INVESTIGATION OF POLLUTANTS, DETERMINATION OF PHYSICO-CHEMICAL CHARACTERISTICS OF THE NAIROBI RIVER AND REMEDIATION OF SOME TOXIC HEAVY METALS USING FISH BONES

BY

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DECLARATION

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

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DEDICATION

I dedicate my work to my husband Charles and my three children Christopher, Christine and Sarah, who continuously supported and encouraged me and made the completion of this degree possible.

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ABBREVIATIONS

µS/cm – Micro Siemens per centimeter

AAS – Atomic Absorption Spectrometry

AMREF – African Medical Research Foundation

BOD – Biochemical Oxygen Demand

COD – Chemical Oxygen Demand

DO – Dissolved Oxygen

e.g. – exempli gratia [for example]

EDTA – Ethylenediamine Tetra acetate

EDXRFA – Energy Dispersive X-Ray Fluorescence Analysis

EMCA – Environmental Management and Coordination Act.

EPA – Environmental Protection Agency

EU – European Union

FET – Field Effect Transistor

GDWQ – Guidelines for Drinking Water Quality

GPS – Geographical Positioning System

HEM – Hexane Extractable Material

IBWA – International Bottled Water Association

ID – Internal Diameter

INST – Institute of Nuclear Science and Technology

KEBS – Kenya Bureau of Standards

KMD – Kenya Meteorological Department

LDL – Low Detection Limit

MCA – Multi Channel Analyser

mg/L – Milligrams per Litre

ND – Not Detected

NTU – Nephelometric Turbidity Units

°C – Degree Celsius

PAHs – Polycyclic Aromatic Hydrocarbons

ppm – Parts per million

TDS - Total Dissolved Solids

TSS - Total Suspended Solids

UNCHS – United Nations Center for Human Settlement

UNEP – United Nations Environmental Programme

UNICEF - United Nations Children's Educational Fund

UV – Ultra Violet

UVA –Ultra Violet Absorber

WHO - World Health Organization

XRFA – X-Ray Fluorescence Analysis

XRF - X-Ray Fluorescence

SYMBOLS

$AgNO_3$ – Silver Nitrate

Ag_2SO_4 – Silver Sulphate

As – Arsenic

$CaCl_2$ – Calcium Chloride

Cl^- – Chloride ion

Cd – Cadmium

CO_2 – Carbon dioxide

Cr – Chromium

Cu – Copper

Fe - Iron

$FeCl_3$ – Iron (III) Chloride

$Fe(NH_4)_2(SO_4)_2.6H_2O$ – hydrated Ferrous Ammonium Sulphate

Ge – Germanium

$HClO_4$ – Perchloric acid

Hg – Mercury

Hg_2SO_4 – Mercury Sulphate

HNO_3 – Nitric acid

Hp – Hyper pure

H_2SO_4 – Sulphuric acid

KCl – Potassium Chloride

$K_2Cr_2O_7$ – Potassium Dichromate

KH_2PO_4 – Potassium Dihydrogen Phosphate

$K_2S_2O_8$ – Potassium Persulphate

$MgSO_4.7H_2O$ – hydrated Magnesium Sulphate

$MnSO_4.2H_2O$ – hydrated Manganese Sulphate

Na – sodium

$Na_2PO_4.7H_2O$ – hydrated Sodium Phosphate

$Na_2S_2O_3$ – Sodium Thiosulphate

NaN_3 – Sodium Azide

$(NH_4)_2MoO_4$ – Ammonium Molybdate

NH_4VO_3 – Ammonium Metavanadate

Ni – Nickel

Pb – Lead

PO_4^{3-} –Phosphate ion

Zn –Zinc

ABSTRACT

A Study was conducted to determine the level of pollution in the Nairobi River. The study covered four sampling sites located along the river, stretching from upstream at Ondiri swamp then moving to Museum Hill Bridge then further down to Race Course and finally downstream at Outer Ring Road Bridge. Sampling was done once a month for a period of six months starting in November 2008 and ending in April 2009. The sampling carried out covered the wet and dry months.

At each sampling site, composite samples of water and sediment were taken. The samples were prepared, preserved and analysed according to standard methods reported in Greenberg et al, (1992). The analysis, identification and quantification of pollutants were carried out at the University of Nairobi, Department of Chemistry.

The parameters investigated included physico-chemical parameters [pH, temperature, conductivity, alkalinity, Total Dissolved Solids (TDS), Total Suspended Solids (TSS), Chemical Oxygen Demand (COD) and Biochemical Oxygen Demand (BOD)], toxic heavy metals [lead, cadmium and Chromium], organics [oil and grease], one nutrient [phosphate] and one anion [Chloride]. The appearance of water was also assessed for turbidity, colour and smell.

Toxic heavy metals were analysed using Atomic Absorption Spectrometry (AAS) and X-Ray Fluorescence (XRF) methods. Some physico-chemical parameters were analysed by colorimetry, volumetric analysis, gravimetric analysis and potentiometric titration, whereas analysis of oil and grease was carried by gravimetric method based on USEPA 1664A.

Data analysis was done using Microsoft office excel and Statistical Programme for Social Scientists (SPSS).

Results found show that in the physico-chemical analysis, pH values ranged from 6.48-8.25 with a mean of 7.10 ±0.49. At each site pH values were within acceptable WHO, EU and KEBS limits for natural water [6.0-8.5]. The conductivity and TDS values were positively correlated and ranged from 196-592 µS/cm with a mean of 510 ±179.5 µS/cm and 98.7-339.3 mg/L with a mean of 251 ±93.7. mg/L. TDS values were below acceptable WHO limits of 1000mg/L, while conductivity values were well above acceptable WHO limits of 0.6 - 1 µS/cm. The temperatures ranged from 19.7-32.2 °C with a mean of 23 ±3.5 °C. The high temperature of 32.2 °C that was recorded at Ondiri Swamp was attributed to time of sampling. TSS values ranged from 20.7-164 mg/L across the four sampling sites with a mean of 66.3 ±38.75. mg/L. High TSS value was recorded at Race Course Bridge, while the lowest value was recorded at Ondiri Swamp.

Dissolved oxygen in water was determined through BOD and COD. The level of BOD ranged from 333 mg/L to 4100 mg/L with a mean of 1435 ±1480.mg/L, while COD values varied between 20 and-706.7 mg/L across the sampling sites with a mean of 260.6 ±248.8 mg/L. High levels of BOD and COD were recorded at Race Course Bridge and Outer Ring Bridge. Both values were well above acceptable WHO (2008) limits of 3 – 6 mg/L.

Concentration of phosphate ions ranged from 1.4 – 8.0 ppm with a mean of 3.9 ±2.65 ppm High concentrations (8ppm) were recorded at Ondiri Swamp and Race Course Bridge in the month of April. In November, the concentration of phosphate ions increased from upstream to downstream

[0 -5.3 mg/L] with a mean of 2.3 ±2.25. mg/L. Chloride ion concentration ranged from 37.3 – 94.4 mg/L with a mean of 62.1 ±18.70 mg/L High concentration values were recorded at Museum Hill Bridge and Race Course Bridge in both the dry and rainy seasons.

Toxic heavy metals were analysed using XRF and AAS technique. Only lead and Chromium were detected. The amount of lead detected using AAS technique ranged from 0.04 to 0.16 ppm with a mean of 0.08 ±0.04 ppm , while that detected using XRF ranged from 32.95 to 176.5 ppm with a mean of 84.9 ±62.09 ppm. Chromium was detected using AAS and values ranged from 0.01 to 0.24 ppm with a mean of 0.1 ±0.08 ppm. In both cases concentrations detected do not comply with WHO (2008) requirements, lead (0.01 ppm) and chromium (0.05 ppm). High lead concentrations were recorded at Race Course Bridge (176.5 ppm).

Experiments were also carried out to assess the remediation capacity of ground fish bones on heavy metals. Water from Outer Ring sampling site was eluted through a column packed with ground fish bones and the eluate analysed using AAS. Results from the analysis indicate a decrease in concentration of lead ions from 0.11 to 0.08, which is 27% reduction. While conductivity values before and after remediation reduced from 200 μ S/cm to 101.6 μ S/cm, this translated to a reduction of 49%. Factors affecting the remediation process were also investigated. These were temperature, surface area, time of contact and mass of fish bones. Langmuir and Freundlich models were used to fit adsorption data for lead ion concentrations determined. From the graphical plots and value for R^2, the Langmuir data gives the best fit indicating that the adsorption process using fish bones is monolayer.

CHAPTER ONE

INTRODUCTION

1.1 General Introduction

The delicate balance between man and the environment no longer exists. It has been disturbed by man's direct and indirect activities (Khopkar, 1995). Although some activities are desirable for human development and welfare, most have contributed to environmental pollution.

Chapter 1 of this study briefly highlights the general background on water pollution, the Nairobi River Basin, problem statement, objectives and justification. Chapter 2 discusses Nairobi as a city, its history and its source of water supply. This will provide information on the kind of scenery that the Nairobi River meanders through. The chapter also summarises the findings of the desk study of the Nairobi River Basin Programme, looks at sources of pollution, treatment of water and the various parameters that were used during investigations carried out in this study. Chapter 3 describes in detail the instruments that were used to analyse the presence of heavy metals in water and sediment. Chapter 4 describes the sampling sites, sampling methods, procedures and reagents used during the study. Chapter 5 discusses results obtained during the investigations and chapter 6 gives the conclusion and recommendations of the study.

1.2 General Background on Water Pollution

Water is one of our planet's most important resources. Without it life would be non existent. Not only is it a habitat and a source of sustenance for animals and plants, human societies depend on fresh clean water for its survival and prosperity.

Worldwide, 1.7 million children under five years die from diarrhoeal diseases caused by drinking contaminated water (Schaefer, 2008). It is therefore incumbent upon society to ensure the availability of clean water. The world is facing a global crisis. Already, deficiencies in water supply and water quality are causing widespread human suffering. 1.1 billion people lack access to clean water, and 2.6 billion do not have access to improved sanitation facilities.

Water comprises 71% of the earth's surface, over 97% of it is salty, and most of the remaining 3% is frozen in the ice polar caps leaving 0.3% which is of use to humanity (UNEP-IETEC, 2008). Man depends on this tiny fraction of water to quench his thirst, water crops and wash away wastes. In industries water has several uses: it is used as a coolant, a solvent, a cleaning reagent, putting out fires and to power industries. The limited supply is over strained.

The indiscriminate release of industrial wastes and agricultural run-off overload rivers and lakes with chemicals, wastes and nutrients in addition to poisoning water supplies. This dirty water is the world's major cause of diseases. According to AMREF (www.amref.org, 2008) 70% of East Africa hospital visits are caused by contaminated water. The monitoring and control of pollutants in the environment has become a major concern to scientists globally. There is great demand to remove harzardous substances and eliminate threats from uncontrolled hazardous waste sites in a cost effective manner (Findley and Faber, 1991).

1.3 Pollution

Pollution is caused by man introducing into the environment contaminants that cause harm, discomfort to humans or other living organisms or damage the environment. The Indian Environment (Protection) Act of 1986 defines pollution as any solid, liquid or gaseous substance present in such a concentration as may be or tend to be injurious to the environment (Mbui, 2007). There are basically three types of pollution: air pollution, water pollution and land pollution. The focus of this study is on water pollution.

1.3.1 Water Pollution

Water pollution occurs when a body of water is adversely affected due to the addition of large amounts of toxic materials to the water. When it is unfit for its intended use, water is considered polluted. (Krantz and Kifferson, 2000). Polluted water can be toxic to human and other living organisms. Biologically contaminated water is water that contains micro organisms such as bacteria or viruses that can lead to infections. Toxic water contains chemical contamination from pesticide run-offs, mine tailings and industrial effluents. Boiling, filtering or chemically treating water can remove or kill micro organisms but will not, remove chemical toxins. (Tyagi. and Mehra, 1992).

Water pollution can be categorized into point and non point source. The non point source, which delivers pollutants indirectly through environmental changes, e .g. fertilizer from a field carried into a stream by rain in the form of run off which in turn affects aquatic life, while the point source is when harmful substances are emitted directly into water at given specific points.

The non point source is difficult to control and accounts for the majority of contaminants in rivers and lakes where there are no storm water treatments.

1.3.2 Sources and Effects of Water Pollution

1.3.2.1 Industrial pollution

Many industrial wastes discharged into water are mixtures of chemicals which are difficult to treat. Some wastes are so toxic that they need to be strictly controlled, making them an expensive problem to deal with. Examples of such pollutants include cyanide, zinc, lead, copper, cadmium and mercury. These substances may enter the water in such high concentrations that fish and other animals are killed instantly. Sometimes the pollutants may enter the food chain and accumulate until they reach toxic levels, eventually killing birds, fish and mammals and humans inclusive.

1.3.2.2 Thermal Pollution

Industries use water for cooling processes, sometimes discharging large quantities of hot water back into rivers. This raises the temperature of water lowering the level of dissolved oxygen, upsetting ecosystem balance in the water and increasing evaporation rates.

