

BY

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This thesis is my original work and has not been presented in part or otherwise for a degree in this or any other university except where indicated by reference.

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DEDICATION

This thesis has been dedicated to my family and in particular to my father, mother, wife and children.

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ABSTRACT

In this work, X-ray fluorescence analysis technique was used to analyze soils, plants, water, sediments and urine samples from a selected area in the Athi River town.

From the analysis, dust from the electrostatic precipitator was found to have very low levels of chromium and lead. For the other elements, dust had high levels, e.g. iron (7480.3 - 9670.7 ppm) and manganese (404.0 - 595.5 ppm). However, the levels were found to be lower than those in the indigenous soil in this region e.g. iron (30180.4 - 53340.7 ppm) and manganese (1320.1 - 1960.5 ppm). Overall, there was an increase in the levels of these metals with distance from the electrostatic precipitator. Thus, the metals in the dust were noted to leach down suggesting they were likely to be available to plants.

From the analysis of plant leaves, the concentrations of metals were found to depend on the levels in the soil, soil type and the organic matter content except for zinc. The metals in the indigenous soil appeared to be more available to plants than those in the dust. Leaves from the three plant species sampled had significantly different levels of heavy metals suggesting that they had different physiological role, different tolerance or different mechanisms of absorption.

In the case of the water samples from the Athi river, the pH values were found to be high (7.20 - 9.45). The concentrations of the metals encountered were also higher than the natural uncontaminated levels e.g. copper (4.6 -17.9 ppb) which was much higher than the reported uncontaminated values (0.2 - 2.2 ppb) for drinking water although they were lower than the W.H.O. highest acceptable values. It was noted that as the distance of the sampling point from the point where a given metal was being discharged increased, the concentration of the heavy metals decreased. This suggested that the river load was within what it could cope up with i.e. removed by the natural self purification of rivers through the process of precipitation and scavenging by microorganisms.

The concentration of elements in sediments from the Athi river were found to be generally high, e.g. chromium (0 - 428.2 ppm), iron (4970.1 - 14520.3 ppm), manganese (313.2 -6410.0 ppm), copper (1.6 - 43.7 ppm), zinc (16.4 - 55.7 ppm), lead (3.3 - 32.7 ppm) and mercury (0 - 23.2 ppm). Despite this, it was noted that that only a small percentage was in solution. This was probably due to the high pH of the water, low solubility product and matrix effects. Generally, the results suggested that the Athi river was only moderately polluted.

Analysis of urine samples from those working in the cement factory had relatively higher concentrations for most of the metals than those not working in the factory (controls) with lead as the only exception.

CHAPTER ONE

1.0.0 INTRODUCTION.

Over the years man has been involved in many activities. These activities in one way or another have been continuously adding pollutants to his environment and ultimately into the cells of plants, animals and microorganisms [1,2]. As such, there has been a growing concern over the environmental degradation resulting from these activities [3]. These activities include; milling, smelting, tanning, farming, welding, manufacturing of finished and intermediate products. The result of all these is an increased level of organic and inorganic pollutants in the plants, soil, air, water and animal tissues [4,5,6,7].

In this work however, only toxic and non toxic heavy metals will be discussed. Heavy metal pollution is not a new phenomenon. It dates as early as 2300 years ago when Hippocrates observed colic among workers in lead smelting industries [1].

Heavy metals as a result of their physical and chemical properties have found many uses in industrial activities, such as, mercury in cosmetics, fungicides, pharmaceutical and marine paints; lead in paints, battery plates, x-ray equipments, as a petrol additive; zinc in torch batteries; chromium in skin tanning; iron in iron and steel industries; cadmium in motor vehicle tires and manganese in fertilizer making industries [1,2,8,9]. As a result of these, the levels of these metals in the cells of both aquatic and non aquatic organisms has increased considerably sometimes to high proportions which are hazardous to the cells of the organisms. This is because of the ability of these elements to accumulate in these cells [1,6,10]. Cadmium, lead, mercury and copper are known to be cumulative [11] and as such, their levels need to be kept low in industrial dust and fumes, industrial and domestic effluents [12].

Heavy metals can basically be divided into two categories namely:

1.1.0 Essential metals.

These include, zinc, iron, chromium (trace), cobalt (trace), manganese and copper (trace) [6,13,14]. These metals are termed essential for they are an integral component of the animal and plant tissues. They help in maintaining certain biochemical processes e.g. catalysis, electron transfer, oxygen transfer, storage and oxidation. However, these useful effects are only realised at relatively low concentrations.

1.2.0 Non essential metals.

In this class, we have mercury, cadmium, arsenic, selenium and lead [11]. These metals are toxic to the organism even at very low concentration and have no known useful biochemical role.

Metals from these two classes are however cumulative in cells with only a few exceptions. This is partly due to their ability to bind to tripolyphosphates in bones thus displacing calcium and partly due to their ability to bind to the sulphydryl group (SH) in proteins [15,16]. Once in the body, they bind to these systems and get immobilized. However, under favourable conditions they sometimes get mobilized especially by chelating agents like ethylenediaminetetraacetate (EDTA). In the immobilized form, these metals are hard to eliminate since proteins are not usually discharged in the kidneys unless under serious kidney damage.

From the above discussion, it is worthwhile mentioning the various modes through which some of these heavy metals get into our environment and ultimately into the cells of both micro and higher organisms.

1.3.0 Industrial activities.

These include the major industrial activities such as milling, welding, tanning, soldering, smelting, manufacturing of various products like insecticides, paint, pharmaceutical, tanning and mercury based cosmetics [1,7,11]. These add dust particles which if inhaled may be harmful to the respiratory system in particular and the body cells in general as a result of their chemical nature or due to their sheer size. These particles differ in their radii and hence have different residence time in the air resulting in different potentials as air pollutants [17]. When these particles finally settle on the surface, they increase the levels of heavy metals in the soil, water and in animals and plant tissues. The other mode through which these metals enter into the cells is by contact with the skin. This occurs when these metals are present in an organic matrix e.g. Lead oleate, lead acetate, methyl mercury, tetraethyl lead, tetramethyl lead and as organic complexes.

1.4.0 Industrial and domestic discharges.

Industrial effluents are sometimes added into the receiving systems directly without any proper treatment thus affecting the quality of the receiving water [8]. This becomes a major environmental problem since most industrial processes require large volumes of water as such, they are constructed near water courses. This means that, if the effluents are discharged without any form of treatment, they enter the water course with a load that is not easily removed by the natural treatment through precipitation and natural traps offered by microorganisms and lower plants which are known to scavenge heavy metals

[6,18,19,20]. The levels of heavy metals in these effluents are sometimes high enough to cause deaths to fish and at times to human beings. Such occurred in Japan's Minamata bay due to methyl mercury.

Therefore, man, animals, plants and lower organisms get exposed to toxic heavy metals via air, soil, water and food [1,2,6,8]. Lastly, it has been noted that, although most elements (metals) have similar sources and mode of attachment to cell molecules, they have different effects on cells [21]. As such, each metal will be discussed separately. However, in some cases, metals argument each other's effect i.e. they show a synergic effect.

1.5.0 LEAD

Lead metal has been in use for at least 6000 years however, its toxic effects were first observed by Hippocrates about 2300 years ago when he noted colic among workers in lead smelting industries [1].

The early use of this metal arose from its chemical and physical characteristics. Today, lead is used in paints, cosmetics, insecticides as lead arsenate, petrol additive as tetraethyl lead and tetramethyl lead and soldering which had been noted by Hoeane [22] to increase the level of lead in canned foodstuffs by a factor of between 4 and 6 [1,6,15].

Lead especially in an organic matrix is easily absorbed through the skin [1]. The inorganic form is however, absorbed through the respiratory system if inhaled (90% of body burden pass through the respiratory system) and through the gastrointestinal tract if ingested. The efficiency of absorption in the gastrointestinal tract is however dependent on the levels of chelating agents in food materials e.g. phatates, acetates but it is usually between 5 and 15 percent.

Lead being a cumulative element is a serious toxin, especially under long term exposure of the subject. This is because it is able to displace calcium in bones and bind to the sulphydryl group (SH) in certain proteins. As such, it is stored in bones (7-11 $mgKg^{-1}$) as tripolyphosphates and in the liver and kidneys (1.0 $mgKg^{-1}$) [22,23]. Some lead is also stored in fatty tissues as organo lead complexes which are soluble in fats.

The effects associated with lead toxicity include; mental retardation, dental carries, impaired growth, oral dyspraxia, impaired immune system due to suppression of plasma immunoglobulin A and G biosynthesis, anaemia due to inhibition of haemoglobin biosynthesis by interfering with -aminolevulinic acid dehydrase (ALA-D) which catalyses the formation of porphobilinogen (PBG) from -aminolevulinic acid (ALA) and haemsynthetase (Haem-S) which in turn catalysis iron incorporation into protoporphyrin 1X (PP1X). It is also thought to lower the life of erythrocytes [1,10,15,16,22,24]. These effects are due to the ability of lead to bind to the sulphydryl (SH) group in proteins leading to protein precipitation or proteinuria.

Lead body burden is difficult to determine due to its high tendency to bind to proteins and the tripolyphosphates in bone, thus getting immobilized. Thus blood and urine are good indicators of short term exposure while hair and nails are good indicators of body burden . The body burden is usually monitored by mobilizing lead with chelating agents such as ethylenediaminetetraacetate (EDTA).

1.6.0 MANGANESE.

Manganese is a widely distributed metal in the earth's crust. In the environment, manganese pollution results from partially and/or untreated industrial effluents if discharged into receiving systems. It may also arise from industrial processes such as milling and grinding of manganese containing rocks. The use of industrial sludge has also been shown by Maina [25] to pollute the environment with manganese (Kariobangi sludge has about 1190 ppm) [25]. Other sources include, phosphate fertilizers, manure, foodstuffs like milk (2050 ppb), nuts, cereals, legume seeds, tea and coffee (20-25 ppm) [26,27].

Manganese is an essential element. It is found in several metalloenzymes like pyruvate carboxylase which catalyses adenosine triphosphate carbon dioxide fixation, in several electron transfer systems like chlorophyll and in several classes of non-specific metal activated enzymes like kinase and transterase.

In the body, manganese is absorbed in the lungs if dust is inhaled (diameter <0.5 micro meter) and in the gastrointestinal tract if ingested. Once in the body, it is stored in the liver. The main channels via which it is excreted are the faeces via bile and the urine. The levels in the urine are dependent on the levels of proteins in the blood due to the high tendency of manganese to form complexes with proteins. Despite the useful effects, manganese when present in high concentration is toxic to growing sheep (400 ppm) and to cauliflower and cabbage (450 ppm). Deficiency on the other hand leads to fecundity, seminal tubular degeneration, spermatogenesis in mice and rats, anomalies in fat and lipid metabolism due to anomalies in the cholesterol biosynthesis [6].

1.7.0 ZINC

Zinc is an integral component of both plants and animals [25]. It gets into the environment, especially water and air from zinc based industries e.g. torch battery, smelting of copper and lead which emit zinc fumes. The usage as a fertilizer of partially treated effluents has been shown to contaminate the soil and consequently the foodstuffs grown on this sludge amended soil (Kariobangi sludge has about 1930 ppm) [25]. Unlike other metals, zinc is non cumulative in cells of plants and animals. Thus, zinc toxicity is rarely witnessed [6]. However, some researchers have tagged levels of zinc above 1000 ppm and 400 ppm as being toxic and phytotoxic to animals and plants respectively. Despite being non cumulative, high zinc levels are sometimes recorded in the tissues. This occurs when a high dose of zinc containing material e.g. zinc sulphate is ingested causing zinc toxicity. The excess amount in the tissues is easily mobilized by chelating agents such as ethylenediamine- tetraacetate (EDTA) and excreted with the urine. This was found to be the case by Hoekstra et. al. [28], who noted that the level of urinary zinc increased though not linearly with the amount of ethylenediaminetetraacetate (EDTA) administered. Moreover, this zinc was found to originate from the body stores and not from an increased zinc absorption in the gastrointestinal tract.

In human and animal bodies zinc is absorbed in the gastrointestinal tract and in the lungs if zinc fumes are inhaled. This leads to respiratory disorders like chronic fever. High levels of zinc are found in the liver and is thought to be the storage organ

[27,28]. At low concentration, zinc is involved in many processes in both plants and animals. These include: catalysis e.g. in carbonic anhydrase for reversible carbon dioxide hydration, hydride transfer in flavin coenzyme dehydrogenase. High levels lead to different complication depending on the chemical form. Thus, zinc sulphate causes drowsiness, lethargy, increased serum, lipid and amylase levels while zinc fumes cause fever and pulmonary disorders. Deficiency leads to skin lesion, skeleton abnormalities, poor testicular organ development in rats and chlorosis in plants [7,23,27,28].

1.8.0 COPPER

Copper is a cumulative essential element in plants and animals [6,25,29]. In living organisms, copper occurs bound to proteins called copper proteins. These proteins have wide range of uses; as oxygen carriers in mollusc and arthropods called hemocyanins; in electron transfer proteins like plastocyanins in higher plants, umecyanin in horse radish, plantacyanin in cucumber and spinach; in oxidases like laccase found in the latex of Japanese lac tree which catalysis the oxidation of ortho and para dihydroxyphenols to quinone, in ceruloplasmin found in the mammalian blood as the blue coloured copper containing glycoprotein of the -globulin which oxidize substrate with molecular oxygen. All these activities are dependent on copper's ability to show variable oxidation states. It is also important in maintaining vascular and skeletal integrity. In the environment, it originates from power plants, municipal waste water, pesticides, erosion of copper containing rocks and from industrial dust. In the soil, its availability is low due to its high tendency to form kinetically inert complexes with organic matter [6]. In water, copper ion exists as the hexahydrate ion ($Cu(H_2O)_6^{2+}$) which is a kinetically labile complex. This ion is thus highly toxic to invertebrates, algae, fish and bacteria.

In man and animals, copper is absorbed in the gastrointestinal tract with the absorption depending on the dietary level, the matrix and the cations present e.g. iron, molybdenum and zinc. These ions are known to lower the absorption efficiency [30]. Once in the body, it is bound to -globulin ceruloplasmin of plasma.

High levels of available copper in the soil have been found to be phytotoxic to plants (5 ppm) causing chlorosis. In animals, high levels in the liver causes wilson disease. While the major storage organs are the liver and the brain.

The main excretion routes are the faeces via bile (0.5 - 2.0 ppm) and a smaller amount through the urine

(2.7-29.9 ppb) which is suspected to be bound to albumin. The urinary levels have been found to be increased by complexing agents such as ethylenediaminetetraacetate (EDTA), 2,3-dimercaptopropanol (BAL) and B'B'dimethylcystein (penicillamine) and certain ailments like nephrotic syndrome (100-600 ppb) [7].

1.9.0 CHROMIUM

Like zinc, chromium is a non-cumulative and essential element in both plants and animals when present in trace amounts [16,31]. However, at relatively higher concentration, it is toxic to animals and highly phytotoxic to plants.

Chromium pollution is becoming increasingly serious. This is partly due to its being widely used especially in welding, chrome plating and tanning and partly due to the ever increasing use of the highly water soluble chromium (VI) which is toxic at a concentration of 5 ppm [16].

In human and animal bodies, chromium is usually absorbed through the gastrointestinal tract if ingested and through the lungs if inhaled. In man and animals, chromium is highly toxic. However, chromium (III) ion (Cr^{3+}) when present in trace amount has been found to act as a glucose tolerance factor. Thus, lack of chromium (III) ion is suspected to be one of the causes of diabetes mellitus [15,28,31]. Unlike most of the other essential metals, chromium level in tissues is very low with the urine being the main excretion route. Under normal circumstances, its level in urine is between 7 and 10 ppb. If present in high concentrations, chromium has been found to cause renal dysfunction, lung cancer (if chromate fumes are inhaled) and it has a primary causative effect. Deficiency on the other hand leads to cardiovascular diseases [28,31]. Analysis of chromium in samples by techniques involving digestion at elevated temperatures usually result in very low yield [28]. This is due to its high losses when samples are heated and also due to the fact that its level is usually low in samples i.e. near the detection limit of most machines. Thus, drying plant materials at 80 ^{o}C results in a 90% loss of chromium [28].

1.10.0 IRON

Iron is an industrial metal that has found wide use in iron and steel based industries. As such, it is found in high concentrations in both industrial and domestic discharges [20,25]. Therefore, utilization of partially or untreated sludge as a fertilizer has been a major source of iron in the environment e.g. Kariobangi sludge has about 40008 ppm [25]. Being an essential element in many living systems it is only very heavy loads that show toxic effects. In animals it is involved in oxygen transfer systems e.g.

haemoglobin and oxygen storage systems in muscles like myoglobin; in electron transfer systems e.g. cytochrome C [1,29].

In the animal bodies iron is absorbed in the duodenum if ingested and is deposited in the lungs causing chronic bronchitis and tracheobronchial disorders if inhaled. The efficiency of iron absorption in the duodenum is dependent on the chemical form and oxidation state. Comar [27] noted that in the presence of chelating agents in foodstuffs e.g. phatates and phosphates with which it forms very stable complexes, the efficiency is very much lowered. He also observed that it is the ferrous form which is absorbed in the duodenum. As such, ferric form is first reduced to the ferrous form before absorption. Thus, the efficiency of iron absorption is increased by reducing agents like ascorbic acid [4,27]. In the body, the main storage organs are the liver where it sometimes causes cirrhosis, the spleen and the bone marrow where it is stored as ferritin or hemosiderin.

The main excretory route for iron is via faeces with a smaller amount through urine [7,27,28]. The urinary level of iron is relatively low due to the low level of free iron in the blood as most occur bound to transferrin and siderophilin which are the iron transfer proteins. These proteins are not normally excreted unless under serious kidney damage.

1.11.0 MERCURY

This is a non essential element that has found many uses in industries e.g. in cosmetics, chlor-alkali, tanning, pharmaceutical, fungicide, marine paints and in paper and pulp [2] and as such, its levels in water have gradually increased [1,6,16]. In the environment, mercury occur either in an organic matrix or in an inorganic form. However, the inorganic form is slowly methylated by certain microorganisms to methyl mercury chloride [2]. This compound easily decomposes to give the highly toxic methyl mercury which is highly absorbed through the skin [6,23,31,32,33].

Once in the body it interacts with subcellular systems via the sulphydryl (SH) group leading to brain and central nervous system disorders, tingling sensation, constricted vision and sometimes death. In the body it accumulates in the kidneys with the main excretion routes being the faeces and the urine. The levels in the urine are increased by mercury mobilizing ligands e.g. ethanol and aminotriazole [16].

With this discussion, the author of this work decided to monitor the levels of these metals in soil, plants, water, sediments and urine samples obtained around Athi River town. X-ray fluorescence analysis technique was used as discussed in chapters two and three.

1.12.0 RESEARCH AIMS AND SIGNIFICANCE.

This research was aimed at determining the levels of iron, zinc, lead, chromium, cadmium, manganese and mercury in soil, plants, water, sediments and urine (for those working in the above cement factory). Sampling was done within the cement factory and in the Athi river, which flows through this region with many upcoming industries which include; a tannery which uses water soluble chromium (VI), a cement company which emits huge volumes of dust containing heavy metals like iron, manganese, copper and traces of other metals. These metals are likely to end-up in the soil within the vicinity; Exide Chloride company which smelt car battery plates and Auto spring company which uses iron and steel. Most of these industries do not pre-treat their effluents properly before discharging them into the sewage system due to lack of trained manpower and proper instruments as had been noted in an earlier work [37]. In addition to this, the town council has no waste treatment works and as such effluents are discharged into the receiving waters without any form of treatment.

Also to be monitored is the effect of the wind on dust scatter. Thus, soil samples in both leeward and wind ward directions was sampled.

Another reason for carrying out this research, was to find out why plants were not growing within the vicinity of the cement industry. Also monitored in this work is the seasonal variation in the levels of these metals in the river especially in the case of chromium. This was thought necessary because the two tanneries in this region dispose of their chromium (VI) containing effluents via the spray system on a piece of land near the river. As such, there is a possibility of these effluents getting washed into the river during the rainy season.

Lastly, the author decided to do this research as no work had been reported that integrated the effects of industrial activities with the levels in soil, plants, water, sediments and urine within and beyond the neighbourhood of industries in the Athi River town.

CHAPTER 2

2.0.0 THEORY OF THE X-RAY FLUORESCENCE ANALYSIS TECHNIQUE (XRFA).

In this technique, x-rays from an x-ray tube or from a radioisotope such as cadmium-109, iron-55 are used [38]. These primary characteristic radiations are then used to excite the elements in the sample being analysed. The secondary characteristic radiations (fluorescence radiation) emitted from the sample are then detected, amplified, shaped and sorted out as per their energies by a system consisting of a pre-amplifier, amplifier and a multichannel analyzer (MCA).

