HEAVY METALS IN WASTES IN MATHARE VALLEY AND FORMULATION OF A WASTE MANAGEMENT DATABASE.

BY

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A thesis submitted in partial fulfilment for the degree of Master of Science of the University of Nairobi.

This is my original work and has not been presented in any other University.

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This work has been submitted for examination with my approval as University supervisor.

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Finally to God from whom all wisdom and knowledge comes from. For He has said in the holy scriptures 'If anybody lacks wisdom, let him ask and it will be given him'

DEDICATION

To my mother.

ABSTRACT

The concentration levels of Cadmium and Lead in garbage waste, water and top soil in Mathare Valley has been investigated using atomic absorption and polarographic techniques. Further to this, a waste management database consisting of literature on waste management technologies was established. In determining the concentrations of the metal ions in the garbage, a digestion procedure was developed for the analysis of the matrix.

In the digestion of garbage samples for the extraction of Cadmium, Nitric, Sulphuric and Perchloric acids in the ration of 2:1:1 maintained at room temperature (23±2°C) for 1 hour was found as the most suitable method for digestion. Higher temperatures were found to be unfavourable. The concentrations in garbage and top soil ranged between 0.01-2.86 mg/kg of dry waste and 1.40-2.13 mg/kg respectively. In water, detectable Cb concentration did not exceed 0.007 ppm. comparatively lower than the WHO limit for drinking water of 0.01 ppm.

In the digestion of garbage samples for the extraction of Lead, Nitric and Perchloric acids in the ratio of 4:1 at room temperature (23±2°C) for 1 hour followed by 40°C for 1 hour was found to be the most appropriate procedure. Concentrations in garbage and top soil ranged between 34.48-54.36 mg/kg of dry weight and 30.84-54.36 mg/kg respectively. In water, detectable Cb concentration did not exceed 0.008 ppm which is lower than the who limit for drinking water of 0.05 ppm.

A drop in the concentration levels in garbage, top soil and water was observed during the rainy season suggesting leaching and dilution effects.

The above results suggest that there is no immediate danger of direct Cadmium and Lead pollution as a result of the garbage dumps, yet the health hazards possed by the presence of these dumps in the vicinity houses should not be overlooked. The information contained in the database showed that methods for the handling of urban waste are available and have been tested in real life situations. The task is to appropriately apply these techniques in Nairobi.

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CHAPTER 1

1.0 INTRODUCTION

Many cities in the developing countries are growing at a very fast rate. This growth rate has many implications among which are the heavy burdens that fall upon the cities in the areas of provision of services to the urban populations e.g. adequate housing, transport, health facilities, schools, social amenities etc. These exploding city sizes are in part indicative of the increase in industrialization and commercial activities. These two factors are no doubt, good pointers of economic development yet on the other hand, this development does bring with it unique problems. Increase in industrialization and population mean that there will be an increase of total amount of waste produced. The waste management systems have to be continually improved and more efficient cost effective methods sought for.

TABLE 1 HUMAN POPULATION FOR SELECT WORLD CITIES

CITY	POPULATION IN THOUSANDS			
ALGERIA	1722(87)	1523(77)	940(66)	266(48)
SINGAPORE	2586(86)	2414(80)	2075(70)	680(47)
CAIRO	6205(85)	5074(76)	4220(66)	2091(47)
KINSHASA	2654(84)	2444(76)	1323(70)	209(47)
TOKYO	8354(85)	8349(80)	8841(70)	5386(50)
NAIROBI	1104(84)	828(79)	509(69)	75(48)
LUSAKA	538(80)	262(69)	31(50)	
MOMBASA	426(84)	341(79)	247(69)	85(48)
NEW YORK	7263(86)	7072(80)	7896(70)	7892(50)

( ) Year of population estimate.

The basic problem encountered in waste management is the question of how to get rid of the waste produced, finding appropriate ways of collecting and disposing of it in an environmentally acceptable manner.

1.1 SOURCES AND COMPOSITION OF WASTE

The major sources of waste in an urban environment include:

i) Industrial establishments.

ii) Commercial and related activities.

iii) Households.

Regarding (i), regulations have been formulated that specify the quantity and state in which the waste produced may be released to the environment. The laws ensure that the impact on the environment is at a minimum. The existence of these laws could be partly attributed to the potentially devastating short and long term effects the pollutants would have on the environment e.g. gaseous emissions leading to acid rain, uncontrolled discharge of waste into river systems endangering life in the river and any potential users. The industries generating the waste have the responsibility of controlling and treating any wastes produced such that they comply with the regulations stipulating the allowable levels in the environment of the waste they are producing.

During the last few years, the subject of waste management has attracted a considerable amount of attention. Incidences of developed countries exporting their industrial wastes to developing countries have featured in news headlines. In cities of the developing countries, dumps of uncollected rotting waste have increasingly become a common site. The responsibility for collecting and disposing of this garbage rests on the municipal councils. Their resources have been stretched to the limits in trying to cope up with the ever increasing quantities.

TABLE 2 WASTE GENERATION CHARACTERISTICS OF FAMILIES[1] FROM UK, ASIA AND MIDDLE EAST

	UK	ASIA	MIDDLE EAST
Size of Household	2.25	6	5
Weight/family/day (kg)	1.90	2.49	5.3
Vol/family/day (l)	14.4	4.32	25.10

TABLE 3 WASTE GENERATION CHARACTERISTICS OF PEOPLE[1] FROM UK, ASIA AND MIDDLE EAST

	UK	ASIA	MIDDLE EAST
Wt/Person/Day (kg/m^3)	0.845	0.415	1.06
Appx. Density (kg/m^3)	132	570	211
Vol./Person/Day (l)	6.4	0.72	5.02

The characteristics in Africa are very similar to those of Asia with large families and relatively low volumes of waste. This is due to the limited use of disposable articles and lower use of packaged products[1]. Vegetable matter makes up to 75% of the waste, while in UK, it is only up to 28%. The major packaging materials, paper glass and plastic make up only 2%, 0.2% and 1% respectively, in contrast to the 28%, 9% and 2% for UK.

TABLE 4 COMPOSITION OF WASTE FOR THREE GIVEN REGIONS, UK, ASIA AND ARAB OPEC COUNTRIES

	UK (%)	ASIA (%)	ARAB(OPEC) (%)
Vegetables	28	75	50
Paper	37	2	16
Metal	9	0.1	5
Glass	9	0.2	2
Textile	3	3	3
Plastics	2	1	1
Other	12	18.7	23

This though can not be taken as the overall picture since even for a given locality the greatly varying economic incomes of the people will in turn affect the composition of waste generated. Table 5 illustrates this variation. The characteristics of the middle class tend to resemble those of ARAB (OPEC) countries.

TABLE 5 VARIATION IN WASTE COMPOSITION FOR THREE DIFFERENT LOCATIONS IN ACCRA, GHANA

	Market Refuse (%)	Middle Class (%)	Public Dumping (%)
Vegetables	96.4	69	90.9
Paper	2.1	15	3.0
Metals	0.01	7.0	2.2
Glass	0.51	1.9	1.1
Textile	0.01	1.5	0.7
Plastics	0.04	3.7	0.5
Other	0.93	1.4	1.6

As the standard of living in the developing countries goes up, it would be expected that the waste patterns will increasingly resemble those already being exhibited by the developed countries i.e high volume, low density and an abundant use of packaging materials. This compounded with the projected sharp increase of populations means that the quantities of waste generated are expected to be enormous.

1.2 WASTE COLLECTION

There are several methods open for use in waste collection depending on the nature and type of waste. In the majority of cases, specialised vehicles e.g. compactors, side loaders, tippers etc are used for this purpose. Other alternatives are also employed, like in Cairo, animal drawn carts are used extensively[2]. The key factor in whatever system is employed for waste collection is the frequency. In the hot and humid countries around the equator, refuse will tend to decompose at a much faster rate than in the temperate regions. This will necessitate higher frequencies of collection. In cases where bulk community containers are being used, failure to collect regularly will lead to the location of the container turning into a disorganised dumping ground creating the very problem the container is supposed to solve. In order to establish a collection frequency, the climatic condition and waste generation rates have to be taken into consideration. There are financial implications of any chosen system which in the developing countries, have to be given closer attention due to lack of funds. A study carried out in the middle east revealed the following concerning the relationship between different methods and cost, Table 6.

Although the communal system looks cheapest, it is in-appropriate for high income residential areas in just the same manner that House-to-house collection would be in-appropriate for high density residential areas because the method requires well planned housing estates that take into consideration the particular method of waste collection. In many cases where un-planned housing estates come up, no provision is made for waste collection. In the slum areas, poor road conditions, where they are available, severely limit the use of any motorised systems of collection requiring alternative options. Use of motorised systems require in addition to good roads, a well planned housing system that will allow for easy access to the different housing units to facilitate for the collection of the waste.

TABLE 6 AN OUTLINE OF SOME MECHANICAL SYSTEMS PROPOSED FOR A MIDDLE EAST CITY[1]

System	Outline	Public Part	Relative cost %
Communal	Central bulk collection by refuse vehicles	Place refuse in nearest neighbourhood bulk container	100
Kerbside	Full access by refuse vehicles to all areas	Place refuse in adjacent kerbside container	110
Kerbside	70% access by refuse vehicles with 30% secondary transfer	Place refuse in adjacent kerbside container	128
Kerbside	30% access by refuse vehicles with 70% secondary transfer	Place refuse in adjacent kerbside container	162
House to House	100% house to house collection	Place refuse in individual household container at dwelling entrance	277

1.3 WASTE DISPOSAL

Disposal forms the major part of any waste management system. The waste having been collected from various areas has to be processed such that the waste is no longer an inconvenient by-product of previous processes. It is desirable that the disposal point be reasonably near the source of the waste to minimise the transportation costs. The nature and composition of the waste also contributes to the final options available for its disposal.

1.3.1 LANDFILL

Waste disposal by landfill method is the most common method employed in the disposal of waste. The method consists of dumping waste at a pre-selected site preferably away from high concentrations of population.

Reclamation of otherwise useless tracts of land can be achieved using this method[3]. The method is reasonably cheap and ideal for dumping of large volumes of non toxic waste, industrial commercial and household. When a great majority of the waste remains inert after burial in the site, however the organic matter biodegrades with time, the rate depending on temperature, moisture content, availability of oxygen and bacteriological composition and content.

Various chemical reactions do take place and with time an aqueous layer of leachate is produced which contains mainly organic compounds. There are also small quantities of inorganic compounds. This leachate forms the major potential source of pollution to the environment, especially as concerns the contamination of underground water systems[4].

1.3.1.1 FACTORS AFFECTING SELECTION OF SITES FOR LANDFILL.

Several factors come into consideration when determining whether a site should be selected or not. The major ones are:

Road access:	The site should have good road access passable during all seasons and capable of handling heavy commercial vehicles.
Distance to site:	Distance to site from the source waste should be within economic delivery range.

Hydrological and geological considerations:	Percolation of rainfall through the landfill could give rise to a highly polluted leachate. the hydrological and geological[4,5] conditions around the site should be well known in order to make contain the leachate and prevent it from escaping into the environment and subsequently polluting the environment.
Covering material:	Availability of covering material within close proximity of the site is essential.

Landfills are used for the disposal of both toxic and non-toxic,though precautions have to be taken when dealing with the former. Large volumes of non-toxic waste are necessary to allow for dispersion of the toxic waste if this is an acceptable method of disposal.

The major problem of environmental concern encountered when dealing with landfill sites is in the control of the leachate[6]. Constant monitoring of ground water systems in order to detect any pollution forms an integral part of the management of the site. The city of Nairobi, like many other cities of the developing nations, uses this method for the disposal of waste. With the increase in number of industries especially those that process chemicals, alternative methods would need to be incorporated in the waste management system.

1.3.2 COMPOSTING

Disposal by composting is suitable for waste containing a high percentage of organic matter which gets decomposed to carbon dioxide, and humus. Tables 4 and 5 show that the waste composition of many cities in the developing countries contain substantial amounts of organic matter making them suitable for disposal via composting. Unfortunately, not many cities have adopted this method of disposal[2] possibly due to the high costs of running the composting plants. Humus obtained from composting the waste could be sold and the income used to offset the costs of running the plants but this requires a well organised system to market the by-product.

1.3.2.1 COMPOSTING PRINCIPLES

Composting of waste is carried out by naturally occurring micro-organisms which grow in mixed organic waste. The process of growth leads to the liberation of CO_2 and water vapour compounded with an increase of temperature. It is essential that a balance is maintained between the heat generated and that which escapes since higher temperatures would kill the heat sensitive bacteria hence promoting the growth of heat tolerant bacteria that may not be desirable[7].

There are three stages through which the waste undergoes before it is fully composted. In the first stage, mesophilic bacteria as well as actinomycestes yeasts and other fungi break down fats, proteins and carbohydrates. During this initial process, the temperature gradually rises to a range of 40°C-50°C. This temperature range is too high for survival of the organisms that initiated the process. The compost goes into the second stage whereby thermophilic bacteria take over from the mesophilic bacteria and continue the process of decomposition process generating heat that causes the temperature to rise to about 70°C. These high temperatures normally kill the majority of pathogenic organisms present in the waste. On exhaustion of food available in the waste, the thermophilic bacteria stop producing heat resulting in cooling of the compost heap. This cooling off stage comprises the third and final stage. The final product is a mass of indigestible residues referred to as humus.

1.3.2.2 FACTORS AFFECTING COMPOSTING

Three factors need to be controlled in order to make good compost. These are:

i) Availability of Oxygen

ii) Moisture content

iii) Fraction of Nitrogen in the waste, (Carbon/Nitrogen (C/N) ratio)

i) Availability of Oxygen

Oxygen is necessary in order for the compost to decompose aerobically. Decomposing of waste anaerobically produces objectionable odours which tend to make people shy away from using it. The temperatures are not as high as those of aerobic decomposition which means that the final product is not adequately disinfected in addition to taking a much longer time. Several methods have been employed to ensure that the compost is sufficiently aerated. Mixing of the compost and pumping air through the system are some of the methods that have been used[8].

ii) Moisture content

Moisture levels of about 50% by weight have been found to be ideal for the growth and multiplication of the bacteria. The upper limits are controlled by the necessity to allow air to diffuse through the compost for reasons outlined in section (i) above[8].

iii) Fraction of Nitrogen (C/N ratio)

C/N ratios in the range of 25-30:1 are suitable for composting. The very high percentage of organic matter of comparably low C/N ratio present in municipal waste (Table 5) require that the substances of high C/N ratio e.g paper be added to elevate the ratio. Sewage sludge has been used on occasions provided that it contains no harmful concentrations of contaminants[9,10].

The following factors have been suggested by WHO[11] for a successful composting program.

a) Suitability of waste.

b) Market for compost within a range 25 km.

c) Support from government ministries concerned with agriculture.

d) An acceptable price for the product.

The output tonnage of a municipal composting plant to be commercially viable on large scale has been estimated to be around 30,000 tonnes per annum. Small scale composting can be carried out especially in agricultural communities where there is an immediate use of the compost. No special equipment is required for this[7].

1.4 COMPUTER INFORMATION SYSTEM

Since the advent of computers in the early 40's, they have played a major role and continue to in the automation of different processes. The main breakthrough in the use of computers occurred in the 80's when technological advances allowed the micro-computer to be affordable by large populations. Formerly, computing was associated with very large machines owned by large organisations, but with the micro-computers now available to the general public, it was inevitable that development of application for use by these new users would start. Word processing, spreadsheets, databases and other packages were developed as the use of micro-computers spread.

The power of the computer lies in its ability to quickly process large amounts of information and to store it for later access. In research, survey of large amounts of data is frequently done and cases may arise when a selection of the references needs collected together. This can be done by manually compiling and storing the information. Manual compilation is adequate when the information at hand is not extensive, but as it is, new items of information keep on being generated, which have to be incorporated into the already existing information base. Carrying out this process manually is very inefficient and very time consuming creating problems in keeping up to date[12,13]. These problems can be alleviated by adoption of computerised information systems.

1.4.1 DATABASES

It is common to find similar information collected and stored together e.g reference books, holdings in specialised libraries etc. As part of the objectives of this study, it was desired to collect together information pertaining to waste management technologies and storing it in computers. Computer programs have been developed for the storing and management of this information and are referred to as database packages. The decision regarding which database package to use is based upon:

i) Type of information, i.e numeric, textual or both.

ii) Intended use of the information.

The information of concern in this study was bibliographic, i.e the description of publications in the field of waste management. The computer program to be used in the storing of the information would need to be able to efficiently store textual data as bibliographic description of publications consists mainly of text of non fixed length. In addition the program need to have very good searching facilities to enable one to locate publications of interest easily.

Several database programs are available on the market geared towards the storing and management of data. There are tailor made programs, though fairly easy to use, they tend to lack flexibility hence limiting their use.[14] UNESCO has developed the CDS/ISIS program, specifically designed to manage bibliographic non-numeric data of varying length.[15,16] Many documentation institutions in the world have adopted the program and in Kenya over 40 are using it[17]. This world wide use facilitate easy exchange of information between the institutions as the need to translate the information into another format is eliminated[18].

1.5 ENVIRONMENTAL ASPECTS OF HEAVY METALS

Many works have been published on the environmental aspects of heavy metals, thus, only a brief outline is going to be given here.

1.5.1 CADMIUM

Cadmium has no known essential function in the human body[19,20]. It's entry into the human body is normally during ingestion of food. It competes with other divalent ions when they are being bound by ligands. Several parts of the body affect the passage of Cadmium. In the gastrointestinal tracts, metal binding ligands released during the digestive process have been found to bind cadmium as opposed to other divalent ions e.g. Zinc. Mucosal cells of the small intestines have been found to concentrate Cadmium. High concentrations of the ion have also been found in the liver and kidneys. Concentrations of 200μg/gram fresh weight causes renal tubular damage.

Apart from dietary intakes, air also contributes to the total amount of Cadmium in the human body (appx 0.03μg /Day). Higher levels are bound to be recorded in more polluted environments.

Low level poisoning normally due to occupational hazards, usually manifests itself in shortness of breath and fatigue. Anaemia and slight liver damage could also occur.

Cases of high level of Cadmium poisoning have been as result of eating highly contaminated food most notable being the case of Fuchu Toyama Prefecture in Japan after the residents had eaten highly contaminated rice. It has been estimated that the intake of Cadmium was about 300μg/day. Itai itai disease characterised by ease of getting fractures of bones, renal dysfunction, excretion of proteins, glucose and amino acid.

1.5.2 LEAD

Like Cadmium, Lead has no known essential function in the body[19]. The main uses of Lead are in batteries, water pipes and as petrol additives. Other areas of use include paints, solder metal etc. It is evident from these uses that the human population is in constant contact with the metal raising the concern over its toxic effects.

Lead is a potential enzyme inhibitor[19,20] because it binds the sulphdryl (SH) group. It also inhibits the synthesis of heme and utilization of iron in the body. Manifestations of Lead poisoning include abdominal colic, anaemia, renal damage and neuropathy. Under normal conditions, the body can excrete upto 0.3 mg. of Lead. Clinical disorders given above start occurring if intake of Lead exceeds 1.0 mg day.[1]

1.6 RESEARCH OBJECTIVES

The current survey shows that there is very little information on the heavy metal content in raw garbage that litters the many areas of the city of Nairobi. The close proximity of the slum dwellers to rarely collected garbage dumps poses a health risk not only due to the pathogenic bacteria that infest these dumps and may easily affect them, but also due to the possible problems related to heavy metal exposure.

Identification of the problems possed by presence of waste in close proximity to human populations, only partly solves it. Of more importance, is to find solutions as to how to effectively control the disposal of waste that is an inherent part of the society. A first step in achieving this objective is to collect together information on waste management and organize it in such a manner that it may be quickly and easily accessed. In summary the objectives of the current research work was to:

(i) Select a representative area which is well known for uncollected, uncontrollable garbage.

(ii) Develop a digestion method suitable for the analysis of garbage.

(iii) Study the garbage from different positions with respect to Lead and Cadmium concentrations from surface layers and inner layers.

(iv) Study the extent of these two metals in the receiving river, particularly during the rainy season.

(v) Set up a bibliographic database on waste management.

Work of similar nature has been carried out in other countries[21] but no information has been found for any such work in Kenya, particularly with respect to closer investigation of non-essential toxic elements, (Pb, Cd) in raw garbage within a slum. The word "slum" in this context refers to a densely populated, low income, congested unplanned housing and uncontrolled home industries. It was with much pain that this project was undertaken from an area which has been neglected over the years by most researchers.