1.3.2.3 Agricultural Pollution

This includes sediments, pesticides sprayed on crops, fertilizers, plant and animal wastes which get into the river through run off from agricultural lands. (Mbui, 2007).This kind of pollution will lead to an increase of BOD for the decomposition of organic wastes, eutrophication when waterways are rich in nutrients causing uncontrolled growth of macrophytes and algal blooms in the water system.

1.3.2.4 Solid Waste Pollution

These include garbage, rubbish, sewage sludge, soil erosions and solid chemicals dump. These will contaminate water; the degree of contamination will depend on the pollutant disposed.

1.4 The Nairobi River Basin

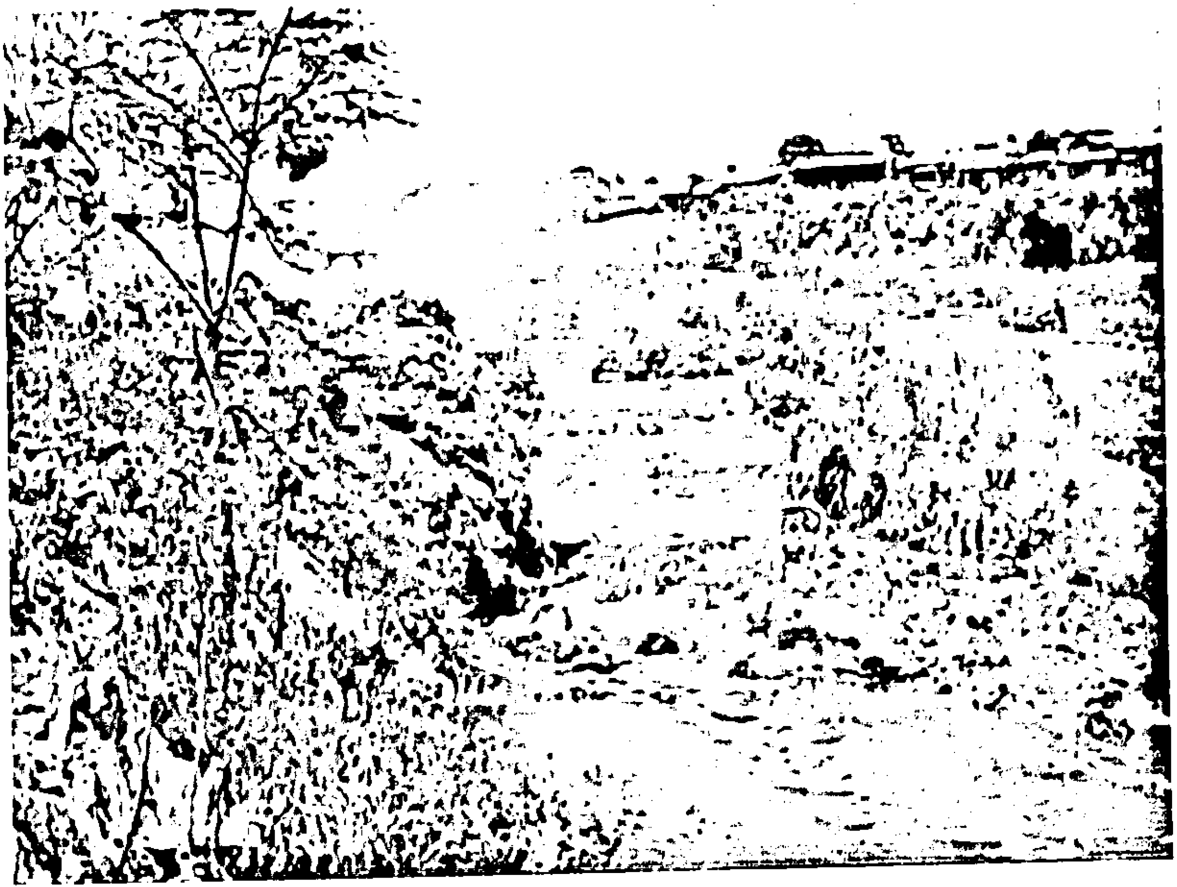
Nairobi River was meant to be a source of clean water for the residents of Nairobi. However, urbanization, high population growth in the city, poor agricultural practices along the Nairobi river basin, human waste from the informal settlement and waste from abattoirs have changed the once cool and clear water to its present polluted state. A solution is required to clean up this vital resource and monitor the various parameters leading to its pollution (NETWAS, 2005).

Nairobi River flows through the Kenyan capital Nairobi. It is the main river of the Nairobi river basin, a complex of parallel streams that join east of Nairobi, meet Athi River and eventually enters into the Indian Ocean. (NETWAS, 2005). The above named activities have put enormous pressure on the river causing serious environmental problems which in turn have significant economic implications.

The polluted river is harnessed for irrigation, its waters used for both livestock and domestic purposes. This may have led to spread of water-borne diseases in riparian communities downstream, loss of biodiversity and reduced availability and access to safe water.

All these impacts affect human health and productivity and challenge Kenya's ability to reach targets under the Millennium Development Goals 7 (Ensure environmental sustainability) and 1 (Eradicate extreme hunger and poverty).

Below is a picture showing part of Nairobi River chocking with trash, garbage and human waste from the slums. This scenario is experienced both here and downstream.



Source: *UNEP, 2009*

Figure 1: Trash and garbage wash down in the Nairobi River

1.4 Problem Statement

Nairobi River is polluted because of the various activities taking place along the river. These range from effluent discharge from industries and the 'jua kali' sector, agriculture, construction, domestic discharge from the informal settlements and burning of solid wastes. All these impact negatively on the quality of water. The river water is coloured, turbid, has odour and is not fit for human consumption, yet farmers along the river water the vegetables with this polluted water.

The activities along the river introduce heavy metals, nutrients, oil and grease as some of the pollutants of concern. With time, these pollutants accumulate in the ecosystem changing the natural water balance and polluting the water, sediment and biota. This creates environmental problems that affect human and aquatic life.

There is not enough information on levels of heavy metals in the Nairobi River. Analysis of studies carried out between 1969 and 2004 is scanty and unreliable. Choice of metals analysed and frequency of sampling was haphazard leading to serious gaps and inadequacy in interpretation of their status. Documented data from the Nairobi River Basin Programme: Phase III indicated that no studies of arsenic, oil and grease were carried out on the Nairobi River for the last 35 years.

To safeguard human health and the environment, it is necessary to understand the sources and quantities of various pollutants in the Nairobi River. This study was conducted to establish the concentrations of oil, grease and heavy metals namely: cadmium (Cd), chromium (Cr) and lead (Pb) in the river. The study also investigated a process of reducing the levels of the toxic heavy metals to maintain safe limits, so that water quality and biological activities in the river are not disturbed.

1.5 Objectives

The main objective of the study was to determine the physico-chemical characteristics of the Nairobi River water, determine its level of pollution and evaluate the effectiveness of ground fish bones as a tool for cleaning up river water polluted with heavy metals, then make recommendations on how to remove or significantly reduce pollutants, so as to restore Nairobi River's ecosystem with clean water.

The following specific objectives were targetted:

1. To determine the physico-chemical characteristics of water at four sampling points (Ondiri Swamp, Museum Hill Bridge, Race Course Bridge and Outer Ring Road Bridge) along Nairobi River. Parameters measured were pH, Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD), temperature, conductivity, Total Suspended Solids (TSS), Total Dissolved Solids (TDS) and alkalinity.
2. To investigate the presence of heavy metals (Pb, Cd, Cr,), inorganic anions (PO_4^{3-}, Cl^-) and organic compounds (grease and oil) in water.
3. To compare concentrations of pollutants found with other given standards (WHO, EU and KEBS).
4. To generate data that may be used to inform policy and other stakeholders to improve water quality and quantity.
5. To investigate the effectiveness of fish bones in heavy metal remediation.

1.6 Justification

Previous reports have not generated reliable data. This study seeks to generate reliable quality data through approved methodology, that can be used to make policy decisions.

CHAPTER TWO

LITERATURE REVIEW

2.1 Nairobi City

Nairobi is the Capital and largest city of Kenya. The City and the surrounding areas make up Nairobi province. The name 'Nairobi' comes from the Masaai word, which means 'the place of cool waters'. However, it is popularly known as the 'green city in the sun'. (pulseafrica.com, 2008). The city is located 140 km south of the equator and 500 km west from the Indian Ocean coast. The city is at latitude 1^0 17'S and longitude of 36^0 49'E. The City lies on the Nairobi River and has an elevation of 1661 m. (5450 ft.) above sea level. It is the most populous city in East Africa with an estimated urban population of between 3 and 4 million in an estimated area of 684 square kilometres. It is the fourth largest city in Africa.

Nairobi is adjacent to the eastern edge of the Rift Valley, minor earthquakes and tremors occasionally occur. The Ngong hills, located to the west of the city, are the most prominent geographical feature of Nairobi area. Mt Kenya is situated north of Nairobi and Mt. Kilimanjaro is towards the south east. Both Mountains are visible from Nairobi on a clear day. The Nairobi River and its tributaries traverse through the Nairobi province (Perspectivetravel.com, 2008).

Nairobi enjoys a fairly moderate climate. The high altitude counts for some chilly evenings, especially in the June/July season when the temperature can drop to 10^0C (50^0F). The sunniest and warmest parts of the year are from December to March, when temperatures average the mid twenties during the day. The mean maximum temperature for this period is 24^0C (75^0F). There are two rainy seasons, but rainfall can be moderate. As Nairobi is situated close to the equator, the difference in temperatures between the seasons is minimal.

2.2 History of Nairobi

Nairobi was originally a place where the Maasai people lived and watered their cattle. With time, Nairobi grew into an urban centre. It became the capital of Kenya in 1905 and a municipality with corporate rites in 1919. After independence in 1963, the city boundaries were extended to Dagoretti, the Nairobi national park, Jomo Kenyatta International Airport and a large area of grassland (Mbui, 2007). In 1972, United Nations Environmental Program (UNEP) was established with its headquarters in Nairobi and in 1976 United Nations Centre for Human Settlement, UNCHS (Habitat) also had its headquarters stationed in Nairobi. The city grew into a modern centre for tourism and diplomacy.

As the city grew, the urban population increased outstripping the available physical and natural resources. The city could no longer provide enough shelter, services and facilities. Several factors compromise the city's water quality, ranging from natural phenomena such as high fluoride content in groundwater, to anthropogenic factors such as poor waste water treatment and environmental degradation both within the city and the surrounding countryside (UNEP, 2009).

2.3 Nairobi Water Supply

The city obtains its water from Ruiru, Kikuyu springs (from Athi River), Sasumua, Chania, Thika and Ndakaini dams (from Tana River catchments). These dams are all on rivers emanating from the Aberdare Forest, one of Kenya's five 'water towers'. The water is treated in three plants Sasumua, Kabete and Ngethu. The supply is managed by the Nairobi Water and Sewerage Company – a subsidiary company of the City Council of Nairobi.

2.4 Nairobi River Basin

The Nairobi river basin consists of three major rivers Nairobi, Mathare and Ngong as indicated in figure 2 below. Previous studies indicate that all the three rivers are highly polluted making the water unfit for human consumption. (Ohayo and Wandiga, 1996)

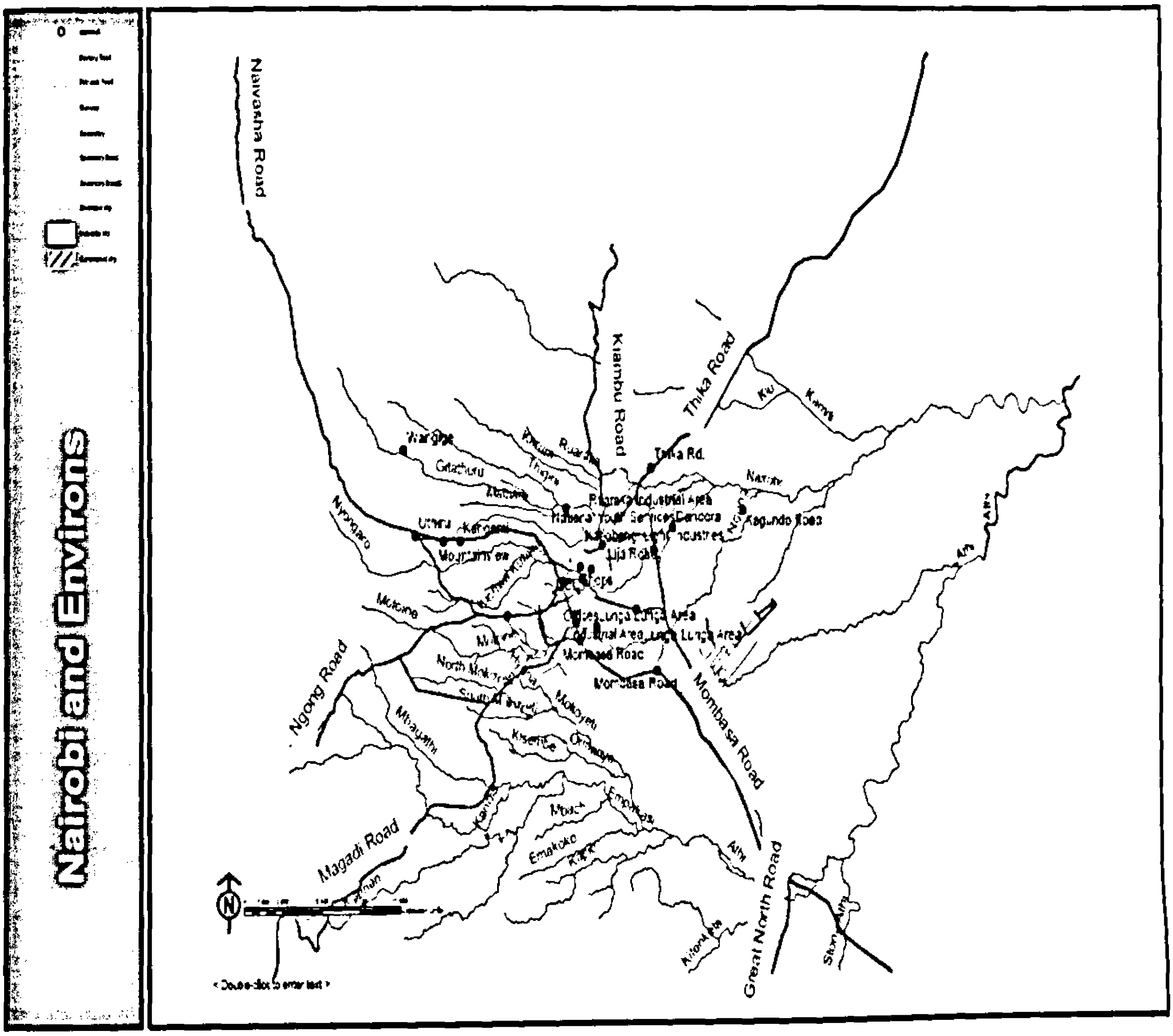


Figure 2.0: Map of Nairobi River Basin

A study on existing water quality assessment of Nairobi Rivers (Wandiga *et al*, 2006) reported a general pollutant concentration increase downstream with intermittent peaks midstream. In general, the river profiles pollution pattern reflected anthropogenic activities that lie along the length as the rivers meander across the city.