2.1.0 DERIVATION OF EQUATIONS USED IN XRFA.

These equations are derived after making the following assumptions:

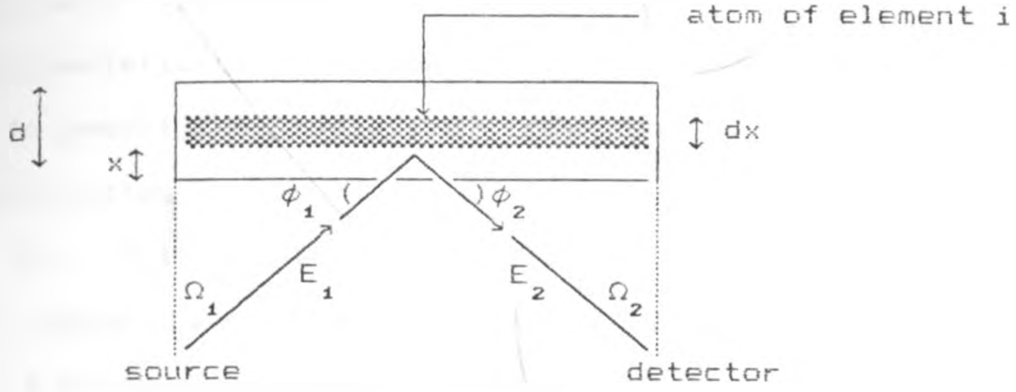
(1) That the sample is of uniform thickness and homogeneous i.e. the density (ρ) is constant throughout the sample.

(2) That the incident primary radiation used to excite the sample is monochromatic.

(3) When measuring the intensity, the spectrometer geometry is taken as fixed.

The spectrometer system consists of a sample, source of radiation and the detector system, figure 1.

figure 1: Schematic diagram of a spectrometer system with a sample.



where,

d - thickness of the sample pellet.

x -depth penetrated by the incident radiation

Ω_1 and Ω_2- are the solid angles.

E_1 - energy of the incident radiation whose intensity is Io.

E_i - energy of the fluorescence radiation of element "i" whose intensity is I_i.

2.1.1 Production of fluorescence radiation.

The primary incident radiation interacts with the inner electrons thus exciting the atom. If the energy (E_i) of the primary incident radiation of intensity Io is greater than the binding energy (Eb) of the electron, an electron is ejected and the vacancy so created is occupied by an outer shell electron in order to maintain the atom at the lowest possible internal energy. Fluorescence radiation is emitted from this electronic transition. The resultant radiation is characteristic of the element being excited.

To detect the radiation from the sample, three probabilities are involved.

(i) P1. This is the probability that the primary incident radiation of intensity I_o will penetrate a depth x in the sample.

$$P1 = I_o\, \Omega_1 \exp -\{\mu(E_i)\rho_i\, x \csc \phi_1\} \text{ ---------(2.1.1)}$$

where,

μ - mass absorption coefficient.

x - depth penetrated by the primary radiation.

I_o - intensity of the primary radiation.

E_1 - energy of the primary radiation.

ρ_i - density of the sample.

(ii) P2. This is the probability that the atom of element "i" will totally absorb the primary incident radiation within a layer dx and get excited through photoelectric effect thereby emitting its characteristic radiation of energy E_i

$$P2 = \sigma_i^{\rho h}\,(E_i)\rho_i \csc \phi_1 (1-1/Jk)^i\, \omega_k^i\, f_\alpha^i\, dx \text{ ---(2.1.2)}$$

where,

$\sigma_i^{ph}(E_i)$ - the photoelectric cross-section of element "i" at primary incident radiation E_i.

$(1- 1/Jk)^i$ - the relative probability that photoelectric effect occurred in the K-shell.

ω_k^i - fluorescence yield for K-shell of element i.e. the efficiency with which fluorescence radiation is produced.

f_α^i - the fraction of the α x-rays to the total series excited.

(iii) P3. - The probability that fluorescence radiation of energy E_i will emerge out of the sample and be detected with a probability $\varepsilon(E_i)$.

$$P3 = \Omega_2 \varepsilon(E_i) \exp-\{\mu(E_1) \rho_i x \csc \phi_2\} \text{---------} (2.1.3)$$

where,

$\varepsilon(E_i)$ - detector efficiency for fluorescence radiation of energy E_i.

If the intensity of the primary radiation is Io then, the contribution of fluorescence x-rays in a layer of thickness dx at a depth x is given by;

$$dI_i = P1.P2.P3$$

$$= I_o\,\Omega_1\Omega_2 \csc\phi_1 \rho_i \sigma_i^{ph}\, E_1 (1 - 1/Jk)^i\, \omega_k^i\, f_\alpha^i\, \varepsilon(E_i)\, e^{(-a\rho x)} dx \quad \text{-----(2.1.4)}$$

where,

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

To get the total mass absorption coefficient for both primary and fluorescence radiation in the sample, equation (2.1.4) is integrated giving equation (2.1.5).

$$I_i = C\left[\frac{\{1-[\exp\}(-a\rho d)_i\}}{a\rho}\right] \text{------------(2.1.5)}$$

Where,

$$C = I_o\Omega_1\Omega_2\csc\phi_1\sigma^{ph}\, E_i(1-1\backslash Jk)^i\omega_k^i\, f_\alpha^i\, \varepsilon(E_i)\rho_i$$

Multiplying and dividing equation (2.1.5) by d, gives equation (2.1.6) below.

$$I_i = C\left[\frac{\{1-[\exp(-a\rho d)_i\}\ d}{a\rho d}\right] \text{--------------(2.1.6)}$$

Also, equation (2.1.6) can be rewritten as equation (2.1.7) below.

$$I_i = G_o\ Ki\ (\rho d)_i\left[\frac{\{1- \exp(-a\rho d)_i\}}{a\rho d}\right] \text{------(2.1.7)}$$

where,

G o is the geometrical factor dependent on the solid angles Ω_1 and Ω_2 given by equation (2.1.8)

$$Go = Io\Omega_1\Omega_2 \csc \phi_1 \text{-----------------} \quad (2.1.8)$$

$$Ki_i = \sigma_i^{ph}(E_i)(1-1/Jk)^i\ \omega_k^i\ f_\alpha^i\ \varepsilon(E_i)$$

This is the relative excitation and detection efficiency. The component $\left\{\frac{1-\exp(-a\rho d_i)}{a\rho d}\right\}$ is the absorption correction factor (A_{corr}).

Thus,

$$I_i = Go\ Ki(\rho d)_i\ A_{corr} \text{-----------------} (2.1.9)$$

where,

$(\rho d)_i$ - mass per unit area in g/cm^2 of a sample pellet of an element being determined.

This correction factor (A_{corr}) approaches unity as the weight of the sample pellet approaches zero i.e. a thin sample. Therefore, the equation for a thin sample becomes.

$$I_i = Go\ Ki\ (\rho d)_i \text{------------------------} (2.1.10)$$

Using equations (2.1.9) and (2.1.10) the absorption correction factor (A_{corr}) is determined. This is achieved by determining both I_i and the mass per unit area of the sample pellet $(\rho d)_i$ (Ki values are tabulated for most elements). The Go value is calculated using equation (2.1.10) and a thin sample of a known element whose mass per unit area $(\rho d)_s$ is known.

For analysis purpose, equation (2.1.9) is utilized. However, the absorption correction factor (A_{corr}) is first determined by making use of a multielement target and drawing a graph of $(a\rho d)_i$ against the corresponding characteristic radiation of zinc, manganese, titanium, bromine and niobium (equation 2.1.11).

$$a\rho d(o) = \ln \left[\frac{I_o^i}{I_1^i - I_2^i} \right] \qquad \text{-----------------(2.1.11)}$$

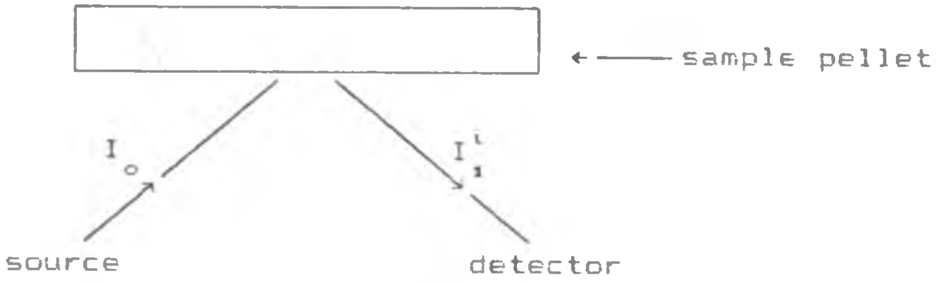
However, for this equation to hold the sample weight must not exceed 0.2g.

2.2 QUANTITATIVE ANALYSIS USING XRFA TECHNIQUE

2.2.1 Determination of aρd(o).

To determine $a\rho d(o)$, thin or intermediate sample (0.2g) are prepared and excited with monochromatic primary radiation I_o from a radioisotope or x-ray tube (figure 2). The elements in the sample after excitation emit their characteristic radiations and the intensities of the photopeaks for titanium, manganese, zinc, bromine and niobium determined. These are the I_1^i values [3,6,39].

Figure 2: Schematic diagram of a sample pellet being excited.



Where,

I_o is the primary incident radiation and

I_1^i is the emergent fluorescence radiation.

A multielement target is then placed on top of the sample and the intensity of the photopeaks determined after excitation with the same incident primary characteristic radiation (figure 3). These are the I_2^i values.

Figure 3: Schematic diagram of a sample and a multielement target being excited.

where,

I_o, is the primary incident radiation.

I_2^i, is the emergent fluorescence radiation.

Lastly, the sample pellet is removed and the multielement target excited. The intensities of the photopeaks of the same elements are recorded. These give the Io values. From the Io, I^i_1 and I^i_2 values for titanium, zinc, manganese, bromine and niobium, the $a\rho d(o)$ are calculated and using equation (2.1.11) below.

$$a\rho d(o) = \ln\left[\frac{I^i_o}{I^i_1 - I^i_2}\right] \text{-----------------(2.1.11)}$$

From a plot of $a\rho d(o)$ values versus energy (E_i) of the characteristic radiation of the above five elements, the $a\rho d(o)$ values of the elements of interest are determined (figure 4).

2.2.2 Calculation of concentration.

Assuming that the sample pellet is thin, the correction factor (A_{corr}) is taken as one. Rearranging equation (2.1.10) gives equation (2.1.12)

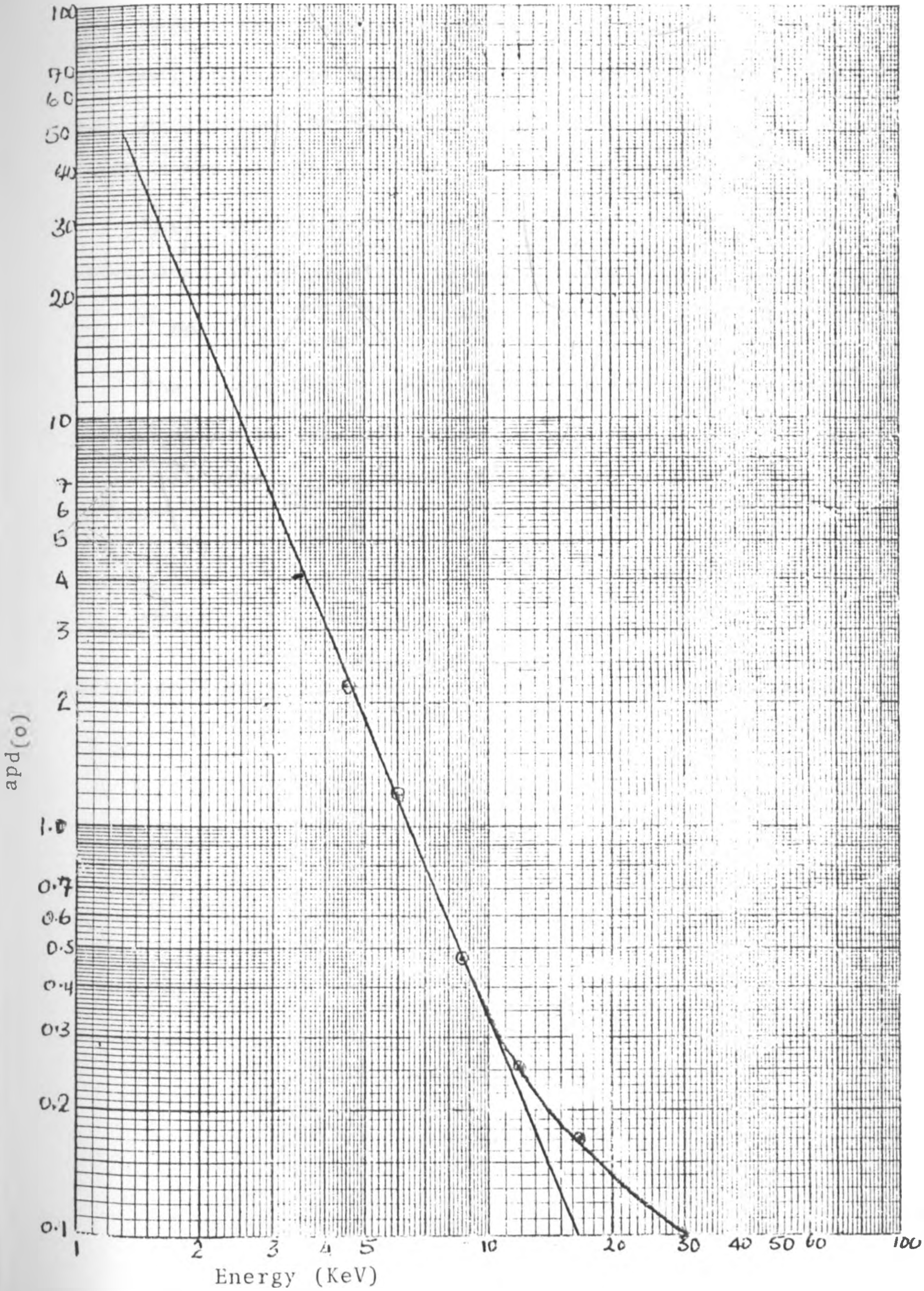
$$(\rho d)_i = \frac{I_i}{Goki} \text{--------------------(2.1.12)}$$

$$(\rho d)_s = \frac{\text{weight of sample (g/cm)}}{\text{surface area of the sample pellet}} \text{----(2.1.13)}$$

The uncorrected concentration (α_{uncorr}) is given by,

$$\alpha_{uncorr} = \frac{(\rho d)_i}{(\rho d)_s} \text{-------------------(2.1.14)}$$

FIG. 4: A GRAPH OF apd(o) AGAINST THE ENERGIES OF THE CHARACTERISTIC RADIATIONS OF TITANIUM, MANGANESE, ZINC, BROMINE AND NIOBIUM



From the absorption correction graph discussed earlier, the $a\rho d(o)$ values are used to calculate the $a\rho d'$ as in equation (2.1.15).

$$a\rho d' = a\rho d(o) \{1- [(1-1/Jk)\ \alpha_{uncorr}]\} \text{------}(2.1.15)$$

The absorption correction factor (A'_{corr}) is calculated using equation (2.1.16) below.

$$A'_{corr} = \frac{1-\exp(-a\rho d')}{a\rho d'} \text{------------------}(2.1.16)$$

The corrected concentration is then calculated using equation (2.1.17) below.

$$\alpha_{corr} = \frac{[(\alpha_{corr}\ .\text{dilution factor})\ 100\ ]\ \%}{A'_{corr}} \text{-----}(2.1.17)$$

Where, the dilution factor is given by,

$$\text{dilution factor} = \frac{(\text{weight of sample + starch})}{\text{weight of sample}} \text{---}(2.1.18)$$

2.3.0 INSTRUMENTATION.

The fluorescence system used consists of ;

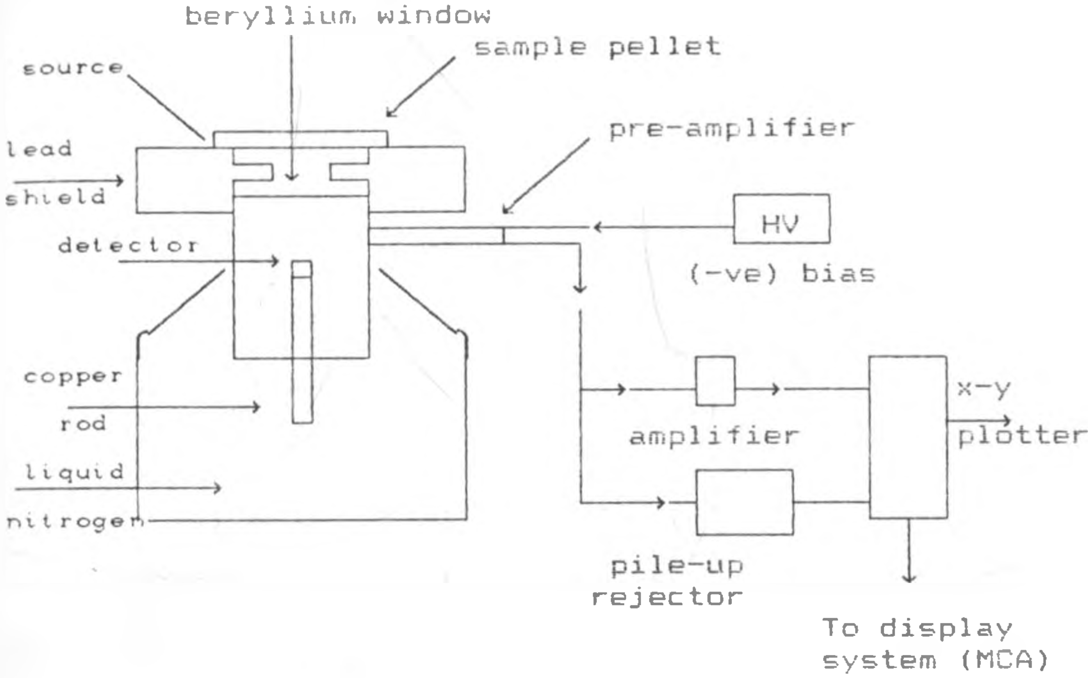
(i) A primary x-ray source. This is either an x-ray tube or a radioisotope.

(ii) Detector system. Here an ORTEC nitrogen cooled Si(Li) semi conductor detector is used whose overall resolution is 200 eV at 5.9 KeV.

(iii) Sample in air. Other systems may have sample in a vacuum or helium.

(iv) Electronic system which consists of a pre-amplifier, main amplifier and a multichannel analyzer (MCA). This is the system which amplifies, shapes and displays the photopeaks (figure 5).

Figure 5: Schematic diagram of a fluorescence system used in the analysis



(i) Data output is either an x-y plotter or a pro-350 micro computer.

(ii) Pre- amplifier for amplification of signals from the Si(Li) semi conductor.

(iii) An amplifier system that shapes-up and sorts out the signals.

(vi) A source that emits a monochromatic primary radiation that is used to excite the elements in the sample being analyzed.

CHAPTER 3

3.0.0 EXPERIMENTAL TECHNIQUE

3.1.0 Apparatus and reagents

In this work, the following apparatus and reagents were used;

1) Analar grade nitric acid and hydrochloric acid.
2) Analar grade ammonia solution.
3) Analar grade sodium diethyldithiocarbamate (NaDDTC).
4) Pure starch powder.
5) Mylar papers and millipore filter papers.
7) Double distilled water.
8) Agate mortar.
9) Pulveriser.
10) Hydraulic press.
11) pH metre.
12) Filtering system fitted with a millipore vacuum pump.
13) Cadmium-109 radioisotope source.
14) A multichannel analyzer system which consists of a multichannel analyzer (MCA), pre-amplifier, amplifier, liquid nitrogen cooled Si(Li) semiconductor detector whose overall resolution was 200 eV at 5.9 KeV.
15) Pro-350 micro computer.
16) An X-Y plotter.

3.2.0 SAMPLING AND SAMPLE PRESERVATION

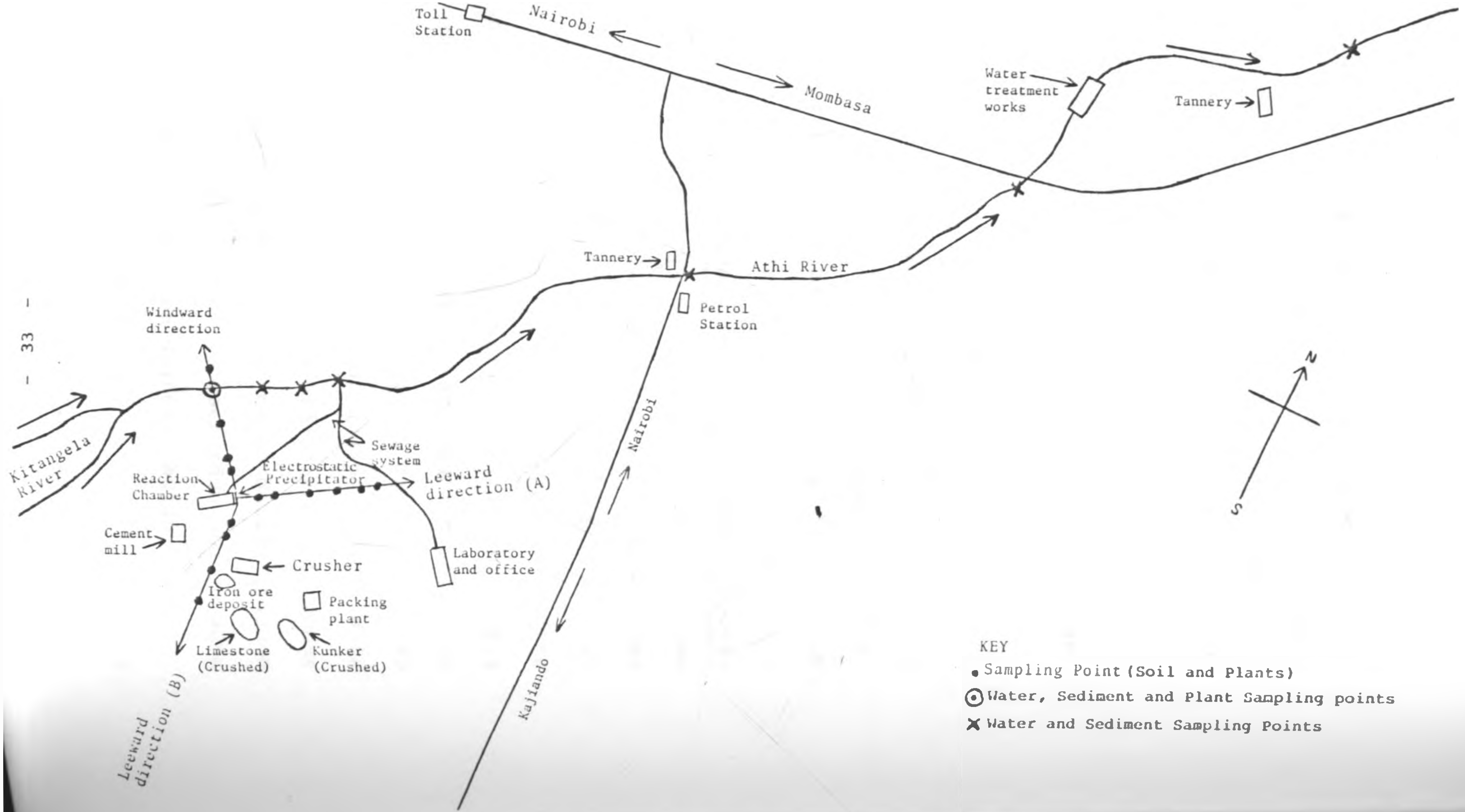
3.2.1 Soil

Soil samples were sampled within the cement factory at different distances relative to the electrostatic precipitator (Figure 6). At each of the locations, Soil samples were sampled up to a depth of 2 feet. This was found necessary in order to monitor the depth profile. The samples were stored in polyethylene containers and sealed to avoid trace metal contamination [40].