CHAPTER 2

2.0 ANALYTICAL METHODS AND INSTRUMENTATION

Several methods of analyses based on instruments exist for the analysis of trace metals in different matrices. These include X-ray fluorescence, Atomic Absorption Spectroscopy, Atomic Emission Spectroscopy and Polarographic techniques. The adoption of any particular method is based upon several factors namely:

i) The scientific objectives.
ii) Safety.
iii) Economy.
iv) Convenience.
v) Availability of the required instrument.
vi) Method sensitivity.
vii) Detection limits, precision, accuracy and reliability.
viii) Level of susceptibility to matrix interference

A balance between the above objectives was sought for in carrying out the research and as a result, Atomic Absorption Spectroscopy and Polarography were selected.

2.1 ATOMIC ABSORPTION SPECTROSCOPY

Atomic absorption spectroscopy has emerged as one of the major instrumental methods of analysis as evidenced by the numerous publications where the instrument has been used. The versatility of the instrument is such that over 70 elements can now be analyzed using the instrument. The use of electrothermal atomizers greatly increases the detection limits of the instrument. Currently the instrument is used in the trace analysis of water and effluent, marine chemistry, foodstuffs, geochemistry, petrochemicals, clinical chemistry and many others. The general concepts and instrumental techniques in atomic absorption spectroscopy have been given ample treatment,[22,23,24] thus only the essentials are going to be reviewed.

2.1.1 ATOMIC ABSORPTION THEORY

Every element has a unique electronic structure associated with it, the normal orbital configuration being referred to as the ground state of the atom. On subjecting the ground state atoms to radiation which corresponds exactly to the energy required for a transition from the ground state to an excited state, absorption occurs. The unabsorbed radiation passes through a monochromator which isolates the desired exciting spectral line and then into the photo detector. Absorption is measured by the difference in transmitted signal in the presence and absence of the absorbing species. The energy absorbed is unique for the absorbing species and hence allows for qualitative analysis. Quantitative analysis is also possible since the amount of light so absorbed has a linear relationship with the number of atoms that had absorbed it. This relationship is defined by Beer's Law:

$$\log \frac{I^{\circ}}{I} = \epsilon bC \qquad (1)$$

where

ϵ = Molar absoptivity

b = Path length

C = Concentration.

2.1.2 INSTRUMENTATION PARAMETERS

The Atomic Absorption Spectrometer can be subdivided into the following parts

- i) Nebuliser system
- ii) Lamp system
- iii) Burner
- iv) Detectors
- v) Read-Out system

2.1.2.1 NEBULISER SYSTEM

The solution under analysis is aspirated into the nebuliser converting it into a mist. The sample aerosol is mixed with the fuel and oxidant in the nebuliser chamber before introduction into the flame. Here, the metal ions are converted into gaseous atoms and subsequently absorption of the relevant energy occur. The magnitude of absorption will be proportional to the concentration of the metal atoms in the flame and hence to the concentration in the solution[24].

2.1.2.2 LAMP SYSTEM

Hollow cathode lamps are used to produce the desired radiation. The cathode of the lamp is made up of the metal under analysis. A monochromator is then utilised to select the desired spectral line to be used in the analysis. Diffraction gratings are preferred over prisms as they offer better accuracy over a wide range of wavelengths.

2.1.2.3 BURNER

It is essential that the flame temperatures used be in the excess of 2000 K, yet again not exceedingly high so as to cause the ionisation of the metal atoms. Table 7 shows the fuel oxidant mixtures and their respective temperatures[25].

TABLE 7 FUEL OXIDANT MIXTURES AND TEMPERATURES

Fuel	Oxidant	Temperature (K)
Acetylene	Air	2400
Hydrogen	Air	2300
Propane	Air	2200
Acetylene	Nitrous Oxide	3200
Hydrogen	Nitrous Oxide	2900
Propane	Nitrous Oxide	3000

In the case of analysis of metals that tend to form refractory compounds e.g. aluminium or Titanium, high flame temperatures have to be utilised

2.1.2.4 DETECTORS

These usually consist of photomultiplier tubes coupled with electronic circuitry to enable high speed detection limits and sensitivity.

2.1.2.5 READ-OUT SYSTEMS

In the older models, dials were common place. Advances in electronics have led to the introduction of digital read-out systems coupled with micro processors that allow for programming of various features which simplify certain procedures.

2.1.2.6 PERKIN ELMER MODEL 2380 ATOMIC ABSORPTION SPECTROMETER

In this study, the above named instrument, which is microprocessor based, was used in carrying out the analysis. The presence of the microprocessor enables one to accurately and conveniently calibrate. In addition, multiple readings can be taken including some statistical treatment of the data. Direct readings of the concentrations of the analytes is also possible via a prior internal calibration of the instrument.

2.2 THEORY OF POLAROGRAPHY

2.2.1 INTRODUCTION

Polarography was introduced as an electroanalytical technique by the Czechoslovak Electrochemist, Jaroslav Heyrovsky in 1922.[26] Applications of polarographic techniques range from the simple classical (DC) Polarography to more complex Differential Pulse Anodic Stripping voltametry (DPASV)[24].

Polarographic analysis is based on the measurement of the half-wave potentials ($E_{½}$). $E_{½}$ corresponds to the inflection point of the polarographic waves, where the current is half the limiting current. The value of $E_{½}$ is characteristic of the substance under analysis and thus can be compared to literature values hence enabling qualitative analysis. This value may be a function of the conditions of the solution under analysis i.e. supporting electrolyte, pH, solvent system and reference electrode.

Quantitative analysis can be carried out by comparing wave areas or wave heights corresponding to diffusion limiting currents of redox with those of standards or comparing them to those of spiked standards.

Reduction reaction follows the following process

$$M^{n+}_{(aq)} + ne \rightarrow M_{(Hq)} \qquad (2)$$

where

n = Number of electrons involved

where the equilibrium potential, E of the amalgam electrode is determined by the ratio of the concentration of a metal M to the concentration of its atoms in the amalgam:

$$E = E^{\circ} + \frac{RT}{nF} \; ln \; \frac{C^{n+}_{m_{(aq)}}}{C_{m_{(Hg)}}} \qquad (3)$$

where

E° = Standard Equilibrium Potential

R = Gas constant

ln = Natural log

F = Faraday constant

$C^{n+}_{m_{(Hg)}}$ = Concentration of the metal in solution

$C_{m(Hg)}$ = Concentration of the metal in amalgam

Since an amalgam is formed when the metal ions discharge at the surface of the electrode, it follows that the concentration in the amalgam must be proportional to the current so produced i.e.

$$C_{m_{(Hg)}} = K'I \tag{4}$$

where

K' = Proportionality Constant

I = Current

The concentration of substances is determined in a solution containing an excess of an indifferent electrolyte referred to as the supporting electrolyte. The supporting electrolyte suppresses the migration of the ions to be determined, thus ions are transported to the surface of the mercury electrode exclusively by diffusion. Under these conditions, limiting current, I_d (maximum diffusion current) is proportional to the concentration of the reducible species in the solution.

$$I_d = K'' C^{\circ}_{m^{n+}_{(Hg)}} \tag{5}$$

where

K'' = Proportionality constant

$C^{\circ}_{m^{n+}_{(Hg)}}$ = Reducible species in the solution

This limiting current corresponds to the complete depletion of the solution in ions to be determined near the drop surface. At any given time after the reaction has started, the current is I lower than I_d, so that the concentration of the metal ions is different from zero and corresponds to a value $C_{m^{n+}_{(aq)}}$ which determines according to equation (2), the electrode potential. Under these conditions, the diffusion current is equal to

$$I = K'' \left(C^{\circ}_{m^{n+}_{(aq)}} - C_{m^{n+}_{(aq)}}\right) \qquad (6)$$

combining with (4) and (5)

$$C_{m^{n+}_{(aq)}} = \frac{(I_d - I)}{K''} \qquad (7)$$

substituting the values of $C_{m_{(Hg)}}$ and m $C_{m^{n+}_{(aq)}}$ from equations (3) and (7) respectively into equation (2):

$$E = E^{\circ} - \frac{RT}{nF} \ln K'K'' - \frac{RT}{nF} \ln \frac{I}{I_d - I} \qquad (8)$$

if I = ½ I_d, then

$$E = E^{\circ} - \frac{RT}{nF} \ln(K^{\prime} K^{\prime\prime} E_{\frac{1}{2}}) \qquad (9)$$

Substituting $E_{\frac{1}{2}}$ in Eq (8), Eq (9) simplifies to

$$E = E_{\frac{1}{2}} - \frac{RT}{nF} \ln \frac{I}{I_d - I} \qquad (10)$$

Eq (10) forms basis of polarographic waves.

Three modes of transport are responsible for the migration of ions in solutions under analysis. The first, migration due to the existence of an electric field. Its effect is eliminated by the use of the supporting electrolyte in concentrations of about 50 to 80 times in excess of the ions under investigation. The second, convection, caused by mechanical agitation of the solution, is reduced to negligible proportions by keeping the solution still. The third, diffusion, caused by a concentration gradient between the electrode surface and bulk of the solution, is the mode that is of interest in polarographic analysis.

2.2.2 DIFFERENTIAL PULSE ANODIC STRIPPING VOLTAMMETRY (DPASV)

Only the DPASV method is going to be reviewed as it was the one of interest to this project. Details of the other methods e.g. DC, Pulse, ASV etc. may be found in literature[24,27].

DPASV combines the best of the polarographic methods having the capacity to determine concentrations up to parts per billion (ppb) level. The material to be analyzed is first pre-concentrated on a hanging mercury drop electrode (HMDE) by application of a potential more negative than the reduction potentials of the species under analysis. In this process the ionic species of the metals are reduced to their metallic form at the electrodes where they amalgamate with the mercury. Subsequently, a gradually increasing positive linear ramp on which a small amplitude pulse has been superimposed is applied to the mercury electrode. As the potential increases the various amalgamated metals get oxidised each beginning at its own redox potential. The oxidation produces a current which is proportional to the concentration of material being oxidised.

2.2.2.1 INSTRUMENTATION

The instrument lay out can be divided into three parts:

i) Oxygen scrubber system

ii) Analytical cell

ii) Polarographic Analyzer and graphic plotter

A schematic diagram of the apparatus setup is shown in the Figure 1.

2.2.2.2 OXYGEN SCRUBBER SYSTEM

Presence of Oxygen in the solution gives rise to complications when carrying out the analysis (see section 3.6). An oxygen scrubbing system is therefore essential for removing traces of Oxygen in the Nitrogen. In this work, amalgamated Zinc in a solution of VCl_2 was used as the scrubbing system.

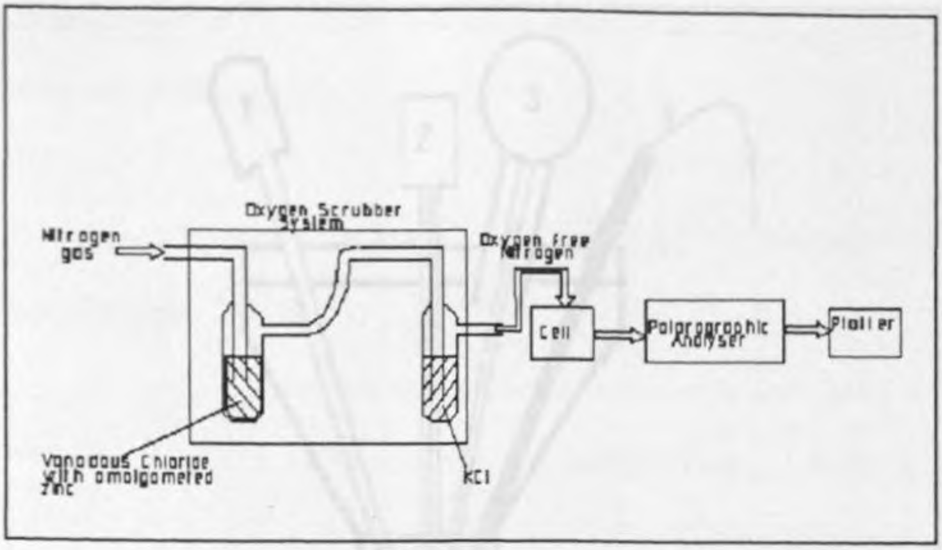

Figure 1 Schematic Diagram of Polarographic analysis system

2.2.2.3 THE POLAROGRAPHIC CELL AND IT'S THREE-ELECTRODE SYSTEM

The cell had attached to it three electrodes, reference electrode consisting of a saturated calomel electrode (SCE), working electrode consisting of a hanging Mercury drop electrode (HMDE) and a platinum counter electrode. In addition, there was attached a Nitrogen gas control tap. A diagram of the cell used is given in Figure 2.

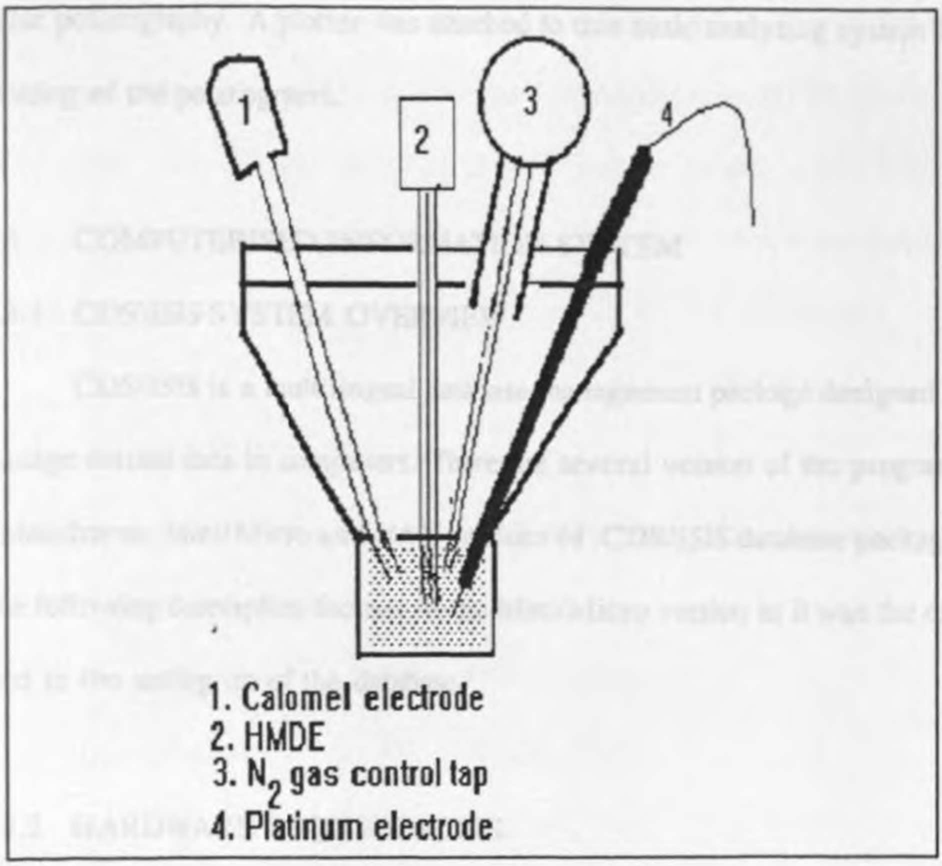

Figure 2 Polarographic Cell and It's Three-Electrode System

2.2.2.4 POLAROGRAPHIC ANALYZER AND PLOTTER

An EG&G Princeton Applied Research corporation Model 174A Polarographic Analyzer was used in this work. This is a very versatile instrument capable of doing DC, sampled DC, differential and integral pulse, direct and differential pulse stripping voltammetry, linear potential sweep and with accessories, other more elaborate types like square wave voltammetry and cyclic voltammetry. It has an initial potential of $\pm$5V with a scan rate of from 0.1mV/sec to 5.0mV/sec and a sensitivity range of .02μA to 10mA full scale. It is capable of giving 5, 10, 25, 50, 100mV pulses for differential pulse polarography. A plotter was attached to this basic analyzing system for plotting of the polarograms.

2.3 COMPUTERISED INFORMATION SYSTEM

2.3.1 CDS\ISIS SYSTEM OVERVIEW

CDS\ISIS is a multilingual database management package designed to manage textual data in computers. There are several version of the program, a Mainframe, Mini/Micro and VAX versions of CDS/ISIS database package. The following description focuses on the Mini/Micro version as it was the one used in the setting up of the database.

2.3.2 HARDWARE REQUIREMENTS

The following are the minimum requirements that are necessary in order to use the program on a micro-computer[28].

- IBM PC/XT/AT or compatibles, 512 RAM (640 RAM highly recommended)
- Dos version 2.0 or later versions.
- At least one floppy disk drive and a hard disk. A printer should be added if printing will be required.

2.3.3 PROGRAM INSTALLATION

Full installation instructions are given in the programs reference manual[28], only the important points are going to be highlighted. The program files are distributed in five different directories on the hard disk. This allows the separation of program files from the data files making it easy for file management activities. The program uses a parameters file, SYSPAR.PAR, which gives one a greater flexibility in defining the default values for the system e.g. default language, inclusion of passwords for access restrictions, distribution of files, and programming of function key.

2.3.4 SYSTEM RESTRICTIONS

The following is a list of system restrictions which are currently effective:

a) Maximum record size 8000 characters.

b) Maximum field size 8000 characters.

c) Maximum number of fields 200.

d) Maximum number of fields in a worksheet page 19.

e) Maximum number of pages in a worksheet 20.

f) Maximum number of stopwords 799.

g) Maximum number of records 16 million, (depending on the disk space available).

h) Maximum size of display format 4000 characters.

2.3.5 PROGRAM DESIGN

The system is menu driven, the services being accessed via the different menus. The services available can be divided into two, user services and system services. The user services consist of:

i) ISISENT: Data entry services for date entry and editing.

ii) ISISINV: Inverted file maintenance for maintenance of database index.

iii) ISISPRT: Sorting and printing services for printing of information.

iv) ISISRET: Information retrieval services for searching and displaying of the information contained in the database.

The above are the most frequently used services when using the database.

System services consist of functions that allow one to alter the structure of the database and various other system attributes. The available functions are:

i) Programming facilities for developing of specific utility programs using Pascal programming language, ISISPAS.

ii) Database definition services for creating and modifying the structure of databases, ISISDEF.

iii) Utility function for creating and editing of system menus and changing of other system attributes e.g. colours, ISISUTL.

iv) Data interchanging functions for exporting and importing of data using the ISO data exchange format 2709.

The different functions of ISIS are accessed via sub-menus that are selected from the main menu. The default setting lists 10 functions in the main menu:

a) Database selection: Selection of the desired database.

b) Language selection: ISIS is currently available in English, French, Spanish and Arabic. It is possible to translate all the system messages into another language e.g. Swahili.

c) Data Entry: This function allows the creation and editing of records

d) Data retrieval: For Browsing of the database and carrying out searches. ISIS search language supports the following features -

   i) Precise terms and right truncation

   ii) OR, AND, and NOT search operators

   iii) Field level and proximity searches. One may restrict the search to one field, an occurance of a repeatable fields and within a specific word separation i.e. adjacent, separated by one word etc.

   iv) Free text searching (used for un-indexed fields)

The different search expressions performed are given a number and saved. They may thus be executed again but only during that particular session. Combining of search expressions using boolean operators AND, OR and NOT to create more precise search formulations is provided for. These combinations obey normal algebraic rules.

The program allows one to save the results of a search in a file which may then be printed using the ISIS print services.

e) Sorting and printing: Options are available to print either the whole database, a range of records or hit records saved during a search. Sorting may be performed prior to printing.

f) Inverted file services: Creation and maintenance of the dictionary of searchable terms is performed here. The Field Select Table (FST), which defines the fields to be indexed, is used in the generation of the dictionary's searchable terms. Five indexing techniques are supported, whole fields, subfield, terms enclosed in <...>, terms enclosed in /.../ and singe words. Stop word files used in the elimination of non significant words e.g. articles etc, may be created for use with the last technique. The maximum length of a search term is 30 characters.

g) Data base definition and modification: Used in the creation or modification of a database structure.

h) Master file services: Importing and exportation of database files and backup.

i) System utilities: Used in editing system menus, creation/editing of user defined menus and changing screen attributes.

j) Programming: A pascal compiler is provided for development of specific applications relevant to one's needs.

Selection of fields to be defined in the database depend on the information and the use to which it would be made. The objective of the study was to create a bibliographic database thus the fields to be defined have to allow for the full bibliographic description of the publication. Table 8 below lists the fields used in the database.