The study also revealed that Nairobi River had the highest number of sampling points and parameters studied. These were classified into six categories i.e. physico-chemical, chemical, organics, pesticides, microbial and macro invertebrates. The river had scanty data of most physico-chemical parameters. The following observations were noted (Wandiga et al, 2006):

a) Biological oxygen demand (BOD) was found to be very high even at the river source (Ondiri swamp 43 mg/l). This clearly indicated that water was polluted with a lot of organic matter. The levels were well above allowable levels by EU standards. 3-6 mg/l for fisheries and aquatic life and 20 mg/l for industrial discharge.

b) The water temperature along the Nairobi River was reported to be increasing steadily. This was attributed to temperature changes from relatively cool Ondiri swamp to generally hot Mwiki area, and also hot water discharge into the river along the profile.

c) Total dissolved solids (TDS) were found to increase down the river in general, but the level of amounts found were below the WHO drinking water of 1000mg/l.

d) Conductivity data were taken from 2 sampling points. Chiromo - 295µS/cm and Museum - 357µS/cm. The high conductivity values may have emanated from fertilizers or a high concentration of soluble salts.

e) The pH of the water was found to be within the 6.5 – 8.5 which is within EU recommended levels.

f) The flow rate was found to be slow, indicating that resident time of most pollutants at any particular point is high.

g) From chemical parameters considered, high levels of phosphate, sulphate and nitrate ions were found, which may have originated from fertilizer run offs and discharges of detergents that are made of phosphates. The ions contribute to algal blooms in water systems. The sediments had an accumulation of heavy metals i.e. Cd, Cr, Fe and Cu, which originated from the informal 'jua kali' sector. The relatively high concentration of Fe may have come from the corrosion of iron sheets and metal works from the slum settlements.

h) Microbial contamination across the river profile showed a general increase.

2.5 Trace Metals

Trace metals occur in extremely small quantities. They are present in animal cells, plant cells and tissue. They are a necessary part of good nutrition, although they can be toxic if ingested in excess quantities. Trace metals include Chromium, Cobalt, Copper, Iron, Manganese, Magnesium, Molybdenum, Selenium, Zinc and other elements that occur in very small amounts (1 to 10 ppm) (Business Dictionary.com, 2009).

The trace metals are further divided into essential and non essential elements. The essential metals maintain the metabolism of the human body and include heavy metals like zinc, copper, and selenium. However, at higher concentrations they can also be toxic.

Heavy metals are dangerous because they tend to bioaccumulate. Bioaccumulation is the increase in concentration of a chemical in a biological organism over time, compared to the chemical's concentration in the environment (Emel, 2009). Heavy metals can enter a water supply system through industrial and consumer waste, or even acid rain breaking down soils and releasing heavy metals into streams, lakes, rivers and groundwater. Non essential metals are not required by living systems and include metals like chromium, cadmium, lead, mercury and arsenic among others.

Human vitamin pills and plant fertilizers both contain trace metals as additional sources for trace metals. Studies carried out on Nairobi River by Budambula, and Mwachiro, (2003); reported the following concentration levels of heavy metals in the Nairobi River; (Kikuyu) 7500 µg/l (Lead), 850 µg/l (Chromium) and 25 µg/l (Cadmium), the concentrations of cadmium found were below the critical level by WHO and KEBS but not for chromium and lead. While Okoth and Otieno (2001) reported (150 µg/l) levels of lead at Chiromo, levels found were below the detectable WHO limits.

2.6 Effects of Heavy Metals on Human Health and the Environment

2.6.1 Cadmium

It is a natural element in the earth's crust. It does not have a definite taste or odour. In industries it is used to make Ni-Cd batteries for mobile phones, plastics and electroplating filaments for incandescent lights. The powder is used in dentistry as an amalgam in the ratio (1:4 Cd:Hg).

Cadmium particles are introduced into the environment by mining, industry and burning of coal and household wastes. Cadmium particles in air travel long distances before falling to the ground or water. Fish, plants and animals take up cadmium from the environment. Cadmium stays in the body for a long time and can bioaccumulate for many years of exposure, although it is eventually excreted.

Sources of contamination include breathing contaminated workplace air, e.g. battery manufacturing, metal soldering/welding, eating contaminated foods like kidney, meats, liver and breathing cadmium in cigarette smoke. In humans, long term exposure is associated with renal dysfunction. High exposure may lead to obstructive lung disease and has been liked to lung cancer. Cadmium may also produce bone effects (osteoporosis) in animals and humans (Lenntech, 2009).

The average daily intake for humans is estimated at 0.15 µg from air and 1 µg from water. While studies carried out indicate smoking 20 cigarettes can lead to inhalation of around 2-4 µg of cadmium, however levels may vary widely (Lenntech, 2009).

Studies carried out by Prof. Manfred Anke and co-workers in 1977 at Jena University, Germany, indicated the essentiality of cadmium to goats. He carried out several experiments.

In Cd-deficiency experiments (< 15μg Cd/kg of feed dry matter) carried out on growing, pregnant and lactating goats. Results of the experiment showed a significant effect on rate of abortion on first insemination, but no effect on feed intake and weight gain. The intrauterine Cd-depleted kids were found to be phlegmatic, moved little, were too lazy to eat or drink and had problems holding their heads erect. In other words, the kids showed symptoms of impaired mobility and muscular weakness, some even died. Those given Cd supplementation (65 μg Cd/kg of feed dry matter) did not suffer from Cd-deficiency symptoms. In man when Cd is considered essential the normal intake is set at >3μg/day. (Anke *et al*, 1977).

Previous studies carried out on cadmium indicate that it was studied only once in 2002 according to the Nairobi River Basin Programme – phase III. The Cd levels found were relatively high; a concentration of 0.14 mg/L was recorded at Naivasha Road Bridge on Nairobi River.

2.6.2 Chromium

Chromium compounds and chromium (III) are not considered health hazards, but Chromium (VI) compounds are toxic; they cause lung cancer to workers working in the paint, pigment and tannery industry. It is irritating to eyes, skin and mucous membranes. Chromium (VI) is carcinogenic. Though toxic, it is still widely used for aerospace and automotive refinishing applications.

Chromium often accumulates in aquatic life, leading to the danger of eating fish that may have been exposed to high levels of chromium. World Health Organisation recommended maximum allowable concentration in drinking water for Cr (VI) is 0.05 mg/L. According to information from the Nairobi River Basin Programme: phase III chromium was only studied once in 2002.

At the time, levels found indicated that the highest concentration of chromium was recorded at Mwiki sampling point (0.015 mg/L) (Lenntech, 2009).

2.6.3 Lead

Lead can be found in all parts of our environment. Most of it comes from human activities like mining, manufacturing and burning fossil fuels. Lead poisoning is one of the most common occupational diseases. Lead once absorbed is distributed to the kidney, liver and stored in the bones. When the bones can no longer take in lead, it is slowly released into the bloodstream, poisoning the victim. Lead affects red blood cells by causing anaemia, damages the liver, kidney, heart and the male reproductive system. It is dangerous to the young and unborn children; it causes premature births, smaller babies, causes a decrease in the mental ability of an infant, cause behavioural problems and stunted growth.

Lead from the soil tends to concentrate in root vegetables (onion) and leafy green vegetables (spinach) (Howard, 2002). In the United Kingdom, it is estimated that the average daily lead intake for adults is 1.6 μg from air, 20 μg from drinking water and 28 μg from food (Lenntech, 2009). However, dietary lead exposure is well below the weekly intake recommended by WHO (25 μg/kg), and UN Food and Agricultural Organisation (0.4 - 0.5 mg). Previous studies indicate that lead was studied only twice during the period 1969 to 2004. It was only analysed at three sampling points in the Nairobi River with the highest concentration of 0.16 mg/L recorded at Naivasha Bridge.

2.7 Oil and Grease

Their source is vegetable and natural oils and hydrocarbons of petroleum origin. Sediments, biota and decaying life forms are often high in natural oils which make up part of the oil and grease measure (Irwin *et al*, 1997). If oil and grease is present in excessive amounts, it may interfere with aerobic and anaerobic biological process and may lead to decreased wastewater treatment efficiency.

Oil pollution is a major contribution to the deterioration of marine water quality. Shipping activities involving tanker and other vessels plying the waters are a source of petroleum hydrocarbons in the waters. Land based industrial and urban sources discharge water that contributes to the overall pollution load in the waters (Pawlak *et al*, 2008). No studies have been reported on concentration of oil and grease in the Nairobi River.

2.7.1 Effects of Oil and Grease on Human Health and the Environment

When oil and grease find their way into the soil or water due to unintentional leakage, they pose risks to both human health and the environment because of poor biodegradation rate and presence of hazardous substances. They also have serious negative environmental and socio–economic impacts. Negative socio-economic impacts would include decreased tourism and closure of recreational and fishing areas. Wildlife is affected in two main ways, toxic contamination (inhalation or ingestion) or by physical contact. Seabirds that spend much of their time near water bodies are more vulnerable to oil spills and suffer from hypothermia because the oil destroys the structure of their protective layer of feathers. This may lead to drowning due to increased weight when the oil covers their bodies, poisoning them or loss of flight which could affect their reproductive capacity. Fish absorb oil in water through their gills and accumulate it within the liver, stomach and gall bladder. They are able to cleanse themselves within weeks of exposure. However, if the fish accumulates oil that is contaminated with Polycyclic Aromatic Hydrocarbons (PAHs) in their edible tissues, they pose a health risk to consumers since they are carcinogenic. trees like mangroves and plants in water systems do not survive in water bodies contaminated with oil and grease, because the oil coats their roots making it impossible for them to take up water and other nutrients required for their growth.

2.8 Water Quality Parameters

2.8.1 Dissolved Oxygen

This is the amount of oxygen dissolved in water; 4 to 6 mg/L (WHO and EU, 2008) is considered the optimum amount for good quality water. This amount maintains aquatic life in water. A lower dissolved oxygen value indicates that the water is polluted. Monitoring the amount of dissolved oxygen provides information on the extent of pollution in the river. Oxygen demanding wastes deplete oxygen from water through aerobic reaction. These wastes include sewage, industrial wastes from food processing plants, effluent from the slaughter houses and meat packing plants. At times when dissolved oxygen is depleted from the water completely, the oxygen demanding wastes will derive oxygen from compounds like phosphates, nitrates and sulphates. This will result in the formation of substances with foul odors (phosphine, amines and hydrogen sulphide). This type of reaction is termed as anaerobic (Mbui, 2007). Therefore, to estimate the amount of pollutants in a water body, biochemical oxygen demand (BOD) and chemical oxygen demand (COD) measurements are used. Studies carried out by Dulo (2001) reported levels of 32 mg/l of dissolved oxygen in Nairobi River. The levels are well above WHO and EU allowable standards of 5 mg/l, indicating that Nairobi River was not polluted.

2.8.2 Biochemical Oxygen Demand (BOD)

Biochemical oxygen demand (BOD) is a chemical procedure that is used to estimate the relative oxygen requirements of waste waters, effluents and polluted waters (Bartram and Ballace, (1996).A sample of water is incubated at 25^0 C for five days. The amount of oxygen consumed is determined chemically before and after incubation. A BOD of 0.75 -1.5 ppm (WHO and EU, 2008) will indicate that the quality of water is good. Therefore BOD is a water quality indicator. Analytical results reported by Dulo (2001) indicate concentration levels of 182.5 mg/l of BOD. This indicates that water quality is not good.