3.2.2 Plants leaves

In this work, leaves from three plant species were sampled from Athi River region and especially the area close to the cement factory where soils were sampled (Figure 6). These plant species were Tagetes minuta (Mexican marigold), Acacia xanthophloea (fever tree) and Schinus molle (pepper tree). They were selected because they were found to flourish extensively in this region. The three plant species were collected within an area of 5 M^2 at each of the selected locations. These locations were within 170 metres from the stack of the electrostatic precipitator which was the main source of the dust. The samples were put in polyethylene containers to avoid trace metal contamination, sealed and stored at 0 °C. This was to minimize growth of microorganisms which tend to decompose the samples [40,41,42,43].

FIGURE 6: SKETCH OF THE ATHI RIVER REGION SHOWING THE VARIOUS SAMPLING POINTS



3.2.3 Urine

The urine samples were taken voluntarily from some of the employees of the cement company and from a control group of volunteers who had not worked in an industry for a couple of years. The subjects selected were requested not to take any alcoholic drinks two days prior to the time when the samples were to be collected as these drinks tend to raise the levels of trace elements in urine [7]. To get an unbiased sample, the urine samples were collected over a period of 24 hours as suggested by Hoekstra et. al. [28]. The samples were grouped as per area in which the subject was working and the period of stay in this region as exposure levels basically depend on these two factors [23]. The pH of these samples were determined before stabilizing them with concentrated nitric acid [6]. They were stored in polyethylene containers to avoid trace metal contamination, sealed and kept at 0^{o}C.

3.2.4 Water

Water samples were taken from the cement company laboratory and the Athi river which flows through this region (Figure 6). Sampling was carried out over a length of about 2.0 kilometres. This length was selected because the effluents from the various industries entered the Athi river along this length. Also sampled, were the sediments at the water sampling points. Sampling was carried out both in the dry as well as in the wet season in order to monitor seasonal variation in the levels of trace elements.

The water samples were then put in plastic containers. Once in the laboratory, the pH of the water samples were measured and concentrated nitric acid added to prevent flocculation, precipitation of metal compounds and reduce adsorption on the sides of the container thus stabilizing the sample [40]. They were then sealed and kept at 0^{o}C.

3.2.5 Sediments

Sediments were sampled from the Athi river at the same points where water was sampled (Figure 6). The samples were put in polyethene containers and sealed.

3.3.0 SAMPLE PREPARATION

3.3.1 Soil and sediments

The soil and sediment samples were oven dried at 105^{o}C [43]. This temperature had been found to be effective in driving out water in soil samples without affecting the dry matter which would otherwise affect the concentration of the elements being determined. The sample was dried until a constant weight was recorded then ground and sieved through a 75 micro meter sieve (this was necessary as the technique is very sensitive to particle size effect) [6]. From this, a known weight was taken (about 1g) and mixed with a known weight of starch (about 2g) which acts as a binder and helps in minimizing enhancement effect. This was thoroughly mixed using a mortar and pestle (this was necessary as this technique is sensitive to inhomogeneity). A known weight (<0.2g) was taken and a thin pellet prepared using a hydraulic press at a pressure of about 7 tons. Several pellets were made from the same mixed sample. The exact weight of the pellet was then determined. The sample was then analysed as discussed earlier using XRFA technique.

3.3.2 Plant leaves

Leaves from Tagetes minuta, Schinus molle and Acacia xanthophloea plant species were collected and washed with distilled water as recommended by several researchers like Hoekstra et. al., Steyn and Walsh et. al. [28,42,43]. They were oven dried at 85 ^{o}C [44] until a constant weight was recorded then ground with a quartz mortar and sieved through a 75 micro meter sieve [43]. This was done to minimize particle size effects as discussed earlier in soil. A known weight (<0.2g) was taken and a pellet prepared as in soil samples above. Again, several pellets were made and analysed.

3.3.3 Urine

From the urine sample, 20 mls were measured out and digested with 1 ml of analar grade nitric acid at 40 ^{o}C to break-up the organic matter [27,30]. The pH was adjusted to 5.0 for most elements and to 3.9 for chromium and manganese using analar grade nitric acid and ammonia solution. 10 mls of a freshly prepared 2% solution of sodium diethyldithiocarbamate (NaDDTC) were added [41] and the sample allowed to stand for about 15 minutes and filtered through a millipore filter paper using a vacuum pump. The sample was again allowed to dry in the oven at 30 ^{o}C and then analysed.

3.3.4 Water

Water samples were first filtered through a number 1 filter paper and 100 mls taken. To each of the samples, 2 mls of nitric acid were added and the sample heated at 40 ^{o}C for about 10 minutes to break-up the organic matter [27,30] which tend to block the millipore paper used in the final filtration. The sample was then allowed to cool and its pH adjusted to 5 using analar grade nitric acid and ammonia solution. This pH value was chosen because the sodium diethyldithiocarbamate (NaDDTC) which is used as a complexing agent works best at this pH [41,45]. However, a pH of 3.9 was selected for manganese and chromium for the same reason [27,41,45].

To this sample, 10 mls of a freshly prepared 2% solution of sodium diethyldithiocarbamate (NaDDTC) were added as a pre-concentrating agent and allowed to stand for about 15 minutes. The sample was then filtered through a millipore paper with the help of a vacuum pump and allowed to dry in an oven at 30 ^{o}C. This drying process was found necessary because water is known to give rise to x-ray attenuation which may lead to serious errors in the concentration values [41]. The sample was then analysed.

3.4.0 SAMPLE AND DATA ANALYSIS

In this work, an x-ray fluorescence analysis (XRFA) technique was used. The XRFA system used consists of a 10 mCi cadmium-109 radioisotope source, a liquid nitrogen cooled ORTEC Si(Li) semi-detector with a 25 micron beryllium window, an S40 canberra multichannel analyzer (MCA) and a Dec Pro-350 microcomputer.

The samples were excited using a cadmium-109 radioisotope source. The emitted fluorescence radiation was then detected using a Si(Li) semi conductor detector. The signals were then amplified, shaped and sorted out by the electronic system as discussed in chapter 2. The intensities of the various photopeaks were determined using a quantitative x-ray analysis program (QXAS) and the corresponding concentrations calculated with the help of a pro- 350 microcomputer.

For soils, sediments and plants samples, an excitation time of 1500 seconds was found appropriate whereas for water and urine samples a time of between 4000 and 6000 seconds was found necessary.

For plants and soils, a multielement target was placed on the sample pellet and the system excited for 500 seconds . Here, only the intensities of the photopeaks for titanium, zinc, manganese, bromine and niobium were determined. Lastly, the multielement target was excited for 100 seconds and the intensities of the above five elements determined. These intensities were used to determine the $\text{apd}_{(o)}$ and the absorption correction factor (A_{corr}) as discussed in chapter two.

3.5.0 Accuracy of the technique (XRFA)

XRFA technique as pointed out earlier in chapter two is suitable for the analysis of both solid and liquid samples. The liquid samples that can be analysed include water, urine and other body fluids, industrial and domestic effluents. For solids, it can analyze plant materials, soil, ores and sewage sludge.

In this work, plant leaves, soil, urine and water were analysed. The accuracy of this technique against other analytical techniques was tested by analyzing standard reference materials i.e. soil-7 and tomato leaves from international atomic energy agency (IAEA).

The results were compared with certified values (IAEA) obtained from several analytical laboratories. The results are tabulated in tables 1 and 2.

From table 1, it was noted that the levels of potassium, calcium, manganese, iron, copper, zinc, lead and strontium were within the certified range (IAEA) with zirconium as the only exception. The other point noted was that the relative error between the certified (IAEA) values and those obtained from XRFA technique were all below 10% with copper and lead as the only exceptions. The high deviation of these two values was attributed to errors arising from the low concentrations involved resulting in a high background. This makes it difficult to determine the area of the photopeaks accurately. The other factor that could have contributed to these deviations is inhomogeneity. This is because it is very difficult to homogenize an element in a sample if present in very low concentrations. However grinding the sample thoroughly minimizes this problem.

TABLE 1 A COMPARISON OF THE LEVELS OF HEAVY METALS IN STANDARD REFERENCE SOIL-7 AS DETERMINED BY XRFA WITH THE CERTIFIED REFERENCE VALUES.

ELEMENTS	XRFA VALUES (ppm)	CERTIFIED VALUES (IAEA) (ppm)	CERTIFIED RANGE (IAEA) (ppm)	RELATIVE PERCENTAGE ERRORS
K	12613.1 ± 281.1	12100	*	4.2
Ca	160144.5 ± 1885.	163000	*	1.8
Ti	2874.6 ± 181.8	3000	2600 - 3700	4.2
Mn	644.8 ± 9.3	631	604 - 650	2.2
Fe	25191.1 ± 587.6	25700	25200 - 26300	2.0
Cu	9.5 ± 1.2	11	9 - 13	13.6
Zn	110.5 ± 8.5	104	101 - 113	6.2
Pb	52.9 ± 9.0	60	55 - 71	11.8
Sr	106.7 ± 6.4	108	103 - 114	1.3
Zr	203.1 ± 6.1	185	180 - 201	9.8

NB.
* not calculated.

It was noted from table 2 that the concentrations of the metals analysed were within the certified reference range (IAEA) with potassium and strontium as the only exceptions. However, the deviation was small and is within analytical errors. It was also noted that the relative errors (percentage) are all below 10%. This was expected as plant materials are very homogeneous compared to soils and do not require a binder.

In conclusion, the technique was found to have an accuracy comparable to that of other analytical techniques and hence suitable for this work.

TABLE 2 A COMPARISON OF THE LEVELS OF HEAVY METALS IN STANDARD REFERENCE TOMATO LEAVES AS DETERMINED BY XRFA WITH THE CERTIFIED REFERENCE VALUES. (concentration in ppm)

ELEMENTS	XRFA VALUES	CERTIFIED VALUES (IAEA)	CERTIFIED RANGE (IAEA)	RELATIVE PERCENTAGE ERRORS
K	45200.5 ± 381.7	44600	44287 - 44912.2	1.3
Ca	30315.0 ± 320.6	30000	29700 - 30300	1.1
Mn	230.8 ± 10.4	238	231.1 - 244.9	3.0
Fe	658.1 ± 13.8	690	666.3 - 713.7	4.6
Cu	11.7 ± 0.7	11	10.0 - 12.0	6.4
Zn	61.6 ± 2.4	62	56.0 - 68.0	0.6
Rb	16.8 ± 1.3	16.5	16.4 - 16.6	1.8
Sr	46.9 ± 3.2	44.9	44.6 - 45.2	4.5

CHAPTER 4

4.0.0 RESULTS AND DISCUSSION

In this chapter, the mean levels of heavy metals in plants, soil, urine, water and sediments are discussed. The results are classified into several classes.

1) Variations in the levels of heavy metals with depth in soil samples, sampled at different locations relative to the electrostatic precipitator within the cement factory.
2) Variation in the levels of heavy metals in soil samples with distance from the electrostatic precipitator.
3) Variation in the levels of individual heavy metals in the leaves of **Schinus molle, Tagetes minuta** and **Acacia xanthophloea** plant species with the levels in the respective soils.
4) Variation in the levels of heavy metals in urine samples of volunteer employees of a cement company working in different departments within the factory.
5) Variation in the levels of heavy metals in water samples, sampled along the Athi river at different distances relative to the point where effluents from the

cement company entered the Athi river. 6) Variation in the levels of heavy metals in sediments, sampled at the water sampling points.

As pointed out earlier, this research was mainly confined to a cement company that was found to emit large volume of dust which covered the soil within the vicinity of this factory. The dust was being emitted by the electrostatic precipitator which had been installed in the reaction chamber (kiln), where the temperature range from 200 ^{o}C to 1600 ^{o}C [46]. Dust from the electrostatic precipitator was analyzed in the laboratory of the cement factory for calcium carbonate, silicates and alumina. For analysis purposes, a dust sample was weighed and about 7.0g of sodium hydroxide pellets added as the digesting media in a gold coated crucible. The sample was digested for 30 minutes at about 900 ^{o}C and then dissolved in 5M hydrochloric acid solution [47,48]. The resultant solution was then used in the analysis [49,50,51,52]. For calcium analysis, a known volume was taken and titrated with ethylenediaminetetraacetic acid (EDTA) and the volume used recorded. This volume was used to calculate the concentration of calcium carbonate (appendix 1). For silicates, the sample was analyzed for silica (SiO_2) levels after a known volume of the digested sample was complexed with a 10% solution of ammonium molybdate and analyzed at 410nm with a Pye Unicam 1800 spectrophotometer. Alumina was analyzed at 365nm using a 0.2% solution of 8-hydroxy-7-iodo-5-quinoline sulphonic acid in a solution of sodium acetate trihydrate in 5M acetic acid. The levels of calcium carbonate, silica and alumina were 65%, 21% and 2.5% respectively.

4.1.0 SOIL

The soil at the sampling points was mainly dust from the precipitator which had a characteristic light yellow colour. The dust had formed a heap about 15 metres high. These samples being mainly dust had high levels of calcium carbonate, silica and alumina with very low levels of organic matter.

Table 3 shows a summary of the levels of heavy metals in soil samples , sampled 30 metres from the electrostatic precipitator at various depths in a windward direction. The various trace elements are itemized below:-

CHROMIUM

Chromium was not detected over the depth range sampled. Thus, the dust was found not to be a potential pollutant with respect to chromium (Table 3).

MANGANESE

The concentrations of total manganese in the soil between 0.0 cm and 30.0 cm deep ranged from 393.4 ppm to 406.2 ppm) with a mean of 401.2 ± 5.6 ppm. The difference was small and insignificant at 95% confidence level as shown by the t-test method. This difference was attributed to experimental error. As the depth increased, the concentrations were notably increasing, registering 559.6 ± 36.2 ppm and 595.5 ±

TABLE 3 THE LEVELS OF HEAVY METALS IN SOIL SAMPLES SAMPLED 30 METRES FROM THE ELECTROSTATIC PRECIPITATOR.
(concentration in µg/g; n=4; Mean, ± standard deviation)

depth(cm)	Cr	Mn	Fe	Cu	Zn	Pb	Hg
0.0	nd	404.0	7620.1	5.5	41.5	11.8	nd
	-	± 33.3	± 370.0	± 0.9	± 3.3	± 1.7	-
15.0	nd	406.2	7480.3	7.3	39.5	11.2	nd
	-	± 215	± 460.2	± 1.0	± 3.2	± 1.7	-
30.0	nd	393.4	5710.3	6.1	65.7	14.1	nd
	-	± 22.5	± 380.7	± 0.7	± 5.2	± 1.1	-
45.0	nd	559.6	9240.0	5.4	65.9	12.8	nd
	-	± 36.2	± 600.0	± 0.3	± 6.5	± 1.2	-
60.0	nd	595.5	9670.7	6.1	66.8	11.6	nd
	-	± 34.9	± 450.2	± 1.1	± 4.8	± 1.8	-

NB.
n - sample size.
nd - not detected.

34.9 ppm at 45.0 cm and 60.0 cm respectively. The increase was attributed to leaching of manganese to lower depths [25, 52,54].

Under condition of reduced oxygen levels, the following reduction occurs (54).

$$MnO_2 + 4H^+ + 2e^- = Mn^{2+} + 2H_2O \quad ----(4.1.1)$$

As a result, the concentration values in the upper depths were lower than those at lower depths. However, there were some anomalies at depths of 0.0 cm and 30.0 cm. The slightly higher levels were thought to have been due to recent dust deposits. As such, the dust was found to have environmental pollution value with respect to manganese, especially if this manganese would be leached and hence available to plants [55].

IRON

The total iron concentrations were found to be comparable at depths of 0.0 cm (7620.5 ± 370.5 ppm) and 15.0 cm (7480.3 ± 460.2 ppm). At 30.0 cm, there was a decrease to 5710.3 ± 380.7 ppm followed by an increase upto 60.0 cm.

Moore [53], working on soil from North East Scotland noted that iron levels usually increase with depth to a maximum and then falls., He had attributed this phenomenon to mobilization of iron from upper soil levels to lower depths. As it leaches down, some get trapped by silicates structure which does not release it readily under conditions of limited oxygen availability and high ionic strength. This was thought to occur at lower depths during the rainy season when the rate of oxygen diffusion was low. Under conditions of low oxygen levels, the following reaction occurs [53,54].

$$Fe(OH)_3 + 3H^+ + e^- = Fe^{2+} + 3H_2O \quad ----(4.1.2)$$

After this reduction process, iron (II) ions, leach down as they are water soluble. This phenomenon was not wholly obeyed as there was always some dust being deposited on the top soil thereby, replenishing leached iron (sampling was done after four months of a dry spell). This would have resulted in higher levels being registered at 0.0 cm and 15.0 cm compared to 30.0 cm. The fact that there was no decrease after the initial increase was thought to be due to the narrow range sampled. Moore [53] had sampled upto a depth of 120.0 cm getting a maximum between 40.0 and 60.0 cm.

Therefore, the dust had a substantial amount of iron that could be leached hence available to plants [54], suggesting its potentiality as a soil contaminant.

COPPER

The levels of copper were noted to increase slightly from 5.5 ± 0.9 ppm (0.0 cm) to 7.3 ± 1.0 ppm

(15.0 cm). This was followed by a mild decrease upto 45.0 cm and then an increase to 6.1 ± 0.7 ppm at 60.0 cm. The initial increase at 15.0 cm was attributed to leaching of copper which was latter being adsorbed on the surface of iron and manganese containing soil matrix at this depth [54]. Under conditions of reduced oxygen levels and water, the following reaction occurs.

$$Cu^{2+} + e^{-} = Cu^{+} \qquad E_o = + 0.167\ V \text{ -----(4.1.3)}$$

This reaction does not normally occur in soil for it is sensitive to low pH and it has a positive redox potential hence not spontaneous [56]. Also, its solubility in water in the presence of high levels of hydroxide and carbonate ions with which it forms insoluble compounds is low [54]. These samples had high levels of calcium carbonate (65%) hence limited leaching. It was thus thought that the concentrations of total copper in soils were dependent on the parent rock and anthropogenic activities [10]. Therefore, the levels of copper were too low to be of any pollution value.

ZINC

The concentrations of total zinc were found comparable at depths of 0.0 cm (41.5 ± 3.3 ppm) and 15.0 cm (39.5 ± 3.2 ppm). Further down, there was an increase to 65.7 ± 6.2 ppm (30.0 cm), 65.9 ± 6.5 ppm

(45.0 cm) and 66.8 ± 4.8 ppm (60.0 cm). This increase was thought to have been due to leaching and adsorption by iron and manganese oxides as this is the common form of these oxides in the soil [54,57,58].

These levels were low to cause any environmental pollution as zinc shows phytotoxicity when the level of available zinc is about 400 ppm [25].

LEAD

The levels of total lead over the depth range sampled were notably constant (11.2 - 14.1 ppm). These differences were small and insignificant at 95% confidence level (t-test) and were attributed to experimental errors [59]. They could have also been due to slight variations in soil levels as lead distribution in soil was noted to be non-uniform by Freiburg [59]. Like copper, lead does not leach down due to its low solubility in the presence of high levels of carbonate ions (1.58×10^{-10} ppm) [60,61].

Despite the low levels of lead in the dust the levels were of concern as lead was likely to be absorbed in the respiratory system if the dust was inhaled. This was likely to occur as inorganic lead is absorbed in the respiratory system and it is cumulative and highly phytotoxic and toxic to plants and animals respectively [1,10,15,22]. This is due to its ability to bind to the sulphydryl group (SH) in proteins and amino acids as discussed in chapter 1.

$$\text{Protein-SH} + \text{Pb}^{2+} + \text{HS-Protein} = \text{Protein-S-Pb-S-Protein} + 2\text{H}^{+} \text{ ----------(4.1.4)}$$

MERCURY

Mercury was not detected in all the soil samples analyzed. This data was taken as reliable as Schindler [62], Maina [25] and Jenkins et. al. [63] working on water, soil and plant samples respectively found this technique (XRFA) to be reliable for mercury determination both in the ppm and ppb range.