TABLE 8. FIELD DEFINITION TABLE OF DATABASE

Tag	NAME OF FIELD	DESCRIPTION OF FIELD	LENGTH	TYPE
5	Bibliographic level code:	Describes type of document i.e monograph, journal etc.	1	A
20	Source of record:	Source of the information concerning the record	3	A
21	Completeness of record:	Indicates how complete the information is	1	A
22	Date record entered:	Date when information was first entered	6	N
23	Date record updated:	Date of latest update	6	N
40	Language of item(s):	Language of publication	30	X
50	Physical medium code:	Physical state of publication	25	X
51	ISBN:	ISBN number of publication	100	X
52	ISSN:	ISSN number of publication	50	X
56	Title:	Title of publication	700	X
57	Other title(s)	Other title(s) of publication	400	X
60	Edition:	Publication edition	50	X
61	Name of person(s):	Authors of the publication	160	X
62	Name of corporate body(ies)	Corporate bodies participating in the publication	500	X

ISBN International Standards Book Number
ISSN International Standards Serial Number

Table 8 cont.

Tag	NAME OF FIELD	DESCRIPTION OF FIELD	LENGTH	TYPE
63	Name of conference(s):	Name of conference that gave rise to the publication	400	X
64	Imprint:	Name of publisher, location and date of publication	260	X
65	Serial numbering:	Serial numbering if publication is a series	80	X
66	Physical description:	Physical description of publication e.g. size, no. of pages etc.	80	X
67	Series note(s):	Notes regarding the series.	300	X
68	Bibliographic relationship:	Bibliographic relationships of serial publications.	300	X
69	Note:	Any relevant information regarding publication.	600	X
70	Serial frequency:	Frequency of the publication in cases of series.	1	A
71	Call number(s):	Library reference number of publication	350	X
72	Subject descriptors:	Subject descriptors of the publication	610	X
73	Main subject(s):	Main subject area covered by the publication	100	X

CHAPTER 3

3.0 MATERIALS AND METHODS

3.1 DESCRIPTION OF SURVEY AREA

Mathare valley is situated towards the north-eastern sector of the city of Nairobi, Figure 3a. It is a slum area with a very high population density. The majority of the houses are built of mud with the exception of commercial premises that are built of cement. There are many small scale industries located within the valley. These include furniture shops, metal workshops, food kiosks, retail shops etc.

The drainage system is not adequate and thus can not meet the needs of the whole area. As a result of this, a large proportion of the waste water resulting from activities carried out within the valley drains into the Mathare river. There are two public water type toilets within the area but are unusable as the drainage system is blocked leaving the residents with the option of pit latrines.

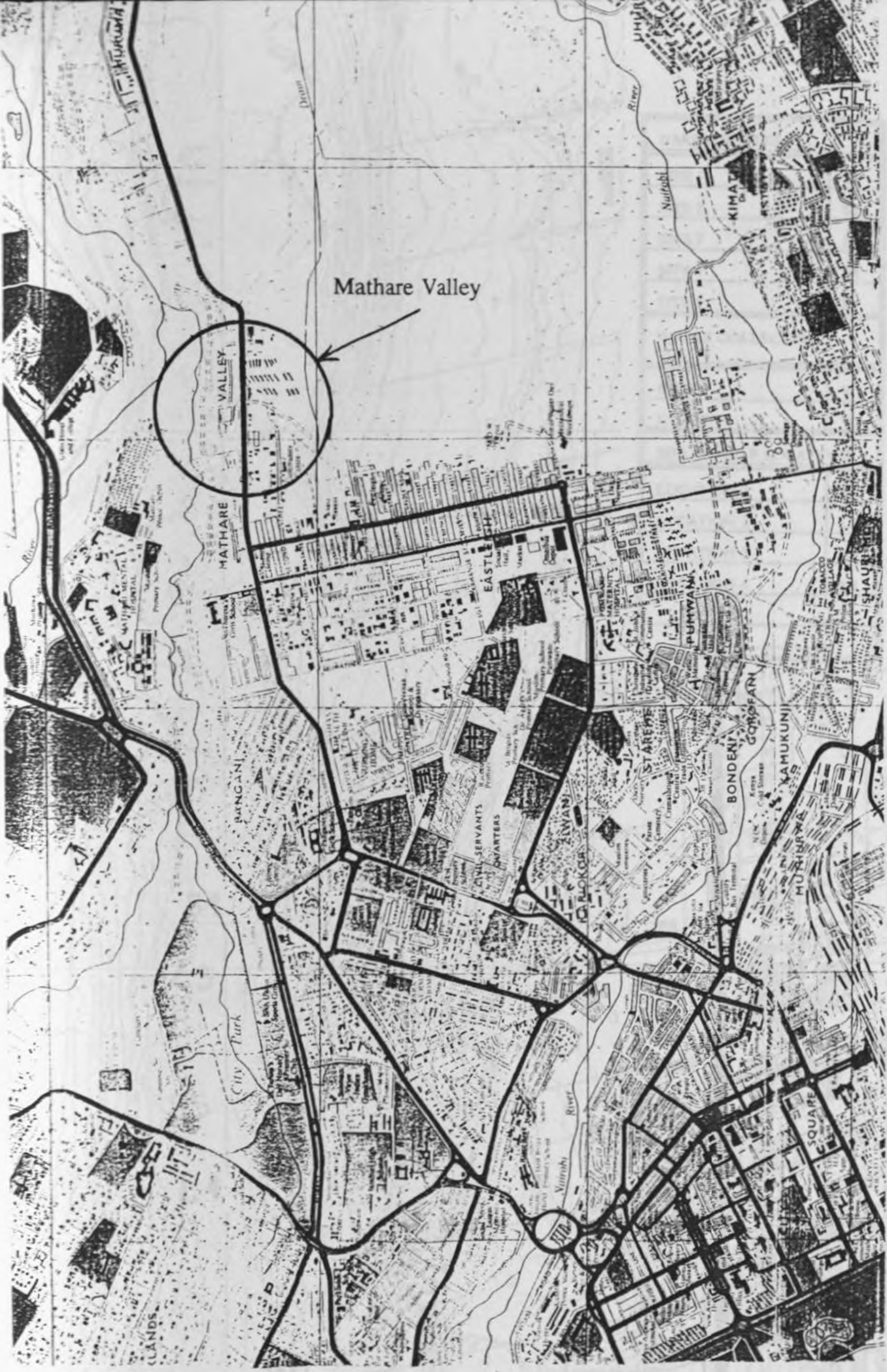

Figure 3a Nairobi Area Map

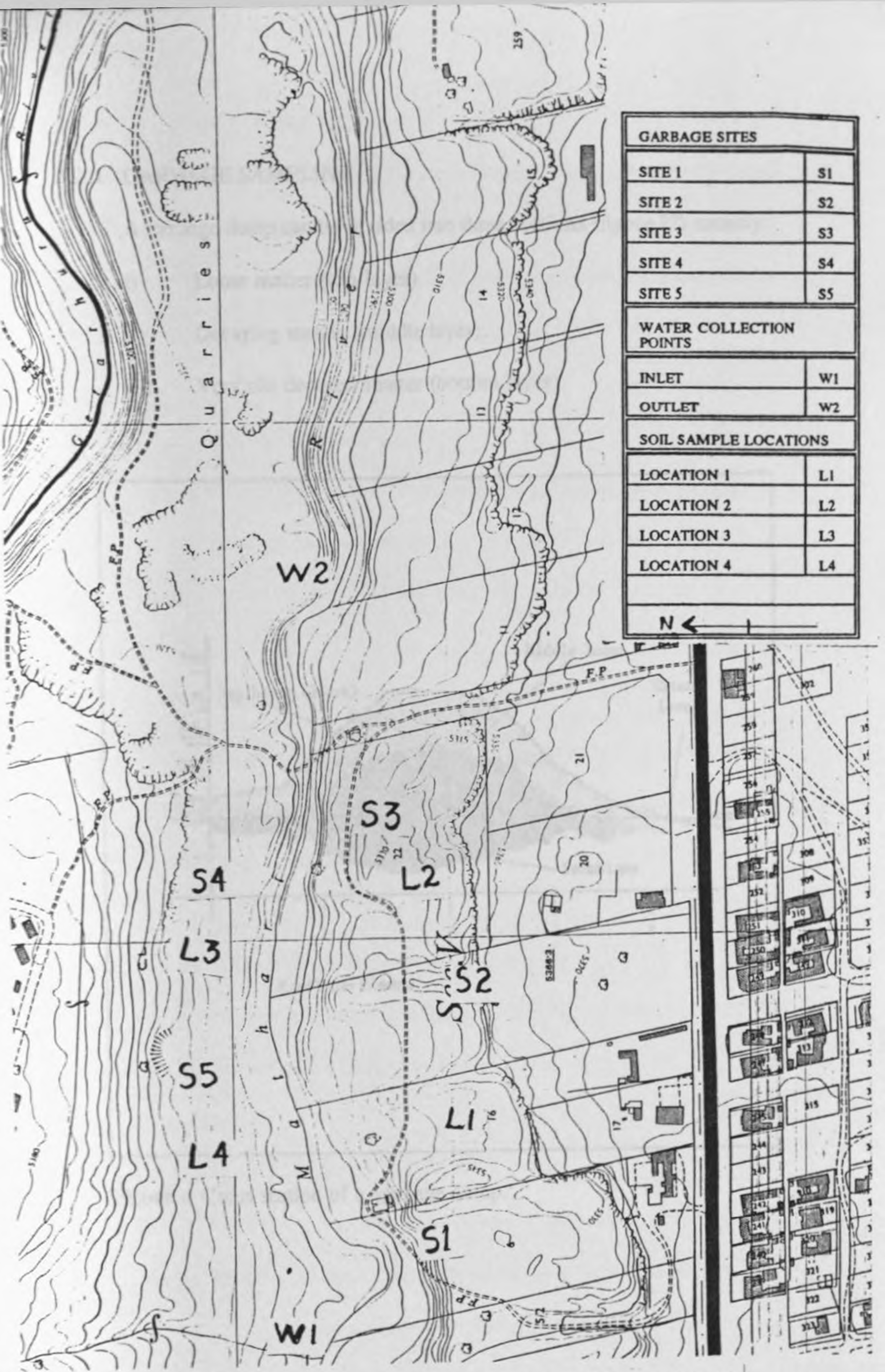

Figure 3b Location of Sampled Sites In The Mathare Valley, Nairobi

3.2.1 GARBAGE SAMPLING

A garbage dump can be divided into three sections (figure ??) namely:

i) Loose matter (top layer).

ii) Decaying matter (middle layer).

iii) Very old decayed matter (bottom layer).

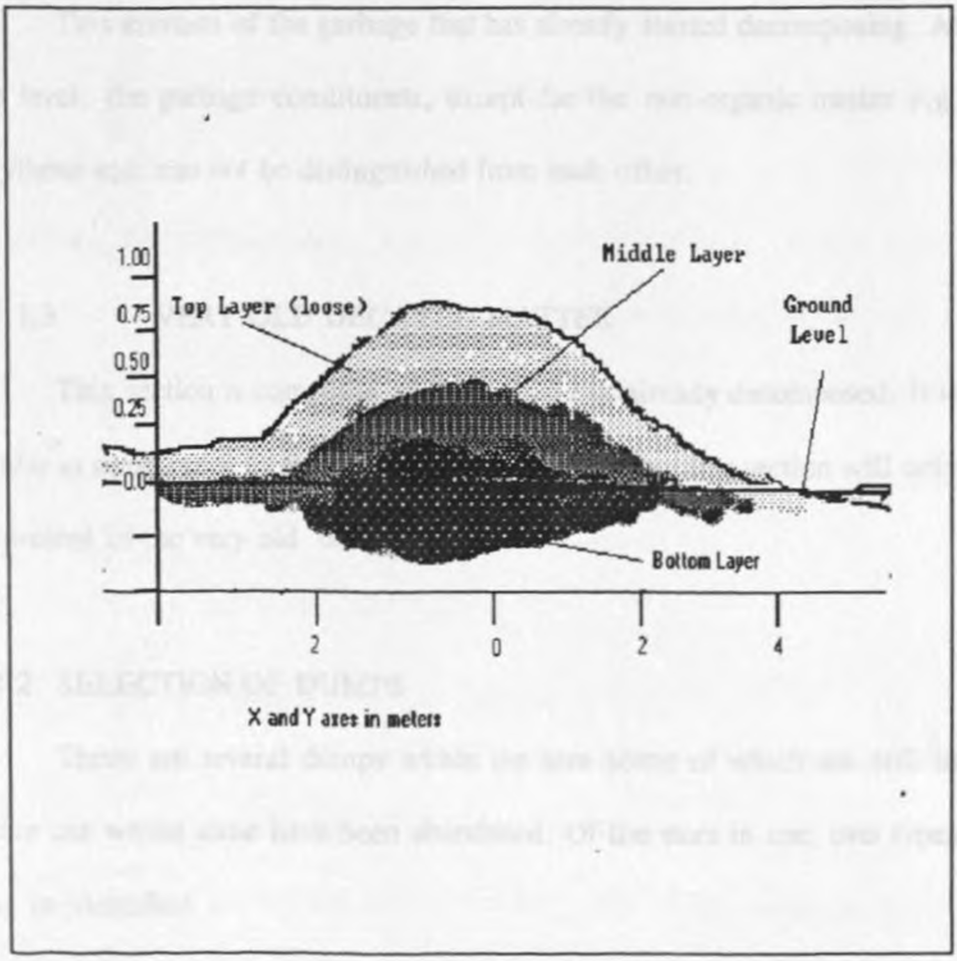

Figure 4 Cross section of a garbage dump.

3.2.1.1 LOOSE MATTER

The loose matter consists of the recently dumped garbage, the different constituents of the garbage still maintaining their unique forms easily distinguishable from each other i.e. pieces of paper, foodstuffs. Separation and classification of these constituents can be carried out at this stage[11].

3.2.1.2 DECAYING MATTER

This consists of the garbage that has already started decomposing. At this level, the garbage constituents, except for the non-organic matter e.g. polythene etc. can not be distinguished from each other.

3.2.1.3 VERY OLD DECAYED MATTER

This section is composed of matter that has already decomposed. It is similar in appearance to the soil. It should be noted that this section will only be present in the very old dumps.

3.2.2 SELECTION OF DUMPS

There are several dumps within the area some of which are still in active use whilst some have been abandoned. Of the ones in use, two types may be identified

i) Shallow:- consisting of mainly loose garbage scattered over the ground. Animals especially goats were found to be the main causes of the scattering of the garbage as they frequent the dumps looking for food. Due to this constant interference by animals, these dumps never form a decomposing section that can be associated with the dump.

ii) Deep:- These cover an area of about 2.5m - 3.0m radius. The animal activity in them is relatively low thus allowing the formation of a definite decomposing section

Presence of a decomposing section in the dump was a major criterion used in the selection of the dumps. It was ensured that the dumps were well distributed around the valley. Figure 3b shows the location of the dumps across the valley marked as sites 1 to 5. It was important to sample at different points in order to report a more reasonable representation of the entire area.

3.3 COLLECTION OF SAMPLES

3.3.1 GARBAGE SAMPLING

Fresh polythene bags were used in the collection of the samples from the selected sites marked in the diagram. The samples were collected from the middle layer. This section was chosen as it reduced the volume of sample to be collected to approximately 1000cm^3. Since it was in the decaying process, it was expected to include all the different types of garbage fairly well homogenised. This represents a good cross-section of the garbage. Sampling from the top layer would have necessitated the collection of large volumes. After collection, the samples were air dried for a period of one week then ground to a fine powder in a glass mortar.

3.3.2 WATER SAMPLING

Two sampling points, as marked in figure 4 as inlet and outlet, were selected for the purpose of carrying out a brief water survey.

Samples were collected between 10.30 a.m. and 11.00 a.m. It was observed that at this time, house-hold activities e.g. washing, were at their highest giving rise to large volumes of waste water. Samples were taken from the middle of the river at a depth of about 30 cm.

All the sample bottles (polythene containers) were first thoroughly washed with soap and water. They were then soaked in Nitric acid for 24 hrs. after which they were rinsed with de-ionised water and subsequently air dried. Samples were collected using 200ml. sample bottles and were immediately transferred to the laboratory and digested promptly.

3.3.3 SOIL SAMPLING

The top soil was collected and put into fresh polythene bags. Stones, pieces of metal, glass etc. and other materials that were easily identifiable as a non integral part of the soil were avoided.

3.4 SAMPLE ANALYSIS TECHNIQUES

3.4.1 GARBAGE AND SOIL

Atomic absorption spectroscopy was adopted in the analysis of the garbage. Selection of this method was based upon optimization of the criteria discussed in section 2.0.

3.4.2 WATER

Polarography was adopted as the method of analysis of the water samples, its selection being based on optimization of the criteria discussed in section 2.0. Rowland W. Odipo[29] has reported levels in the ppb range thus further favouring the use of polarography.

EG&G Princeton Applied Research corporation Model 174A Polarographic Analyzer was used and the results recorded using an Omnigraph 2000 plotter. A three electrode system consisting of HMDE, Calomel and Auxiliary electrode made of platinum wire was employed.

3.4.2.1 CLEANING OF POLAROGRAPHIC CELL

In order to avoid leaching of metals from the cell into the solution, prior cleaning with concentrated Nitric acid and thoroughly rinsing with deionised water was carried out before the analysis of samples.

3.4.2.2 HMDE PREPARATION

Dirt of any kind in the capillary, which is of very fine bore, is a major hazard. It was necessary to ensure that the mercury used was clean. In order to achieve this, impure mercury was distilled and further cleaned by filtering through Whatman No. 41 using the pin-hole screen drying technique. Cleaning of the capillary was always done before filing up with fresh mercury or when any of the factors below was observed during the analysis.

i) Breaking of Mercury thread

ii) Noisy stripping curves

iii) No output signal

3.4.2.3 CLEANING OF HMDE CAPILLARY

Mercury still in the capillary was discharged into a reservoir of used mercury and cleaning carried out in the following manner. 1 M Nitric acid was sucked through the capillary for a period of 1 hour. This was followed by sucking of de-ionized water for another 1 hour and finally air for another 1 hour.

3.4.2.4 FILLING OF CAPILLARY

Filling of the capillary was done as recommended in the manufacturer[30] manual. Care had to be taken in order not to have trapped air in the capillary. This was evidenced by a considerable retraction of the mercury thread when a drop was dislodged. A properly filled capillary will exhibit a suck back not exceeding 5mm. If at this stage the mercury kept flowing out after dislodging of a drop, then it was indication that either the mercury being used was dirty thus needing further cleaning or the capillary was dirty requiring a complete clean up.

3.5 REAGENTS

All reagents used in this work were of analar grade. They included, $CdCl_2$, $Pb(NO_3)_2$, HCl, and H_2SO_4.

3.5.1 PREPARATION OF STANDARD SOLUTIONS

Cadmium nitrate and Lead nitrate were used in preparing 1000 ppm stock solutions of the metal ions. These were then stored in plastic bottles from which standard solutions were made by serial dilution as and when required.

3.5.2 PREPARATION OF ULTRA PURE POTASSIUM CHLORIDE

Analar grade Potassium Chloride may still have trace amounts of heavy metal contaminants. In order to use it as a supporting electrolyte, it was necessary to eliminate these trace amounts which was achieved by controlled potential electrolysis in a cell made up of platinum anode and mercury pool as cathode. 100ml of the supporting electrolyte was introduced into the electrolysis cell and electrolysed for 24 hours at a current of 0.2mA. During this period, the solution was constantly kept stirred by bubbling Nitrogen gas through it. Metals dissolved in the solution were deposited in the mercury pool. At the end of the electrolysis period, the electrolysed solution was extracted from the cell using a pipette and stored. It should be noted that the extraction was carried out with the cell still on to avoid redissolving of the metals which may occur if the current is switched off with the solution still in contact with the mercury[31].

3.5.3 PREPARATION OF ULTRA PURE HCl AND AMMONIA

Ultra pure HCl and Ammonia were required for adjusting the pH of the sample solutions. The high level of purity was a prerequisite in order to avoid introducing contaminants into the solution under analysis. Purification by isothermal distillation at room temperature used in the preparation of the pure solutions. 500ml of concentrated Hydrochloric acid and concentrated Ammonia solution to be purified were each placed in a desiccator inside which there was 200ml of de-ionised water. They were then left to equilibrate. After a period of 72 hours, the beakers which originally had contained de-ionised water were each found to have solutions of about 1 M. of the respective solution[31].

3.6 OXYGEN SCRUBBING SYSTEM

3.6.1 OXYGEN COMPLICATIONS

Presence of oxygen in the solution can cause severe problems in carrying out analysis[32]. Complications due to Oxygen will arise due to its voltametric behaviour and through its associated reactions. The following equations show what may occur at the HMDE:

$$O_{2(g)} + 2H^+_{(aq)} + 2e^- \rightarrow H_2O_2 \qquad (i)$$

$$O_{2(g)} + 2H_2O_{(l)} + 2e^- \rightarrow H_2O_{2(g)} + 2OH^-_{(aq)} \qquad (ii)$$

$$O_{2(aq)} + 4H^+_{(aq)} + 4e^- \rightarrow 2H_2O_{(l)} \qquad (iii)$$

Equations (i) and (ii) occur at an $E_{1/2}$ of between -0.5 ± 0.05 V and 1.3 ± 0.05 V versus saturated calomel electrode (SCE). This is also the same range of potential that most reductions of metals occur and hence oxygen may bring about the overlapping of peaks in addition to new peaks. The formation of Hydrogen peroxide ion in (i) and (ii) is an invidious reaction to other electroactive species since it can function as both an oxidising agent or reducing agent. The presence of the peroxide ion may also cause pH changes within the vicinity of the HMDE increasing the chances of precipitation of heavy metals in turn diminishing the diffusion currents. As a result of the forgoing reactions, it was necessary to ensure that all traces of oxygen in the system were removed. This was done using the Vanadous Chloride Scrubbing system.