2.8.3 Chemical Oxygen Demand (COD)

Chemical Oxygen Demand is a measure of the concentration of substances in a water supply that can get attacked by a strong oxidizing agent in standardized analysis. COD will measure the amounts of organic compounds in water. It is expressed in milligrams per litre (mg/l), which indicates the mass of oxygen consumed. COD gives an indication of the toxicity of pollutants as well as biologically resistant organic substances in water. It should not exceed 50 mg/l (WHO, 2008). According to the Nairobi River Basin Programme COD is one of the least studied parameters of the Nairobi River. However, according to studies carried out by Dulo (2001) concentration levels of COD were found to be 49.5 mg/L.

2.8.4 Total Suspended Solids (TSS) and Turbidity

Total Suspended Solids is a non-point source pollution. It is a major, largely uncontrolled cause of water degradation. Major contributor of TSS pollution include storm water runoff, agricultural activity near the river, excess sediment from river bank erosion and excess nutrients from fertilizer use.

Suspended solids interfere with biological primary production (photosynthesis) for aquatic plants. TSS will increase turbidity of the water and prevent growth of organisms that require light energy. Hence levels of nutrients in water systems are likely to rise. TSS discharge standards for waters should not exceed 30 mg/L (EU, 2008). Studies carried out (Dulo, 2001) in the Nairobi River indicated concentration levels of 116.43 mg/L. This exceeded allowable limits of <30 mg/L, indicating that the water was polluted.

2.8.5 Total Dissolved Solids (TDS)

TDS measures compounds which are in their ionic form in the water. They are charged particles. When compounds undergo dissolution the concentration of ions in water will increase as well as conductivity of water. TDS discharge standards should not exceed 1200 mg/L (WHO, 2008).

TDS analysis carried out on the Nairobi River indicated that levels were very high. Studies carried out by Gaciri and Ngecu (1998) found levels that ranged from 105-390 mg/L with a mean of 205 mg/L.

2.8.6 *Phosphorus*

Phosphorus occurs in natural waters almost solely as phosphates (Greenberg *et al*, 1992). These phosphates occur in solution, in sediment, biological sludge and in bodies of aquatic organisms. The phosphates arise from a variety of sources. Condensed phosphates that are added to water supplies during treatment, or when water is used for laundering, Orthophosphates which are applied to agricultural land as fertilizer and Organic phosphates which are formed by biological processes. The presence of phosphate compounds stimulates algal productivity and enhances eutrophication processes (UNEP, UNESCO & WHO, 1996). In the analysis of phosphorus, one can measure reactive phosphorus by colorimetric method and total phosphorus which measures all forms of phosphorus present in a sample, regardless of form is initially digested then analysed by colorimetric procedure. Okoth and Otieno (2001), reported high levels of phosphates along the Nairobi River ranging from 2000 to 3340 μg/l.

2.8.7 *Chloride*

The concentration of chloride varies from sample to sample. It has no adverse effect on health, but it gives bad taste to drinking water. A salty taste in water depends on the ions with which chlorides are associated, with sodium ions the taste is detectable at about 250 mg/L, but with calcium or magnesium ions the taste may be undetectable at 1000 mg/L (Bartram and Ballance, 1996). High chloride content has a corrosive effect on metal pipes and structures and is harmful to most plants. The amount of chloride ions in water can be determined either by potentiometric titration, Mohr's or Volhard's method (Khopkar, 1995). The three methods are excellent for the analysis of dissolved chloride.

2.8.8 Alkalinity

The alkalinity of water is its capacity to neutralise acid i.e. buffering capacity. A buffer is a solution to which an acid can be added without changing the concentration of hydrogen ions appreciably. It protects a water body from fluctuations in pH. The amount of a strong acid needed to neutralise the alkalinity is called total alkalinity, and is expressed in mg/L as calcium carbonate ($CaCO_3$). The alkalinity of some waters is due only to the bicarbonates of calcium and magnesium. The pH of such water does not exceed 8.3 and its total alkalinity is identical with its bicarbonate alkalinity. Water having a pH above 8.3 contains carbonates and possibly hydroxides in addition to bicarbonates (UNEP & WHO, 1996).

2.8.9 Conductivity

The ability of water to conduct an electric current is called conductivity. The conductance is the measure of concentration of mineral constituents present in water. Conductivity is measured in microsiemens per centimetre ($\mu S\ cm^{-1}$). It relates to TDS, high TDS relates to high conductivity. The measurement should be made in the field because conductivity changes with storage time (UNEP &WHO, 1996).

2.8.9.1 pH

The pH of a river indicates how acidic or basic the water is on a scale from 0 to 14. On this scale, 7 is neutral, 6 to 0 is acid with 0 being the most acidic. 8 to 14 is base with 14 being the most basic. pH of unpolluted waters will depend on the local geology and physical conditions. pH of unpolluted water is around 6 to 8.5. A pH of 5.5 to 8.2 is generally thought to be the healthiest for diverse aquatic life, especially fish, but the optimum pH for a species depends on temperature, dissolved oxygen. and alkalinity of the water.

The pH of the river depends on the waste added to the water. A sudden change in pH causes some dissolved materials to become toxic to aquatic life. If the pH suddenly becomes very acidic or very alkaline, this could be due to industrial waste. If there is an increase in pH while at the same time there is a decrease in D.O. and an increase in ammonia, nitrates and phosphates, then a sewerage discharge is suspected (UNEP & WHO, 1996).

2.8.9.3 Colour

Colour occurs due to the presence of coloured organic matter e.g. humic substances, metal compounds like iron or manganese or highly coloured industrial wastes. Drinking water should be colourless. It was important to note for the presence or absence of colour at the time of sampling.

2.8.9.4 Taste and Odour

Odour is caused by presence of organic substances, biological activity or industrial pollution. When water tastes it is due to presence of inorganic compounds of metals like Mg, Ca, Na, Cu, Fe and Zn (UNEP &WHO, 1996).

2.9 Water Quality Parameters and Standards.

Ensuring drinking water safety is a challenge in every part of the world, from water piped into homes, to rural wells and water provided to refugee camps in an emergency. Contamination of drinking water is too often detected only after a health crisis, when people have fallen ill or died as a result of drinking unsafe water. The World Health Organization (WHO), European Union (EU), Kenya Bureau of Standards (KEBS) and many other existing standards have released permissible limits for domestic water supply.

The Environmental Management and Coordination Act (EMCA, 2004) has released quality standards for sources of domestic water and effluent discharge into the environment. When compared with quality standards quoted by WHO and EU, some heavy metals (mercury, cadmium, chromium, zinc, arsenic and nickel) and some anions (bromide) are omitted, possibly because not enough research has been done on the water systems to know exactly their level of pollution.

However, with increase in number of cottage industries in the city of Nairobi, EMCA needs to indicate the allowable concentrations of heavy metal ions.

Potable water is intended for human consumption and is stored in sealed bottles or other containers with no added ingredients. In various parts of the world, water guidelines control water quality. Some of the guidelines that will be considered in this study will include: WHO, EU and KEBS

The allowable levels of various parameters for potable water are presented in the following two tables.

Table 2.0: Physical Parameters

Parameters	**(WHO) Guidelines**	**(EU) Guidelines**	**(KEBS) Guidelines**
Colour	Colourless	Colourless	15 true colour units
Odour	Odourless	Odourless	Odourless
pH	6-8.5	6-8.5	6.5-8.5
Conductance	250 μS/cm	250 μS/cm	-
Dissolved oxygen	5 mg/l	5 mg/l	-
Turbidity	Acceptable to customers	Acceptable to customers	5 max. (NTU)

Sources: (KEBS, 2001; WHO, 2008; EU, 2008).

Table 2.1: Inorganic Parameters

Parameters	**(WHO) Standards mg/l**	**(EU)Standards mg/l**	**(KEBS) Standards mg/l**
Chloride	5	250	250
Fluoride	1.5	1.5	0.13
Nitrate	50	50	1.2
Cadmium	0.05	0.05	Not mentioned
Chromium	0.05	0.05	Not mentioned
Zinc	3	0.1-5.0	5
Mercury	0.001	0.001	Not mentioned
Iron	Not mentioned	<0.05	0.3
Arsenic	0.01	0.01	Not mentioned
Manganese	<0.05	<0.05	0.1
Magnesium	Not mentioned	Not mentioned	100
Carbonates	Not mentioned	Not mentioned	Nil
Sulphates	Not mentioned	Not mentioned	400
Sodium	Not mentioned	Not mentioned	200
Potassium	Not mentioned	Not mentioned	6.4
Lead	0.05	0.05	nil

Source (KEBS, 2001; WHO, 2008; EU, 2008)

Worldwide scientists and groups are seeking ways of cleaning up polluted waterways. Environmental clean up is not cheap, the costs involved are prohibitive. Clean up needs concerted effort of all those sharing clean up costs and the goodwill of the government.

The Rhine River, Europe's longest river became so polluted that it was sometimes referred to as 'Europe's sewer'. Approximately 60 million people living close to its banks depended on the river for their drinking water (Groot, 2006).

Companies which provided drinking water faced enormous costs in treating the water to make it fit for human consumption. Their frustration resulted in the establishment of the Reinwater Foundation that fought to get the river cleaned up. It took the concerted effort of five European countries through which the Rhine flows to clean up the river. The governments set up a string of purification plants along the river and successfully detoxified the river.

Africa is a continent which has some of the poorest nations of the worlds, over 300 million people have no access to safe water and one third of the deaths are caused directly or indirectly by contaminated water (UNEP, 1999).

The state of water quality has deteriorated to unacceptable levels, through eutrophication, existence of heavy metal pollutants, persistent organic pollutants and acidification processes, even contaminating the fragile underground aquifers (Gash *et al*, 2001).

In some districts in Kenya, Uganda, Tanzania and South Africa, fluoride levels in underground water ranges up to 25 mg /l far above the 1.5 mg/l limit value for Guidelines for Drinking Water Quality (GDWQ). In these countries, the populations suffer from dental and severe skeletal fluorosis (Marrakech, 2004).

Clear political commitment and leadership at the highest level is required to ensure that adequate intra-governmental interaction happens (UNEP, 2008). The government needs to acquire the right technology to deal with high levels of pollution in water systems and be more forceful in dealing with those who pollute the Nairobi River.

2.9.1 Water treatment

2.9.1.1 Water Purification

Water purification seeks to convert polluted water into water that is acceptable for drinking, recreation and some other purpose. Techniques such as filtration and exposure to chemicals that kill micro organisms in the water are a common means of purification. The use of chlorination remain the most widely used purification option, other approaches use ultraviolet radiation, filters of extremely small pore size that can exclude viruses and use of ozone (Abel, 1996). Depending on the situation and the intended use, a combination of these techniques can be used.

2.9.1.2 *Solar Water Disinfection*

This is a method of disinfecting water using only sunlight and transparent plastic PET bottles only. The bottle is exposed to sunlight for six hours. UV radiation of the sun will kill diarrhoea generating pathogens in polluted drinking water (Ahuja, 2009).

Solar radiation has 3 effects:

- UV-A – interferes directly with the metabolism and destroys cell structures of bacteria.
- UV-A (wavelength 320-400nm) reacts with oxygen dissolved in water to produce oxygen free radical and hydrogen peroxide which damage pathogens.
- The infra red radiation heats the water disinfecting it.

In Kibera, people put their bottles on the iron roofs; this will ensure that their drinking water is free from micro-organisms.

2.9.1.3 Toxic Metal Removal

Several methods have been devised to remove heavy metal ions from water systems. According to studies (Chikhi et al, 2006) heavy metals are removed using a suitable complexing agent like EDTA which chelates the cations and prevents the complex formed from passing through the semi-permeable membrane, hence increasing metal retention. The process is termed ultrafiltration. On a large scale the method would be expensive in trying to remediate a large water body.

Charcoal is obtained by burning wood, coconut husks, animal bones and carbon-containing materials. The charcoal is activated by two processes: Chemical activation – where acid is mixed with source material in order to cauterize the fine pores and Steam activation – which is achieved with steam and it develops a myriad pores with an enormous surface area. The carbonized material is mixed with gases at high temperature to activate it. Activated carbon is used in metal extraction, water purification, air filters in gas masks and many other applications (Warren et al, 1993).

tudies indicate that bone black may be used as a filtration material to remove heavy metal contamination from both drinking water supplies and from waste water. It was found that bone black articles can reduce lead concentration initially present in the range of 200-300 ppm to as low as 1 ppm r less, or Cadmium (Cd) concentration of around 50 ppm have been reduced to 0.1ppm. Bone black is eadily available and inexpensive.

According to experimental studies (Dahbi *et al*, 2002) the ability of bone charcoal to remove Cr (III) from aqueous solutions by adsorption was investigated. 3g of bone charcoal was added to water ontaining Cr (III) and stirred for 30 minutes. The bone charcoal was sieved out. The amount of Cr (III) n the water was greatly reduced. When bone charcoal was treated with NaOH and HCl it provided an nhancement of Cr (III) retention.