In order to obtain a wide ranging understanding of the levels of the trace elements in the region, analysis was performed with samples from a different direction (leeward direction (A)) and distance from the electrostatic precipitator as opposed to that shown in table 3 above.

Table 4 shows a variation of the levels of heavy metals in soil samples, sampled 40 metres from the electrostatic precipitator in a leeward direction. The top soil at the sampling points was mainly dust changing to black cotton soil with increase in depth. Individual elements in table 4 are discussed in more detail below:

CHROMIUM

Chromium was not detected in the top soil as in table 3. This was attributed to dust from the precipitator which had very low total chromium concentrations. Further down, its concentration increased to 10.3 ± 1.6 ppm, 18.9 ± 4.0 ppm, 13.9 ± 3.9 ppm and 14.8 ± 4.1 ppm at 15.0 cm, 30.0 cm, 45.0 cm and 60.0 cm respectively.

From the above concentration values, the levels of chromium were noted to increase to a maximum at 30.0 cm and then stabilized.

In soil, chromium exist as the water insoluble chromium (III) ion which is the stable oxidation state [31]. The maximum value at 30.0 cm was thought to have

TABLE 4 THE LEVELS OF HEAVY METALS IN SOIL SAMPLES SAMPLED 40 METRES FROM THE ELECTROSTATIC PRECIPITATOR. (concentration in ug/g; n=5; Mean, ± standard deviation)

depth(cm)	Cr	Mn	Fe	Cu	Zn	Pb	Hg
0.0	nd	404.2	9010.1	10.7	39.3	10.8	nd
	-	± 23.0	± 280.0	± 2.2	± 3.4	± 1.5	-
15.0	10.3	950.0	7010.0	14.2	66.5	6.5	nd
	± 1.6	± 80.0	± 240.0	± 2.4	± 5.5	± 0.9	-
30.0	18.9	430.6	7880.0	7.9	51.4	7.9	nd
	± 4.0	± 44.2	± 210.0	± 1.3	± 4.0	± 1.7	-
45.0	13.9	339.5	8960.2	6.7	5.1	7.5	nd
	± 3.9	± 29.3	± 330.1	± 1.2	± 3.9	± 1.6	-
60.0	14.8	424.6	10120.4	6.0	56.2	8.0	nd
	± 4.1	± 24.5	± 410.0	± 1.1	± 4.5	± 1.8	-

NB.

n - sample size.
nd - not detected.

been due to leaching of the slightly soluble chromium (IV) ions in the top soil after the oxidation of chromium (III) ions. This was then thought to have resulted in low concentrations at these depths. This oxidation requires oxygen hence it may not have occurred far from the soil surface especially in the rainy season when the level of oxygen in the soil is low [15,64].

Therefore, the concentration at depths of 45.0 cm and 60.0 cm could have been dependent on the levels in the parent rock as the rate of leaching was expected to be low.

MANGANESE

The concentration of total manganese was noted to increase from 404.2 ± 23.0 ppm (0.0 cm) to 950.0 ± 80.0 ppm (15.0 cm). As had been pointed out earlier, the top soil consisted mainly of dust from the electrostatic precipitator. This dust had substantial amount of manganese which could be easily leached (Table 3) to lower depths during the rainy season for manganese is a mobile element [53]. This might be the reason why the concentrations at depths of 45.0 cm and 60.0 cm i.e. 339.5 ± 29.3 ppm and 429.6 ± 24.5 ppm respectively were low. These concentrations were considered to be the non-anthropogenic levels hence dependent on the levels of this metal in the dust which in turn depend on the parent rock [54]. At a depth of 15.0 cm there was a change in the soil type to black cotton soil. This soil being a zeolite had a high adsorption capability for manganese. Thus, the levels of manganese at 15.0 cm were ever increasing as the top soil was being replenished by the falling dust, thus offering a reservoir for manganese.

Therefore, the level at a depth of 15.0 cm was thought to have been partly due to non-anthropogenic manganese and partly due to leached manganese from upper soil as the increase and subsequent decrease were so drastic as to be accounted for by the natural inhomogeneity in the distribution of metals in soils [10,53].

IRON

The level of total iron in the top soil was higher than that at a depth of 15.0 cm. This was thought to have been due to dust from the precipitator which had high levels of iron and was continuously replenishing the top soil. With increase in depth, the concentration of total iron decreased and then increased upto a depth of 60.0 cm. This increase was attributed to leaching from upper soil as zeolite do release adsorbed iron and also because iron (II) ions are soluble over the whole pH range encountered in soil. However, in the presence of extremely high levels of carbonate ions its solubility is lowered to about 3.5% and hence the slight differences in concentration with increase in depth [53,55].

COPPER

The levels of total copper were notably variable over the depth range sampled. They were high in the top soil (10.7 ± 2.2 ppm) increasing to 14.2 ± 2.4 ppm (15.0 cm) and then decreased upto 60.0 cm. The high level of copper in the top soil was attributed to anthropogenic copper in the dust. This after being mobilized was thought to leach down and later adsorbed by manganese and iron oxides as the two metals exist in that form in the soil (manganese being a better adsorber for copper than either organic matter or silicates) [64,66]. This was suggested to be the reason why copper had a maximum at 15.0 cm where the level of manganese was 950.0 ± 80.0 ppm (Table 3). As the depth increased, the strongly bound copper could not be easily mobilized (eq. 4.1.3).

This is due to its positive redox potential hence not spontaneous [54,56]. As such, concentrations at lower depths were taken as the natural levels.

ZINC

The concentration of total zinc in the top soil (39.3 ± 3.4 ppm) was notably lower than those at lower depths which were, 66.5 ± 5.5 ppm, 51.4 ± 4.0 ppm, 46.1 ± 3.9 ppm and 56.2 ± 4.5 ppm at 15.0 cm, 30.0 cm, 45.0 cm and 60.0 cm respectively. The low concentration in the top soil was probably due to leaching which resulted in slightly high levels further down. The fact that these values were comparable suggests that they were from the same parent rock and hence they were the natural levels [54,65,67].

LEAD

The concentration of total lead in the top soil (10.8 ± 1.5 ppm) was notably higher than those at lower depths. The level in the top soil was comparable to that in the dust (Table 3). This was expected as Lead ions are highly insoluble and are not expected to leach down especially in the presence of the carbonate ion which lowers their solubility to less than 1.58×10^{-10} at $25\ ^{o}C$ [60,61].

Further down, the levels were comparable (6.5 - 0.9 ppm). The differences in these values were small and insignificant at 90% confidence level and were within experimental errors near the detection limit (5.0 ppm) [59]. The slight differences could also have been due to inhomogeneity in the distribution of lead in soils [59]. Thus, the concentrations of lead at various depths were thought to have been basically dependent on the natural levels.

Therefore, the dust was found to have more lead than the indigenous soil. This suggests that the dust was a potential soil contaminant with respect to lead.

An interesting feature at sampling point 90 metres away from the precipitator, was that soil samples sampled at all depths were mainly dust possibly from the electrostatic precipitator, crusher and an iron ore storage site.

Table 5 shows a summary of the levels of heavy metals in soil samples, sampled at a distance of 90 metres from the electrostatic precipitator in a wind ward direction. At the sampling points, there was the main crusher that crushed the rocks used in cement manufacture. Dust from this crusher was noted to have been falling on the soil at the sampling points. Nearby, there was also an open storage site for crushed iron ore. This iron ore was sometimes being washed away by water especially during the rainy season. It was also being blown away by the wind to soil within the the vicinity. These activities were thought to result in an increased level of iron, chromium and zinc at the sampling points. The soil type at the sampling points was noted to change with depth from greyish brown to brown.

CHROMIUM

The concentrations of total chromium were generally high. The oxidation state of chromium was not determined but it was thought to be the slightly water soluble chromium (III) ion which is the most stable form of chromium in soil [31].

As had been pointed out earlier, the colour of the soil changed from greyish brown to brown with increasing depth. The colour change was attributed to dust from the crusher, the electrostatic precipitator and the iron ore storage site. During the rainy season, iron ore was being washed away and deposited on this soil. The dust from the three sources was suspected to have had appreciable amount of chromium as a rock having the same chemical composition as the rock used in cement manufacture had chromium concentrations averaging about 33.6 ± 5.1 ppm. Thus, the levels of chromium at depths of 0.0 cm (66.6 ± 11.4 ppm) and 15.0 cm (67.5 ± 6.7 ppm) were comparable followed by a significant increase at 30.0 cm (76.5 ± 11.7 ppm). This increase of about 10 ppm was significant at 95% confidence level as showed by t-test and might have been due to anthropogenic activities, moderate leaching or the levels present in the parent rocks.

Therefore, the levels at various depths were attributed to anthropogenic activities and in particular to dust from the iron ore storage site, the crusher and the electrostatic precipitator.

TABLE 5 THE LEVELS OF HEAVY METALS IN SOIL SAMPLES SAMPLED 90 METRES FROM THE ELECTROSTATIC PRECIPITATOR.
(concentration in ug/g; n=4; Mean, ± standard deviation)

depth(cm)	Cr	Mn	Fe	Cu	Zn	Pb	Hg
0.0	66.6	487.2	11950.2	10.4	103.2	56.7	nd
	± 11.4	± 39.5	± 650.3	± 2.0	± 16.5	± 6.3	-
15.0	67.5	384.8	11910.3	9.1	90.7	10.6	nd
	± 6.7	± 18.7	± 720.4	± 2.3	± 6.1	± 2.2	-
30.0	76.5	411.4	11130.9	14.1	96.7	22.5	nd
	± 11.7	± 31.5	± 634.7	± 2.5	± 10.6	± 4.0	-
45.5	73.6	531.0	15277.5	15.1	97.6	42.2	nd
	± 13.5	± 40.6	± 564.9	± 2.4	± 4.4	± 3.1	-
60.0	715	3115	13010.4	12.3	97.0	43.1	nd
	± 13.5	± 29.1	± 610.2	± 1.9	± 0.4	± 4.6	-

NB.
nd - not detected.
n - sample size.

MANGANESE

The concentrations of total manganese were notably comparable over the depth range sampled although there were slight variations due possibly to leaching. The levels at various depths were 487.2 ± 39.5 ppm (0.0 cm), 384.8 ± 18.7 ppm (15.0 cm), 411.4 ± 37.5 ppm (30.0 cm), 531.9 ± 40.6 ppm (45.0 cm) and 310.5 ± 29.1 ppm (60.0 cm). Moore (53), had reported that the levels of manganese increase, stabilize and then decrease with depth. This pattern seems to have been observed if it was not for the concentration in the top soil. The high level in the top soil was thought to have been due to dust from the crusher. This dust was continuously replenishing the metals being leached. Therefore, the concentrations at lower depths were attributed to leaching and the natural levels.

IRON

The concentrations of total iron in the soil samples were generally higher than those present in the dust from the electrostatic precipitator (Table 3). The high levels were attributed to the iron ore being brought by water and wind from an iron ore storage site i.e. due to anthropogenic activities [54]. Here, leaching was expected to have had minimal effect as most of the iron was from the iron ore. Leaching probably contributed to slight increases beyond 30.0 cm as most of the iron at this point was from an iron ore storage site. This iron exist as the insoluble iron (III) ions whose rate of reduction to iron (II) is mild as iron is moderately mobile [54].

COPPER

The concentrations of total copper were comparable over the depth sampled with no outright variation. However, there was some correlation between the levels of manganese and iron in the soil and the levels of copper. This correlation might have been dependent on the high ability of these metals in the soil to adsorb copper or due to these metals being associated with copper in the parent rock [53,64,67].

ZINC

The levels of total zinc were comparable over the depth sampled. This suggests that there was only slight leaching to lower depths and that the dust had a substantial amount of zinc. This had been noted to be the case as the dust from the electrostatic precipitator had about 53.4 ± 12.9 ppm.

Another notable observation was that the concentration of total zinc in the top soil was much higher than at the lower depths with the difference being attributed to recent dust deposits. The slight decrease at 15.0 cm (90.7 ± 6.1 ppm) was probably due to leaching of zinc to lower levels thus explaining the increase with increase in depth. Unlike most of the other metals, leaching of zinc does not depend on the level of available oxygen (zinc does not show variable oxidation states) [66]. As such, leaching of zinc depends on the type of the soil.

LEAD

Variation in the concentrations of total lead with depth did not show any explainable pattern. Unlike most of the other metals, it was noted that leaching of lead would have had insignificant effect as the top soil had high levels of calcium carbonate which lower its solubility to about 1.58×10^{-10} ppm at 25 ^{o}C [60,61]. Thus, the high level in the top soil (56.7 ± 6.3 ppm) might have been due to continued deposition of dust which had significant amount of lead (Table 3). The sharp decrease at 15.0 cm (10.6 ± 2.2 ppm) might have been due to slight leaching to lower depths or due to the natural level (non-anthropogenic) [59]. However, the latter was thought to apply as levels at lower depths could not be explained by leaching and were thought to be the natural ones. Freiburg [59], had noted similar distributions in soils. He had attributed the levels to inhomogeneity of lead in soils and to anthropogenic activities. Generally, scanning through tables 5, the levels of the elements analysed (except chromium and lead) were found to drop at 15.0 cm, increase upto 45.0 cm and then decrease.

Table 6 shows a summary of the levels of heavy metals in soil samples, sampled 120 metres from the electrostatic precipitator in a windward direction.

At the sampling point, the samples were rocky, hence it was not possible to sample upto 60.0 cm. Soil samples at the sampling points had the characteristic yellow colour of the dust from the electrostatic precipitator. When these samples were analyzed for silica and calcium carbonate, they were found to contain 25% and 49% respectively [46].

The sampling points, were only 2 metres from the Athi river thus, they were usually being covered by water during the rainy season. This water was analyzed and found to contain some lead (Table 18).

CHROMIUM

The sampling points were far from the electrostatic precipitator hence received minimal amount of dust. As such, dust had no effects on the levels of chromium in the top soil. The elemental levels registered at different depths were thought to have been dependent on the parent rock.

The levels of chromium in the soil were found to be comparable over the depth sampled (28.6 - 35.1 ppm) except in the top soil where the concentration was

TABLE 6 THE LEVELS OF HEAVY METALS IN SOIL SAMPLES SAMPLED 120 METRES FROM THE ELECTROSTATIC PRECIPITATOR.
(concentration in ug/g; n=4; Mean, ± standard deviation)

depth(cm)	Cr	Mn	Fe	Cu	Zn	Pb	Hg
0.0	41.3	360.7	7390.1	9.3	56.2	27.5	nd
	± 8.8	± 28.7	± 302.3	± 0.9	± 3.3	± 3.1	-
15.0	29.3	398.2	7650.2	8.9	58.2	21.0	nd
	± 3.9	± 14.9	± 280.1	± 1.3	± 5.0	± 2.1	-
30.0	35.1	405.8	7400.3	12.3	48.2	20.2	nd
	± 7.0	± 31.2	± 340.3	± 2.5	± 6.9	± 2.2	-
45.0	28.6	498.5	8260.8	8.4	51.6	21.3	nd
	± 4.2	± 29.5	± 350.4	± 1.1	± 3.0	± 2.8	-

NB.
n - sample size.

found to be 41.3 ± 8.8 ppm. The high level of chromium in the top soil was thought to be due to precipitation as the river water at the sampling contained substantial amounts of chromium.

As in the earlier discussion, leaching was expected to be minimal as the soil had high carbonate content which lowered solubility of chromium [6,31]. Also the rate at which water would percolate down was expected to be very low because the sampling points were rocky [6,31].

It was noted that the dust had no detectable amount of chromium as was the case with rocks (Table 6) which had the same chemical composition as the raw materials used in cement manufacture [46]. This was attributed to losses of chromium at elevated temperatures in the reaction chamber as had been noted by Hoekstra et. al. [28].

MANGANESE

Unlike chromium, manganese levels were noted to increase with depth. Thus, the level in the top soil was 360.7 ± 28.7 ppm increasing to 398.2 ± 14.9 ppm and 405.8 ± 31.2 ppm at 15.0 cm and 30.0 cm respectively. This increase was attributed to leaching and partly to the natural levels. It was thought that the latter was more applicable as manganese mobilization depend on the levels of oxygen and water in the soil [53,54]. At the sampling points, the soil was rocky and hence, the rate of diffusion of oxygen and percolation of water would be low resulting in minimal leaching. Also, the low rate of diffusion, percolation of oxygen and water respectively could not account for the high levels at 45.0 cm (498.5 ± 29.5 ppm). The range of these values was however small (360.7 ppm - 498.5 ppm with a mean of 415.8 ± 50.7 ppm) especially when they were from a rocky sampling point. Therefore, they were taken to have been from a similar origin hence they were the natural levels.

IRON

The levels of total iron were noted to increase gradually with depth in agreement with Moore [53]. This increase was partly attributed to the natural distribution and to leaching of the metal from the upper levels [54,55]. The range from 7390.1 ppm (0.0 cm) to 8260.8 ppm (45.0 cm) with a mean of 7675.5 ± 353.6 ppm was small for rock sample. This suggested that the samples were from the same parent origin. This range compared well with that of the dust (5710.3 ppm - 9240.0 ppm with a mean of 7944.3 ± 1413.1 ppm. The slight differences were attributed to limestone and iron ore added to the basic raw materials used in cement manufacture [46]. Therefore, this area could be a possible position where the company would mine the required basic raw material.

COPPER

As in the other metals above, the levels of copper were almost constant (8.4 - 12.3 ppm). The differences in levels registered at different depths were insignificant. This suggests that there was no leaching as this would have resulted in a significant decrease and then a significant increase with depth [53,54,67]. This phenomenon was noted in most of the samples analysed. It was attributed to its being immobilized by organic matter, silicates and the oxides of iron and manganese and to the positive redox potential of the reduction reaction i.e. reduction from copper (II) to copper (I) ions as in the equation below [56,66].

$$Cu^{2+} + e^{-} \rightleftharpoons Cu^{+} \quad E_o = + 0.167\ V \text{ -----(4.1.3)}$$

ZINC

Zinc concentration was found to vary over a small range (48.2 ppm - 58.2 ppm) with a mean of 53.6 ± 3.9 ppm. This as in the other metals suggests that the samples were from the same parent origin. The mean of these samples was noted to compare well with that of the dust (55.8 ± 12.5 ppm). There was however a slight general decrease which was thought to arise from the natural variations [10].

LEAD

The levels of total lead were generally comparable over the whole depth sampled. This suggested a common parent origin. As in other elements (Table 6), there were slight differences in the concentrations. This was attributed to the natural inhomogeneous distribution of lead in soils especially if present in trace amounts [59]. However, the levels especially in the top soil were high. This was thought to have been a result of lead precipitation as the river water had significant amount (Table 18). These sampling points, in general, had a rock whose elemental composition was closely related to that of the rock used as a raw material by the cement company.

Table 7 gives a summary of the levels of heavy metals in samples sampled 150 metres from the electrostatic precipitator in a leeward direction . The soil at the sampling points was of black cotton type with no noticeable light yellow colour that characterized the dust.

CHROMIUM

The range of the total chromium concentration was small over the depth range sampled (12.2 - 18.1 ppm) with a mean of 15.3 ± 2.2 ppm although there was a break at 60.0 cm (5.2 ± 1.2 ppm).

Limo [31], suggested that in soil, chromium exists as chromium (III) ions which are almost insoluble. He had found that the levels of chromium in plants did not depend on the total chromium levels in the soil even when the levels were below the phytotoxic levels. However, other researchers had found a correlation between the levels of water soluble chromium (VI) and that present in the plants [15]. As a result, leaching was expected to be minimal as in the other samples. It was thus found difficult to account for the low level of chromium at 60.0 cm as inhomogeneity would have affected all depths.

MANGANESE

The levels of manganese were found to vary over a moderately small range (1271.5 -1960.5 ppm) with a mean of 1546.6 ± 285.7 ppm. The low levels at 0.0 cm

TABLE 7 THE LEVELS OF HEAVY METALS IN SOIL SAMPLES SAMPLED 150 METRES FROM THE ELECTROSTATIC PRECIPITATOR.
(Concentration in ug/g; n=4; Mean, ± standard deviation)

depth(cm)	Cr	Mn	Fe	Cu	Zn	Pb	Hg
0.0	12.2	1320.1	30180.4	13.4	90.6	14.9	nd
	± 2.2	± 120.0	± 1220.3	± 1.6	± 8.3	± 1.4	-
15.0	18.1	1271.5	53340.7	28.9	103.9	15.8	nd
	± 2.8	± 96.0	± 2003.2	± 8.1	± 6.6	± 1.9	-
30.0	19615	52710.1	20.9	106.7	13.2	nd	
	± 2.6	± 110.8	± 2360.8	± 4.1	± 7.3	± 2.8	-
45.0	14.4	1820.7	45900.2	11.9	135.7	14.5	nd
	± 2.9	± 100.3	± 1313.6	± 2.3	± 9.9	± 1.0	-
60.0	5.2	1360.1	35800.1	8.9	103.3	14.9	nd
	± 1.2	± 70.0	± 1870.2	± 2.1	± 10.7	± 2.4	-

NB.
n - sample size.
nd - not detected.

and 15.0 cm were considered to have been as a result of leaching to lower depths with a resultant high levels at 30.0 cm and 45.0 cm.