3.6.2 VANADOUS CHLORIDE SCRUBBING SYSTEM

Nitrogen used in deaeration needed to be of high purity. Although specially manufactured pure Nitrogen was used, it was necessary to further clean it to remove any traces of Oxygen. In this project Vanadous Chloride was used as the scrubbing agent. It was prepared by boiling 2g of ammonium metavanadate with 25ml of concentrated hydrochloric acid and diluting with water to 250 ml. The solution so produced was bluish green and contained vanadium in various high oxidation states. It was then transferred into the glass washing tower and amalgamated zinc added to reduce it to the +2 oxidation state. In addition, to this basic scrubbing system, a washtower of 0.1M KCl was attached whose purpose was to ensure that the moisture content of Nitrogen bubbling through the analyte was of the same concentration as the supporting electrolyte. Nitrogen to be scrubbed was first bubbled through the vanadous solution then through the KCl solution. Exhaustion of the scrubbing solution was detected when the characteristic bluish green colour changed to a violet colour. Regeneration was achieved by either adding a few millilitres of concentrated HCl, more amalgamated zinc or both the reagents.

3.7 ESTABLISHMENT OF SAMPLE DIGESTION PROCEDURE

3.7.1 DIGESTION PROCEDURE FOR GARBAGE SAMPLES

Raw garbage is heterogenous consisting of various types of components. The composition of the garbage will depend upon the source, whether industrial, commercial or domestic. The garbage analyzed mainly arose from domestic activities hence mainly organic in nature. It should be noted though that other factors do govern its very nature e.g. domestic waste from a high income area will differ in composition from one arising from a low income area. Considering the above reasons, a digestion method suitable for the matrix under study was developed.

In developing the method, three factors were taken into consideration:

i) Acid ratios.
ii) Temperature.
iii) Time.

Literature survey[33,34] showed that Nitric acid was a popular constituent of the acid combinations employed. Sulphuric acid and Perchloric acid also featured but not to the same level as Nitric acid. It was thus decided to include

Nitric acid in different ratios but vary the composition of Perchloric and Sulphuric. Table 9 lists the four different acid ratios which were selected and used with three different digestion programme.

TABLE 9 DIGESTION PROGRAM

	DURATION OF HEATING		
ACID RATIOS	Step 1	Step 1 & Step 2	Step 1,Step 2 & Step 3
1:1:0	X	X	X
2:1:0	X	X	X
1:0:1	X	X	X
4:0:1	X	X	X

Acid ratios-Nitric acid:Sulphuric acid:Perchloric acid.
(Room Temperature:- 23 ± 2°C)
Step 1:- Room Temp 1hr.
Step 2:- 40°C 1hr.
Step 3:- 60°C ½ hr.

1.0 ± 0.1g samples of the finely ground garbage were weighed into digestion tubes in triplicate. To this 12 ml of a mixture of the acids was added, the respective quantities being governed by the desired ratios. Nitric acid and Sulphuric acid (in the cases where they were used) were first added drop by drop. After the subsiding of the initial violent reaction, perchloric acid was added (in the cases where it was a constituent). The samples and acids were kept thoroughly mixed by constantly shaking the tubes. A water bath was utilised in the digestion programmes that required heating. At the end of a digestion period, the tubes were left to cool before adding 5ml of deionised water and filtering. The filtrate was subsequently diluted to 50ml in a 50ml volumetric flask.

The Atomic Absorbtion Spectrophotometer was first optimised for the metal under consideration as per the manufacture's instructions[25] before proceeding with the analysis. From the results, it was possible to deduce the optimum digestion conditions for analysis of each metal ion.

3.7.2 DIGESTION PROCEDURE FOR SOIL SAMPLES

The method developed for the digestion of garbage samples was used in the digestion of soil samples.

3.7.3 DIGESTION PROCEDURE FOR WATER SAMPLES

The analysis of water using polarography is well documented[35,36,37]. The following method was adopted for analysis of water samples in this project:

The best pH for the analysis of the samples was first determined by analyzing a given sample at different pH's and observing at which pH the machine was most sensitive to the sample thus giving the highest responses[38].

5ml of the water sample was measured out into a beaker that had been thoroughly washed, i.e. first washing with soap and water, soaking overnight in 1M Nitric acid finally rinsing with deionised water. To this sample 5ml. of concentrated Nitric acid was added and the mixture evaporated to near dryness. The residual solution was washed into a 50ml. volumetric flask and diluted to the mark.

9.5ml of the sample and 0.5ml of 1M ultra pure KCl were put into the analysis cell. The pH was then adjusted to the required value after which the solution was degassed by bubbling Nitrogen through the solution for 10 minutes while stirring. After this period, the solution was blanketed with Nitrogen gas and deposition step of the ions carried out for 1 minute. The stirrer was then switched off to allow for the convection currents to cease after which stripping was carried out. This procedure was repeated with a cumulative addition of 10 μl of a mixed standard consisting of 6 ppm of Cd^{+2} and 10 ppm Pb^{2+} until a total of 100 μl had been added.

The polarograms were obtained with instrumental setting as given below:

Polarographic settings

Scan Rate	5mV/sec
Scan direction	+
Range	1.5 volts
Initial Potential	1200 mV.
Modulation Amplitude	50 mV
Operation Mode	Differential Pulse
Current Range	2-5 μA
Low Pass filter	Off

Recorder Settings

X-axis	40 mV/cm
Y-axis	0.4 V/cm

3.8 BIBLIOGRAPHIC DATA COLLECTION

Bibliographic information for the setting up of the database was collected from four libraries, UNEP, British Council, Chiromo and Jomo Kenyatta Memorial libraries. At the UNEP library, it was found that the information was computerised which made possible the transfer of information using computer diskettes. A search in the system for publications dealing with waste management was carried out and the hit records transferred onto diskettes. The information on these diskettes was then imported into the computer in the department. In the other libraries, the relevant publications had to be looked for manually and their information entered in data-entry forms. This information was then typed into the computer. A sample of the data entry forms used is given in Appendix II.

CHAPTER 4

4.0 RESULTS AND DISCUSSION

4.1 OPTIMUM A.A.S. OPERATING CONDITIONS FOR Cd AND Pb DETERMINATION

In carrying out the analysis, it was found necessary to optimise the operating parameters of the machine. This was found necessary in order to obtain the highest sensitivity possible that would enable analysis of very low levels of metals. Table 10 lists the optimum operating conditions found suitable for carrying out the analysis. These were established by optimising the absorbance of a given standard solution by varying oxidant and fuel flow rates. For the other parameters, standard values for either of the lamps were used.

TABLE 10 OPTIMUM OPERATING CONDITIONS OF A.A.S FOR CADMIUM AND LEAD

	CADMIUM	LEAD
LAMP CURRENT (mA)	4	10
SPECTRAL BAND PASS (nm)	0.7	0.7
WAVELENGTH (nm)	328.8	283.3
OXIDANT (AIR) FLOW RATE	50	50
ACETYLENE FLOW RATE	15	15

-Only basic calibration features were checked in order to obtain maximum sensitivity

4.1.1 DETECTION LIMITS

The detection limits, technically defined as 95% certainty in detecting an ion in the solution, and sensitivity of the instrument were determined and compared with the manufactures values. These two parameters give an indication of the performance state of the instrument. The detection limit was determined by serially diluting and measuring the absorption of a standard solution until the value observed was twice the noise level. Table 11 lists the detection and sensitivity limits for the machine.

TABLE 11 DETECTION AND SENSITIVITY LIMITS

EXPECTED[25]			EXPERIMENTAL	
ELEMENT	DETECTION LIMIT (mg/l)	SENSITIVITY	DETECTION LIMIT (mg/l)	SENSITIVITY
CADMIUM	0.001	0.025	0.005	0.025
LEAD	0.01	0.5	0.056	0.537

The results showed that there has been a slight deterioration of the detection limits by probably aging effect of the instrument, although not so adverse as to affect the carrying out of the analysis since standards were analyzed at the same conditions as the samples. Nevertheless, close monitoring of its performance was maintained.

4.1.2 VERIFICATION OF BEERS LAW

Verification of the law was essential in order to establish the range in which the concentration and instrumental effects are not active. Figures

5a,5b 6a,and 6b show the calibration graphs obtained for the metal ions determined. The ranges covered by the graphs constitute the range of results that would be devoid of concentration related deviations.

4.2 EVALUATION OF ANALYTICAL PROCEDURE FOR GARBAGE ANALYSIS

As reflected in the objectives of this work, it was important to vary the literature suggested conditions for different environmental samples, due to the disparity of the matrices likely to be encountered, and thus obtain a suitable digestion procedure for the matrix under investigation. A substantially large percentage of the matrix was found to be organic matter mixed with distinguishable pieces of glass, metal, pieces of polythene and other plastics.

A survey of literature citing the use of wet digestion method as the technique for analysis, showed a prevalence of Nitric, Sulphuric and Perchloric acids[39,40,41,42]. It was also found that of the three acids, Nitric acid featured the most frequently. It was thus adopted as the main constituent of all the different acid mixtures.

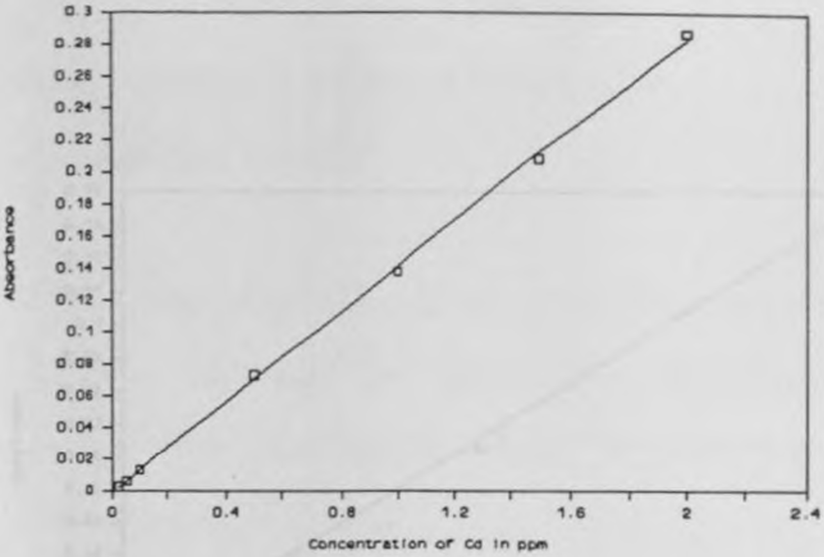

Figure 5a. A.A.S Calibration Graph For Cadmium.

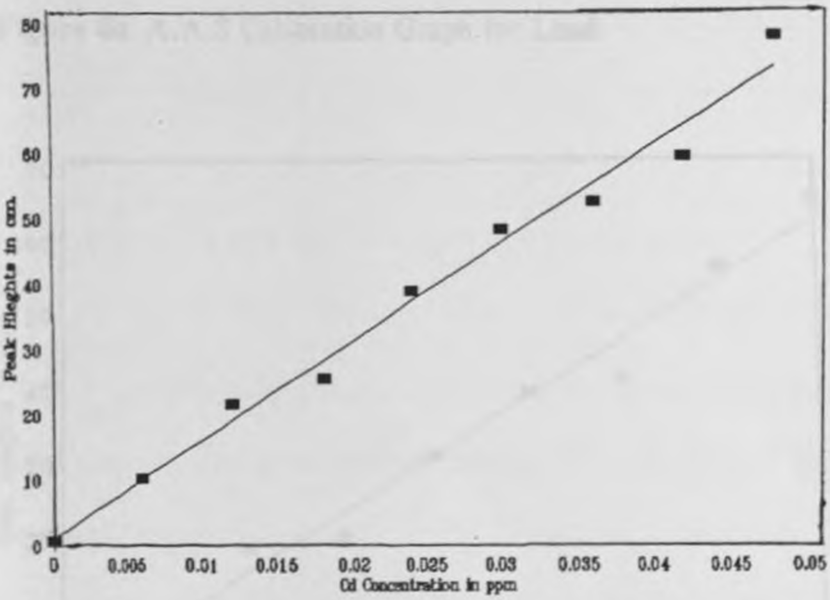

Figure 5b Polarography Calibration graph for Cadmium

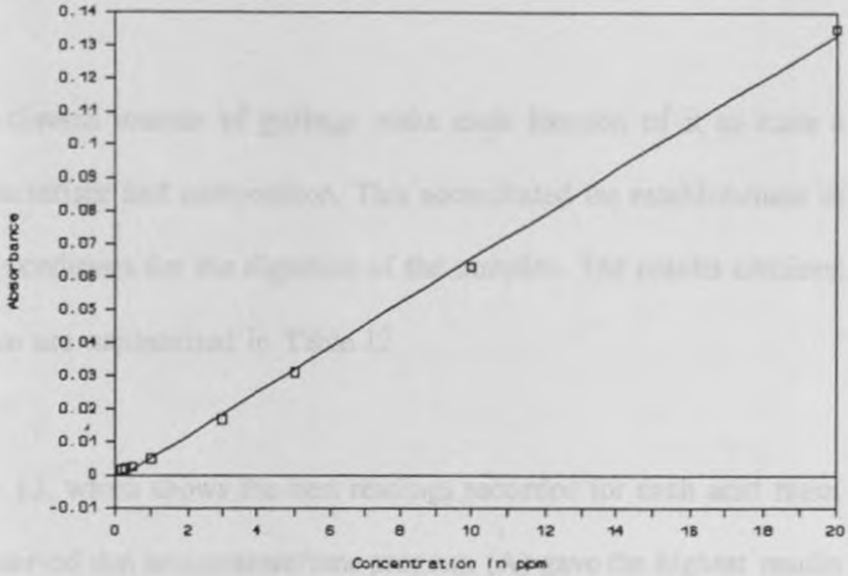

Figure 6a. A.A.S Calibration Graph for Lead.

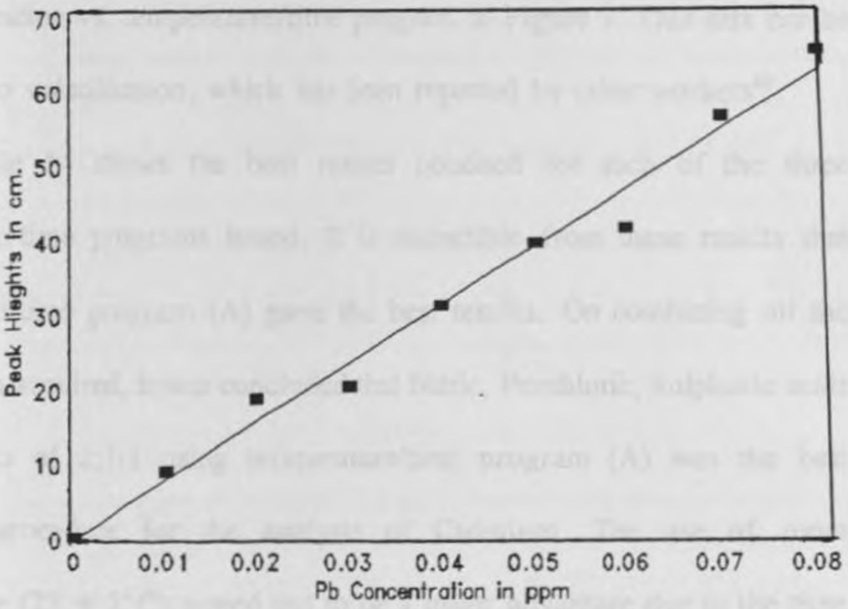

Figure 6b Polarography Calibration graph for Leadm

4:2:1 DETERMINATION OF A SUITABLE EXTRACTION PROCEDURE FOR CADMIUM.

The diverse sources of garbage make each location of it to have a unique characteristic and composition. This necessitated the establishment of appropriate conditions for the digestion of the samples. The results obtained for Cadmium are summarized in Table 12.

From Table 13, which shows the best readings recorded for each acid ratio, it can be observed that temperature/time program (A) gave the highest results for Cadmium in three out of the 4 methods that were tested. An increasing loss of Cadmium on temperature increase was observed as seen from the plot of concentration vs. temperature/time program in Figure 7. This loss can be attributed to volatilisation, which has been reported by other workers[43].

Table 14 shows the best results obtained for each of the three temperature/time programs tested. It is deductible from these results that temperature/time program (A) gave the best results. On combining all the information acquired, it was concluded that Nitric, Perchloric, Sulphuric acids in the ratio of 2:1:1 using temperature/time program (A) was the best digestion procedure for the analysis of Cadmium. The use of room temperature (23 ± 2°C) turned out to be a major advantage due to the time and energy saved in carrying out the analysis. This cost saving element is important especially for environmental laboratories charged with the routine monitoring of trace heavy metals. These results suggest the importance of preliminary work in determining the appropriate temperature/time program other than just picking literature values

TABLE 12 EFFECT OF TEMPERATURE ON THE EXTRACTION AND QUANTITATIVE DETERMINATION OF CADMIUM BY AAS.

	TEMPERATURE/TIME PROGRAM		
ACID RATIOS	A	B	C
1:1:0	0.035±0.007	0.021±0.009	0.021±0.008
2:1:1	0.102±0.009	0.070±0.010	0.063±0.009
1:0:1	0.056±0.009	0.028±0.009	0.028±0.008
4:0:1	0.0560.009	0.060±0.006	0.063±0.008
Mean Values	0.062±0.008	0.045±0.010	0.044±0.010

A:- Room temperature (23 ± 2°C) 1 hr.
B:- (A) followed by 40°C for 1hr.
C:- (A), (B) followed by 60°C for ½ hr.
Concentration values in ppm.

TABLE 13 EFFECT OF ACID RATIO ON EXTRACTION OF CADMIUM

ACID RATIO	CONCENTRATION ppm	PROGRAM
2:1:1	0.102±0.009	A
1:1:0	0.035±0.007	A
1:0:1	0.056±0.009	A
4:0:1	0.060±0.006	B

TABLE 14. EFFECT OF TEMPERATURE/TIME ON EXTRACTION OF CADMIUM

TEMP/TIME. PROG	ACID RATIO	CONCENTRATION in ppm
A	2:1:1	0.102±0.009
B	2:1:1	0.070±0.010
C	2:1:1/4:0:1	0.063±008/0.063±0.010

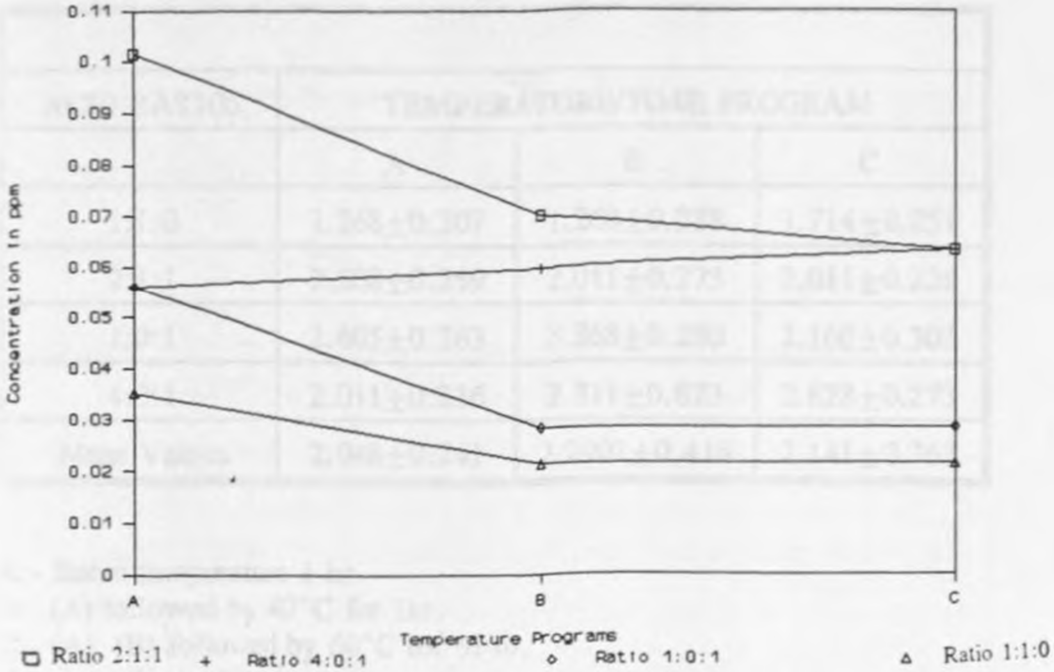

Figure 7. Cadmium Concentration vs. Extraction Temperature/Time Program for different acid ration.