Other studies carried out to remove trace metals from water systems include the cassava tuber bark waste (Horsfall *et al*, 2003). It was able to remove on average 45.61 mg/g Cd^{2+}, 54.21 mg/g Cu^{2+} and 20.95 mg/g Zn^{2+} from a solution containing 100 mg/L Cd^{2+}, Cu^{2+} and Zn^{2+}

2.9.1.4 Bioremediation

This is nature's way to a cleaner environment. It is a process that uses micro-organisms, fungi, green plants or their enzymes to return the natural environment to its original condition (Wikipedia, 2008).

2.9.1.5 Phytoremediation

This is a form of biotechnology where plants remove, degrade or stabilize complex environmental contaminants. These are heavy metals like mercury, zinc, cadmium, arsenic, tin and copper (AGBI-TECH INFOSOURCE, 1999). Plants like lettuce, parsley, dill and onion have been used to clean up sediments contaminated with heavy metals (Tokalioglu et al, 2006). The plants have microbes that live on their root system; they absorb, oxidise and store pollutants within their cells or break them down to less toxic form. The clean up exercise is green, clean, inexpensive but very slow.

Espinoza-Quinones *et al* (2005) performed experiments using several healthy acclimatized plants, the aquatic macrophytes *Salvinia sp.*was used to remove heavy metals from polluted river water in a pond. Experimental results indicated that the plant salvinia sp showed a promising potential for removal of metals from pond water.

2.9.1.6 Adsorption Process

Adsorption is the physical adherence of ions and molecules onto the surface of another molecule. Adsorption may be used to clean up polluted water. Adsorption mechanisms can be categorised as either physical adsorption (physisorption) or chemical adsorption (chemisorption) (Attahiru, 2003).

In physical adsorption, the molecules of the adsorbate are held by weak forces of attraction to the surface of the adsorbent. These are van der Waals forces. The heat of adsorption is 20 - 40 kJ/mol. If temperature is raised, the kinetic energy of the molecules increases and they leave the surface of the adsorbent. Therefore raising the temperature lowers the extent of adsorption

Chemical adsorption involves the formation of a chemical linkage between the adsorbed molecule and the surface of the adsorbent. This process is highly selective and only particular types of molecules are adsorbed by a solid in chemisorption.

The process depends on the chemical properties of the gas/ion and the adsorbent, and will be accompanied by high heat changes of 40 to 400kJ/mol. The process is not reversible and is an exothermic process.

2.9.1.7 Remediation using fish bones

The advantages of fish bones is that they contain little fluorine and almost no metals, they are highly porous with a large surface area for reactions, and they are an extremely good buffer especially for acidic waters that occur in acidic mine drainage.

Therefore most water will be buffered to normal pH range of between 6 and 8. This makes them ideal for use in treating and immobilising metals in soils, water and waste forms. They have been effectively used to reduce zinc, cadmium, lead, copper, nickel, uranium, barium, caesium, strontium, plutonium, thorium, most lanthanides and actinides in sediment, soils and water systems (Wikipedia, 2009). Fish bones are composed of phosphate compounds.

They provide phosphate ions that combine with metal ions in solution to form metal phosphate precipitate, at the same time buffering the pH of the water and adsorbing metals onto their own surfaces. The time period, over which the remediation occurs, depends on the water chemistry, total metal inventory and the amount of fish bone used in a particular situation.

Fish bone can be mixed with polluted sediment to study how effective they are as clean up agents. Alternatively, crushed fish bones can be packed in a column, and highly polluted water passed over it. The polluted water and the eluate can be analysed using Atomic Absorption Spectrometry (AAS) or X-Ray Fluorescence (XRF).

Experiments conducted by Jill Pasteur *et al* (2005), in which 1 g/L aqueous suspensions of fish bone were reacted with 10^{-4} M $Pb(NO_3)_2$ in a solution buffered at pH 6 and agitated on a rotary shaker. The solution when analysed for dissolved lead after 4 hours showed that concentration levels of lead had decreased to less than 5×10^{-8} M, and a fine white precipitate had formed in suspension.

Similar studies carried out by Darafsh *et al* (2008), on the application of fish scale as bio-indicator for heavy metal pollution, found considerable high concentration levels of lead (22.22 mg/g) adsorbed on scales of fish. These findings indicate that fish bone and scales can be used to remediate water systems polluted with heavy metals.

2.9.1.8 *How Fish Bones Clean Contaminated Water*

When water contaminated with toxic heavy metals is introduced into a column packed with ground fish bones, three processes take place, precipitation, filtration and adsorption (Moore and Edgewood, 2001). In precipitation, the fish bones release phosphate (PO_4^{3-}) ions in solution which react with metal ions to form insoluble metal phosphate as indicated in equation 1.

$M^{2+}_{(aq)} + PO_4^{3-}{}_{(aq)} \rightarrow M_3(PO_4)_2{}_{(s)}$ ....Equation 1

Filtration is carried out by the metal phosphate in that the precipitate is capable of selectively trapping and removing heavy metal contaminants while allowing water and other contaminants to pass through (Moore and Edgewood, 2001).

The metal phosphate plays another role in that it will slow down the flow of water in the column, increasing contact time between the water and fish bone, hence increasing rate of adsorption. When all the phosphate ions in solution have been precipitated, the metal ions are then adsorbed on the surface of the fish bone until equilibrium is set up between the adsorbed metal ions and the metal ions in solution. These reactions are indicated in equations 2 and 3. Mass of fish bone used has a finite number of adsorption sites, when all the available sites have been taken up by the metal ions, no more adsorption takes place.

$F\text{-}Ca_{(s)} + M^{2+}_{(aq)} \rightarrow F\text{-}M_{(s)} + Ca^{2+}_{(aq)}$ .... Equation 2
(Fish bone)

$M^{2+}_{(s)} \leftrightarrow M^{2+}_{(aq)}$ .... Equation 3

CHAPTER 3

INSTRUMENTATION

3.1 Analytical methods and instrumentation for heavy metal analysis

Several methods of analysis based on instruments exist for analysis of heavy metal in different matrices. These include X-Ray Fluorescence (XRF), Atomic Absorption Spectrometry (AAS), Atomic Emission Spectroscopy (AES) and Polarographic techniques. The adoption of any particular method depends on a number of factors, namely safety, cost, convenience, availability of the instrument, method sensitivity, detection limits, precision, accuracy and reliability. Based on the above factors the X-Ray Fluorescence and Atomic Absorption Spectrometry were selected to analyse the presence of toxic heavy metals in water and sediment, and to determine which instrument was more sensitive, precise and reliable. The choice of these two methods was based on their availability, relatively fast, safe to use, convenient for the analytical method studied and assisted to meet the specific objectives cited.

3.2 The general concept for Atomic Absorption Spectrophotometry

Every atom has a unique electronic structure with an orbital configuration designated as the 'ground state'. When energy of the right magnitude is applied to an atom, the energy will be absorbed and subsequently an outer electron will be promoted to a higher energy level. This state is unstable, so the electron will immediately return to normal lower energy level reverting the atom to its 'ground state'. In atomic spectroscopy, either the energy absorbed during the excitation process or the energy emitted in the decay process is measured. The wavelength of the light emitted is a unique property of each individual element.

In absorption spectrophotometry, the absorbance of each element analysed has a linear relationship with its concentration in the sample being analysed (Onyari, 1985).

3.2 Atomic Absorption Spectroscopy

This is one of the most widely used methods in analytical chemistry. It is used as a quantitative tool in the chemical laboratory. The AAS phenomenon is divided into two major processes:-

The production of free atoms from inorganic analytes in solution, and the absorption of radiation from an external source by the atoms as they move from ground state to excited state providing the analytical data. The AAS has been used to analyse over 70 elements (Mirikau, 1992). The more sophisticated AAS system has a microcomputer that enables the instrument to calculate the best analytical curves using up to 5 standards compute ratios, apply statistical techniques and present results in graphical or tabular form (Willard et al, 1986). The only liability of the AAS is the need for a different hollow cathode lamp for each element to be analysed.

3.3 Atomic Absorption Spectrophotometer (AAS)

The main components of the AAS comprise of Nebuliser system, Lamp system, Burner, Detectors and Read-out system.

3.3.1 Nebuliser system

The solution under analysis is aspirated into the Nebuliser converting it into vapour. The sample aerosol is then mixed with fuel and oxidant in the Nebuliser chamber before introduction into the flame. At this point, the metal ions are converted into gaseous atoms absorbing energy in the process. The magnitude of absorption is proportional to the concentration of metal atoms and hence concentration in the solution.

Nebulisation is governed by several factors like viscosity, surface tension and density of the sample solution, the flow rate of the nebuliser gas and aspirated solution as well as the velocity of the nebulizing gas. Changes in viscosity and surface tension can be avoided by preparing samples and standards similarly, and avoiding total acid or salt concentration greater than 0.5%.

3.3.2 Lamp system

The desired radiation is produced by hollow cathode lamps. The cathode of the lamp is made of the metal under analysis. The monochromator is used to select the desired spectral line to be used in the analysis.

3.3.3 Burner

The temperature used by the burner exceeds 2000 K. Extremely higher temperatures should be avoided to prevent the ionisation of metal atoms. A suitable flame is one that has a proper temperature and fuel/oxidant ratio to carry out the functions of the flame. Table 3.0 gives the temperatures for some common pre mixed flames.

Table 3.0: Temperatures of fuel/oxidant mixtures

Fuel	Oxidant	Temperature (K)
Acetylene	Air	2400
Hydrogen	Air	2318
Propane	Air	2198
Acetylene	Nitrous oxide	2800
Hydrogen	Nitrous oxide	2963
Propane	Nitrous Oxide	3000

Source: Willard et al, (1986)

The exact value depends on the fuel/oxidant ratio and is generally highest for a stoichiometric mixture. The optimum temperature depends on the excitation and ionisation potentials of the analyte. Table 3.0 shows that fuel/nitrous oxide produces a higher flame temperature than the fuel/air flame temperature. The hotter flame allows for the sensitive analysis of additional elements whose refractory oxides are not reduced to the atomic state in the fuel/air flame.

3.3.4 Detectors

They consist of photomultiplier tubes coupled with electronic circuitry to enable high speed detection limits and sensitivity. The detector read-out unit possesses high speed electronics that can track the signals and signal processing that allows measurement of rapid events.

3.3.5 Read-out systems

This is composed of digital read-out systems coupled with micro processors that allow for programming of various features which simplify certain procedures.

3.4 X-Ray Fluorescence

The fluorescent emission of x-rays provides one of the most potent tools available to the analyst for the identification and measurement of heavy elements in the presence of each other and other elements (Ewing, 1985). X-Ray fluorescence spectrometry is widely accepted as a highly versatile and potentially accurate method of elemental analysis (Jenkins *et al*, 1985).

With the development of the Energy Dispersive X-Ray Fluorescence Analysis (EDXRFA) there was simultaneous recording of the entire fluorescent energy spectrum.

This method has several advantages; It uses weak excitation sources such as radioisotopes, the sample specimen can be in any form i.e. solid, powder, liquid, slurry, etc, multi elemental analysis can be done, the use of prepared set of standard in evaluation of elemental concentrations is minimal, it has a high sensitivity and requires 10 seconds for analysis and it is non destructive.

The method however, fails with elements lighter than sodium. Determination of elements present in low concentration is also limited by matrix effect: the emitted radiation is greatly absorbed by the other elements of the specimen samples in which the main constituents are elements of high atomic weight. These elements will absorb a higher percentage of the radiation than would be absorbed by light elements.

3.5 X-Ray Fluorescence Analysis

In this method, a sample is irradiated by a primary beam of x-rays. The primary beam consists of photons with greater energy than the most energetic of the expected secondary x-rays to be emitted by the sample. The x-rays interact with the atoms in the sample, where each heavy element in the sample produces characteristic secondary radiation lines, which are used to identify the elements present in the sample. The flux of the secondary characteristic radiation of a particular element is proportional to the concentration of that element in the sample.

3.5.1 X-Ray Fluorescence Instrumentation

It consists of the x-ray excitation source and the x-ray spectrometer. The x-ray spectrometer is composed of the following; Solid state detector, silicon-lithium (Si (Li)) or hyper pure Germanium (HpGe) detector, Pre-amplifier, Amplifier and a Multichannel Analyser (MCA). A microcomputer with its input and output devises is connected to the spectrometer to assist in handling and analysis of spectral data.

A schematic representation of the XRFA unit and radioisotope excitation system is given in figures 3.1 and 3.2. The functions of the various components are provided in the subsequent subsections.