Further down, the concentration of manganese at 60.0 cm was much lower. This was also noted in chromium above and it was suggested that there could have been a slight change in the soil structure resulting in differences in the natural levels [25,54].

IRON

As in manganese above, iron concentrations were found to have a maximum value at about 30.0 cm which was in agreement with the work of Moore [53], in which he had found a maximum at a depth of between 1.3 and 60.0 cm followed by a decrease. He attributed this variation to leaching from the upper soil to low depths if there are no anthropogenic activities which would adversely contaminate the top soil. Therefore, the pattern in the iron concentrations were attributed to leaching for they were found to increase to a maximum then decrease. However, unlike manganese, the range of these values was large (30180 - 53340 ppm).

COPPER

Like in other samples discussed earlier, the levels of copper were notably high at depths where the levels of iron and manganese were high. This was in agreement with the hypothesis that the two metals when present in a soil matrix adsorb copper strongly with only limited tendency to release it [54,58]. Here, the levels of total copper were found to increase appreciably from 13.4 to 28.9 ppm. At these depths (15.0 cm and 30.0 cm), the levels of these metals in the soil were notably high. Further down, leaching of copper was thought to have been hindered by an increase in the acidity of the soil as a result of reduced rate of oxygen diffusion especially in the rainy season. Thus, the concentration values at lower depths were taken as the natural levels [54,67,68].

ZINC

The concentration of total zinc was notably lower in the top soil compared to the other depths which had comparable concentration (103.3 - 135.7 ppm) with a mean of 112.4 ± 15.5 ppm. This deviation was relatively small suggesting a possible similar parent origin [10,54,69]. The low level in the top soil was attributed to leaching to lower depths.

LEAD

The concentrations of total lead over the depth range sampled were comparable (13.2 - 15.8 ppm) with a mean of 14.7 ± 0.8 ppm. The slight differences were within experimental errors and they could have been due to inhomogeneity of lead in soils [59,70,71]. As such, the concentration values were taken as the natural levels.

Table 8 shows a summary of the levels of heavy metals in soil samples, sampled at a distance of 170 metres from the electrostatic precipitator in a leeward direction. The soil type at the sampling points was dark loam up to a depth of 45.0 cm, beyond which it was of black cotton type.

The top soil was noted to have high levels of organic matter from decaying plant matter as it had been covered with decaying plant leaves. The sampling points were far from the precipitator thus, experiencing minimal effects of dust from the electrostatic precipitator.

CHROMIUM

Unlike the soil at 150 metres from the electrostatic precipitator, the soil sample at 170 metres had no detectable amount of chromium. This was attributed to differences in soil type having different natural levels.

MANGANESE

The concentration of total manganese decreased from 1610.0 ± 120.0 ppm (0.0 cm) to 1280.3 ± 80.1 ppm at 15.0 cm. There was then an increase to a comparatively constant value at 30.0 cm and 45.0 cm i.e. 1710.1 ± 90.3 ppm and 1670.0 ± 200.1 ppm respectively and a sharp increase at 60.0 cm (15010.0 ± 660.8 ppm).

TABLE 8 THE LEVELS OF HEAVY METALS IN SOIL SAMPLES SAMPLED 170 METRES FROM THE ELECTROSTATIC PRECIPITATOR.
(concentration in ug/g; n=4; Mean, ± standard deviation)

depth(cm)	Cr	Mn	Fe	Cu	Zn	Pb	Hg
0.0	nd	1610.0	42510.3	45.5	217.1	29.7	nd
	-	± 120.0	± 1472.6	± 7.7	± 23.5	± 4.9	-
15.0	nd	1280.3	368615	59.5	302.5	28.3	nd
	-	± 80.1	± 1520.3	± 6.3	± 20.9	± 4.1	-
30.0	nd	1710.1	25800.2	12.3	151.2	24.7	nd
	-	± 90.3	± 961.5	± 2.2	± 13.1	± 2.6	-
45.0	nd	1670.0	24820.1	11.6	182.7	24.6	nd
	-	± 200.1	± 840.4	± 2.9	± 22.1	± 2.8	-
60.0	nd	15010.2	39750.3	35.5	159.9	30.8	nd
	-	± 660.8	± 2970.2	± 4.4	± 10.0	± 3.5	-

NB.

nd - not detected.
n - sample size.

The high level of manganese in the top soil was considered to have been from decayed plant matter. Maina [25] had found animal manure which is basically from plant matter to have about 2257 ppm of manganese.

Manganese is known to bind to organic matter more strongly than to silicates [25,31]. Also, organic matter has a lower tendency than silicates to let go its metal content so that it may undergo reduction from manganese (IV) to manganese (II) (eq. 4.1.1) which is the mobile oxidation state of manganese in soil [25,31,54,55,74]. As such, leaching from the top soil was thought to be minimal. Also, it was thought that the high level in the top soil despite leaching was due to replenishment by decaying plant matter.

The increased levels with depth were linked to leaching as the amount of organic matter was expected to decrease with depth and also to the indigenous soil levels [55,58]. At 60.0 cm, the concentration of manganese was much higher than could have been accounted for by leaching. This was attributed to the natural soil levels for there was a change in the soil type i.e. from dark loam to black cotton soil which sometimes has very high levels of manganese. [55].

IRON

Like manganese above, the level of iron was noted to be high in the top soil (42510.3 ± 1472.6 ppm).

This was again attributed to high levels of organic matter and the replenishment of leached amount by decaying plant matter [25,55]. Maina [25], had found the concentration of iron in animal manure to be about 41775 ppm. Like in all other metals, organic matter bound iron shows limited tendency to leach down due to its low release from the matrix before its reduction to the mobile iron (II) ion (eq. 4.1.2) [54,55,74]. As such, appreciable leaching was only anticipated at lower depths.

Again, the level of iron at 60.0 cm was higher than at other depths. The reason was possibly due to change in the soil type i.e. from loam soil to black cotton soil. The latter usually has high indigenous iron levels.

COPPER

The concentrations of total copper were notably high at 0.0 cm (45.5 ± 7.7 ppm) and 15.0 cm (59.5 ± 6.3 ppm). The high levels were attributed to decaying plant matter, high levels of organic matter and the high concentration of manganese and iron in the soil which bind copper strongly thereby immobilizing it [10,54,65,69]. Unlike copper bound to an inorganic matrix, copper bound to organic matter is not easily mobilized via its reduction to copper (I) ion (eq. 4.1.3). This was considered to have been the reason why copper levels were much lower at lower depths despite the high levels in the top soil [57,58]. Thus, the levels at 30.0 cm (12.3 ± 2.2 ppm), 45.0 cm (11.6 ± 2.9 ppm) and 60.0 cm (35.5 ± 4.4 ppm) were taken as the natural levels. The concentration value at 60.0 cm was attributed to change in the soil type [54].

ZINC

As expected, the level of zinc was notably high in the top soil as is usual with most of the metals that are normally assimilated by plants for physiological activities [25]. This was thought to have been as a result of decayed plant materials.

Unlike other elements, leaching of zinc does not depend on levels of diffused oxygen as it does not show variable oxidation state [54]. As such, the amount of zinc leached depends on the level of free zinc. Therefore, the concentration values at depths of 30.0 cm (151.2 ± 13.1 ppm), 45.0 cm (182.7 ± 22.1 ppm) and 60.0 cm (159.9 ± 10.0 ppm) were attributed to the natural levels and slight leaching.

Therefore, it was thought that the high levels of zinc in the upper depths was due to the presence of organic matter bound zinc which could not be easily leached. Also, zinc was thought to have been getting gradually replenished by the decaying plants.

LEAD

The concentrations of total lead were found to be slightly higher in the upper depths i.e. 29.7 ± 4.9 ppm (0.0 cm) and 28.3 ± 4.1 ppm (15.0 cm). These levels were probably due to the amount being added by the decaying plants

Lead being a poorly absorbed metal by plant was expected to be in low concentration in plants. As such, increase due to decayed plants was therefore small [70]. Harrison et. al. [70], working on leaves of Acalypha wilkensiana plant grown on soils having variable amounts of available lead noted that the plants assimilated less than 10% of lead. He found that in soils from Jalan pudu and Jalan parlimen having 561 ppm and 595 ppm of available lead only 49 ppm and 32 ppm were found in the leaves respectively. As the depth increased, the concentrations recorded were considered to be the natural levels, as the amount of lead that is usually leached is small. This was in agreement with the work of Chapman [72] and Filipek et. al. [73].

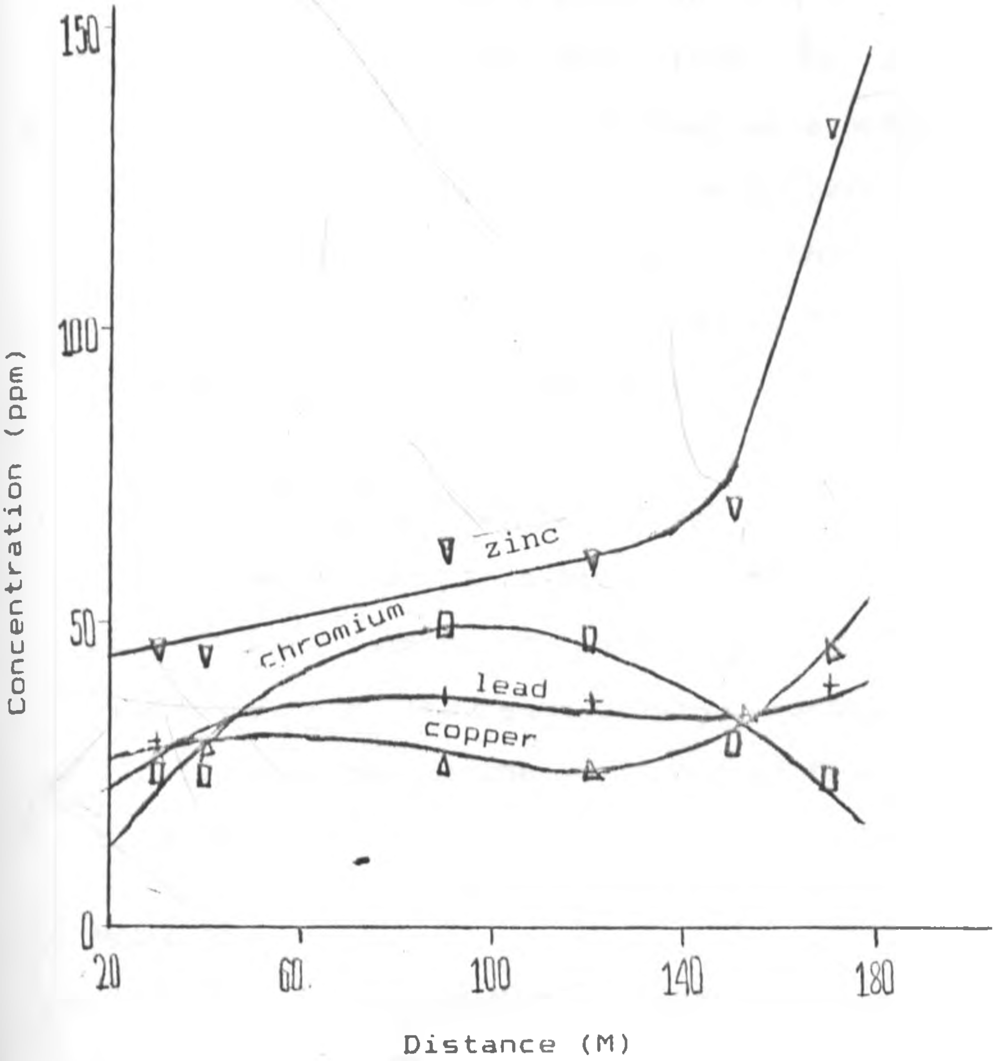
In order to come up with a wide ranging perspective regarding the extent of dust scatter, it was found necessary to include distance profile studies. This was carried out to determine the effect of the wind on the distribution of trace metals in soil samples. This type of study would be very useful particularly when it comes to a question of future residential and possible agricultural areas within the company's environment. Overall, two leeward directions (A and B) and a windward direction were investigated (Figure 6).

Table 9 and figure 7 show a summary of the levels of heavy metals in the top soil samples, sampled at different locations in a direction towards the administration block which was in a leeward direction (A) (Figure 5). Samples that were sampled near the main stark from the electrostatic precipitator received substantial amount of dust (Table 9). As such, the levels of heavy metals in these samples were slightly different from the rest of the samples in the same direction.

CHROMIUM

The top soil at distances of 30 metres and 40 metres was covered with dust from the electrostatic precipitation. These samples had no detectable amount of chromium. This was attributed to loss of chromium

FIGURE 7: VARIATION IN THE LEVELS OF CHROMIUM, COPPER, ZINC AND LEAD WITH DISTANCE FROM THE ELECTROSTATIC PRECIPITATOR IN A LEEWARD DIRECTION (A)



in the reaction chamber as discussed earlier [28], that is heating samples above 90 °C drives off most of the chromium. Further away, from the electrostatic precipitator, the levels of dust were notably low as the light yellow colour which characterized the dust was not evident. The soils were either black cotton type (90-150 metres) or dark loam at 170 metres.

Therefore, the levels in the top soils at a distance of 30 to 40 metres were dependent on the levels in the dust and to a lesser extent on leaching. The concentrations at a distance of 90 metres and 120 metres were almost the same, suggesting that they could be from the same origin. Further away, the levels decreased as the soil changed from black cotton to dark loam.

MANGANESE

As in chromium above, the levels of manganese upto 40 metres were comparable to those in the dust (Table 4). As the distance increased, the effect of dust diminished and at 90 metres it had only minimal effects. However, manganese levels were uniform between 90 and 120 metres suggesting related parent origin. Beyond 120 metres, the levels were noted to increase with increasing distance. This was attributed to changes in the soil type which have different natural levels.

IRON

Iron levels up to a distance of 40 metres compared well with the levels in the dust. Infact, upto this distance the top soil was entirely dust from the stark of the electrostatic precipitator. Beyond this, the effect of dust was not felt and the levels were dependent on natural soil levels. At distances between 90 and 120 metres, the levels were comparable however, beyond these distances, the levels increased due to a change in the soil type as in manganese above.

COPPER

The level of total copper between 30 and 40 metres was slightly higher than in dust but was comparable. The difference was thought to arise from analytical errors near the detection limit or to a high background count.

As the distance increased the levels of copper increased but they were still low as levels in un-contaminated soil are usually low. However, some soils e.g. those obtained from Bahati and Solai had high levels in which case the amount of available copper content was low [75]. Copper show phytotoxicity at concentrations as low as 5 ppm [25].

ZINC

Zinc concentrations were noted to increase with distance from the precipitator although the levels near the precipitator i.e. 30 metres and 40 metres were low and comparable. The difference was again attributed to pollution from the dust and variation in the soil type, hence different natural levels.

LEAD

The concentration of total lead in the dust between 30 metres and 40 metres was lower than the concentration at the other sampling points. The low lead levels in the dust compared to the level in the parent rock (Table 7) and this was attributed to loss in the reaction chamber due to the high temperature involved in the cement manufacture (200 ^{o}C - 1600 ^{o}C) and dilution by limestone and iron ore which are added to the raw materials with low level of lead [46].

The variation in lead levels registered with increasing distance were attributed to soil type and anthropogenic activities.

Therefore, it was found that the levels of heavy metals were dependent on the amount of dust. However, the dust was noted to have lower levels than the indigenous soil. Despite the low levels, the fact that the dust was not as compact as the indigenous soil meant that it was likely to add more particulate matter into the air thereby contaminating the air.

For the purpose of correlating the two major directions of the wind, a windward direction was also considered, as opposed to a leeward direction (A) discussed above (Figure 6).

Table 10 and figure 8 show a summary of the levels of heavy metals in soil samples, sampled in a windward direction. Analysis in this direction indicated that, samples close to the electrostatic precipitator had increased levels of heavy metal present in the dust i.e. iron, copper, manganese, and lead. As the distance increased, the amount of dust in the soil samples decreased and the levels of heavy metals approached those in the indigenous soil which had similar chemical composition as the raw material (Kunkur) used in cement manufacture [46].

CHROMIUM

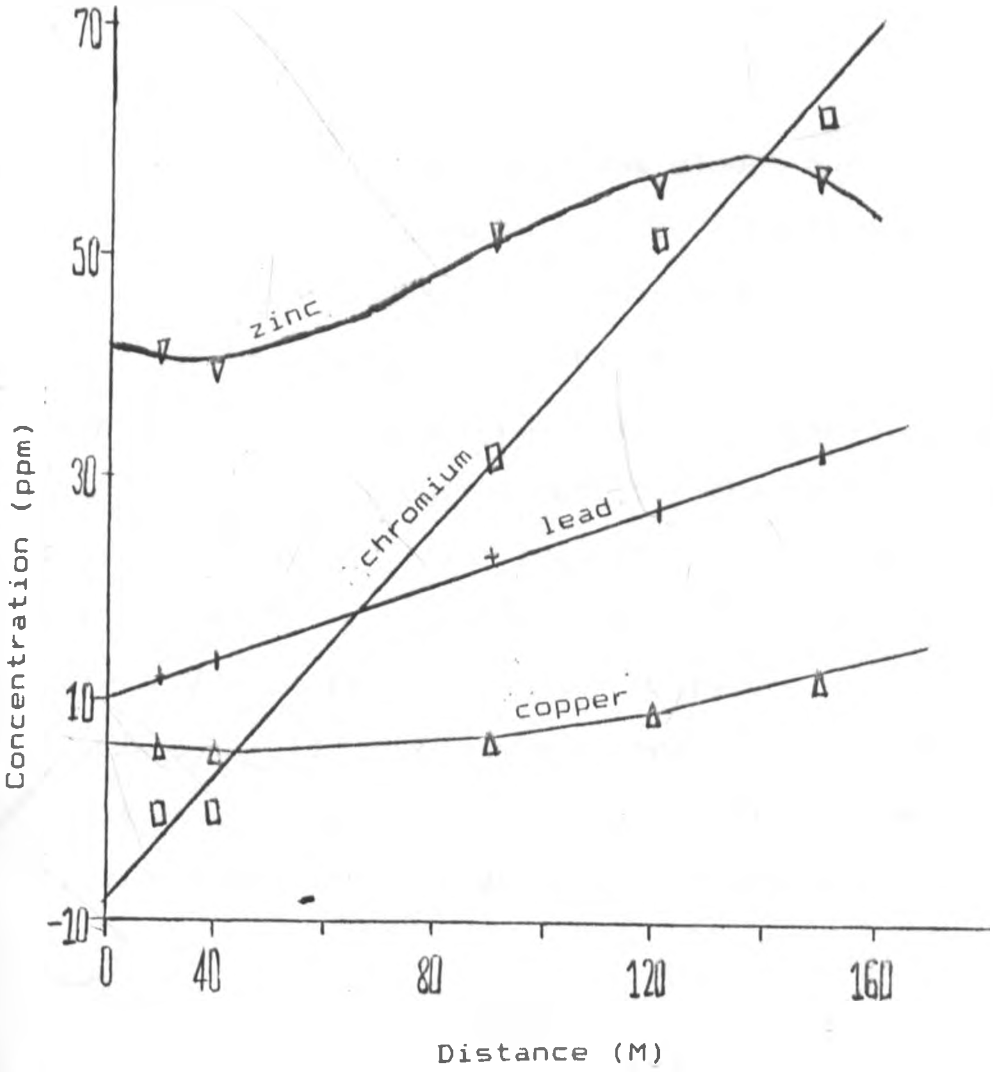
The soil samples at a distance of 30 to 40 metres contained mainly dust from the electrostatic precipitator. The chromium concentration was low hence not detected. The low level of chromium compared to the raw material (Table 6) was thought to have been partly due to chromium loss in the reaction chamber [28] and partly due to dilution by limestone and iron ore which have low level of chromium [46]. As the distance increased, the amount of dust in the top soil decreased and beyond 90 metres, the soil samples were almost free from dust. This resulted in an

TABLE 10 THE MEAN LEVELS OF HEAVY METALS IN SOIL SAMPLES SAMPLED AT DIFFERENT LOCATIONS IN A WIND WARD DIRECTION WITHIN THE FACTORY. (concentration in ug/g; n=4; Mean, ± standard deviation)

Distance (M)	Cr	Mn	Fe	Cu	Zn	Pb
30	nd -	404.0 ± 33.3	7620.1 ± 370.0	5.5 ± 0.9	41.5 ± 3.3	11.8 ± 1.7
40	nd -	393.3 ± 35.9	7568.7 ± 356.2	5.5 ± 0.4	39.4 ± 4.9	13.5 ± 2.1
90	32.4 ± 4.5	376.7 ± 25.7	7710.2 ± 410.3	6.4 ± 0.8	51.7 ± 6.3	22.8 ± 2.4
120	51.3 ± 8.8	360.7 ± 28.7	7390.1 ± 302.3	9.3 ± 0.9	56.2 ± 3.3	27.5 ± 3.1
150	62.7 ± 7.6	361.9 ± 36.7	6987.4 ± 280.7	12.5 ± 5.1	57.3 ±.5.1	32.8 ± 3.2

NB.
nd - not detected.
n - the sample size

FIGURE 8: VARIATION IN THE LEVELS OF CHROMIUM, COPPER, ZINC AND LEAD WITH DISTANCE FROM THE ELECTROSTATIC PRECIPITATOR IN A WINDWARD DIRECTION



increased level of chromium as the indigenous soil had some chromium.