4.2.2 DETERMINATION OF BEST DIGESTION PROCEDURE FOR LEAD.

Just as in the case of Cadmium, a suitable digestion method for Lead had to be established. It could not be assumed that the procedure found favourable for Cadmium would be appropriate for Lead. Table 15 summarises the Lead results obtained for the test sample.

TABLE 15 EFFECT OF TEMPERATURE ON THE EXTRACTION AND QUANTITATIVE DETERMINATION OF LEAD BY AAS.

ACID RATIOS	TEMPERATURE/TIME PROGRAM		
	A	B	C
1:1:0	1.268±0.207	1.268±0.288	1.714±0.251
2:1:1	2.308±0.259	2.011±0.273	2.011±0.226
1:0:1	2.605±0.263	3.868±0.280	2.160±0.303
4:0:1	2.011±0.236	2.311±0.823	2.828±0.273
Mean Values	2.048±0.241	2.2902±0.416	2.141±0.263

A:- Room temperature 1 hr.
B:- (A) followed by 40°C for 1hr.
C:- (A), (B) followed by 60°C for ½ hr.
Concentration values in ppm.

TABLE 16 EFFECT OF ACID RATIO ON EXTRACTION PROCEDURE FOR LEAD

ACID RATIO	CONCENTRATION ppm	PROGRAM
1:1:0	1.714±0.288	C
2:1:1	2.308±0.259	A
1:0:1	3.868±0.280	B
4:0:1	2.011±236/2.011±823	A/B

Compared to the results obtained for Cadmium, Table 15 and Table 16 showing the highest readings obtained for each method indicate that Lead analysis is favoured at higher temperatures. The increase in concentration readings is observed in all the cases with the exception of the 2:1:1 acid ratio.

Although this trend would have been expected to continue with increase in temperature, the reaction became too violent at temperatures in excess of 60°C giving rise to erroneous results due to the probable loss of Lead due to spillage. These results form a basis for future work in determining the ideal acid ratio combinations for use in analysis. Moreover, the results give the expected concentrations as a function of temperature and time of digestion.

TABLE 17 EFFECT OF TEMPERATURE/TIME PROGRAM ON EXTRACTION PROCEDURE FOR LEAD

TEMP.PROG	ACID RATIO	CONCENTRATION in ppm
A	1:0:1	2.605±0.259
B	1:0:1	3.868±0.273
C	4:0:1	2.828±0.273

Table 17 above shows the highest readings obtained for each temperature/time program. These results show that extraction of Lead is favoured by acid combinations not containing Sulphuric acid. This is further evidenced by the comparatively poor results that were recorded for the 1:1:0 acid ratio (Table 15) when Sulphuric acid constituted 50%. This can be accounted for by the probable formation of Lead Sulphate which is highly insoluble, thus reducing the concentration of Lead ions in the solution and hence in the subsequently analyzed solution. Elimination of Sulphuric acid leaves two acids only, suggesting an economical digestion procedure. Figure 8 shows that there was no apparent relationship between the Lead concentrations recorded and the temperatures used in the extraction procedures. From the data obtained, it can be concluded that Nitric/Perchloric acids in the ratio of 1:1, using temperature programme (B) was probably the best method for analysis of Lead as it gave the best results. It was thus adopted in all the analysis of Lead in all subsequent samples.

No single digestion method was found suitable for the extraction of both Cadmium and Lead as the factors favouring either of the metals were different. Higher temperatures were found to be favourable for Lead but unfavourable for Cadmium. In the case of acids presence of Sulphuric acid was unfavourable for Lead but had no adverse effect on Cadmium. The standard deviations of the results obtained for the different procedures was very large suggesting that results obtained were independent from each other.

4.3 VARIATION OF CONCENTRATIONS OF ELEMENTS WITH RESPECT TO SEASONS.

The variation of amounts of Cadmium and Lead in the garbage with respect to time was determined. This was done in order to establish the possible effects of environmental conditions on the amounts present in the garbage at any given time. Of these, the major consideration was the rainfall effects which probably wash away the elements due to non compactness of the garbage and leaching.

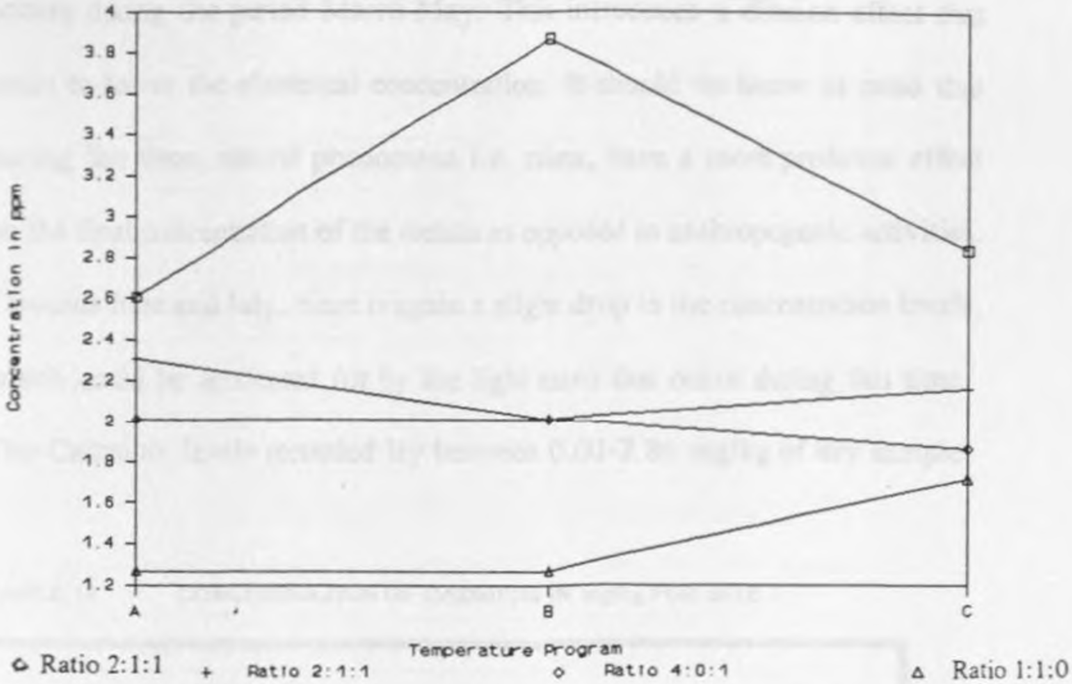

Figure 8. Lead Concentration Vs. Extraction Temperature/Time program for different acid ratios

4.3.1 CADMIUM IN GARBAGE

The results of the amounts of Cadmium found in the five garbage sites are summarised in Tables 18-22. Figures 9a-11b show the plots of concentration values obtained for the sites versus months, figures suffixed (a) being plots of the individual values of the three locations sampled in each site versus the months while those suffixed (b) being plots of the averages of the three sampled locations versus months. The graphs suffixed (b) were plotted in order for general patterns of the concentration-time relationships to be established.

With the exception of Site 1, there was a drop in overall concentration of the metal between the months of March and April but began to increase around May-June. This decrease can be accounted for by the heavy rains that occurs during the period March-May. This introduces a dilution effect that tends to lower the elemental concentration. It should be borne in mind that during this time, natural phenomena i.e. rains, have a more profound effect on the final concentration of the metals as opposed to anthropogenic activities. Towards June and July, there is again a slight drop in the concentration levels, which could be accounted for by the light rains that occur during this time. The Cadmium levels recorded lay between 0.01-2.86 mg/kg of dry sample.

TABLE 18 CONCENTRATION OF CADMIUM IN mg/kg FOR SITE 1

Month	Sample 1[a]	Sample 2[a]	Sample 3[a]	Range	Mean[b]
March	0.250±0.055	0.454±0.038	0.372±0.040	0.25-0.45	0.36
April	0.535±0.020	0.494±0.029	0.576±0.022	0.49-0.58	0.54
May	0.494±0.015	0.372±0.040	0.291±0.030	0.29-0.49	0.39
June	0.006±0.041	0.413±0.025	0.209±0.020	0.01-0.41	0.21
July	0.250±0.030	0.087±0.027	0.372±0.025	0.09-0.37	0.24

[a] Each entry is an average of three samples from the same point.
[b] A measured average for the whole garbage area.

TABLE 19 CONCENTRATION OF CADMIUM IN mg/kg FOR SITE 2

Month	Sample 1[a]	Sample 2[a]	Sample 3[a]	Range	Mean[b]
March	1.675±0.042	1.716±0.091	1.472±0.067	1.47-1.72	1.621
April	1.390±0.051	1.797±0.059	1.594±1	1.38-1.80	1.594
May	2.082±0.022	1.879±0.132	2.286±0.077	1.88-2.29	2.082
June	2.856±0.071	2.042±0.104	2.449±0.087	2.04-2.86	2.449
July	1.716±0.059	2.530±0.063	2.530±0.075	1.72-2.53	2.259

TABLE 20 CONCENTRATION OF CADMIUM IN mg/kg FOR SITE 3

Month	Sample 1^a	Sample 2^a	Sample 3^a	Range	Mean^b
March	1.699±0.033	1.699±0.083	1.699±0.058	1.70	1.699
April	1.397±0.069	1.829±0.055	1.613±0.025	1.40-1.83	1.613
May	1.742±0.031	1.526±0.041	1.699±0.055	1.53-1.74	1.656
June	2.088±0.036	1.872±0.028	1.656±0.050	1.66-2.09	1.872
July	2.174±0.062	1.526±0.023	1.742±0.036	1.53-2.17	1.814

TABLE 21 CONCENTRATION OF CADMIUM IN mg/kg FOR SITE 4

Month	Sample 1^a	Sample 2^a	Sample 3^a	Range	Mean^b
March	1.699±0.017	1.699±0.013	2.131±0.015	1.70-2.13	1.843
April	1.397±0.013	1.829±0.010	1.397±0.016	1.40-1.83	1.541
May	1.699±0.011	1.699±0.007	2.131±0.020	1.70-2.13	1.843
June	2.088±0.006	2.520±0.014	2.088±0.008	2.09-2.52	2.232
July	1.742±0.008	1.742±0.011	1.742±0.012	1.74	1.742

TABLE 22 CONCENTRATION OF CADMIUM IN mg/kg FOR SITE 5

Month	Sample 1^a	Sample 2^a	Sample 3^a	Range	Mean^b
March	1.612±0.017	1.554±0.189	2.131±0.062	1.55-2.13	1.766
April	1.397±0.030	1.829±0.022	1.498±0.026	1.40-1.83	1.575
May	1.601±0.041	1.648±0.030	2.234±0.031	1.60-2.23	1.828
June	2.174±0.022	2.045±0.028	2.108±0.033	2.05-2.17	2.109
July	1.740±0.019	1.648±0.025	1.723±0.035	1.65-1.74	1.704

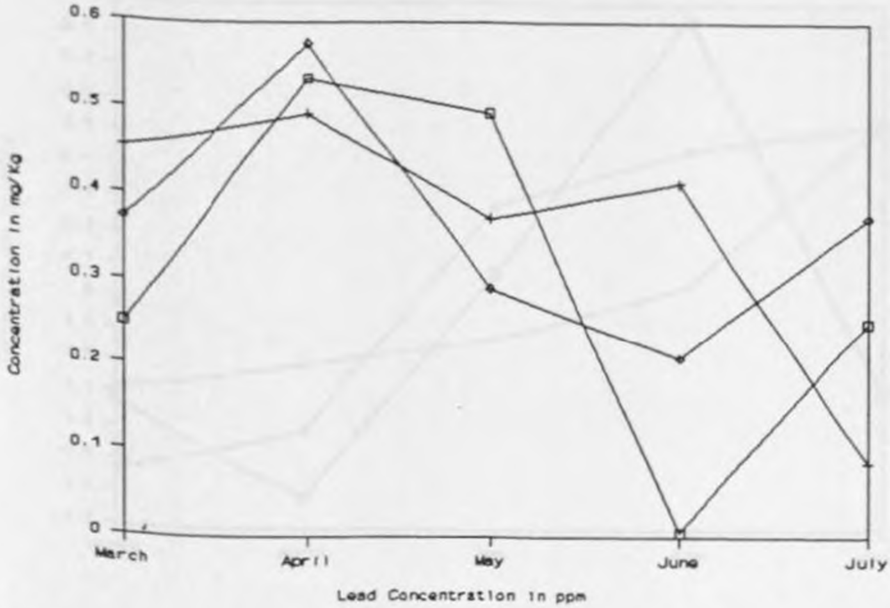

Figure 9a Fluctuations in Cadmium Content of Garbage sampled at Monthly intervals between March and July 1989 at Site 1.

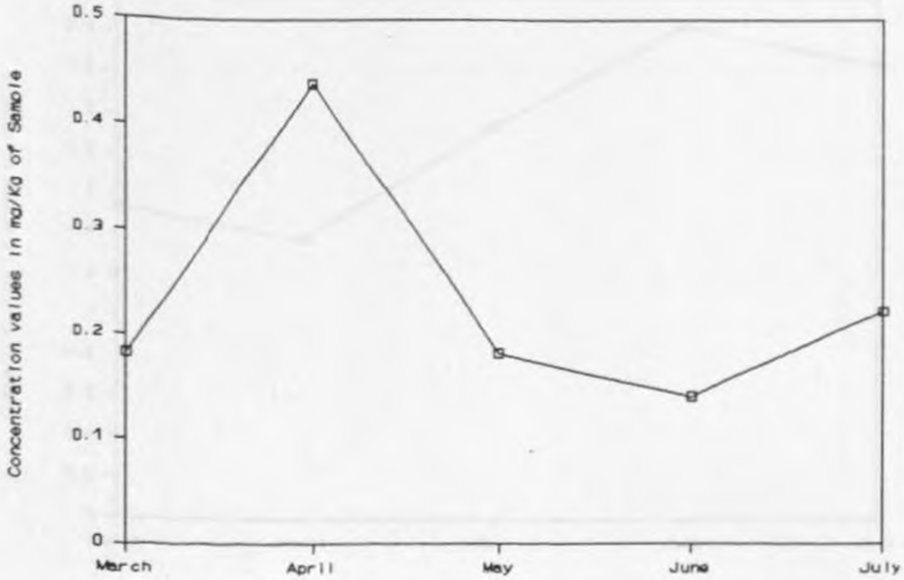

Figure 9a Mean Fluctuations in Cadmium Content of Garbage sampled at Monthly intervals between March and July 1989 at Site 1.

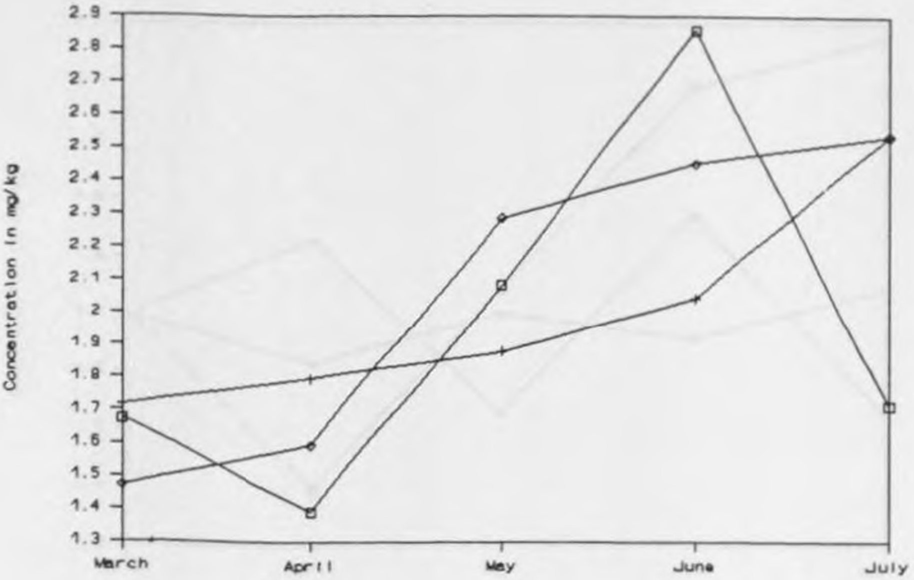

Figure 10a **Fluctuations in Cadmium Content of Garbage sampled at Monthly intervals between March and July 1989 at Site 2.**

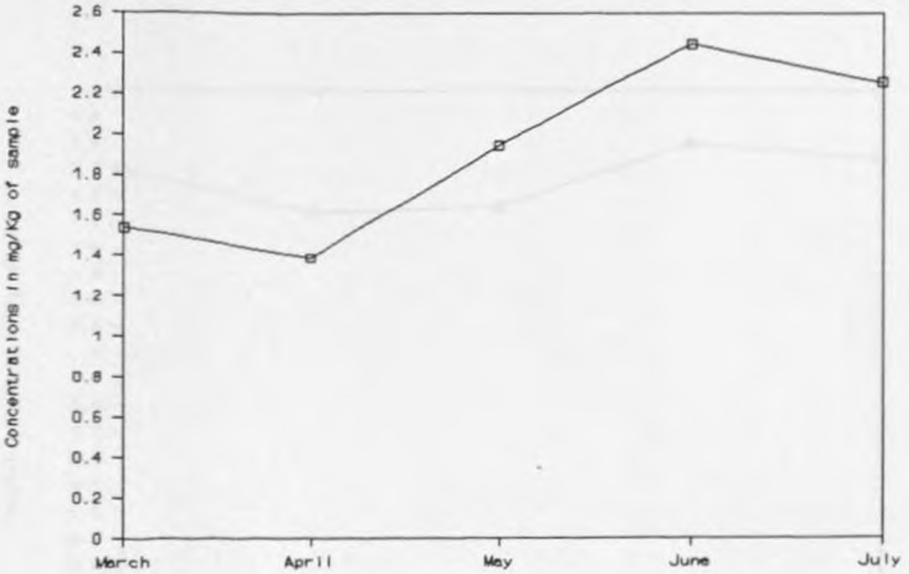

Figure 10b **Mean Fluctuations in Cadmium Content of Garbage sampled at Monthly intervals between March and July 1989 at Site 2.**

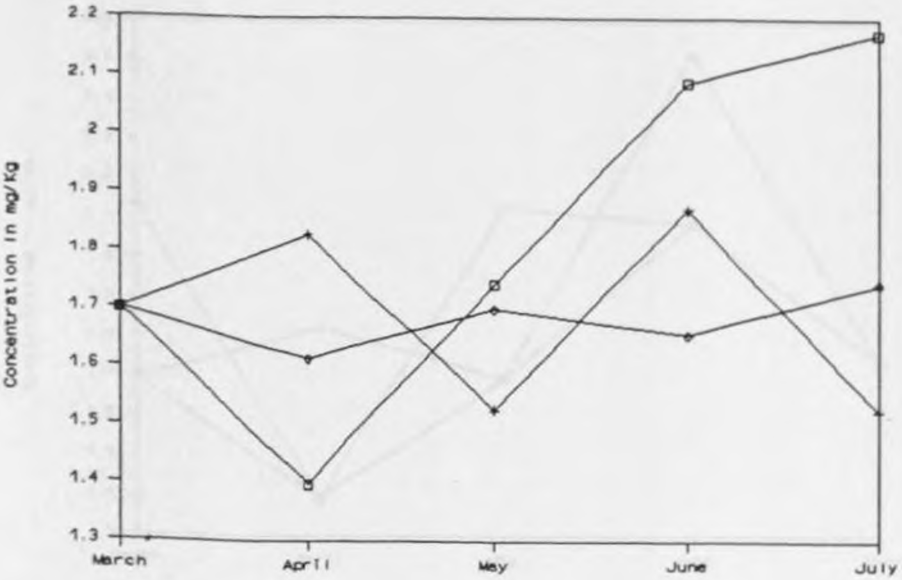

Figure 11a Fluctuations in Cadmium Content of Garbage sampled at Monthly intervals between March and July 1989 at Site 3.