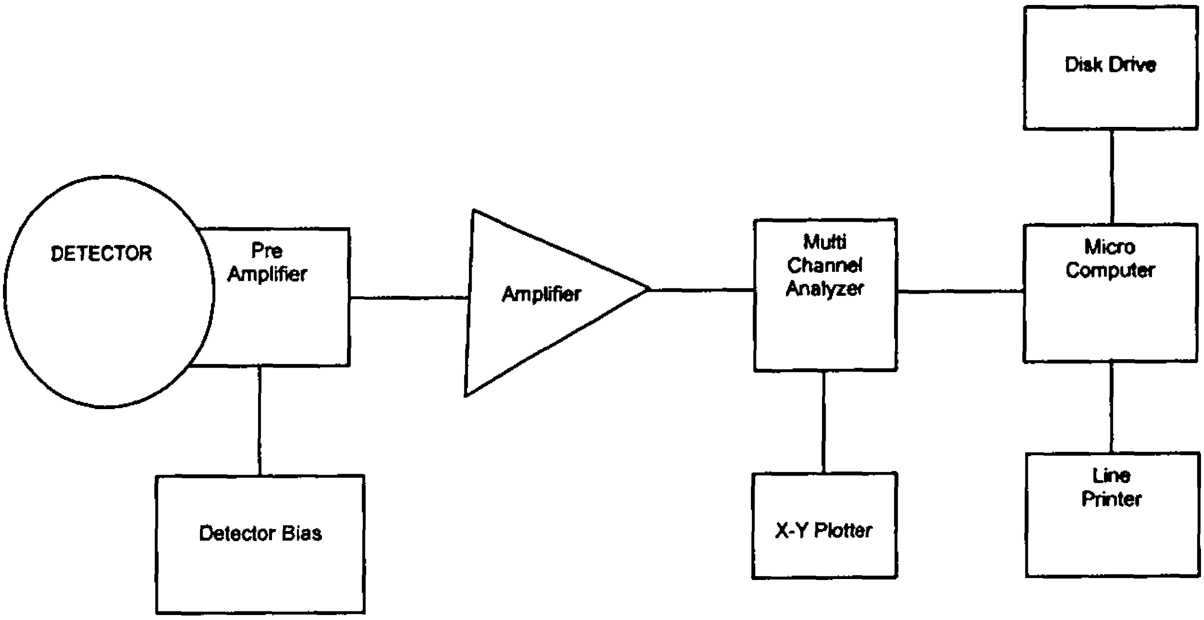


Figure 3.1 A representation of XRFA Unit (Kinyua, 1982)

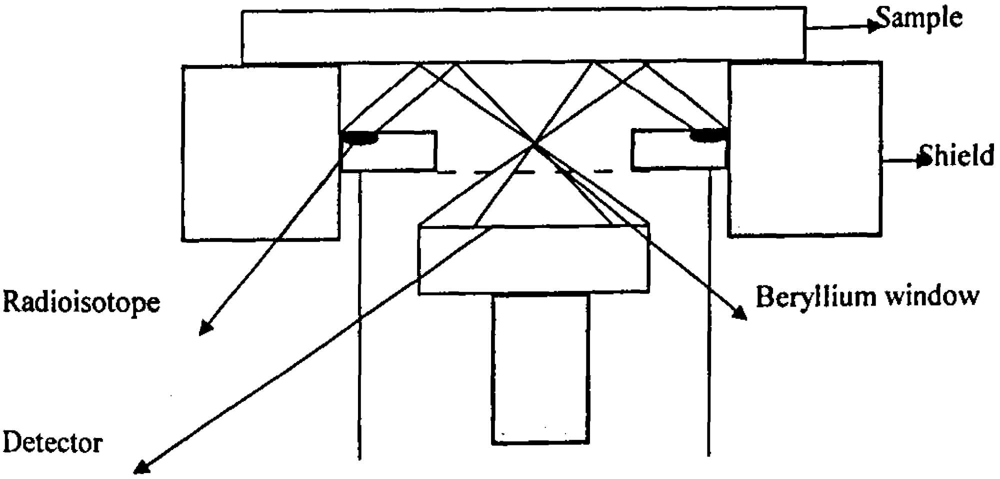


Figure 3.2: Schematic representation of radioisotope excitation system with annular (Tissue, 1996)

3.5.2 Solid state detector

The detector is a crystal of germanium or silicon that is processed to form a diode. A practical detector requires that other sources of charge carriers be minimised. This is accomplished in large crystals by compensating for impurities with lithium in a process known as lithium drifting. Lithium drifted crystals, as well as high purity germanium crystals that does not require compensation, are operated at liquid nitrogen temperature to reduce thermal noise.

Lithium drifted germanium or silicon lithium detectors, must be maintained at liquid nitrogen temperature at all times for the lithium to remain in place, while hyper pure germanium detectors can be left at room temperature when not in use.

3.5.3 Pre-amplifiers

They convert the burst of electrons resulting from absorption of x-rays into a voltage signal which maybe conveniently transmitted to the measurement system. The pre-amplifier is also required to minimise any source of noise which may degrade the resolution of the spectrum. This is achieved by using a Field effect transistor (FET) input charge sensitive pre-amplifier. The pre-amplifier is located at the detector to reduce capacitance of the leads, which degrade the rise time as well as attenuate the signal.

3.5.4 Amplifier

The amplifier serves to shape the pulse as well as to amplify it linearly and make the pulses suitable for the precise pulse height analysis by the multichannel analyser (MCA). This function is achieved by 'pulse shaping' techniques in order to obtain the optimum in energy resolution and count-rate performance. A near Gaussian shape is produced with time constant of 6-10 μ seconds.

3.5.5 Multichannel Analyser (MCA)

It sorts out the pulses from the amplifier according to their pulse heights and accumulates the respective pulse height distribution in its memory. The MCA also includes a microprocessor which is pre-programmed to perform simple data analysis operations like energy calibration, integration, subtraction of background etc.

To achieve optimum energy resolution and count rate performance, the stability and linearity of the mentioned electronic devices is very important. Stability can be maintained by having all the electronic systems permanently 'on' with constant amplification adjusted.

3.5.6 Sensitivities for elemental determination

To estimate the lowest measurable concentration of a particular element in a sample, the measurable limiting intensity has been found using the following relation:-

I_l limit $=3\sqrt{I_B}/t$

Where:-

I_B = background count rate in the region of the peak of element in counts/sec.

t = counting time

The background of x-ray spectra originates mainly from the scattering of primary and fluorescent radiation by the sample, sample holder and surroundings of the detector (Lieser, 1979). Other contributions to the background come also from the incomplete charge collection with sensitive volume of the detector (Kinyua, 1982).

Sensitivity is a measure of signal magnitude that produces a signal at 1%. While detection limit is a measure of the smallest concentration which can be determined with specified precision or reproducibility (Perkin, 2004).

3.5.7 Equipment used in the analysis of other Parameters

The following equipment was used to analyse other parameters. Various chemicals and sediment samples were weighed using an electrical analytical balance. [Model-Fisher scientific 160 A] for maximum accuracy. Sediment samples used in making pellets were weighed using a digital electrical balance (Grant SUB 28). The concentration of chloride ions in the water samples was determined using a potentiometer [Multimeter] that was attached to a silver-calomel combination electrode. In the adsorption experiments, the solution mixtures were agitated on an orbital shaker (Stuart Scientific mini orbital shaker SO5). Total phosphorus in the water samples was analysed using a UV-VIS Spectrophotometer (Analogue spectrophotometer S104). The pH of water samples was determined using a pH meter. (H1 9321 microprocessor) and conductivity was determined using a conductivity meter (Jenway 43D). Total dissolved solids (TDS) in the water samples were measured using a DO meter- 200 Jenway. Temperature adsorption experiments and Biochemical oxygen demand (BOD) were controlled and maintained in a thermostat water bath (Grant SUB28). Rotary evaporator (Labconco) was used to distil off excess hexane in the analysis of oil and grease. It was attached to a vacuum pump (Welch 1399 DuoSeal). A digital thermometer was used to record the temperature of the water at each sampling site. For preservation of water and sediment samples, an ice box was used in the field, while a freezer was used in the laboratory. An oven (Binder E28£04-71528) was used to dry sediment samples, evaporate excess hexane in extraction of oil and grease and drying of filter papers in determining total suspended solids (TSS). Another oven (model: Mammoth) was used to dry glassware. Hot plates (BIBBY HB502) were used in the digestion of water, sediment and determining the chemical oxygen demand (COD) in water samples.

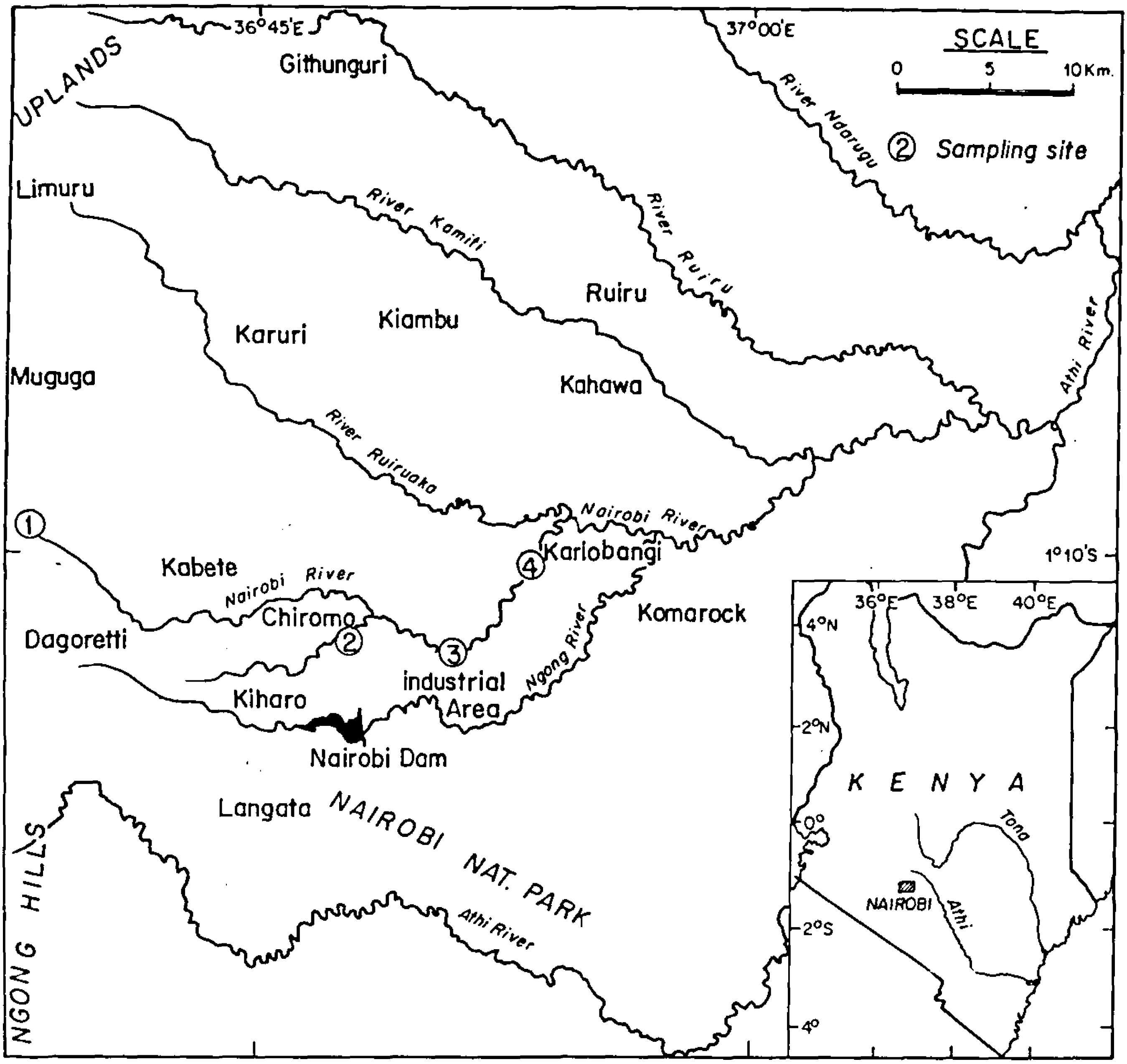
CHAPTER 4

METHODOLOGY

4.1 Brief Introduction

This chapter identifies the sampling sites, gives a list of chemicals and apparatus and a description of the methodologies used during the study. A map of the Nairobi River sampling sites is portrayed in Figure 4.0. The sites are labelled 1, 2, 3 and 4. The four sampling sites were identified on the basis of accessibility and proximity to sources of pollutants such as agriculture, the cottage industries and human settlements. Samples were collected during the wet and dry months. Composite samples of water and sediment were collected in triplicate giving a total of 12 water and 12 sediment samples collected during each sampling. Sampling was carried out once a month for a period of six months.

A representation of Nairobi River indicating the four sampling sites is shown in Figure 4.0, while the site descriptions are given in Table 4.0.



Source: *Cartographer, Department of Geology (2009)*

Figure 4.0: *A Representation for Nairobi River indicating the four sampling sites.*

Table 4.0: Distribution and GPS positions of sampling sites

Sampling sites	GPS location	Altitude	Physical location	Site description
Ondiri Swamp (1)	01° 1S' 10S 036° 39' 48E	1970m	Kikuyu Township	Agricultural
Museum Hill (2) Bridge	01° 16' 28S 036° 48' 44E	1674m	Museum off Waiyaki way	Residential
Race Course (3)	01° 16' 59S 036° 50' 01E	1655m	Race course Road	Industrial
Outer Ring (4)	01° 15' 51S 036° 52' 46E	1616m	Outer Ring Road	Industrial/Residential

4.2 Description of Sampling Sites

4.2.1 Ondiri Swamp

Ondiri Swamp is the source of Nairobi River. Figure 5.1a (Appendix Ia) shows a photograph of the headwaters of Ondiri Swamp. The water is turbid and green-yellow in colour due to algae and cow dung present in the water. The cow dung is introduced into the water by the cows that come to drink. The headwaters were not sampled. Figure 1c (Appendix 5.Ic) is a photograph showing the waters that were sampled for analysis. The water is black in colour, this is due to the decaying vegetation underneath which forms peat and humic acid.