MANGANESE

The level of manganese was almost constant over the distance range sampled (404.0 - 360.7 ppm). This was expected as the rocks in this region had the same chemical composition as the rock used in cement manufacture (being ground), hence comparable levels with those in the dust except for chromium and lead. Thus, if it were not for the natural inhomogeneity and differences in the rate of leaching for different soil matrix, the differences in concentration at different distances would have been even smaller. The levels of manganese in the dust were slightly higher due to the limestone and iron ore added in the crusher.

IRON

As in manganese above, the concentrations of total iron were comparable over the distance sampled (6987.4 - 7710.2 ppm). It was noted that the concentrations of iron in soils having dust from the electrostatic precipitator were higher than the rest of the soil samples. This was expected because iron ore was being added to the raw materials before being crushed hence higher levels in the dust.

COPPER

The concentrations of total copper were noted to increase with increasing distance from the electrostatic precipitator i.e. with decreasing levels of dust. [46,75]. The low levels of copper in the dust could have been due to the limestone and iron ore added to the rocks being crushed. Limestone and iron ore usually have very low levels of copper hence acted as diluents. It was also noted that probably, the dust allowed more water to percolate through compared to the rock resulting in more copper leaching down in the case of dust. In nature, distribution of copper is inhomogeneous with different soil types having different natural levels [25,54].

ZINC

Like copper, the levels of zinc increased slowly with distance from the electrostatic precipitator i.e. with decreasing amount of dust. This was accounted for using the same reasons as in copper above i.e. the raw materials, iron ore and limestone which acted as diluents for they have lower levels of zinc [46]. Lastly, the rock being crushed might have had higher levels of zinc for it was mined in a different region.

LEAD

The levels of lead increased as the amount of dust decreased. This increase was attributed to the low level of lead in the dust (Table 3). This was probably due to loss of lead in the reaction chamber (200 °C - 1600 °C), dilution by iron ore and limestone [46,68]. Moreover, there could have been some mild effect from leaching. Here, the dust would allow more water to percolate down carrying some lead compounds with it resulting in higher levels at lower depths.

In order to determine the extent to which the dust from the cement industry was being carried away by the wind, it was found necessary to monitor another leeward direction (B) (Figure 6). This direction was towards the residential quarters.

Table 11 shows a summary of the levels of heavy metals in soil samples, sampled in a leeward direction (B). A plot of the variation in the levels of these metals with distance is shown in figure 9. The sampling points were near the crusher hence much of the dust in this region was from the crusher rather than from the electrostatic precipitator. In the crusher, there was no heating, hence the levels of heavy metals in the dust were expected to be comparable with those in the raw materials (Table 6). However, there were slight changes due to the addition of Limestone and iron ore which tend to increase the levels of iron and manganese and decreased the levels of the other elements as a result of dilution.

CHROMIUM

The concentrations of total chromium were generally noted to increase with distance although there was a decrease at 120 metres. They registered 36.8 ± 6.2 ppm (30 metres), 38.4 ± 11.8 ppm (40 metres), 66.6 ± 11.4 ppm (90 metres) and 58.6 ± 6.7 ppm (120 metres). Sampling beyond 120 metres was not

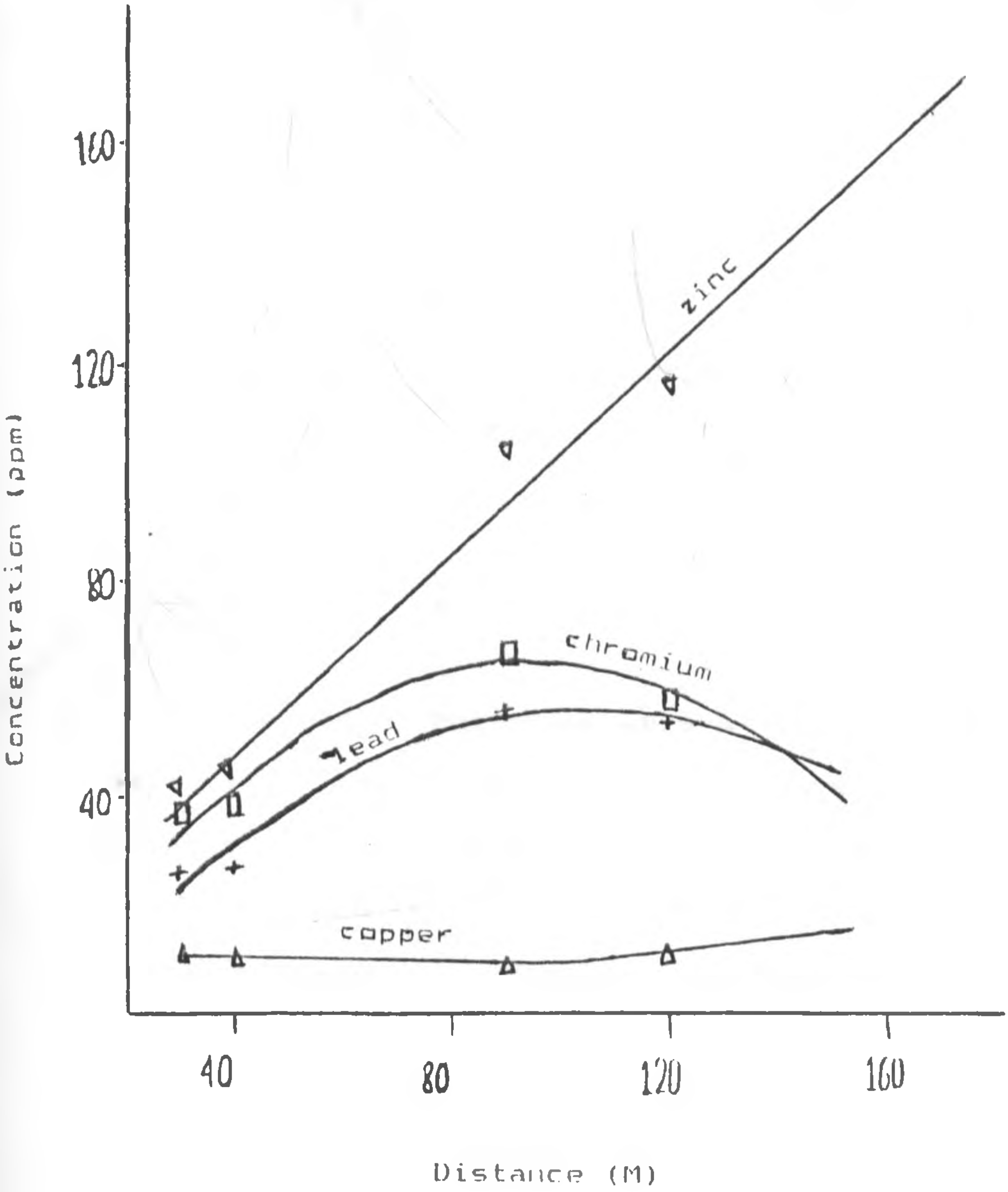
TABLE 11 THE MEAN LEVELS OF HEAVY METALS IN SOIL SAMPLES SAMPLED AT DIFFERENT LOCATIONS IN A LEEWARD DIRECTION (B) WITHIN THE FACTORY. (concentration in ug/g; n=4; Mean, ± standard deviation)

Distance (M)	Cr	Mn	Fe	Cu	Zn	Pb
30	36.8	364.8	7485.9	11.8	37.4	26.2
	± 6.2	± 43.3	± 358.2	± 1.4	± 2.4	± 3.8
40	38.4	372.1	7893.4	11.1	43.9	27.7
	± 11.8	± 33.4	± 242.1	± 1.8	± 3.1	± 5.2
90	66.6	487.2	11950.2	10.4	103.2	56.7
	± 11.4	± 39.5	± 650.3	± 2.0	± 16.5	± 6.3
120	58.6	476.9	10567.4	12.3	115.7	54.2
	± 6.7	± 32.5	± 580.9	± 1.9	± 18.4	± 4.7

NB.

n - the sample size

FIGURE 9: VARIATION IN THE LEVELS OF CHROMIUM, COPPER, ZINC AND LEAD WITH DISTANCE FROM THE ELECTROSTATIC PRECIPITATOR IN A LEEWARD DIRECTION (B)



possible for it was in a different industry where permission to sample was not granted.

The low levels of chromium at distances less than 90 metres was attributed to dust from the precipitator, which had low concentration of chromium. The soil at these distances were basically dust from the precipitator. As the distance increased, the amount of dust from the precipitator decreased with that from the crusher increasing. This was because the sampling points were getting closer to the crusher. This was noted to result in an increase in the levels of chromium as the raw materials had some chromium.

MANGANESE

The levels of manganese were almost constant with only mild increases with distance from the precipitator. The levels were comparable with those in the dust from the electrostatic precipitator. The slight increase with distance was thought to arise from dust carried by water and wind from a nearby open iron ore storage site. This ore was suspected to have substantial amounts of manganese.

IRON

The concentrations of total iron as in the case of manganese above, were comparable to those in the dust from the precipitator (Table 10) up to a distance of 40 metres. This was again expected as no iron containing additives were being added between the crusher and the reaction chamber where the electrostatic precipitator was situated. As the distance increased, the concentration of iron increased drastically. This was attributed to wind and water which had blown and washed away iron from a nearby open iron ore storage site.

COPPER

The concentrations of total copper were almost constant over the whole distance range sampled (10.4 - 12.3 ppm). The differences were attributed to inhomogeneity of copper in rocks and also to experimental errors. The latter was thought to have had a significant effect as the concentrations were approaching the detection limit [76]. However, concentrations of total copper were notably higher than those in the dust from the precipitator (Table 3). As in table 10 it was suggested that the low levels of copper were due to dilution by limestone and iron ore which usually have low levels of copper [2,46].

ZINC

Unlike copper above, the concentrations of total zinc increased with distance from the electrostatic precipitator. At distances of 30 and 40 metres the levels were 37.4 ± 2.4 ppm and 43.9 ± 3.1 ppm respectively. These levels were comparable to those in the dust (table 10). As the distance increased, the levels increased drastically and at 90 and 120 metres, they were 103.2 ± 16.5 ppm and 115.7 ± 18.4 ppm respectively. These values were no longer comparable with those in the raw materials (Table 6). The high levels at distances beyond 90 metres were difficult to account for. As such, it was suggested that sampling beyond 120 metres was necessary. However, this was not possible as permission to sample the soil was not granted by the owners of the company.

LEAD

The concentrations of total lead were noted to increase with increase in distance from the precipitator with the levels at 30 metres (26.2 ± 3.9 ppm) and 40 metres (27.7 ± 5.2 ppm) agreeing well with those in the dust (Table 6).

Further away, the levels increased to 56.7 ± 6.3 ppm and 54.2 ± 4.7 ppm at 90 and 120 metres respectively. These increases could not have been accounted for by the levels of this metal in the dust from the crusher. As such, the levels were attributed to the natural levels in the soil and to a lesser extent to iron ore and limestone. As in the case of zinc above, it was necessary to determine the concentration of lead in soil samples beyond 120 metres. This would yield the exact amount of these metals in the un-contaminated soil as opposed to that near the crusher which contained both dust and soil.

4.2.0 PLANT LEAVES

Trace metal ions are known particularly for their role in the maintenance of healthy plant life. Excesses or deficiencies have effects on the plant growth and morphology. The levels of these metals in different plants and species are known to vary [77]. They depend on their physiological role and the plant's ability to tolerate their toxic effects [9,29]. Thus, plants like Lychnis alpina, Campanula rotundiflora and Astragalus flourish well in soils having toxic levels of copper, lead and uranium respectively. The ability of these plants to tolerate the high levels of these elements is thought to be dependent on one or more of the following mechanisms [29,42,78].

(a) External mechanisms where the metal is not available to the roots for it is insoluble in water, is in chelated form and/ or the concentration of the freely diffusible metal is small.

(b) The roots might have selective cell wall for particular toxic metal ions or the plant release substances that render toxic metals insoluble or unavailable.

(c) The metal while in the plant is bound to complexes hence they do not have any physiological role e.g. iron, copper, zinc and chromium are bound to citrates, proline complexes, galacturonate, and oxalato complexes.

(d) The metal ions are rapidly excreted after being taken-up by the plant or the plant changes slightly physiologically thereby producing high levels of the enzymes that are being inhibited. It may also use a different pathway for the products.

(e) The plant might be requiring these elements for its metabolism e.g. copper in ascorbic acid oxidases and iron in peroxidases.

For soils having high pH, the concentration of soluble iron (III) ions decrease rapidly per every unit increase in the pH. Thus, at a pH of 9 the total iron (II) and iron (III) concentration is about 10 - 20 moldm^{-3} [29]. When this occurs, the roots of plants release H^{+} and reducing agents and accumulate citrates in a bid to increase the rate of iron absorption. Also, calcium reduces the availability of iron, zinc, and manganese in soil to plants. This is due to the ability of calcium to decrease acidity thus lowering the solubility of these metals [29,78].

In the light of the above discussion, with reference to the uptake of metal ions by plants, it was found necessary to investigate the effects of dust produced by the cement industry on the levels of heavy metals in the leaves of the three plant species mentioned earlier. The metals anaylsed are itemized below:

CHROMIUM

In general, the leaves of the three plant species studied were noted to have an increased levels of chromium with increase in the amount present in the soil (Table 12). However, there was no correlation between the levels in the soil and those manifested in the leaves. This was considered to have been dependent on chromium's low availability as had been noted by Limo [31]. This was thought to be due to the low solubility of chromium (III) (the stable state of chromium in the soil) which had to be oxidized to chromium (IV) before being taken up by plants. As such, its levels in plants depends on the available amount present in the soil. The available amount was expected to increase with increased total amount in the soil although not linearly. For example, at 40 metres from the precipitator the mean level of chromium in the soil, **Acacia xanthophloea, Tagetes minuta and Schinus molle** were 11.5 ± 6.4 ppm, 8.6 ± 0.5 ppm, 20.4 ± 1.9 ppm and 8.4 ± 0.2 ppm respectively

TABLE 12 VARIATION IN THE MEAN LEVELS OF CHROMIUM IN PLANT SPECIES GROWN ON SOIL AT DIFFERENT LOCATIONS.

(concentration in ug/g* ; Mean, ± standard deviation)

Soil or Plant species	Soil n=4	Acacia xanthophloea n=5	Tagetes minuta n=10	Schinus molle n=5
Distance (M)	Cr	Cr	Cr	Cr
30	nd	2.9	4.3	2.4
	-	± 0.3	± 0.9	± 0.8
40	11.5	8.6	20.4	8.4
	± 6.4	± 0.5	± 1.9	± 0.2
90	70.9	23.5	25.8	19.8
	± 3.7	± 2.1	± 2.7	± 3.5
120	33.6	18.4	22.6	15.9
	± 5.1	± 0.4	± 1.8	± 1.7
150	13.3	11.1	19.6	18.5
	± 4.5	± 1.2	± 1.1	± 0.8
170	nd	3.2	4.7	2.5
	-	± 0.2	± 0.3	± 0.2

NB.

nd - not detected.

n - sample size.

* - for plants, the concentrations are for dry weight.

(Table 12). At 90 metres the levels in soil, **Acacia xanthophloea, Tagetes minuta and schinus molle** were 70.9 ± 3.7 ppm, 23.5 ± 2.1 ppm, 25.8 ± 2.7 ppm and 19.8 ± 3.5 ppm respectively (Table 12). The increase in the total chromium levels in the soil were about six fold while those registered in the leaves were comparable.

It was also noted that different plant species assimilate chromium differently as the levels in the leaves of these plant species analyzed were very variable (Table 12). This was thought to be the case as physiologically active leaves are known to give a good indication of the trace metal ion state in a plant [15,65]. However, it seemed from the analysis that there was a limit in the amount of chromium that a given plant species could assimilate. This was thought to be the case as the amount registered in different plant species decreased as the total amount in the soil samples increased. It also appeared as though different plants had different mechanisms for chromium absorption as different species had variable levels for the same total chromium concentration in soil. The concentrations registered in the leaves suggested therefore that the dust had lower levels of chromium than the indigenous soil as had been postulated (4.1.0).

MANGANESE

As had been pointed out earlier, manganese is an essential metal in plants. However, its levels in plant vary depending on its role in the plant and its availability in the soil [10]. In the leaves of the three plant species analyzed, the concentrations ranged from 26.9 - 225.5 ppm (Table 13). This range was suggested to be due to differences in the abilities of different plant species to tolerate manganese and its availability in different soil types.

The mean concentration of total manganese in soil samples, sampled at a distance between 30 and 120 metres were comparable with a range from 415.8 - 509.8 ppm. In plant growing on these soils the range was from 33.5 - 123.8 ppm, 64.6 -225.5 ppm and 26.9 - 166.1 ppm for **Acacia xanthophloea, Tagetes minuta and Schinus molle** respectively. These ranges showed that the amount of available manganese in soil was different for different plants. The differences observed may be attributed to differences in mineral uptake by different plants species. In some soil samples e.g. those at 30 and 120 metres, the levels of available manganese was thought to be low as the plants growing on this soil had low manganese values. This was perhaps due to the high amount of calcium ions present (appendix 1) which tend to raise the pH

TABLE 13 VARIATION IN THE MEAN LEVELS OF MANGANESE IN PLANT SPECIES GROWN ON SOIL AT DIFFERENT LOCATIONS.

(concentration in ug/g[*] ; Mean, ± standard deviation)

Soil or Plant species	Soil n=4	Acacia xanthophloea n=5	Tagetes minuta n=10	Schinus molle n=5
Distance (M)	Mn	Mn	Mn	Mn
30	471.7 ± 87.2	33.5 ± 2.2	64.6 ± 3.5	26.9 ± 3.3
40	509.8 ± 222.5	50.6 ± 3.2	99.9 ± 4.0	28.8 ± 3.2
90	425.6 ± 77.2	123.8 ± 12.5	225.5 ± 9.2	123.7 ± 10.2
120	415.8 ± 50.7	74.1 ± 5.4	92.6 ± 14.6	166.1 ± 15.1
150	1546.6 ± 285.7	53.8 ± 3.6	133.6 ± 9.6	142.9 ± 12.3
170	1567.6 ± 169.7	193.2 ± 13.3	210.3 ± 10.1	185.7 ± 15.2

NB.
n - sample size.
* - for plants, the concentrations are for dry weight

and thereby, lowering its solubility [29,78]. Further away, the levels of total manganese in the soil samples increased although they were still comparable. However, the concentration of manganese in the leaves of the three plant species were still variable e.g. 53.8 ± 3.6 ppm, 133.6 ± 9.6 ppm and 142.9 ± 12.3 ppm at 150 metres and 193.2 ± 13.3 ppm, 210.3 ± 10.1 ppm and 185.7 ± 15.2 ppm at 170 metres for **Acacia xanthophloea, Tagetes minuta and schinus molle** respectively. The comparatively lower levels at 150 metres were due to a high clay content which tend to bind manganese more strongly while the soil at 170 metres had high levels of organic matter which is more available to plant [31,42,78].

IRON

Like manganese iron has a physiological role in plants. Generally, its levels are usually high in plants. This was noted to be the case as its levels ranged from 212.6 - 2780.3 ppm (Table 14) for different plant species growing on soil having variable amounts of total iron. However, the levels were found to be variable in the three plant species growing on soil having different amounts of total iron. This was possibly due to differences in tolerance and the physiological roles. Again as in the case of manganese, the levels of iron in plants growing at 30, 120 and 150 metres were much lower than those at 40, 90, and 170 metres. This was again attributed to high calcium levels at 30 and 120 metres and binding by zeolites at 150 metres [29,78]. The tolerance and mechanisms for iron absorption in the three plant species were thought to be different as leaves of **Schinus molle** showed comparable iron levels inspite of the variable concentration in the soil samples.

It was also noted as for manganese above that, availability of iron bound to organic matter was much higher than that bound to silicate structures. Thus, at 150 and 170 metres the levels in the soil were 43586.3 ± 9209.7 ppm and 33948.3 ± 7282.4 ppm respectively while those in **Acacia xanthophloea,**

TABLE 14 VARIATION IN THE MEAN LEVELS OF IRON IN PLANT SPECIES GROWN ON SOIL AT DIFFERENT LOCATIONS.

(concentration in ug/g [*]; Mean, ± standard deviation)

Soil or Plant species	soil n=4	Acacia xanthophloea n=5	Tagetes minuta n=10	Schinus molle
Distance (M)	Fe	Fe	Fe	Fe
30	7944.3 ± 1412.1	225.2 ± 34.7	544.9 ± 815	277.5 ± 25.9
40	8596.1 ± 1063.6	564.2 ± 51.2	1270.2 ± 110.3	319.5 ± 23.8
90	12655.9 ± 1440.7	1510.2 ± 170.3	2360.8 ± 190.7	397.5 ± 32.1
120	7675.4 ± 353.7	456.7 ± 515	527.9 ± 35.2	3915 ± 70.9
150	43586.3 ± 9209.7	314.1 ± 14.0	436.2 ± 14.3	285.2 ± 9.7
170	33948.3 ± 7282.4	2780.3 ± 190.2	1290.6 ± 70.9	212.6 ± 12.4

NB.
n - sample size.
* - for plants, the concentrations are for dry weight.

Tagetes minuta and Schinus molle were 314.1 ± 14.0 ppm, 436.2 ± 14.3 ppm and 285.2 ± 9.7 ppm (150 metres) and 2780.3 ± 190.2 ppm, 1290.6 ± 70.9 ppm and 212.6 ± 12.4 ppm (170 metres) respectively. The amount of iron absorbed did not linearly depend on the total amount present in the soil.