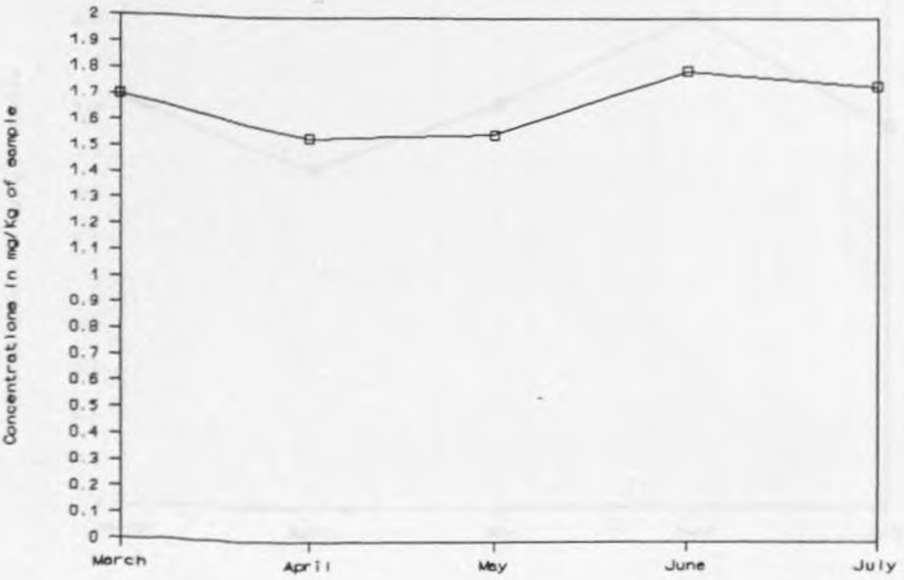

Figure 11b Mean Fluctuations in Cadmium Content of Garbage sampled at Monthly intervals between March and July 1989 at Site 3.

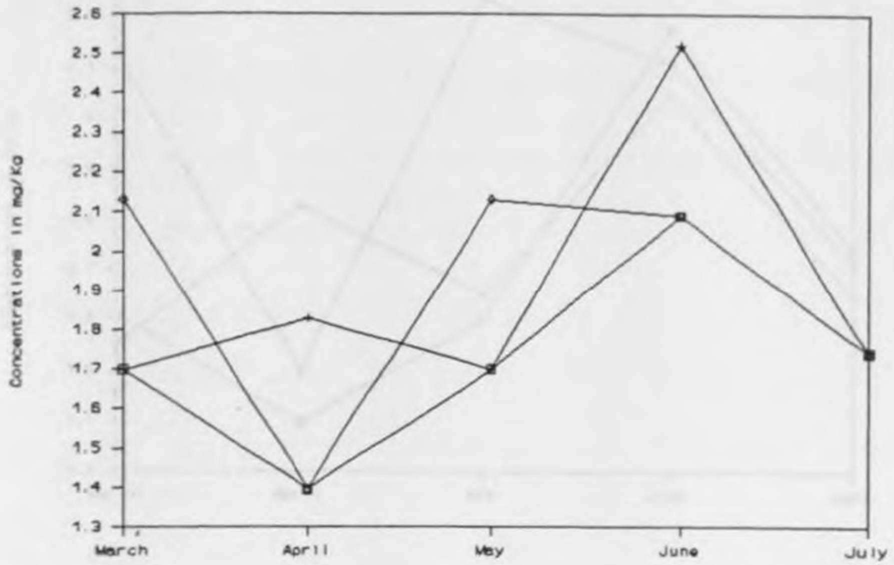

Figure 12a Fluctuations in Cadmium Content of Garbage sampled at Monthly intervals between March and July 1989 at Site 4.

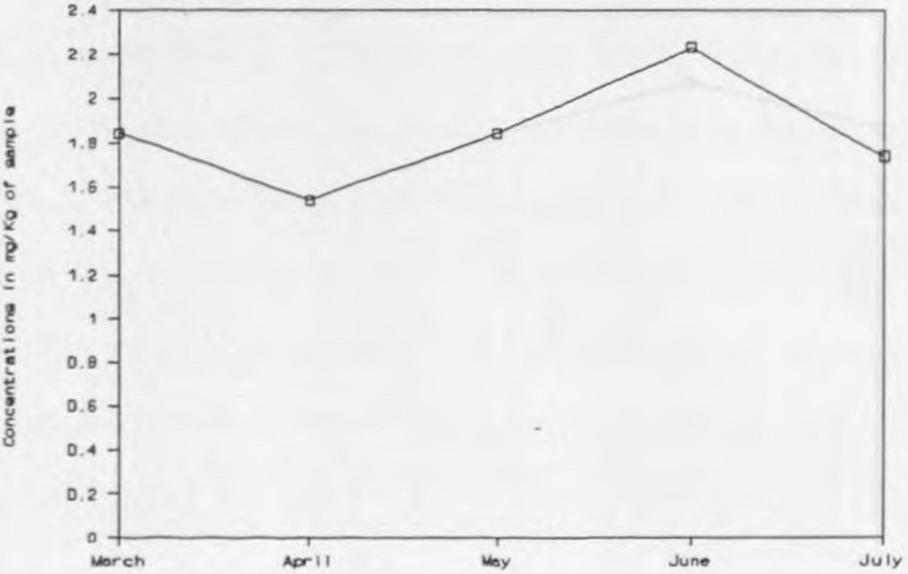

Figure 12b Mean Fluctuations in Cadmium Content of Garbage sampled at Monthly intervals between March and July 1989 at Site 4.

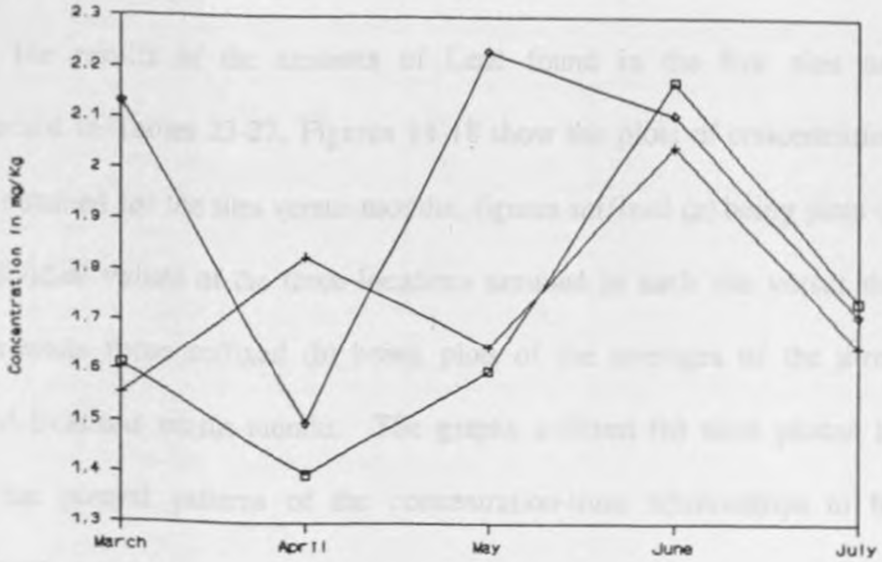

Figure 13a Fluctuations in Cadmium Content of Garbage sampled at Monthly intervals between March and July 1989 at Site 5.

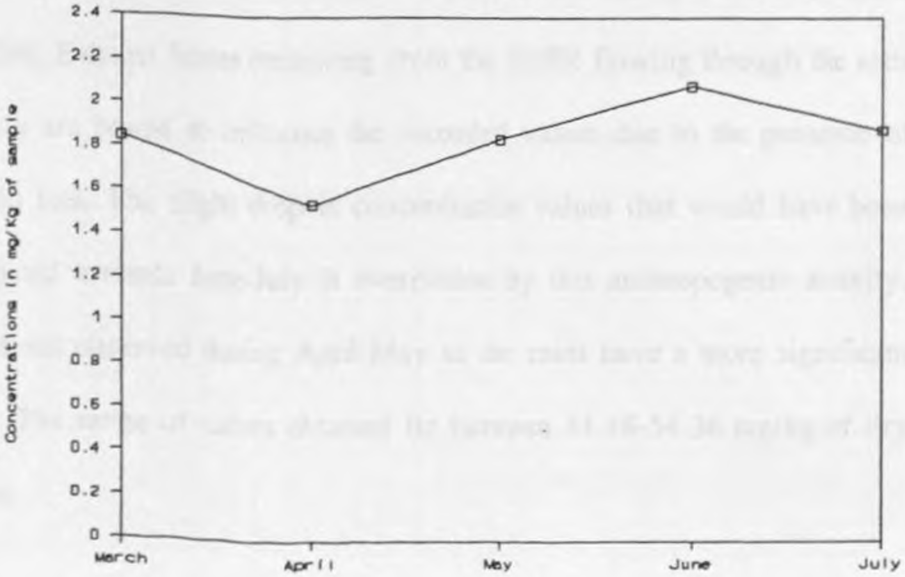

Figure 13b Mean Fluctuations in Cadmium Content of Garbage sampled at Monthly intervals between March and July 1989 at Site 5.

4.3.2 LEAD IN GARBAGE

The results of the amounts of Lead found in the five sites are summarised in Tables 23-27. Figures 14-18 show the plots of concentration values obtained for the sites versus months, figures suffixed (a) being plots of the individual values of the three locations sampled in each site versus the months while those suffixed (b) being plots of the averages of the three sampled locations versus months. The graphs suffixed (b) were plotted in order for general patterns of the concentration-time relationships to be established.

Sites 2, 4 and 5 follow the same pattern as that of Cadmium thus the same reasons that accounted for the pattern observed for Cadmium would account for the pattern observed for Lead. The location of sites 1 and 3 i.e. next to the road introduce a factor that would affect the level of Lead recorded. Exhaust fumes emanating from the traffic flowing through the area of study are bound to influence the recorded values due to the presence of Lead in fuel. The slight drop in concentration values that would have been anticipated towards June-July is overridden by this anthropogenic activity. This is not observed during April-May as the rains have a more significant effect. The range of values obtained lie between 34.48-54.36 mg/kg of dry sample.

TABLE 23 CONCENTRATION OF LEAD IN mg/kg FOR SITE 1

Month	Sample 1[a]	Sample 2[a]	Sample 3[a]	Range	Mean[b]
March	43.296±2.189	44.078±4.300	40.950±3.909	40.95-44.08	42.775
April	40.169±3.127	39.387±1.798	39.387±2.424	39.39-40.17	39.648
May	34.476±2.893	34.696±2.736	37.041±1.642	34.48-37.04	35.404
June	39.387±2.658	38.605±2.033	40.950±3.284	38.61-40.95	39.647
July	44.859±3.596	44.078±1.564	47.205±2.345	44.08-47.21	45.381

[a] Each entry is an average of three samples from the same point.
[b] A measured average for the whole garbage area.

TABLE 24 CONCENTRATION OF LEAD IN mg/kg FOR SITE 2

Month	Sample 1[a]	Sample 2[a]	Sample 3[a]	Range	Mean
March	43.296±4.500	43.296±1.800	43.296±1.200	43.29	43.296
April	34.696±3.300	31.568±2.400	39.387±2.700	31.57-39.39	35.217
May	39.387±5.250	40.169±2.475	37.823±1.875	37.82-40.17	39.126
June	43.296±1.575	35.478±1.200	39.387±1.275	35.48-43.30	39.387
July	35.478±2.250	37.041±1.125	38.605±3.000	35.48-38.61	37.041

TABLE 25 CONCENTRATION OF LEAD IN mg/kg FOR SITE 3

Month	Sample1[a]	Sample2[a]	Sample3[a]	Range	Mean
March	46.521±6.500	46.521±1.560	44.169±3.380	44.17-46.52	45.737
April	41.033±4.030	42.601±2.730	42.601±2.470	41.03-42.60	42.078
May	42.601±5.590	36.329±3.380	41.917±4.420	36.33-42.60	40.282
June	38.681±5.980	41.817±3.510	41.033±4.680	38.68-41.03	40.510
July	46.521±1.950	46.521±3.770	46.521±4.290	46.521	46.521

TABLE 26 CONCENTRATION OF LEAD IN mg/kg FOR SITE 4

Month	Sample 1[a]	Sample 2[a]	Sample 3[a]	Range	Mean
March	38.539±1.930	40.108±4.825	33.048±2.220	33.05-40.11	37.232
April	34.617±4.150	30.650±2.702	34.617±1.834	30.65-34.62	33.295
May	33.833±2.991	35.401±2.413	35.401±3.571	33.83-35.40	34.878
June	38.539±4.439	36.186±1.834	46.383±2.702	36.19-46.54	40.369
July	38.539±3.571	38.539±2.316	38.539±2.895	38.539	38.539

TABLE 27 CONCENTRATION OF LEAD IN mg/kg FOR SITE 5

Month	Sample 1[a]	Sample 2[a]	Sample 3[a]	Range	Mean
March	46.521±3.449	54.362±3.025	46.521±1.452	46.52-54.36	49.135
April	42.601±1.452	51.227±2.057	50.442±1.694	42.60-51.23	48.090
May	42.601±2.299	42.601±1.634	48.874±1.876	42.60-48.87	44.692
June	46.521±2.481	45.737±1.331	48.089±1.997	45.74-48.09	46.782
July	48.874±2.239	38.681±1.634	46.521±2.178	38.68-48.87	44.692

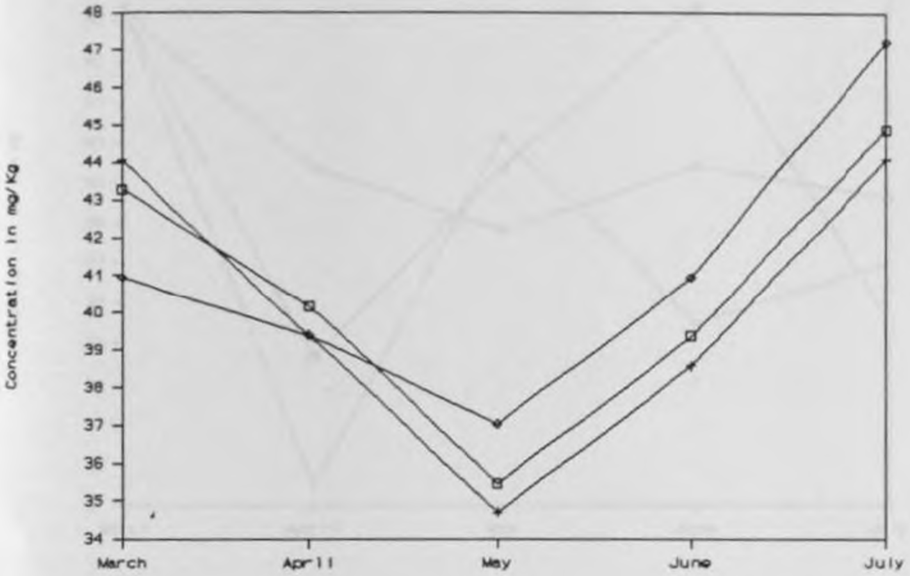

Figure 14a Fluctuations in Lead Content of Garbage sampled at Monthly intervals between March and July 1989 at Site 1.

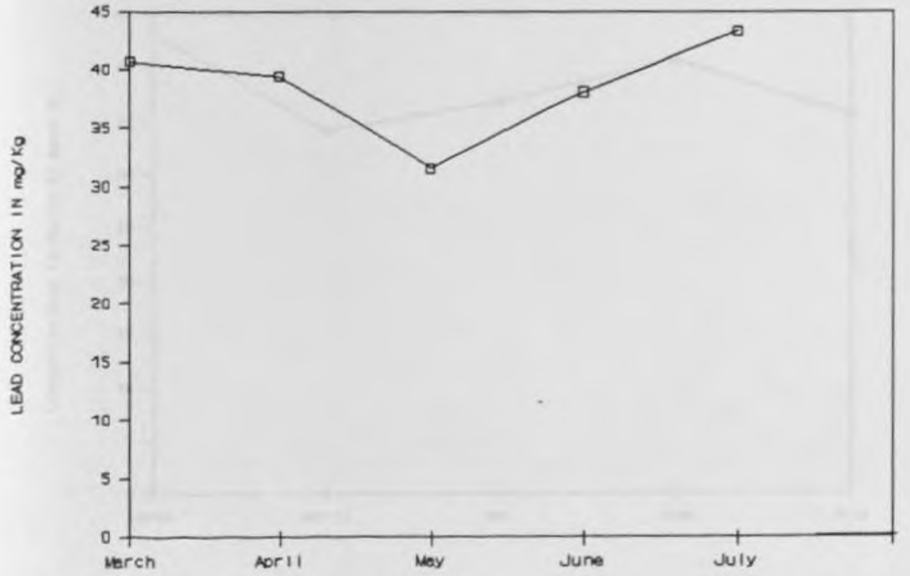

Figure 14b Mean Fluctuations in Lead Content of Garbage sampled at Monthly intervals between March and July 1989 at Site 1.

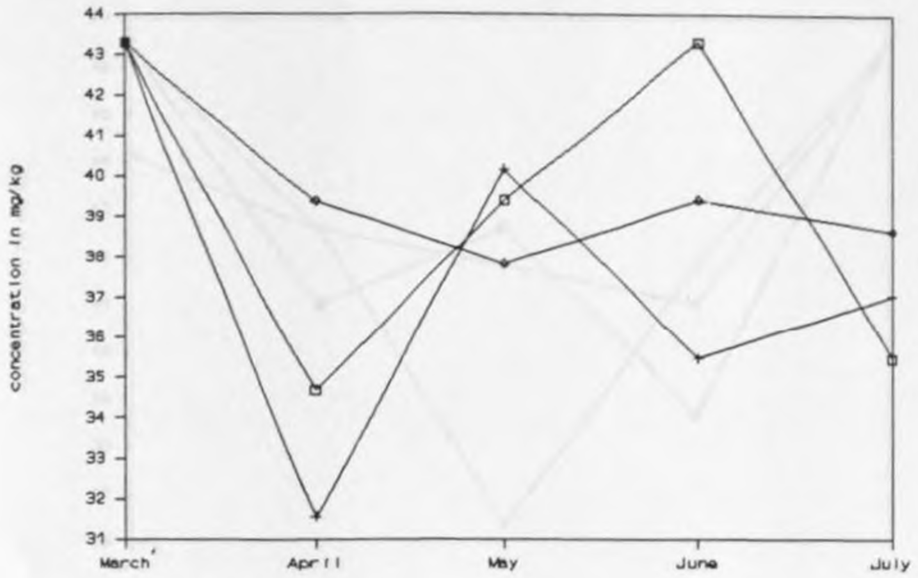

Figure 15a Fluctuations in Lead Content of Garbage sampled at Monthly intervals between March and July 1989 at Site 2.

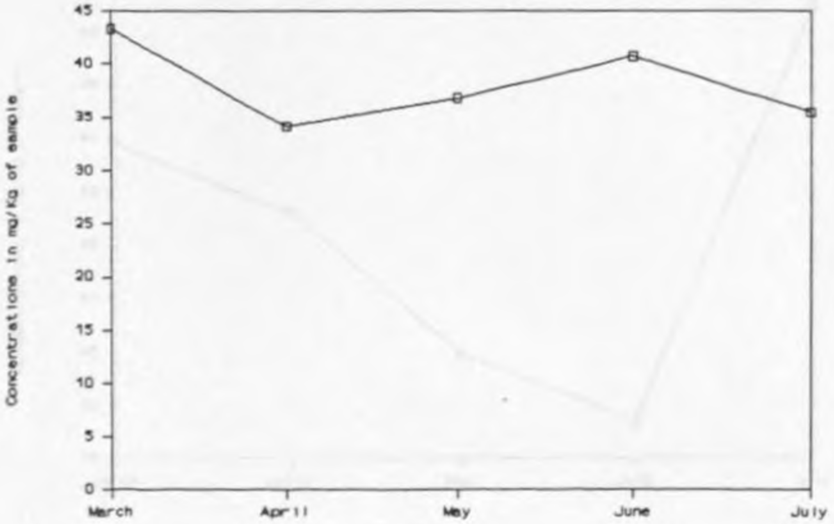

Figure 15b Mean Fluctuations in Lead Content of Garbage sampled at Monthly intervals between March and July 1989 at Site 2.