Figure 5.1b (Appendix 1b) is a photograph indicating the activities taking place at Ondiri Swamp. It captures agricultural activities; sukuma wiki, spinach, bananas, tomatoes, potatoes are grown at this site. This is the fourth sampling site and is situated upstream of the Nairobi River profile.

The water in Figure 5.1d (Appendix Id) is polluted; it is dark and oily in appearance, because of the water pumps used to irrigate the vegetables. The water pumps are oiled and greased to keep them running well. There were also algae in the water.

4.2.2 Museum Hill Bridge

Sampling at Museum Hill captures the residential areas of Lavington, Kileleshwa, Riverside and Chiromo Campus hostels, Chiromo Campus laboratories and offices. Figure 5.2a (Appendix IIa) is a photograph of Museum Hill Bridge sampling site; it is the third sampling site upstream on Nairobi River. Before this site are two tributaries, Kirichwa kubwa and the Nairobi River that flows through Riverside Bridge. Both confluence at the Museum Hill Bridge.

Figure 5.2b (Appendix IIb) captures possible sources of pollution of the river at this sampling site. Traffic of motor vehicles on the road releases gas emissions from the car exhausts this may also contribute towards pollution of the water system or other pollutants that may be washed off the road into the river. This was the third sampling site. There was stagnant water that was green in colour; this indicated the presence of nutrients in the water. Figure 5.2c (Appendix IIc) shows that there was beautification around the site and possibly the City Council of Nairobi use manure or fertilizers to plant flowers. The run-off from this source may have contributed to the green algae observed in the river at this site.

4.2.3 Race Course Road Bridge

The appearance of water in figure 5.3a (Appendix IIIa) indicates that it was polluted. It was dark, turbid, and murky with solid wastes strewn beside and in the river. Parts of the wastes are computer motherboards, waste papers, domestic wastes from food kiosks and faecal coliforms. The figure also shows a parking boy asleep on top of some waste papers. Race Course represents midstream point of the water and is the second sampling site in this study.

Other than the solid wastes shown in the above figure5.3b (Appendix IIIb), the dark tunnel is used as an open toilet by the parking boys. It was very filthy and is contaminated with urine and faecal coliforms. There was also illegal dumping of domestic waste from nearby food kiosks.

There was clearing of debris and vegetation around this site. Loose soil and wind blown dust arising from these activities contribute to the turbidity and total suspended solids in the river.

4.2.4 Outer Ring Bridge

This is situated downstream and is the first sampling point. It captures wastes from industries, the jua kali' sector in industrial area, and waste water from residential areas in Eastlands. The green vegetation in figure 5.4a (Appendix 1Va) indicates the water was rich in nitrates and phosphates. There was a car scrap yard nearby. Figure 5.4b (Appendix 1Vb) clearly shows the state of water at this site. The water was turbid and coloured, raw sewage flows directly into the river giving it a green coloured appearance. Solid wastes were also thrown into the river interfering with its flow rate.

Figure 5.4c (Appendix 1Vc) shows burning of solid wastes and car tyres by the river which contributes to the dark colour of the water and turbidity. Loose soil and wind blown dust also contributed to the turbidity of the water at this site.

4.3 Chemicals

All chemicals used were of analytical grade quality. The chemicals were supplied by Scielab Chemical Suppliers. Chemicals used in the study included potassium chloride, methyl orange powder, hydrated manganese sulphate [$MnSO_4.2H_2O$], laboratory grade soluble starch, sodium hydroxide, sodium iodide, sodium azide, calcium chloride, ferric chloride, potassium dihydrogen phosphate, potassium hydrogen phosphate, sodium phosphate, salicylic acid crystals, sodium thiosulphate, magnesium sulphate, ammonium chloride, potassium dichromate, silver sulphate powder, 1;10 phenanthroline monohydrate, phenolphthalein powder, hydrated ferrous sulphate, ferrous ammonium sulphate, mercuric sulphate powder, potassium persulphate, ammonium metavanadate, ammonium molybdate, and lead nitrate.

The following reagents were also used in analysis: concentrated hydrochloric acid, perchloric acid, concentrated nitric acid, ethanol and concentrated sulphuric acid.

4.4 Glassware and apparatus

An assortment of glassware was used in the analysis carried out. This included boiling tubes, burettes, pipettes, beakers, separating funnels, round bottomed flasks, titration flasks, watch glasses, measuring cylinders, amber bottles used in the collection of water samples, polypropylene bottles, volumetric flasks, magnetic stirrer used in the analysis of chloride ions, filter funnels, desiccators, incubation bottles, refluxing flask, reflux condenser and a Buchner funnel.

4.4 Glassware Treatment

Two point five (2.5) litre amber bottles and all glassware that were used for sampling and analysis were thoroughly washed with detergent, rinsed with dilute nitric acid, washed again with detergent and finally rinsed with distilled water. They were then allowed to dry prior use.

4.5 Sample Collection and Preservation

4.5.1 Water

Water samples were collected in triplicate in 2.5 litre amber bottles. Water samples for BOD and COD analysis were separated and placed in 500 ml bottles and stored in the freezer at 4 °C to prevent oxidation of organic matter. While water samples for heavy metals were preserved immediately on site with 5 ml of 70% nitric acid.

4.5.2 Sediment

Composite samples of sediment were mixed in a stainless steel bowl using a spatula and placed in three 500 g polypropylene jars and stored in the freezer at 4° C.

4.6 Sample Preparation

4.6.1. Water

Water that was used for adsorption experiments was filtered first using size 54 Whatman filter paper to remove suspended particles that may block adsorption sites.

4.6.2 Sediment

Sediment samples were analysed for the presence of lead, chromium and cadmium. Sediment samples were removed from the freezer and allowed to thaw. 40 g of sediment samples were weighed in porcelain crucibles and dried in the oven at temperature of 105 °C for 24 hours to remove moisture. The dried samples were ground to fine powder using a pestle and mortar. Gravel, small stones and large organic residues were removed. The ground sediment was sieved using 2 mm mesh sieve to ensure homogeneity.

4.6.3 Preparation of Fish Bones for Adsorption Experiments.

Fish bones from the Nile Perch species commonly known as 'Mbuta'were purchased from Gikomba Market in Nairobi. The bones were first washed with warm water to remove flesh on the bones then rinsed several times with distilled water. The bones were then dried in the sun for a period of two weeks. They were then ground using a mechanical grinder and sieved. Different mesh sizes were used to produce different size particles of ground fish bone. Sieves used were numbers 44, 52 and 60 corresponding to mesh sizes 355, 300 and 250 microns.

The ground fish bones were used in adsorption experiments.

4.7 Sample Analysis

4.7.1 Water

4.7.1.1 Temperature

The temperature of the water was recorded by immersing a digital thermometer in the river at each of the four sampling points.

4.7.1.2 pH

A pH meter model H1 9321 microprocessor was calibrated with two standard buffer solutions, Solution 1 whose pH is 4 and solution 2 whose pH is 7, after calibration the electrode was rinsed in distilled water, and then dried with soft tissue. The pH reading was taken by immersing the electrode in the water sample.

4.7.1.3 Conductivity

This was carried out using the Jenway 43D conductivity meter. The meter was calibrated using 0.1M potassium chloride (KCl) solution, and set at the documented cell constant i.e. k =0.98. The electrode was washed first with distilled water then dried with soft tissue, the water samples were placed in a 100 ml. beaker and the readings were taken by immersing the electrode in the water sample. The data was generated at 25^0 C by keeping the sample solutions in water bath for 20 minutes prior to each reading.

4.7.1.4 Alkalinity.

20 ml. of each water sample was placed in a conical flask, and titrated with 0.02 N hydrochloric acid using 3 drops of methyl orange as an indicator. The titration was carried out three times.

4.7.1.5 Total Suspended Solids (TSS)

Filter papers were dried in an oven at 105^{0}C for five hours until a constant dry weight was obtained. They were then transferred into desiccators for final drying. 100 ml. of each sample was taken and filtered using a Buckner funnel fitted to a vacuum pump. The filter paper was transferred into an oven where it was dried, cooled in a desecrator and reweighed. The process of drying, cooling and reweighing was repeated until a constant weight was obtained.

4.7.1.6 Total Dissolved Solids (TDS)

50 ml of water sample was measured in a measuring cylinder and placed in a 100 ml. beaker. The conductivity meter was set at TDS in ppm. The electrode was washed with distilled water, dried with tissue then was dipped in the water sample to record the TDS until a constant reading is obtained.

4.7.1.7 Biochemical Oxygen Demand (BOD).

Procedure

15 litres of distilled water was placed in a clean 20 litre bucket. 5 ml. of each of the following reagents previously prepared were added to the water; magnesium sulphate solution, which was prepared by dissolving 22.5g $MgSO_4.7H_2O$ in distilled water and diluting to 1 litre, Calcium chloride solution, was prepared by dissolving 27.5 g of $CaCl_2$ in distilled water and diluting to 1 litre, Ferric chloride solution, was prepared by dissolving 0.25 g of $FeCl_3.6H_2O$ in distilled water and diluting to 1 litre, Phosphate buffer solution was prepared by dissolving 8.5 g KH_2PO_4, 21.75 g K_2HPO_4, 33.4 g $Na_3PO_4.7H_2O$ and 1.7 g NH_4Cl in distilled water and diluting to 1 litre. The resultant solution was aerated by swirling it in the bucket. 1 litre of the solution was measured in a measuring cylinder, transferred into three 300 ml capacity incubation bottles. The incubation bottles were completely filled with enough water and stoppered tightly ensuring no air bubbles. These solutions served as the blank.

1 ml. of water samples from Race Course and Outer Ring Road Bridge sampling sites, and 3 ml. water samples from Ondiri Swamp and Museum Hill Bridge sampling sites were each diluted to 1 litre with water solution prepared in the bucket. The diluted water samples were transferred into incubation bottles and stoppered tightly ensuring no air bubbles. 1 ml. of the following solutions were then added to the three blank solutions in the incubation bottles; Manganese sulphate solution, Alkali-iodide azide reagent and concentrated sulphuric acid. The incubation bottles were then stoppered carefully to exclude air bubbles, each bottle was inverted a few times until dissolution was complete. 202 ml of solution in each incubation bottle that served as the blank was titrated with 0.025 M $Na_2S_2O_3$ solution to a pale straw colour. Then a few drops of starch solution were added and titration continued to first disappearance of blue colour. This was the initial dissolved oxygen. The remaining incubation bottles containing diluted water samples were placed in a water bath thermostatically controlled at 25 ± 1°C for five day incubation. After the five day incubation, the dissolved oxygen in the sample dilutions was determined.

Calculation

Calculation of BOD was carried out using the following formula (Greenberg et al, 1992):

BOD_5 mg/L = $(D_1 - D_2)$ (1000) /P

Where:

D_1 = DO of diluted sample immediately after preparation, mg/L.

D_2 = DO of diluted sample immediately after 5 day incubation at 25°C, mg/L

P = volume of sample used.

4.7.1.8 Chemical Oxygen Demand (COD).

Chemical oxygen demand was determined using the dichromate reflux technique; this is an open reflux method. This technique is preferred because of its superior oxidising ability, it is applicable to a wide variety of samples and is easy to manipulate (Greenberg et al, 1992).

Procedure

10 ml of distilled water was placed in a 500 ml refluxing flask. This was the blank. Then 3 ml of water samples from Ondiri Swamp and Museum Hill were each diluted to 10 ml and placed in a 500 ml refluxing flasks. For Race Course and Outer Ring 1 ml of water sample was taken. The sample volumes are varied due to pollution levels. Where pollution levels are high less water is taken. To each flask the following were added; 1 g of mercuric sulphate ($HgSO_4$) to complex chlorides, 10 ml of 0.25 N potassium dichromate, 25 ml of sulphuric acid reagent and a few anti bumping granules.

Each flask was attached to a reflux condenser, placed on a hot plate and refluxed for two hours. The flasks were cooled to room temperature. 4 drops of ferroin indicator was added to each flask. The contents of each flask were titrated against 0.1 N ferrous ammonium sulphate to the first red brown endpoint.

The FAS prepared must be standardised daily by the following procedure:

Dilute 10 ml of standard potassium dichromate to 100 ml with distilled water, slowly add 30 ml of concentrated sulphuric acid and cool to room temperature. Titrate with FAS titrant using 3 drops of ferroin indicator to red-brown endpoint.

Normality of FAS = ($K_2Cr_2O_7$) (0.25) / (ml FAS required)

Calculation

COD was calculated using the following formula: COD (mg/L) = [(a-b) (N) x 8000]/V

Where:

a = volume of FAS used for the blank.

b = volume of FAS used for water samples.

N = normality of FAS titrant and V = volume of sample used.