COPPER

Unlike the other metals mentioned earlier, copper's availability was not affected by calcium levels as had been noted by Hay and Farago [29,78] (Table 15). It depended on the organic matter content, levels of manganese and iron ions in soil [10,15,54,57]. In this research, soil samples having different amounts of total copper registered similar amounts in the plant species (Table 15). This was probably due to similarities in its role, tolerance and the available levels. Copper was thought to have accumulated in these plant species as most of them showed higher levels than those present in the respective soil samples [29, 78].

ZINC

Zinc is an essential element in plants thus, plant absorb this metal readily. From the analysis, the levels of zinc for different plant species were found to vary over a small range (Table 16) unlike what was evident in most of the other metals. The ranges were 21.6 - 61.6 ppm, 62.9 -156.9 ppm and 45.1 -58.7 ppm for **Acacia xanthophloea, Tagetes minuta and Schinus molle** respectively. The small ranges were thought to be due to zinc being very essential to plant, its high availability and the readiness with which plant absorb it [10,15,25,31]. As with the other metals, plants growing on soils with high calcium levels were noted to register lower levels of zinc as had been noted by Farago [78] and Hay [29].

The levels of zinc registered in the plant leaves did not depend on the total zinc concentration in the soil. For example, when the concentrations in the soil were 51.9 ± 9.2 ppm, 108.0 ± 14.9 ppm and 202.7 ± 34.9 ppm, the levels in **Acacia xanthophloea** were 49.2 ± 4.9 ppm, 33.1 ± 2.5 ppm and 61.6 ± 4.7 ppm respectively (Table 16). This was attributed to the fact that the metal was not cumulative and that plants take only the amount needed for their physiological activities. The differences were probably due to differences in the physiological roles as it was very difficult to sample leaves from plants of the same age [43,65,78].

LEAD

From the analysis, the levels of lead in the three plant species were generally low (Table 17). This was perhaps due to the fact that the metal is not essential to plants and therefore, is not readily available [10,15,70,71]. However, it was noted that **Tagetes minuta** assimilated it pretty well, suggesting that the plant had a higher tolerance for this metal than the rest of the plants. This might have been due to poor selectivity of the cell wall through which this metal must pass through or due to differences in absorption mechanisms as discussed earlier [29,63,78]. In zeolites (clay) and soil having high levels of calcium (dust) the amounts of lead in the plants were much lower than those having high organic matter content (170 metres). This was attributed to its immobilization by the lattice structures and the higher rate of absorption of organic matter bound lead by plants [10,70,71].

TABLE 15 VARIATION IN THE MEAN LEVELS OF COPPER IN PLANT SPECIES GROWING AT DIFFERENT LOCATIONS.

(concentration in ug/g * ; Mean, ± standard deviation)

Soil or Plants	soil n=4	Acacia xanthophloea n=5	Tagetes minuta n=10	Schinus molle n=5
Distance (M)	Cu	Cu	Cu	Cu
30	6.1 ± 0.7	9.2 ± 1.6	24.2 ± 4.2	22.2 ± 3.0
40	9.1 ± 3.0	6.8 ± 0.9	32.3 ± 3.6	20.4 ± 2.5
90	12.2 ± 2.2	15.1 ± 3.3	31.5 ± 3.2	17.1 ± 2.9
120	9.7 ± 1.5	9.4 ± 1.9	35.8 ± 4.6	28.8 ± 4.0
150	16.8 ± 7.2	9.2 ± 1.2	22.7 ± 3.0	29.2 ± 15
170	32.9 ± 8.7	37.9 ± 3.5	33.2 ± 3.2	26.4 ± 4.1

NB.
n - sample size.
* - for plants, the concentrations are for dry weight.

TABLE 16 VARIATION IN THE MEAN LEVELS OF ZINC IN PLANT SPECIES GROWN ON SOIL AT DIFFERENT LOCATIONS.

*
(concentration in ug/g ; Mean, ± standard deviation)

Soil or Plant species	Soil n=4	Acacia xanthophloea n=5	Tagetes minuta n=10	Schinus molle n=5
distance (M)	Zn	Zn	Zn	Zn
30	55.9 ± 12.6	21.6 ± 1.7	62.9 ± 5.8	45.1 ± 5.1
40	51.9 ± 9.2	49.2 ± 4.9	90.4 ± 8.4	55.3 ± 5.8
90	97.0 ± 4.0	34.4 ± 3.5	114.4 ± 14.4	56.9 ± 6.5
120	53.6 ± 3.9	31.5 ± 2.8	88.5 ± 5.4	58.7 ± 7.7
150	108.0 ± 14.9	33.1 ± 2.5	85.8 ± 7.9	55.7 ± 2.4
170	202.7 ± 34.9	61.6 ± 4.7	156.9 ± 9.3	39.3 ± 2.1

NB.
n - sample size.
* - for plants, the concentrations are for dry weight.

TABLE 17 VARIATION IN THE MEAN LEVELS OF LEAD IN PLANT SPECIES GROWING AT DIFFERENT LOCATIONS.

*
(concentration in ug/g ; Mean, ± standard deviation)

TABLE 17 VARIATION IN THE MEAN LEVELS OF LEAD IN PLANT SPECIES GROWING AT DIFFERENT LOCATIONS.

(concentration in ug/g * ; Mean, ± standard deviation)

Soil or Plant species	Soil n=4	Acacia xanthophloea n=5	Tagetes minuta n=10	Schinus molle n=4
distance (M)	Pb	Pb	Pb	Pb
30	12.3 ± 1.0	nd -	4.1 ± 1.1	nd -
40	8.1 ± 1.4	nd -	5.9 ± 0.4	nd -
90	35.0 ± 16.4	8.3 ± 1.3	13.8 ± 1.7	4.2 ± 1.2
120	22.5 ± 2.9	5.1 ± 1.1	10.2 ± 2.2	14.1 ± 2.6
150	14.7 ± 0.8	4.8 ± 0.2	7.0 ± 1.1	5.1 ± 0.2
170	27.6 ± 2.6	15.1 ± 3.5	29.7 ± 2.2	12.8 ± 2.1

NB.
nd - not detected.
n - the sample size.
* - for plants, the concentrations are for dry weight.

4.3.0 WATER AND SEDIMENTS

As had been discussed earlier in chapter 3, water and sediments were sampled at different locations along the Athi river (Figure 6). At each of the sampling locations, water and sediments were taken. For water, sampling was done both in the dry and rainy season (Table 18).

In this research, it was found that there was a general decrease in the levels of heavy metals during the rainy season. This was probably due to dilution by the large volumes of water encountered. However, chromium was found to register higher levels at point 500^{b} in the rainy season. This was attributed to discharges from a nearby tannery.

Another observation was that at 500^{b} metres the levels of all the heavy metals were high in both water and sediment samples (Tables 18 and 19). These increases were attributed to the following anthropogenic activities that were noted to take place at this point.

(1) A nearby tannery was suspected to dispose partially treated chromium containing effluents into the river.

(2) A petrol station and a car wash whose waste water was being channeled into the Athi river. This water was suspected to contain lead and other compounds from petroleum

TABLE 18 THE MEAN LEVELS OF HEAVY METALS IN WATER SAMPLED ALONG THE ATHI RIVER AT VARIOUS POINTS IN THE DRY AND WET SEASON.
(concentration ng/ml)

Distance (M)	pH	Cr	Mn	Fe	Cu	Zn	Pb	Hg
100*	7.96c	0.9	19.5	191.3	7.1	15.1	nd	nd
	7.20d	nd	15.4	145.3	4.6	10.9	nd	nd
50*	8.03c	nd	30.4	281.1	9.1	33.3	3.8	nd
	7.78d	nd	27.3	293.2	6.5	30.1	2.3	nd
0a	8.07c	nd	23.1	247.5	17.9	28.4	1.8	nd
	7.61d	nd	20.5	230.7	13.4	25.8	nd	nd
500b	9.45c	12.5	142.5	34.3	17.5	27.5	1.2	3.0
	8.62d	15.2	102.8	26.8	6.3	8.8	nd	1.9
1000b	8.56c	2.3	3.0	145.0	13.8	26.3	1.3	1.2
	7.83d	5.0	1.2	104.9	9.2	18.0	1.3	nd
1500b	8.41c	2.5	5.2	165.1	10.5	19.8	nd	nd
	7.75d	3.6	1.8	136.7	8.7	14.1	nd	nd

NB. Elements analysed at pH of 5.0 except for Cr and Mn where a pH of 3.9 was used.

nd - Not detected

* - Up stream i.e. before the point where the effluents from the cement industry entered the Athi river.

a - The point where effluents from the cement industry entered the Athi river.

b - Down stream i.e. after the point where effluents from the cement industry entered the Athi river.

c - During the dry season.

d - During the wet season.

TABLE 19 THE MEAN LEVELS OF HEAVY METALS IN SEDIMENTS SAMPLED ALONG THE ATHI RIVER AT VARIOUS POINTS IN THE DRY SEASON.
(concentration ng/ml)

Distance (M)	Cr	Mn	Fe	Cu	Zn	Pb	Hg
100*	nd	1230.0	14520.3	1.6	41.3	5.8	nd
50*	1.3	1470.0	8210.2	2.4	27.5	29.3	nd
0[a]	nd	1064.5	8250.6	5.3	16.8	32.7	nd
500[b]	428.2	6410.0	66510.0	43.7	52.6	9.1	23.2
1000[b]	38.4	334.7	6369.5	6.5	55.7	8.6	1.2
1500[b]	23.5	313.2	4970.1	6.1	16.4	3.3	1.0

NB.

nd - Not detected

* - Up stream i.e. before the point where the effluents from the cement industry entered the Athi river.

a - The point where effluents from the cement industry entered the Athi river.

b - Down stream i.e. after the point where effluents from the cement industry entered the Athi river.

products.

(3) A bleaching and dyeing industry which also discharge its effluents into the river.

(4) There were empty containers that had been dumped at this point.

The above activities were suspected to add heavy metals although more work need to be done to determine the contamination arising from each activity.

Another observation was the change in the pH values downstream although it was generally high at all the sampling points. The high pH, resulted in most of the heavy metals except those in an organic matrix being precipitated as was expected [6,79]. The high pH values were attributed to various activities in this region that required basic media e.g. dyeing. It could also have been due to the dissolution of carbonate as the river bed was basically of a rock with high levels of calcium carbonate.

The levels of most of the metals analysed were found to fall below the recommended W.H.O. highest desirable levels [6], although they were higher than the natural un-contaminated values [20] (table 18).

Also noted was that effluents from the cement company which joined the Athi river at point 0^{a} had high levels of suspended matter (cement dust). This resulted in an increase in the levels of iron, manganese, copper and zinc. This was due to the fact that water samples were first being digested with nitric acid before filtration to break-up the organic matter [41].

Lastly, the level of lead at 50[*] was notably higher. This was probably due to discharge from a battery plate smelting plant nearby. With the above general discussion, individual elements are now discussed.

CHROMIUM

The concentrations of total chromium in the water samples and sediments were below the detection limit of the technique except after 500[b] metres due to chromium from a nearby tannery (Table 18 and 19). This chromium when disposed is in an oxidation state of (VI) and with time it was thought to have been reduced to the stable oxidation state of (III) which is relatively insoluble [31]. This was thought to have been the case because if chromium existed as chromium (VI) the levels in water would have been higher as chromium (VI) is highly soluble [6,10,31]. The levels in sediments were attributed to washed down soil by water from a plot of land on which discharges from a tannery were being disposed. This was thought to happen especially during the rainy season.

The drop in chromium concentration with increase in distance from the point where discharges from the tannery industry entered the Athi river was attributed to the self purification of water systems [6,79].

MANGANESE

The levels of manganese in water were generally lower than the W.H.O. highest acceptable value of 50 ppb except at only one point (500^{b}) where levels were 142.5 ppb during the dry season (Table 18). This value however, was lower than the maximum allowable i.e. 500 ppb in water. The value at this point was attributed to the four anthropogenic activities mentioned earlier (4.3.0).

In sediments, the levels of manganese were high (Table 19). The high concentrations were attributed to high levels in the soil and also to dissolution of calcium carbonate resulting in a higher ratio of manganese in the remaining sediments. This manganese was thought to exist in an oxidation state of (II) which is strongly bound to silicate [54]. Thus, it was not easily dissolved by water, hence its low level in water samples compared to the sediments.

IRON

The concentrations of total iron were all below the W.H.O. Highest acceptable values in drinking water (300 ppb) (Table 18). They were also lower than the maximum allowable level i.e. 1.0 ppm. This suggested that the river was not polluted significantly with respect to iron except at two locations i.e. at point 50^* (281.1 ppb) and at point 0^a (247.5 ppb).

At the point where the effluents from the cement factory are discharged i.e. point 0^a (Table 18) the level in solution was much lower as most of the iron was in the suspended matter. Also, it was suggested that at point 50^*, the levels might have been in the biota as the river bed had a green covering possibly due to blue green algae. These micro-plants in water have been noted to trap heavy metals thereby accumulating them in their cell wall [15]. This was thought to have been the reason why all the metals analyzed were in high concentration at point 50^* i.e. both in water and sediments (Table 18 and 19).

At point 500^b the level of iron in water was very low compared to that in the sediments. This was attributed to the high pH which might have resulted in the precipitation of most of the iron probably as iron (III) carbonate [6]. The higher load of iron in the sediments was thought to have been dependent on the anthropogenic activities mentioned earlier (4.3.0).

COPPER

The concentrations of total copper in the water samples were higher than those in the natural un-contaminated water (0.2 - 2.2 ppb) (Table 18). However, the levels were lower than the W.H.O. highest desirable level of 50 ppb and maximum allowable level of 1.0 ppm.

The concentrations found in sediments were all comparable with a mean of 6.0 ± 0.5 ppm except at point 500^{b} where the level was 43.7 ppm (Table 19). This high level was attributed to the many anthropogenic activities at this point as discussed earlier (4.3.0).

In the water samples, the levels were found to have been dependent on the levels in sediments. However, at point 500^{b} the levels were comparable to those at the other sampling points despite the high levels in the sediment. This was attributed to the high sensitivity of copper (II) ion to pH [81]. Further down, the levels of copper decreased due to the natural purification of water. [6,79].

ZINC

The concentration values of total zinc were all above the natural un-contaminated values i.e. 0.3 - 4.3 ppb (Table 18). However, they were below the W.H.O. highest acceptable and maximum allowable levels i.e. 5.0 ppm and 15.0 ppm respectively.

The levels of zinc in sediments were generally low varying from 16.4 ppm to 55.7 ppm (Table 19). In water, the levels ranged from 15.1ppb and 33.3 ppb in the rainy season (Table 19).

Unlike copper, the levels of zinc in water samples at point 50^* were found to be high. This was again attributed to its possible accumulation in the cells of the blue green algae e.g. chlorella which might have been suspended in water [15]. The decrease with distance downstream was again thought to have been due to the natural purification of water [6,77].

LEAD

In sediments, the concentration values of total lead were generally high (Table 19). However, the concentrations in water were found to be within the natural un-contaminated levels (0.2 - 2.5 ppb) except at point 50^* where the level was high i.e. 3.8 ppb (Table 18). However, this concentration was below the maximum allowable level i.e. 100 ppb. The low dissolution was attributed to the high pH of the water [6,79,81]. The maxima in both the sediments and the water samples was at point 50^* and to a lesser extent at point 0^a. These values were attributed to the discharges from a car battery smelting plant and the amount present in the soil respectively.

MERCURY

The concentration of total mercury was generally very low in most of the water samples (Table 18). However, at point 500^b the levels in both water and sediments were detectable (Table 18 and 19). The levels at this point were slightly higher than those in un-contaminated water i.e. 0.1 ppb [79,80]. However, they were found to be within the W.H.O. maximum permissible level (1-5 ppb).

The levels in sediments were generally low with notably high levels detected at point 500^{b} (23.2 ppm). This level was of some concern as some microorganisms are able to methylate inorganic mercury to the highly water soluble and toxic methyl mercury [6,7,10].

4.4.0 URINE

As discussed in chapter 3, urine from volunteer employees from a cement industry were sampled. The results were grouped as per the departments, and are tabulated in table 20.

The pH of the urine samples were measured with a pH metre. It was noted that the pH values of the urine samples of those working in the chemical laboratory were generally higher than for those in the other departments (Table 20). This was thought to have been due to fumes from chemicals e.g. ammonia solution used in the various determinations as there was no fume cardboard. It was also noted that the technicians were not using pipette fillers instead, they were sucking solutions directly. The pH of the urine samples from the workers from the other departments were acidic as expected due to uric acid [7].

Another notable observation was that the levels of heavy metals in the urine of the control group were lower than those in the three departments.

Lastly, the levels in the urine of those working in the cement industry were found to be within the reported range except for lead which was low [7,10,27,82,83]. However, Comar [27] had suggested that the body has a limited ability to excrete lead

TABLE 20 THE MEAN LEVELS OF HEAVY METALS IN URINE SAMPLE OF VOLUNTEERS IN A CEMENT INDUSTRY.
(concentration in ng/ml)

Area[a]	pH	years[f]	Cr	Mn	Fe	Cu	Zn	Pb	Hg
Controls*	5.97	-	5.8	11.5	243.5	20.0	325.0	27.5	nd
	+1.40		± 2.1	± 6.5	± 66.5	± 12.0	± 215.0	± 12.5	-
Chemical Lab[b]	5.69	10	nd	nd	176.7	24.3	296.7	nd	nd
	6.25	7	14.6	2.3	450.2	19.8	303.3	3.0	nd
	7.92	10	17.5	7.4	110.0	15.2	230.0	5.9	nd
	8.12	7	nd	19.5	233.3	20.8	170.0	nd	nd
	8.16	9	nd	nd	223.3	11.8	280.0	nd	nd
Mean[c]	7.23	8.6	6.4	5.8	238.7	18.4	256.0	0.6	nd
± std	±1.05	± 1.4	± 7.9	± 7.3	± 114.4	± 4.4	± 50.1	± 0.8	-
Cement Mill[d]	5.78	10	27.6	17.3	180.1	27.1	310.0	16.6	nd
	5.42	7	30.3	20.8	410.2	38.4	396.7	nd	nd
	5.37	10	24.8	12.3	203.4	22.7	460.2	nd	nd
	5.60	17	nd	30.5	233.3	33.2	393.3	nd	nd
	8.16	9	nd	nd	223.3	11.8	280.0	nd	nd
Mean[c]	6.07	10.6	16.6	12.6	250.1	26.7	368.0	1.1	nd
± std	±1.06	±3.4	± 13.6	± 10.5	± 82.1	± 9.1	± 64.9	± 2.2	-

NB: Elements analysed at pH of 5.0 except for Cr and Mn where a pH of 3.9 was used.

TABLE 20 (Cont...)

Area[a]	pH	years[f]	Cr	Mn	Fe	Cu	Zn	Pb	Hg
Controls[*]	5.97	-	5.8	11.5	243.5	20.0	325.0	27.5	nd
	±1.40		± 2.1	± 6.5	± 66.5	± 12.0	± 215.0	± 12.5	-
Packing Plant[e]	5.44	15	9.5	83.3	846.7	53.3	386.7	26.2	nd
	5.62	16	17.8	31.7	230.0	14.0	536.7	13.7	nd
	5.44	12	27.9	24.1	263.4	25.3	256.9	12.7	nd
	5.23	10	nd	25.4	123.6	40.0	613.3	2.3	nd
	5.66	9	31.6	11.0	216.7	32.1	166.7	10.8	nd
	5.44	11	nd	27.9	183.4	13.0	346.7	nd	nd
	5.62	10	nd	21.0	286.8	31.1	346.9	11.5	nd
Mean[c]	5.49	11.9	12.4	32.1	307.4	29.8	379.1	3.7	nd
± std	±0.14	± 2.5	± 12.6	± 21.8	± 226.0	± 13.2	± 142.4	± 2.6	-

NB.

* - mean values for the control group.

a - department of the volunteer employee.

b - Chemical laboratory department.

c - mean value for pH, years and levels of heavy metals for those working in the same department

d - cement mill department.

e - Packing plant department.

f - years an employee has been in a particular department.

unless under kidney failure and that urine is only a minor excretion route. Most of the lead in foodstuffs is lost through the faeces.

CHROMIUM

The concentration of chromium in urine from the control group ranged from 0.0 ppb to 10 ppb with a mean of 5.8 ± 2.1 ppb (Table 20). This mean was within the reported range (7.2 - 11.9 ppb) [7,82].

The levels in the urine of those working in the cement company (subjects) were found to be higher than those in the control group. For those working in the chemical laboratory, the levels were variable, ranging from undetected value to 17.5 ppb with a mean of 6.4 ± 7.9 ppb. For those in the other two departments, the levels were much higher with a mean of 16.5 ± 13.6 ppb and 12.4 ± 12.6 ppb for the cement mill and packing plant respectively. These values were relatively higher than those in the control group.

As a result, it was suggested that the activities taking place were increasing the levels of chromium in the body. Analyses of the raw materials and dust from the crusher had shown detectable amounts of chromium (Table 6 and 9). It was also noted that the levels in the urine samples of those working in the packing plant and cement mill were higher than the reported values [7,27,82].

MANGANESE

Like chromium, the levels of manganese in the control group were found to compare well with the reported values [7] (Table 20). They ranged from 5.1 ppb - 18.0 ppb with a mean of 11.5 ± 6.5 ppb. It was also noted that the urine from those who were in the highly dusty sections i.e. packing plant (32.1±21.8 ppb) and cement mill (12.6 ± 10.5 ppb) had higher levels of manganese value than in the chemical laboratory (5.8 ± 7.3). These levels were notably higher than those in the control group and the reported range except for those from the chemical laboratory [7]. This was thought to have been due to dust which had been noted to contain appreciable amounts. In fact, there was a correlation between the extent of dust exposure in a department and the levels of heavy metals in the urine.