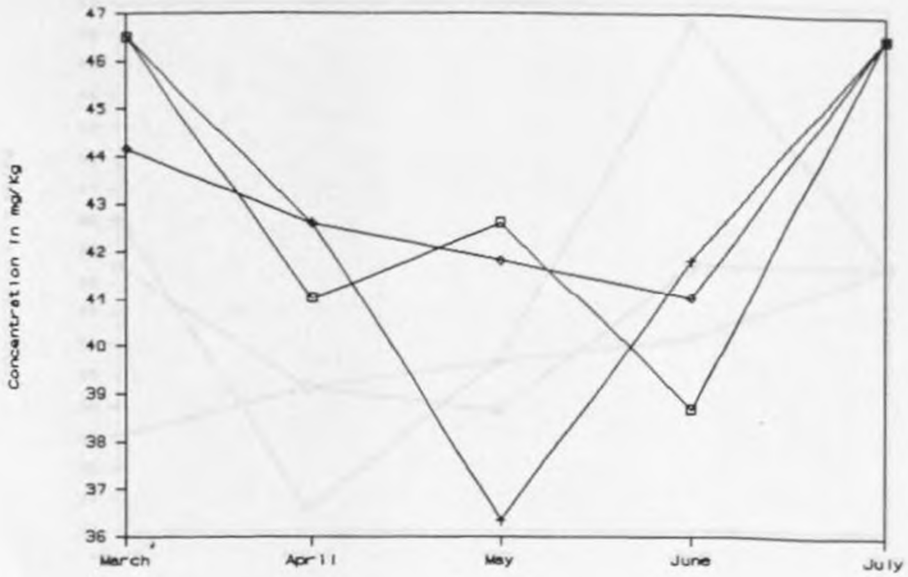

Figure 16a Fluctuations in Lead Content of Garbage sampled at Monthly intervals between March and July 1989 at Site 3.

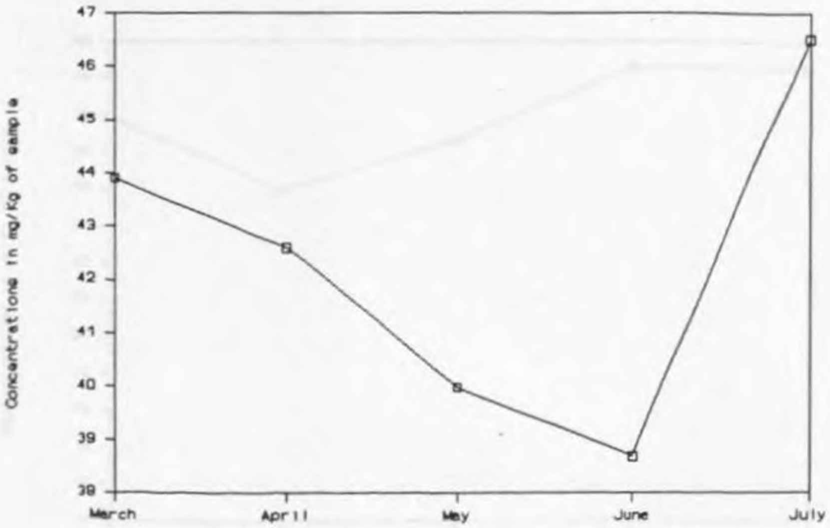

Figure 16b Mean Fluctuations in Lead Content of Garbage sampled at Monthly intervals between March and July 1989 at Site 3.

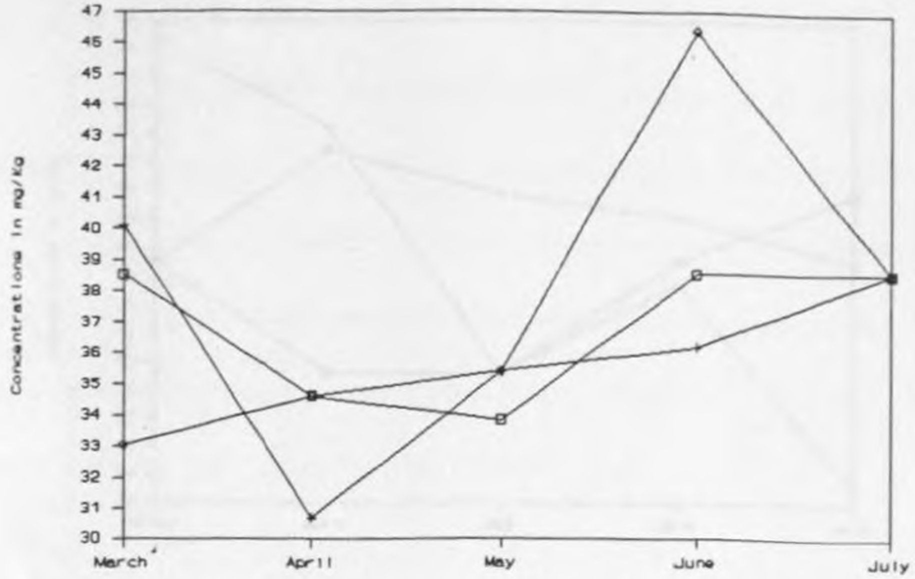

Figure 17a Fluctuations in Lead Content of Garbage sampled at Monthly intervals between March and July 1989 at Site 4.

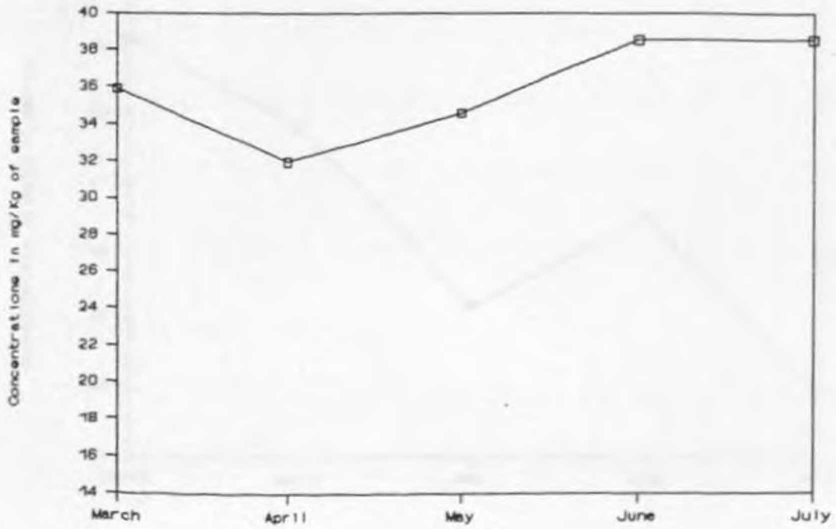

Figure 17b Mean Fluctuations in Lead Content of Garbage sampled at Monthly intervals between March and July 1989 at Site 4.

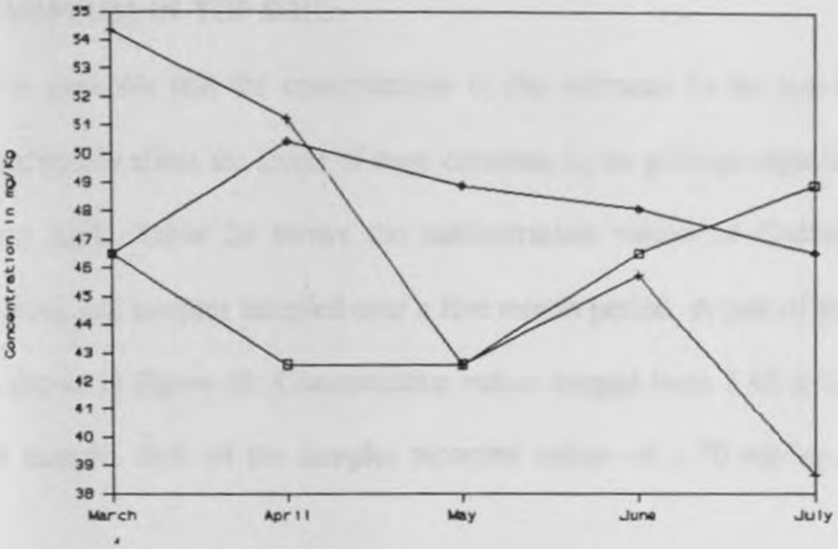

Figure 18a Fluctuations in Lead Content of Garbage sampled at Monthly intervals between March and July 1989 at Site 5.

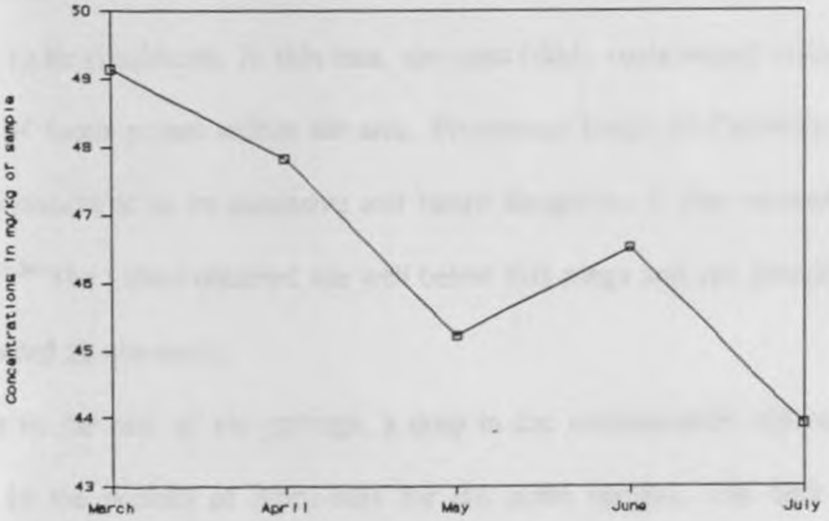

Figure 18b Mean Fluctuations in Lead Content of Garbage sampled at Monthly intervals between March and July 1989 at Site 5.

4.3.3 CADMIUM IN TOP SOIL

It is probable that the concentration of the elements in the top soil could significantly affect the levels of these elements in the garbage especially if they are high. Table 28 shows the concentration values of Cadmium obtained from soil samples sampled over a five month period. A plot of these values is shown in Figure 19. Concentration values ranged from 1.40 to 2.13 mg/kg of sample. 68% of the samples recorded values of 1.70 mg/kg and above.

The values obtained compared favourably with those that have been reported in literature for urban garden soils which ranged from 0.02 - 13.6 mg/kg[44,45,46]. For a conclusion to be drawn as to whether the levels obtained are dangerous or not, paths that might lead to the element being ingested by man need to be considered. In this case, the most likely route would involve ingestion of foods grown within the area. Phytotoxic levels of Cadmium in soils are considered to be excessive and hence dangerous if they exceed 3 ppm.[47,48,49,50] The values obtained are well below this range and can therefore be considered as non-toxic.

As in the case of the garbage, a drop in the concentration values is observed in the periods of April-May for the same reasons. The lack of adequate vegetation to act as soil cover results in erosion taking place during the rainy season. An inverse proportionality between concentration and depth has been reported[51,52] and would thus account for the decrease in concentration level of the metal with the washing away of the top soil.

TABLE 28 CONCENTRATION OF CADMIUM IN mg/kg FOR TOP SOIL

Month	Location 1*	Location 2*	Location 3*	Location 4*
March	1.70±0.177	1.87±0.130	2.13±0.094	1.70±0.125
April	1.61±0.190	1.40±0.075	1.87±0.240	1.83±0.175
May	1.70±0.235	1.48±0.170	2.13±0.185	1.70±0.065
June	1.92±0.088	1.92±0.135	2.00±0.110	2.13±0.150
July	1.74±0.047	1.74±0.165	1.74±0.155	1.74±0.075

* Each entry is an average of three samples from the same point.

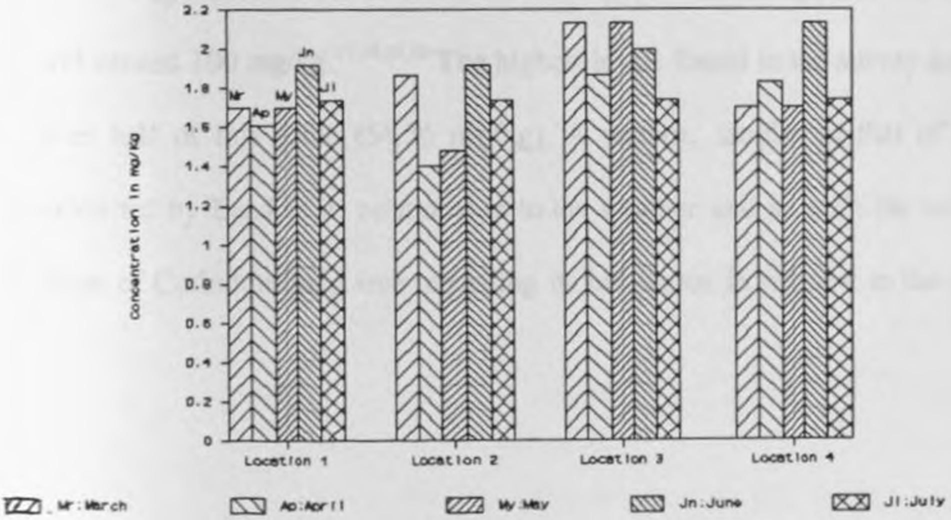

Figure 19. **Cadmium concentration values for a 5 month period at 4 selected locations.**

4.3.4 LEAD IN TOP SOIL

As in the case of Cadmium, the Lead values in the top soil were determined. Table 29 shows the concentration levels of Lead obtained from the soil samples over the five month sampling period. A plot of the values is shown in Figure 20. The concentration values ranged from 30.84 mg/kg to 54.36 mg/kg. 80% of the samples recorded concentration values above 47.00 mg/kg. These values compare very well with those reported in literature[44,45,46,53,54]. Roadside values of Lead have been reported as high as 7000 mg/kg[55].

Phytotoxic levels of Lead are considered to be excessive when levels in the soil exceed 100 mg/kg.[47,48,49,50] The highest levels found in the survey are just slightly over half of this value (54.36 mg/kg). A pattern, similar to that of Cadmium, is exhibited by Lead in its relationship to the weather and as such the same reasons as those of Cadmium hold true regarding its behaviour in relation to the rains.

TABLE 29 CONCENTRATION OF LEAD IN mg/kg FOR TOP SOIL

Month	Location 1*	Location 2*	Location 3*	Location 4*
March	46.52±1.625	54.36±3.500	54.36±4.250	50.44±3.125
April	42.60±1.616	50.44±2.250	48.87±6.250	50.44±3.372
May	44.95±4.007	50.44±4.000	30.84±9.250	50.44±5.752
June	49.66±3.129	54.36±5.250	38.68±2.350	54.36±3.576
July	52.01±0.753	54.36±1.300	50.44±5.500	54.36±2.518

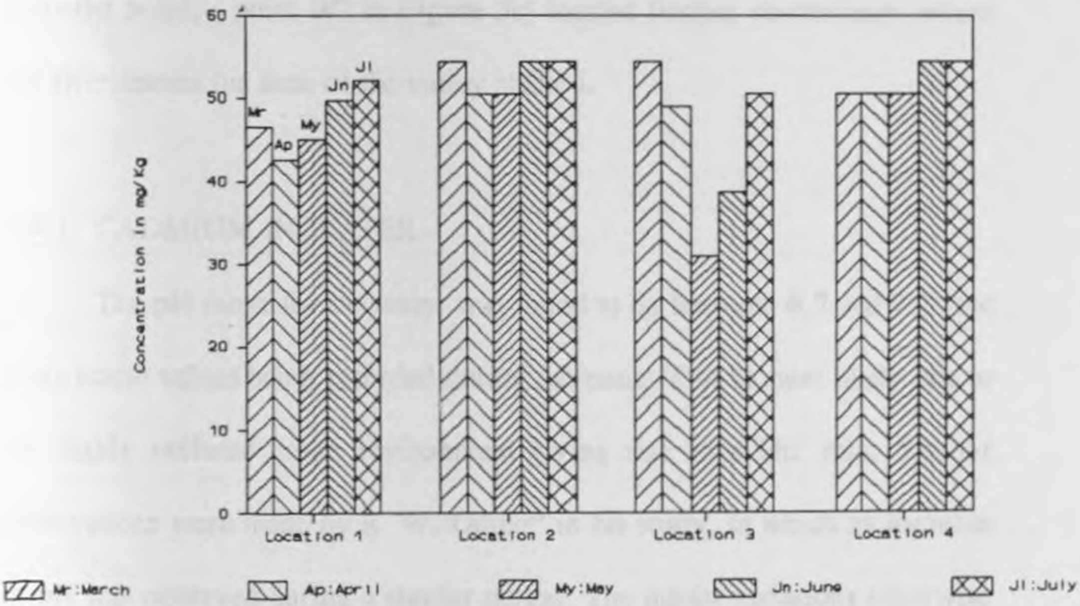

Figure 20 lead concentration values for a 5 month period at 4 selected locations.

4.4 ELEMENTAL CONCENTRATIONS IN RIVER WATER

A large amount of waste generated within the valley ends up in the river. Waste water from the many activities carried out, wash-aways during the rainy season, all get carried away by the river. This does imply that a survey of the concentrations of the elements in the river could give a picture of the pollution extent of these metals in the surrounding area. To evaluate the composition of the elements in the water, samples were taken from the inlet point, (point W1 in Figure 3b) located where the river entered the valley and an outlet point, (point W2 in Figure 3b) located further downstream where the river leaves the area of the valley studied.

4.4.1 CADMIUM IN WATER

The pH range for the water was found to lie between 6.7 and 7.2, the more acidic values being recorded during the rains. This is most likely due to the highly polluted urban environment giving rise to acidic rain. Similar observations were made by R. W. Odipo[29] in his study, in which an increase in pH was observed during a similar period. The minor variations otherwise observed were primarily due to the effluents discharged into the river.

It can be observed from Table 30 that the effluent discharged from the valley did not have a significant effect on the final concentration of Cadmium in the water. Except for week 10 where the difference between the inlet, (incoming waters) and outlet (outgoing waters) was 29 ppb, the difference between the concentrations were less than 10 ppb.

Very high inlet values of Cadmium were recorded between weeks 9 and 16 as compared to the preceding period. In addition, the same period recorded relatively high difference values for the ion. These two factors contrast the results recorded for weeks 1 to 9. The period between weeks 9 and 16 coincides with the time of low or no rainfall. It is thus probable that the rains introduce a dilution factor due to increased volume of water which in turn reduces the concentration in the water. The high value obtained for week 10 may have arisen from a non routine activity occurring at that time that resulted in discharge of high levels of Cadmium into the river.

Table 30 CADMIUM CONCENTRATION VALUES FOR WATER

MONTH	WEEK	CONCENTRATION IN ppm x 100		INLET-OUTLET DIFFERENCE IN ppm x 100	AVG. DIFFERENCE FOR MONTH	pH OF WATERS
		OUTLET	INLET			
	1	1.327±0.010	0.692±0.023	0.635	0.21	6.8
APRIL	2	0.489±0.011	0.386±0.024	0.103		6.9
	3	0.300±0.014	0.297±0.014	0.003		6.7
	4	0.240±0.020	0.157±0.018	0.083		6.9
	5	0.138±0.026	0.109±0.016	0.029	0.39	6.7
MAY	6	0.092±0.027	0.091±0.034	0.001		6.9
	7	0.080±0.015	0.078±0.019	0.002		7.0
	8	1.532±0.01	0.013±0.028	1.519*		7.1
	9	12.317±0.034	11.620±0.033	0.697	1.01	7.2
	10	8.792±0.030	5.870±0.029	2.922*		7.0
JUNE	11	5.790±0.034	5.370±0.017	0.420		7.0
	12	2.811±0.019	2.811±0.022	0.000		6.9
	13	2.781±0.028	2.088±0.013	0.693	0.33	7.0
JULY	14	2.088±0.037	1.620±0.017	0.468		6.9
	15	1.551±0.027	1.484±0.026	0.067		7.0
	16	3.732±0.014	3.635±0.013	0.097		7.0

* Exceptional values

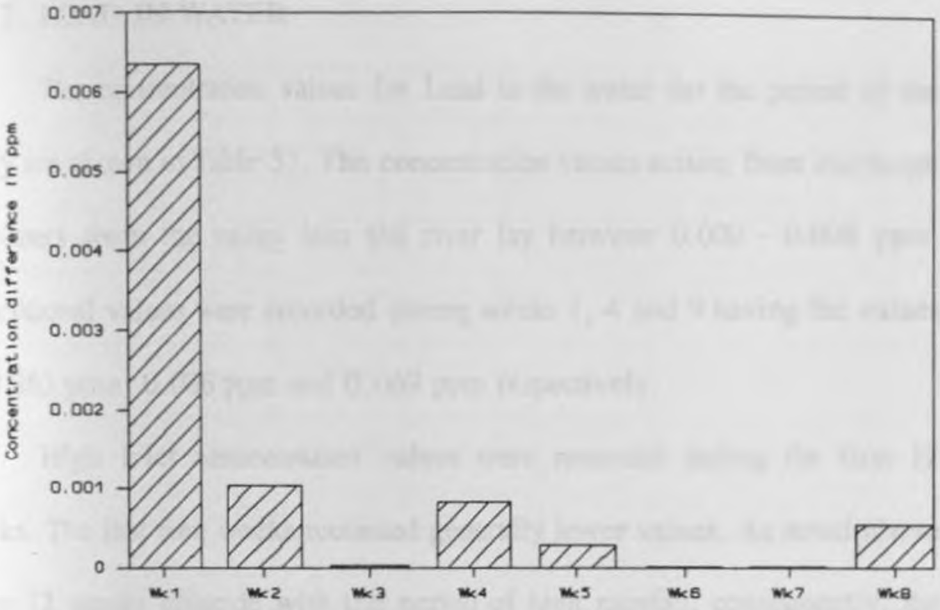

Figure 21 Difference between inlet and outlet concentrations of Cadmium in river water vs. Weeks for weeks 1 - 8.