IRON

The mean concentrations of iron were found to be comparable in all the four groups of subjects sampled (Table 20). Controls (243.5 ± 66.5 ppb), chemical laboratory (238.7 ± 114.4 ppb), cement mill (250.1 ± 82.1 ppb) and packing plant (307.4 ± 226.0 ppb). These levels were within the reported range (200 - 300 ppb) except for those in the packing plant. Underwood [7], Comar [27] and Pirzio-Biroli et. al. [84] had noted that the iron state in the body does not necessarily depend on levels in foodstuffs or exposure. They had attributed this to the limited ability of the body to excrete iron. As such, iron homeostasis is maintained through the adjustment of its absorption. Thus, the amount of iron absorbed depends on the body needs unless in the presence of reducing agents like ascorbic acid or chelating agents like phatates which increase and decrease the rate of iron absorption respectively [7,85]. Consequently, high iron levels in urine are rarely encountered. It was however noted that there was a slight increase with increased exposure to dust. This suggested that the dust had a significant effect on the iron state in the bodies of employees.

In conclusion, iron toxicity was not anticipated among the factory workers except for those working for a long time in the packing plant and cement mill.

COPPER

As in the other metals discussed earlier, the levels of copper in urine samples were found to be high in departments with high levels of dust although they were within the reported range (2.7 - 29.9 ppb) [7,27,28] (Table 20). The mean concentrations were 18.4 ± 4.4 ppb, 26.7 ± 9.1 ppb and 29.8 ± 13.2 ppb for those working in the chemical laboratory, cement mill and packing plant respectively. This data indicates that the body burden was not very high as the urine is the main excretion route for copper [7,86]. Again, the data seems to suggest that there was a correlation between the extent of exposure to dust and the concentration of heavy metals in the urine. Therefore, the dust was thought to have potential pollution value especially to those working in the cement mill and packing plant.

ZINC

Like the other metals, zinc levels were found to be high in the urine of those working in both the cement mill and the packing plant compared to the chemical laboratory (Table 20). This phenomenon was attributed to dust as there was a general correlation between the extent of exposure to dust and the levels manifested in the urine. The concentrations encountered were slightly higher than the reported values (200 -300 ppb) [1,7,15,27,28,82].

Unlike most of the other metals, the concentration values in urine samples from the cement factory were comparable to those in the controls group. This suggested that the increase due to dust was not very significant. Thus, zinc toxicity was not expected as the metal is not cumulative. However, urine is not a good indicator of the zinc state in the body as faeces is the main excretory route [7].

LEAD

Unlike all the other metals analyzed, lead concentrations in urine samples from those working in the cement company were much lower than those in the control group (27.5 ± 12.5 ppb) (Table 20) and the reported values (10 - 80 ppb) [1,7]. The mean of those in the chemical laboratory, cement mill and packing plant were 0.6 ± 0.8 ppb, 1.1 ± 2.2 ppb and 3.7 ± 2.6 ppb respectively.

Lead levels in the environment are known to be dependent on the industrial activities [1,15,23] and that the levels in the subject's blood and urine are dependent on environmental exposure. As such, the ambient level of lead and time of exposure are the main determining factors of the body load. Therefore, the high levels in the controls were attributed to a higher ambient lead level as they were from people living in Nairobi city which had a much heavier traffic and many more industrial activities. This was taken to be the case as several researchers had found high levels of lead in urban environments having heavy traffic [10,15,87,88,89]. The ambient levels by various researchers were variable; Pattenden [87] found 407.8 ngm^{-3} in Swansea (Wales), Cawse [88], found 31ngm^{-3} in non urban Wraymires (UK), and MC Innes [89], found 277ngm^{-3} in urban United Kingdom.

From another research [10], it was found that there was a correlation between the ambient levels and those in the blood e.g. in rural and urban U.S.A. where the ambient levels were 0.5 ugm^{-3} and 3.8 ugm^{-3} respectively, the levels in the blood of those living there were 16.0 ppm and 30.0 ppm respectively. Consequently, the lower levels in the urine of those working in the cement company were attributed to low ambient levels and the low rate of absorption of inorganic lead in the respiratory system compared to organic lead from motor vehicles exhaust fumes [1,7,10,82].

CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

In this work, the accuracy of the XRFA technique was tested using standard reference materials i.e. soil-7 and tomato leaves.

From the analysis, the technique was found to have an accuracy comparable to that of other analytical techniques. This was concluded as the concentrations of the metals determined were within the reported range. Also, the errors in the calculated mean were generally less than 10%.

In the case of soil-7, the accuracy was good for most of the metals determined except for lead and copper. For these metals, the errors in the calculated mean were above 10% although the mean concentration values were within the reported range.

Therefore, the technique was found to be accurate enough for the analysis of iron, manganese, zinc, copper, chromium, lead and mercury in samples.

Soil

From the analysis of soil samples, the following was evident. Dust from the electrostatic precipitator was found to have very low concentrations of lead and chromium. Therefore, it was considered not to pose any environmental pollution with respect to these metals. Infact, it was found that the indigenous soil had higher concentrations of these metals than the dust from the electrostatic precipitator. However, the dust from the crusher was found to have high concentrations of these two metals. The difference was attributed to loss of these two metals in the reaction chamber where temperatures were high. For the other metals, it was noted that the dust had a substantial amount of each. However, they were lower than those present in the indigenous soils. Despite this, the dust could pose some problems as there was a likelihood of those working in this region inhaling it thus, damaging the lungs or increasing the body burden in the long run with respect to these metals.

Lastly, metals present in dust were being leached hence available to plants. Therefore, depending on the amount available and the physiological role of the metal, there was a possibility of these metals being phytotoxic. Chromium and copper were more likely to be in this class as they are known to be phytotoxic even at very low concentrations. Therefore, the dust was found to be an environmental pollutant.

Plant leaves

Plant species growing on dust from the precipitator registered low concentrations of heavy metals. This was in support of the soil data that most of the metals in the dust were generally unavailable to plants probably due to high pH, high calcium levels and the fact that metals were present in unavailable form for "effective uptake". Leaves from the different plant species sampled registered variable concentrations. This suggested that different plants have different abilities to assimilate heavy metals maybe due to differences in the selectivity of the cell wall, mechanism of absorption, tolerance of the species to these metals and the physiological role and activity of the individual metal.

Plants growing on soils having high levels of organic matter were noted to register higher levels of heavy metals. This was probably due to high availability of these metals to plants. The concentrations, registered in the plant leaves were noted to increase with increases in the total amount present in the soil although not linearly. Copper concentrations in plants were generally low although it is an essential element in plants. This was attributed to its high phytotoxicity even at relatively low concentration.

water

From the analysis, the levels of iron and manganese were found to be higher than the natural un-contaminated levels and the W.H.O. highest acceptable values in drinking water, However, they were found to be lower than the maximum allowable values in drinking water. This suggested that although the river was polluted with respect to these metals it was still fit for drinking.

Lead, chromium and mercury were in a class of their own. Their levels were found to be within the natural un-contaminated levels except at one or two points. However, at these points they were still lower than the W.H.O. highest accepted values. Despite the low levels, these metals were of concern as they are cumulative in tissues and highly toxic. These metals were also thought to pose a serious danger to humans living near the sampling points as the Athi River town water treatment works was a rapid sand filter which does not remove metal ions effectively. However, further downstream this danger was considered to be less as the pH of the river was high. Consequently, these metals were rapidly being precipitated resulting in lower levels downstream. As such, the river was found to be relatively less polluted with respect to most of the metals studied.

sediments

The levels of the metals analyzed were relatively high in the sediments except for chromium and mercury which were high at only one location. This being the result of the high pH which favours precipitation of metal ions. Thus, their levels in water were generally low. This was in agreement with water data that the river was generally polluted with respect to iron, manganese, copper, zinc and lead.

Urine

From the analysis, it was found that the levels of all the metals in the urine samples from those working in the cement industry were higher than those from the controls except for lead.

It was also noted that there was a correlation between the extent of occupational exposure to dust and the levels of metals in urine.

The data for lead showed that the pollution arising from dust was not as adverse as that in the urban environments having heavy traffic, as the urine from the controls, who were from Nairobi city had much higher mean levels (273 ± 12.5 ppb) than those working in the chemical laboratory (0.6 ± 0.8 ppb), cement mill (1.1 ± 2.2 ppb) and packing plant (3.2 ± 2.6 ppb). This suggested that the rate of absorption of inorganic lead in the respiratory system was lower than that of organic lead from motor vehicles.

Therefore the dust was found to pose a pollution danger especially to those working in the cement mill and packing plant although to a lesser extent compared to urban environments.

With this discussion, the following was recommended; that blood sampling and analysis for those working in the cement industry needed to be carried out. This was found very necessary especially for those working in the cement mill and packing plant where urine was found to have very high levels of heavy metals.

Water from the Athi river also need to be sampled and analysed especially for mercury and chromium which were found to be present in appreciable amount near the petrol station and the tannery. Also, to be monitored are the heavy metals present in the empty containers dumped in the Athi river.

Lastly, the effectiveness of the water treatment works for the Athi River town residents needed to be determined as the water near the treatment plant had substantial amounts of heavy metals.

The available content of heavy metals in the soil was found necessary as it gives a better correlation between the levels in the soil and those manifested in the plants.

It was also noted that the levels of heavy metals in the soil in a leeward direction (B) increased drastically beyond 120 metres. Thus, soil sampling beyond this distance was found necessary.

It was also found necessary that air sampling and analysis for heavy metals be carried out. This was suggested as some of the dust particles have a long residence time in the air and some volatile elements lost in the reaction chamber might be resident in the air.

Lastly, as the plants were found to assimilate heavy metals in the dust, it would be worthwhile to sample edible plants for uptake of the same metals.

Finally, it is worthwhile noting that a paper entitled "Analysis of the levels of heavy metals in plants, water, soil, and human urine in the Athi River region" was written out of this work. It was written in collaboration with Dr. G. N. Kamau (Chemistry Department, University of Nairobi), Prof. A. H. S. Elbusaidy (Chemistry Department, University of Nairobi), A. M. Kinyua (Center for Nuclear Science Techniques, University of Nairobi) and Dr. Deng (Chemistry Department, Kenyatta University). The paper was presented at the eleventh annual medical Scientific conference organised by KEMRI.

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APPENDICES

LABORATORIES
ANALYSIS REPORT

DATE OF ANALYSIS ....

ANALYSIS OF KILN DUST ORIGIN ....

ANALYST ....

WEIGHT OF SAMPLE 0.32g DATE ....

CHECKED BY ....

SiO_2 – 410 mμ

TOTAL O.D. 0.948

less BLANK O.D. 0.045

SiO_2 O.D. 0.903

% SiO_2 21.4

Al_2O_3 – 365 mμ

TOTAL O.D. 1.235

less BLANK O.D. 0.480

R_2O_3 O.D. 0.755

less O.D. due to Fe_2O_3 0.214

Al_2O_3 O.D. 0.541

% Al_2O_3 2.5

Fe_2O_3 – 600 mμ

TOTAL O.D. 0.182

less BLANK O.D. 0.037

Fe_2O_3 O.D. 0.145

3.39

CaO – E.D.T.A.

Factor x 4.7323

mls. of E.D.T.A. 10.85

CaO = x X mls. of E.D.T.A.

4.7323 x 10.85

% CaO 64.87

L.O.I.

C + Sample (B.I.) 30.6566

C + Sample (A.I.) 30.6009

C 29.6566

L.O.I. 0.0557

% L.O.I. 5.57

SO_3

Nephelometer reading ....

% SO_3 ....

% $CaSO_4$ $2H_2O$ ....

TOTAL CO_2 – (Vol.)

a = ... ml.

b = ... ml.

c = ... ml.

Factor ....

% Total CO_2 – – ....

MgO – E.D.T.A.

Factor x 3.402

Mls of E.D.T.A. 11.30

MgO = x X (Total mls. less mls for CaO)

3.402 x 0.45

% MgO 1.53

INSOLUBLE RESIDUE

C + Ins. residue 29.4660

– C 29.3088

Ins. Residue 0.1572

% Ins. Residue 15.72

SO_3 (GRAVIMETRIC)

C + $BaSO_4$ ....

– C ....

$BaSO_4$ ....

SO_3 = $BaSO_4$ X 0.343 ....

% SO_3 = 2.42

$CaSO_4$ $2H_2O$ = $BaSO_4$ X 0.0738 ....

% $CaSO_4$ $2H_2O$ = ...

$MgCO_3$ (Vol.)

$MgCO_3$ = 2.12 (a–b–2c)

% $MgCO_3$ = ...

% MgO = $MgCO_3$ X 0.478

% MgO = ...

Calcul. $CaCO_3$ = CaO X 1.7848

% Cal. $CaCO_3$ = ...

Calcul. $MgCO_3$ = MgO X 2.0915

% Cal. $MgCO_3$ = ...

FREE CaO

n of Hcl. 0.1058

mls. of Hcl. 4.90

F. CaO = ml X n X 2.804 mg.

% F. CaO 1.45

RESULT

L.O.I. ....

SiO_2 ....

Al_2O_3 ....

Fe_2O_3 ....

CaO ....

MgO ....

SO_3 ....

Na_2O + K_2O ....

Sum ....

MS ....

MA ....

L.S.F. ....

L.C.F. ....

F CaO ....

C_4AF ....

C_3A ....

C_2S ....

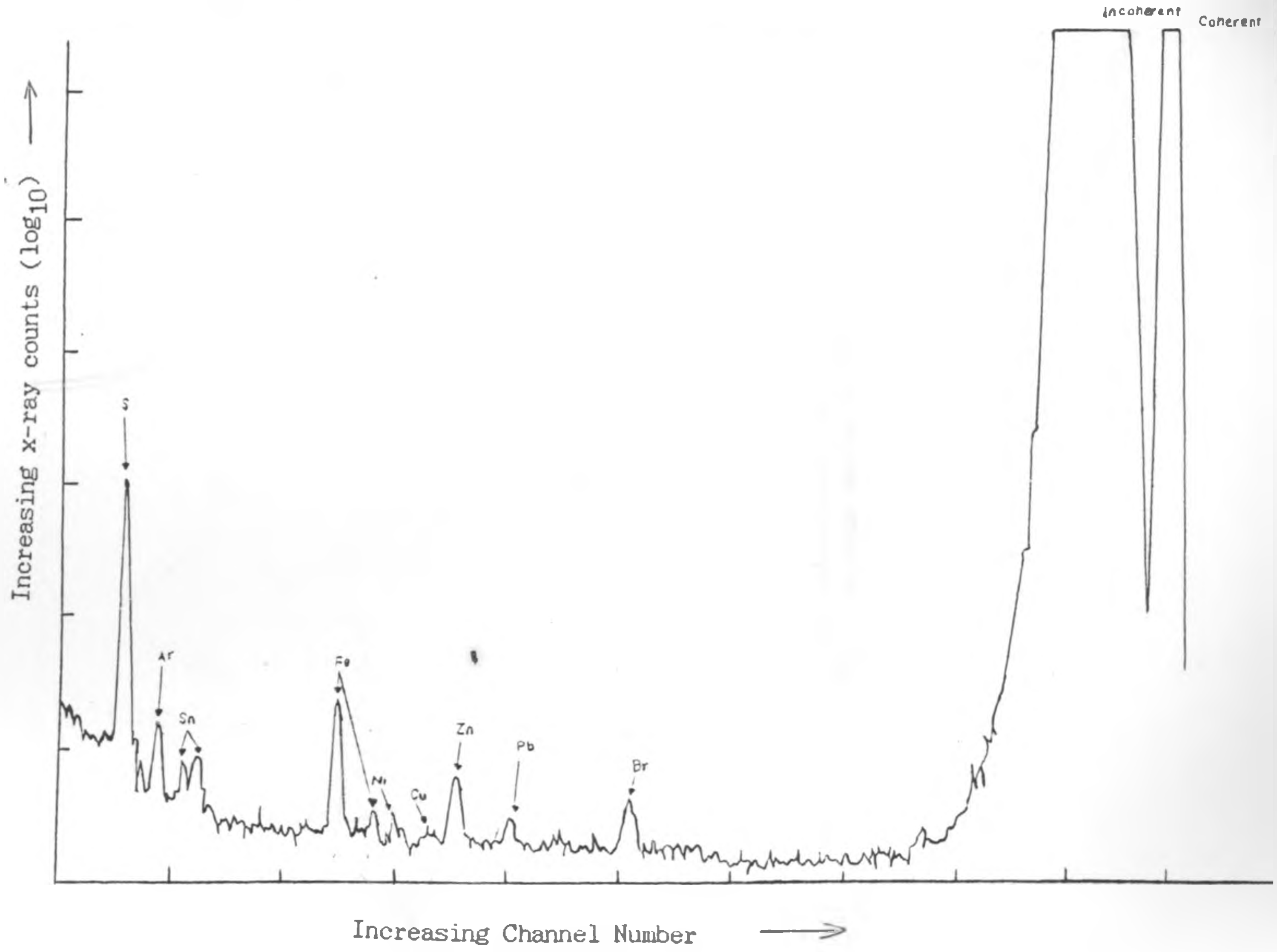
C_3S ....

Total CO_2 ....

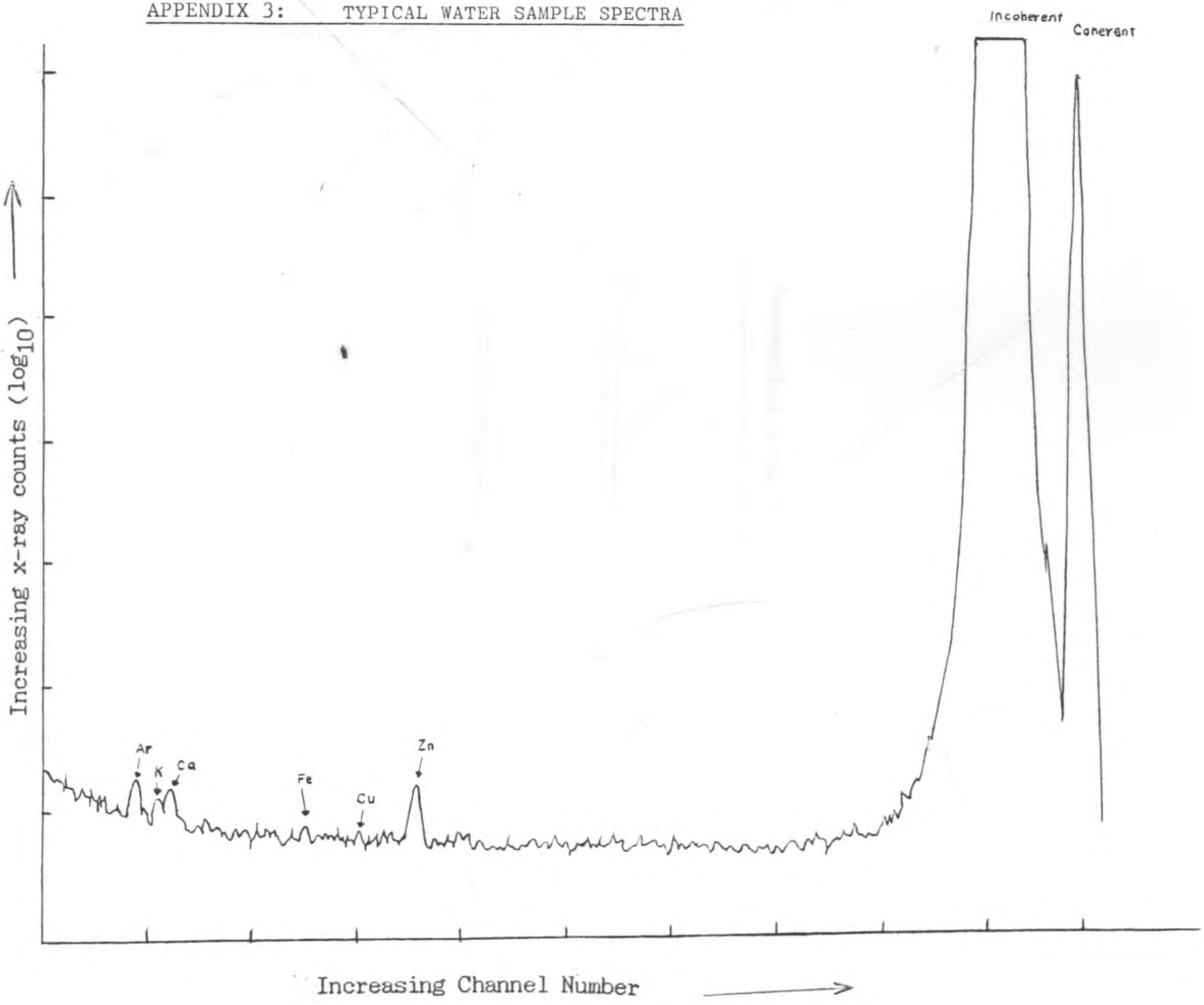
$CaSO_4$.$2H_2O$ ....

Ins. Residue ....

APPENDIX 2: TYPICAL URINE SAMPLE SPECTRA



APPENDIX 3: TYPICAL WATER SAMPLE SPECTRA



APPENDIX 4: TYPICAL SOIL SAMPLE SPECTRA