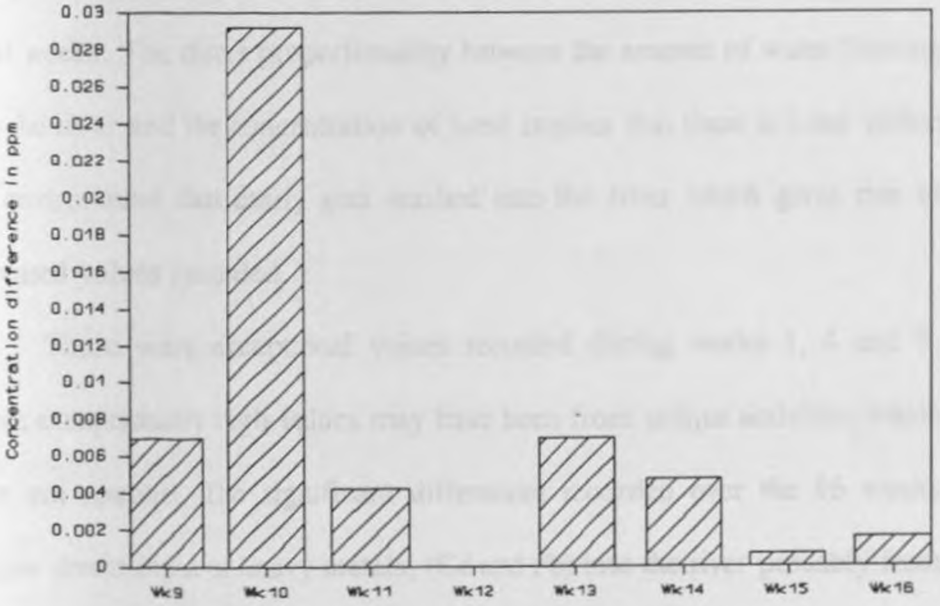

Figure 22 Difference between inlet and outlet concentration of Cadmium in river water vs. Weeks for weeks 9 - 16.

4.4.2 LEAD IN WATER

The concentration values for Lead in the water for the period of the study are shown in Table 31. The concentration values arising from discharge of waters from the valley into the river lay between 0.000 - 0.008 ppm. Exceptional values were recorded during weeks 1, 4 and 9 having the values of 0.263 ppm, 0.036 ppm and 0.069 ppm respectively.

High inlet concentration values were recorded during the first 12 weeks. The last four weeks recorded generally lower values. As noted above these 12 weeks coincide with the period of high rainfall, consequently, the high inlet values of Lead may be attributed to the water flowing into the river during this period having high Lead concentrations.

Regarding the concentration of Lead arising from activities in the valley, the average values for the first eight weeks are higher than the latter eight weeks. The direct proportionality between the amount of water flowing into the river and the concentration of Lead implies that there is Lead within the environment that easily gets washed into the river which gives rise to increased values recorded.

There were exceptional values recorded during weeks 1, 4 and 9. These exceptionally high values may have been from unique activities which were not routine. The significant differences recorded over the 16 weeks suggest direct input of heavy metals, (Cd and Pb) into the river probably from Jua kali type and a wide range of home industries in the highly congested area.

TABLE 31 LEAD CONCENTRATION VALUES IN WATER

MONTH	WEEK	CONCENTRATION IN ppm x 10		DIFFERENCE IN ppm x 10	AVG. DIFF. FOR MONTH x 10	pH of WATERS
		OUTLET	INLET			
APRIL	1	5.870±0.152	3.242±0.131	2.628*	0.769	6.8
	2	0.482±0.011	0.403±0.032	0.079		6.9
	3	2.791±0.023	2.781±0.018	0.010		6.7
	4	2.610±0.021	2.252±0.025	0.358*		6.9
MAY	5	1.081±0.035 0	1.063±0.029	0.018	0.053	6.7
	6	1.001±0.031	0.935±0.041	0.066		6.9
	7	3.133±0.028	3.051±0.025	0.082		7.0
	8	0.371±0.024	0.324±0.034	0.047		7.1
JUNE	9	1.146±0.046	0.459±0.042	0.687*	0.186	7.2
	10	0.434±0.044	0.432±0.033	0.002		7.0
	11	0.285±0.043	0.257±0.025	0.028		6.9
	12	0.223±0.021	0.195±0.033	0.028		7.0
JULY	13	0.184±0.035	0.171±0.026	0.013	0.010	7.0
	14	0.173±0.042	0.153±0.023	0.020		6.9
	15	0.149±0.037	0.146±0.034	0.003		7.0
	16	0.113±0.012	0.110±0.021	0.003		7.0

* Exceptional values

Lead values varied between 25.0-134.0 ppm

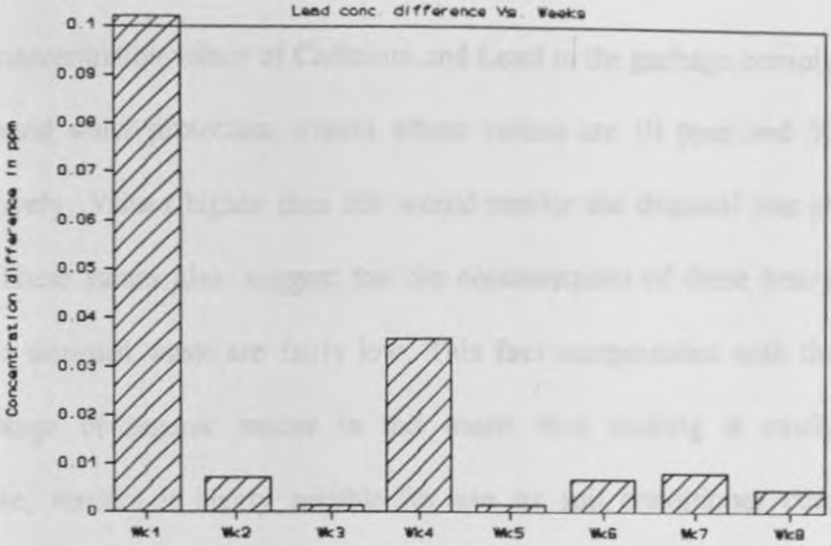

Figure 23 Difference between inlet and outlet concentrations of Lead vs. Weeks for weeks 1 - 8.

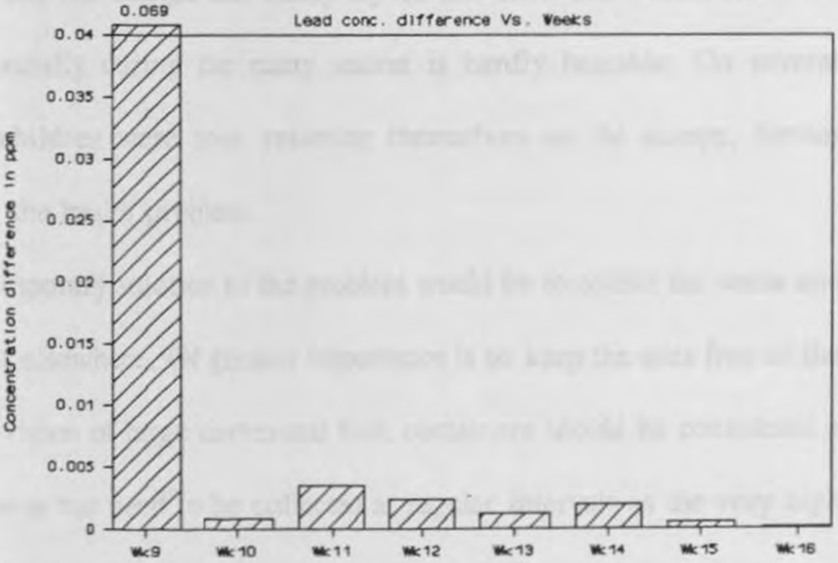

Figure 24 Difference between inlet and outlet concentrations of Lead vs. Weeks for weeks 9 - 16.

4.5 CONCLUSION

The concentration values of Cadmium and Lead in the garbage comply with the ground water protection criteria whose values are 10 ppm and 50 ppm respectively. Values higher than this would render the disposal site as dangerous. These values also suggest that the concentration of these heavy metals in the disposed waste are fairly low. This fact compounded with the high percentage of organic matter in the waste thus making it easily biodegradable, renders it highly suitable for use as soil conditioner cum fertilizer[2]. The waste need not be transported from the location but could be used for the purposes stated above for the improvement of the general surroundings of the area. Never the less the waste as it is poses a great danger to the residents. The very close proximity of the dumps to the houses implies that flies from the dumps can easily fly to and fro. The stench from the dumps, especially during the rainy season is hardly bearable. On several occasions, children were seen relieving themselves on the dumps, further aggravating the health problem.

A temporary solution to the problem would be to collect the waste and dispose of it elsewhere. Of greater importance is to keep the area free of the dumps. Provision of large communal bulk containers should be considered a priority. These too need to be collected at regular intervals as the very high population density would generate large quantities of waste that would require regular collection. An improvement of the sanitary facilities is of paramount importance.

The concentration of Cadmium and Lead in the river are well under the WHO standards[56]. These two parameters do not fully describe the quality of the water. Levels of BOD, COD, dissolved solids, suspended solids, Chlorides, Nitrates and Total phosphates also need to be taken into consideration. The valleys contribution to the total Cadmium concentrations in the river, Table 32, is fairly high. For Lead, disregarding the times of exceptionally high values, the values are 13% or less which may be significant. A more comprehensive study needs to be done to establish the quality of the river waters over a greater distance.

TABLE 32 PERCENTAGE CONTRIBUTION OF CADMIUM AND LEAD IN THE OUTLET WATER BY THE VALLEY.

		CADMIUM (ppm x 100)			LEAD (ppm x 10)		
MONTH	WEEK	OUTLET A	IN-OUT DIFF. B	$(\frac{B}{A})$ %	OUTLET C	IN-OUT DIFF. D	$(\frac{D}{C})$ %
APRIL	1	1.327±0.010	0.635	47.85	5.870±0.152	2.628*	44.77
	2	0.489±0.011	0.103	21.06	0.482±0.011	0.079	16.39
	3	0.300±0.014	0.003	1.00	2.791±0.023	0.010	0.36
	4	0.240±0.020	0.083	34.58	2.610±0.021	0.358*	13.72
MAY	5	0.138±0.026	0.029	21.01	1.081±0.035	0.018	1.67
	6	0.092±0.027	0.001	1.09	1.001±0.031	0.066	6.59
	7	0.080±0.015	0.002	2.50	3.133±0.028	0.082	2.62
	8	1.532±0.010	1.519*	99.15	0.371±0.024	0.047	12.67
JUNE	9	12.317±0.034	0.697	5.66	1.146±0.046	0.687*	59.95
	10	8.792±0.030	2.922*	33.23	0.434±0.044	0.002	0.46
	11	5.790±0.034	0.420	7.25	0.285±0.043	0.028	9.82
	12	2.811±0.019	0.000	0.00	0.223±0.021	0.028	12.56
JULY	13	2.781±0.028	0.693	24.92	0.184±0.035	0.013	7.07
	14	2.088±0.037	0.468	22.41	0.173±0.042	0.020	11.56
	15	1.551±0.027	0.067	4.32	0.149±0.037	0.003	2.01
	16	3.732±0.014	0.097	2.60	0.113±0.012	0.003	2.65

4.6 RECOMMENDATIONS

Solutions to the waste problem do not just mean the provision of adequate facilities for the collection and disposal of waste, a social programme to educate the people on waste management also needs to be initiated. The public needs to be aware of the dangers and risks associated with uncontrolled dumping of waste. The local populations needs to be involved in the waste management programme to alleviate the burden on the civic authorities. The tendency of dumping waste at specific locations could be taken advantage of by providing more communal bins. This would encourage their use for disposing of the waste. With this set up, waste collection is cheaper and easier as compared to the house to house collection. The use of biodegradable waste as garden manure after composting also needs to be encouraged among the city residents who have small backyard gardens. Alternative non-conventional methods of waste collection needs to be adopted by the municipal authority in Nairobi, an example of which could be drawn from Cairo where hand carts have been used.

All literature dealing with the different aspects of waste management cited in this work, has been computerised and can thus be easily accessed. It is essential to keep the database up to date if it is to serve its main objective of being a centralised source of information on waste management.

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54. Baltrop, D., Significance of lead-contaminated soils and dusts for human populations, paper presented at International Symposium on Environmental Lead research, Dubrovinik, Yugoslvia, May 1975.

55. Olson, K. W. and Skogerboe, R. K., Identification of soil lead compounds from automotive sources, Environmental Science Technology, Vol 9, pp. 277 1975.

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APPENDIX I

Listing of a search of publications in the database dealing with disposal of industrial wastes.

SEARCH EXPRESSION: Waste Disposal * Industrial waste

TITLE: Proceedings of the Third International Symposium, Alexandria, Egypt, June 1985.

CORP. BODY: UN. ESCWA. Environment Co-ordination Unit, ESCWA.

CONFERENCE: Management of Industrial and Hazardous Wastes (3rd : 1985: Alexandria, Egypt).

IMPRINT: [Alexandria, Egypt : Alexandria University], 1985.

NOTE: At head of title: Economic and Social Commission for Western Asia, Environment Co-ordination Unit.

CALL NUMBER: Pol,, Wast,, 69.

KEYWORDS: Industrial pollution; Waste disposal; Waste utilization; Wastes; Harmful products; Industrial wastes; Toxic waste disposal; Western Asia.

SOURCE OF RECORD: epl.

LANGUAGE OF PUBLICATION: eng.

TITLE: Treatment and disposal of pesticide wastes, edited by Raymond F. Krueger, James N. Seiber.

AUTHOR(S): Krueger, Raymond F. Seiber, James.

IMPRINT: Washington, D.C. : American Chemical Society, c1984.

SERIAL NOTES: ACS symposium series ; no.259.

NOTE: Based on a symposium sponsored by the Division of Pesticide Chemistry at the 186th meeting of the American Chemical Society, Washington, D.C. Aug. 28-Sept.2, 1983.

ISBN: 0-8412-0858-1.

CALL NUMBER: Pol,, Wast,, 74.

KEYWORDS: Waste disposal; Pesticides; Wastes; Chemicals; Industrial wastes; Recycling.

SOURCE OF RECORD: epl.

LANGUAGE OF PUBLICATION: eng.

TITLE: The state of the environment : a report prepared for the Irish Minister for the Environment, editor, David Cabot.
AUTHOR(S): Cabot, David.

CORP. BODY: Ireland. An Foras Forbartha.

IMPRINT: Dublin : An Foras Forbartha, 1985.

ISBN: 0-85053-007-6.

CALL NUMBER: Man,, Soe,, (415), 1.
KEYWORDS: Environmental quality; Environmental data; Urban environment; Water resources; Water quality; Air pollution; Noise pollution; Waste disposal; Industrial wastes; Agricultural wastes; Ireland.

SOURCE OF RECORD: epl.

LANGUAGE OF PUBLICATION: eng.

TITLE: Strategies, technologies and economics of waste water management in ECE countries : a report on prevailing practice and recent experience in domestic sewage purification and industrial waste-water treatment with special emphasis on advanced techniques, prepared under the auspices of the ECE Committee on Water Problems.

CORP. BODY: UN. ECE.

IMPRINT: New York : United Nations, 1984.

CALL NUMBER: Pol,, Wast,, 84.

KEYWORDS: Sewage; Waste disposal; Recycling; Industrial wastes; Sewage treatment plants; Water pollution; Europe.

SOURCE OF RECORD: epl.

LANGUAGE OF PUBLICATION: eng.

TITLE: Estilos de desarrollo de la industria manufacturera y medio ambiente en América Latina.

CORP. BODY: UN. ECLAC. UNEP.

EDITION: 1st edition.

IMPRINT: Santiago de Chile : CEPAL, 1982.

SERIAL NOTES: Estudios e informes de la CEPAL ; 11.

NOTE: Joint project of ECLAC and UNEP. Bibliography: p.175-180.

CALL NUMBER: Dev,, Econ,, Ind,, 39,, c.2.

KEYWORDS: Industrial pollution; Industrial development; Industrial wastes; Waste disposal; Latin America.

SOURCE OF RECORD: epl.

LANGUAGE OF PUBLICATION: spa.

TITLE: Treatment and discharge of industrial wastewater in the Mediterranean area : report on a WHO workshop, Venice, 10-14 June 1985.

CORP. BODY: WHO. Regional Office for Europe.

IMPRINT: Copenhagen : Regional Office for Europe, World Health Organization, 1986.

SERIAL NOTES: Environmental health series ; 08.

CALL NUMBER: Hlth, 80, v.8.

KEYWORDS: Recycling; Solid wastes; Industrial wastes; Waste disposal; Mediterranean countries; Sewage.

SOURCE OF RECORD: epl.

LANGUAGE OF PUBLICATION: eng.

TITLE: Management of industrial wastewater in developing nations : proceedings of the international symposium, Alexandria, March 1981, edited by David Stuckey and Ahmed Hamza.

AUTHOR(S): Stuckey, David C. Hamza, Ahmed.

CORP. BODY: Egypt. Academy of Scientific Research and Technology. Alexandria University. High Institute of Public Health.

IMPRINT: Oxford : Pergamon Press, 1982.

NOTE: Sponsored by the High Institute of Public Health, Alexandria University and the Academy of Scientific Research and Technology, Egypt.

ISBN: 0-08-026286-4.

CALL NUMBER: Pol, Wast, 71.

KEYWORDS: Sewage; Industrial wastes; Waste disposal; Pollution control.

SOURCE OF RECORD: epl.

LANGUAGE OF PUBLICATION: eng.

TITLE: Manejo de los desechos industriales peligrosos en México, Fernando Ortiz Monasterio, Cristina Cortinas de Nava, María de Lourdes Maffey García.

AUTHOR(S): Ortiz Monasterio, Fernando. Cortinas de Nava, Cristina. Maffey García, María de Lourdes.

EDITION: 1st edition.

IMPRINT: México : Fundación Universo Veintiuno, 1987.

SERIAL NOTES: Colección medio ambiente ; 02.

ISBN: 968-6198-01-6.

CALL NUMBER: Pol, Wast, (72)1.

KEYWORDS: Industrial wastes; Waste disposal; Mexico.

SOURCE OF RECORD: epl.

LANGUAGE OF PUBLICATION: spa.

TITLE: Hazardous waste minimization : a strategy for environmental improvement, H.M. Freeman.

AUTHOR(S): Freeman, H.M.

Journal: International Journal of Air Pollution Control and Waste Management - 38(1) January 1988 : 59-61.

KEYWORDS: Hazardous wastes; Industrial wastes; Waste disposal.
SOURCE OF RECORD: epl.

LANGUAGE OF PUBLICATION: eng.

TITLE: Toxic organic chemicals in porous media : [papers presented at the second International Workshop on Behavior of Pollutants in Porous Media, sponsored by IUPAC and IAHS and held at Bet Dagan, Israel, during June, 1987], edited by Z. Gerstl ... et al.

AUTHOR(S): Gerstl, Zev.

CORP. BODY: International Union of Pure and Applied Chemistry, IUPAC. International Association of Hydrological Sciences, IAHS.

CONFERENCE: International Workshop on Behavior of Pollutants Porous Media (2nd : 1987 : Bet Dagan, Israel).
IMPRINT: Berlin : Springer-Verlag, 1989.

SERIAL NOTES: Ecological studies ; 73.

NOTE: Includes bibliographical references.

ISBN: 3-540-50799-X.

CALL NUMBER: Pol, Water, Gr/1.

KEYWORDS: Groundwater; Water pollution; Environmental aspects; Water quality; Water management; Toxic substances; Waste disposal; Pesticides; Industrial

APPENDIX II

Data Entry form used in collection of bibliographic information.

Bibliographic level code: m Source of record: epl Completeness of record: a
Date record entered: _____ Date record updated: _____
Language of item(s): eng__________________ Physical medium code:ptd__
ISBN: ____________________

ISSN: ____________________

Title: ^a____________________

Other title(s): ____________________

Edition: ____________________

Name of person(s): ____________________

Name of corporate body(ies): ____________________

Name of conference(s): ____________________

Imprint: ____________________

Serial numbering: ____________________

Physical description: ____________________

Series note(s): ____________________

Bibliographic relationship: ____________________

Note: ____________________

Serial frequecy: _

Call number(s):

Subject descriptors: <

Main subject(s): <