4.7.1.9 Total Phosphorus

Total phosphorus represents all the phosphorus present in a sample regardless of form. The amount of total phosphorus present in the water samples was determined by first digesting the water sample using persulphate followed by vanadomolybdophosphoric acid colorimetric method (Greenberg et al, 1992).

4.7.1.9.1 Digestion

Procedure

50 ml of water sample was put in a 250 ml titration flask. One drop of phenolphthalein was added, when a red colour developed, sulphuric acid was added drop wise until the colour was discharged followed by 1 ml of H_2SO_4 and 0.5 g solid $K_2S_2O_8$. The contents of the titration flask were boiled gently for 40 minutes until the volume reduced to 10 ml. the resultant solution was cooled and diluted to 100 ml. with distilled water.

4.7.1.9.2 Vanadomolybdophosphoric acid colorimetric method (Greenberg et al, 1992)

Procedure

10 ml of 0.25% NH_4VO_3 was mixed with 10 ml of 5 % $(NH_4)_2MoO_4$ to form the vanado-molybdate reagent. This was transferred into a boiling tube. 1 ml. of phosphate standard solution [1000 ppm] was added to 9 ml. of deionised water to form a 100 ppm solution. 1 ml of 100 ml standard solution was added to 9 ml. of deionised water to form a 10 ppm solution. Appropriate portions of standard phosphate solutions were transferred into test tubes to obtain solutions of concentrations 2, 4, 8, 10 and 12 ppm. The blank was deionised water which had a concentration of 0 ppm. 5 ml water samples were placed in test tubes. The solutions in the test tubes were treated as follows; Two drops of $HClO_4$, followed by 1 ml of vanado-molybdate reagent were added. The contents were mixed thoroughly and diluted to 10 ml using deionised water. The absorbance of each solution was read and recorded at 470 nm using the Analogue Spectrophotometer S104.

4.7.1.9.3 Chloride Ions

The analysis of chloride ions was determined by potentiometric titration (Skoog et al, 1992). 50 ml of water sample was measured using a 100 ml measuring cylinder and transferred into a 100 ml beaker. A stirrer was placed into the beaker; silver calomel electrodes connected to a potentiometer were dipped into the water sample in the beaker. Silver nitrate solution from a burette was added to the water sample in the beaker and the potentiometer reading recorded after every 0.5 ml volume of $AgNO_3$ solution added until the total volume added was 5 ml, the endpoint for each solution was determined graphically.

4.8.2.0 Aesthetic parameters

Colour and odour were detected using senses.

4.8.2.1 Sample Analysis of Heavy Metals

4.8.2.1.1 Sediment

The sediment was analysed using AAS and XRF.

In the AAS analysis, the operating parameters of the machine were optimised to obtain the highest sensitivity possible that will enable the analysis of very low levels of the heavy metals. The parameters are summarised in Table 4.1.

Table 4.1: Operating conditions of AAS for As, Cr, Cd and Pb

	As	Cr	Cd	Pb
Lamp current [mA]	10	7	3.5	8
Spectral band pass [nm]	0.1	0.1	0.1	0.1
Wavelength [nm]	189.0	425.4	326.1	405.8.
Oxidant [air] flow rate [µg/ml]	3.5	3.5	3.5	3.5
Acetylene flow rate	1.5	4.5	1.5	1.5

Source: Geology and Mines, 2009

4.8.2.1.2 Digestion of sediment sample for AAS analysis.

1±0.01g of dried ground sediment was transferred into a 250 cm^3 beaker. 4 ml (1:1) HNO_3 and 10ml (1:4) HCl were added to the contents in the beaker. The beaker was covered with a watch glass, placed on a hot plate for reflux extraction of analytes. The sample was heated and gently refluxed for 30 minutes. The sample was allowed to cool, transferred into a 100 ml volumetric flask and diluted to the mark. Suspended solids were filtered out using a 54 size Whatman filter paper. The filtrate was analysed using Atomic Absorption Spectrophotometer (AAS) for content of toxic heavy metals.

Preparations of acids used in sediment and water sample digestion were done as follows; (1:1) HNO_3:H_2O was prepared by taking 500 cm^3 of concentrated nitric acid, adding 400 cm^3 of distilled water and diluting to 1 litre mark. (1:4) HCl:H_2O was prepared by taking 200 cm^3 of concentrated hydrochloric acid, adding 400 ml distilled water and diluting to 1 litre mark. (1:1) HCl:H_2O was prepared by taking 500 cm^3 of concentrated hydrochloric acid, adding 400 ml distilled water and diluting to the 1litre mark (Wandiga et al, 2009).

4.8.2.1.3 Digestion of water samples for AAS

50 ml of water sample was placed in 100 ml beaker for wet digestion and another 50 ml of deionised water was placed in a 100 ml beaker, this was the blank. To each solution, 2 ml (1:1) HNO_3 and 1ml (1:1) HCl was added. Each beaker was covered with a watch glass and placed on a hot plate. The solutions were gently evaporated at a temperature between 80° -140° until dense white fumes of HCl disappeared. The heating was continued for 20 minutes until less than 10 ml of original sample remained. The solution was cooled to room temperature, placed in a 50 ml volumetric flask and diluted to the mark. Suspended particles were filtered out using a 54 size Whatman filter paper. The filtrate was analysed for Cadmium (Cd), Chromium (Cr) and Lead (Pb) using an Atomic Absorption Spectrophotometer.

4.8.2.1.4 Sediment preparation for X-Ray Fluorescence (XRF)

The analysis of heavy metals was carried out at the Institute of Nuclear Science and Technology (INST), University of Nairobi using the Energy Dispersive X-Ray Fluorescence (EDXRF) with XRF qualitative technique. This was used to measure the elemental composition of the sediment. The method is simple, fast, most accurate and most economic analytical method. Results from this analysis were compared with those of Atomic Absorption Spectrophotometer.

Procedure

50 ± 0.01g of sediment sample was weighed. The sample was oven dried to constant weight at 105 ± 0.1°C. It was then ground to fine powder using a pulveriser. The sediment powder was sieved to 150μm. 1.5 g of powder was portioned out, 0.15g of starch was added and the mixture of starch and dried sediment were pressed into pellets of 25 mm diameter. 3 pellets each weighing 0.5g were prepared using steel die hydraulic press of pressure of 10 tons with 25 ton press. Each pellet was then placed in the Energy Dispersive X-Ray Fluorescence for analysis; the excitation time for analysis was 1500 seconds. Each pellet was then covered with a molybdenum plate and its intensity determined after 10 seconds.

The XRF Technique was followed by spectrum analysis, a method that is both qualitative and quantitative. The method uses radioactive cadmium (^{109}Cd) and an Axil programme to determine the elements present in each pellet and their concentration in parts per million (ppm). Each element analysed using the EDXRF had its own detection limit, which was calculated using the following formula;

Detection limit = $\sqrt{R_b} \times 3 \times C / P_A$

Where:

P_A = Peak Area

R_b = Background count rate and C = Concentration of metal analysed

4.8.2 2 Oil and Grease Analysis

4.8.2.2.1 Quality Control (QC)

A matrix spike was prepared by spiking one gram of motor engine oil into 500 ml of distilled water in triplicate. The samples were acidified to pH < 2 and extracted three times with 30 ml of hexane in a 1 litre separating funnel.

The extracts were chemically dried over anhydrous sodium sulphate (Na_2SO_4) and the solvent evaporated. The Hexane Extractable Materials (HEM) was desiccated and weighed. The mean % recovery (X) was established using the following expression:

$$X = \frac{x_1 + x_2 + x_3}{n}$$

Where: -

X = % recovery of each sample

n = number of samples

x_1, x_2 and x_3 = masses of motor engine recovered

4.8.2.2.2 Extraction

A clean boiling flask was heated in an oven at 105°C for two hours. It was then transferred into a desiccator to cool to room temperature for 45 minutes. The cooled flask was weighed on a calibrated Fischer Electrical Balance. 500 ml of water samples were measured using a 500 ml measuring cylinder and transferred into one litre separating funnels. The pH of the water samples were adjusted to less than two. The pH was verified using a pH meter. 30 ml of hexane was added to each sample, the funnel was shaken vigorously for two minutes releasing pressure each time and then left to stand for ten minutes. The samples were extracted three times with 30 ml of hexane until a total of 90 ml of hexane had been added. Sodium Chloride was added to break any emulsions present. The lower aqueous layer was removed. Glass wool was placed in glass funnel and 10g of baked anhydrous sodium sulphate was added and rinsed with 5 ml of hexane. The hexane layer from the separating funnel was drained through the sodium sulphate into the preweighed round bottomed flask.

4.8.2.2.3 Gravimetric Method

The extract was concentrated by evaporating the solvent to dryness using a rotary evaporator. The boiling flask was immersed in hot water. After distillation, the flask was put in the oven at 70^0C to dry for 45 minutes, cooled in a desiccator before reweighing. The cycle of drying, cooling in a desiccator and weighing was repeated until the weight loss was less than 4% of the previous weight.

HEM = Total weight of boiling flask less tare weight is determined using the following equation;

HEM (mg/l) = (A – B) /V

Where:-

A = weight of flask + HEM (mg)

B = weight of empty flask (mg) and

V = volume of the sample

4.8.2.3 Investigating the Effectiveness of Fish Bones to Remove Heavy Metals

Two water samples labelled A and B from Outer Ring Road Bridge sampling site (With highest concentration of lead ions) were treated as follows;

Sample A

50 ml of sample A was placed in a 100 ml beaker, its pH and conductivity determined using a pH and a conductivity metre. The sample was then acid digested using 2 ml of (1+1) $HNO_3:H_2O$ and 1 ml (1+1) $HCl:H_2O$ until the volume reduced to 10 ml The digested water sample was allowed to cool, and then filtered into a 50 ml volumetric flask using size 54 Whatman filter paper and diluted to the 50 ml mark using distilled water. The sample was then transferred into a propylene bottle, and taken to Geology and Mines, Department of Natural Resources and Environment for AAS analysis.

Sample B

A column measuring 41 cm by 2.5 cm internal diameter was fitted with cotton wool plug then packed with 30 g of ground fish bone. 50 ml of filtered sample B was introduced into the column, the eluate obtained was collected into a 100ml beaker, its pH and conductivity determined using a pH and a conductivity meter. The eluate was then acid digested using 2 ml (1+1) HNO_3:H_2O and 1 ml (1+1) HCl:H_2O until the volume reduced to 10 ml It was allowed to cool then filtered into a 50 ml volumetric flask using size 54 Whatman filter paper and diluted to the 50 ml mark using distilled water. The sample was then transferred into a propylene bottle, and taken to Geology and Mines for AAS analysis.

4.8.2.4 Investigating Factors that Affect the Remediation Process.

The following experiments were carried out using a standard solution of 60 ppm of lead. In each experiment, the sorption capacity of fish bones for lead nitrate (Pb^{2+}) was studied.

4.8.2.4.1 Effect of Contact Time

5g portions of ground fish bones [mesh number 60] were weighed into seven different 50 ml conical flasks. To each conical flask, 50 ml of 60 ppm lead nitrate was added. The conical flasks were placed in an orbital shaker set at 250 revolutions/minute for different times [5, 10, 20, 30, 40, 50 and 60 minutes]. The solution mixtures were then filtered using size 54 Whatman filter paper into polypropylene bottles. The concentration of lead nitrate in the filterate was analysed using AAS.

4.8.2.4.2 Effect of Temperature

5g portions of ground fish bones [mesh number 60] were weighed and placed into six different conical flasks to which 50 ml of 60 ppm of lead nitrate was added. Each flask was placed in a thermostat water bath set at different temperatures [25° C, 30° C, 35° C, 40° C, 45° C and 50° C].

The temperatures are thermostatically controlled at ±0.1°C and shaken for 30 minutes. The resultant mixtures were filtered into polypropylene bottles using size 54 Whatman filter paper. The concentration of lead nitrate in the filtrate was determined using AAS.

4.8.2.4.3 Effect of Particle Size

5g of ground fish bones of different particle size [mesh numbers 44, 52 and 60] were placed in three different 50 ml conical flasks. 50 ml of 60 ppm of lead nitrate were added to each flask; the flasks were then placed on a mini orbital shaker and allowed to equilibrate at 250 rev/min for 30 minutes. The contents of the conical flasks were filtered into a polypropylene bottle using size 54 Whatman filter paper. The concentration of lead nitrate in the filtrate was determined using AAS.

4.8.2.4.4 Effect of Mass of Ground Fish Bones

5g, 10g, 15g, 20g, 25g and 30g portions of ground fish bones were weighed within an accuracy of ±0.01 g and placed into six 50 ml conical flasks. 50 ml of 60 ppm of lead nitrate was added to each flask and allowed to equilibrate on a mechanical shaker at 250 rev/min for 30 minutes. The contents of each conical flask were filtered into a polypropylene bottle using size 54 Whatman filter paper. The concentration of lead nitrate in the filtrate was determined using AAS.

4.8.2.5 Adsorption Isotherms

Adsorption isotherms for lead (II) nitrate (adsorbate) on ground fish bones (adsorbent) were carried out following mechanical shaking using a mini orbital shaker. Equilibrium relationship between the adsorbent and adsorbate were described by adsorption isotherms. This is the ratio of quantity of lead nitrate adsorbed and those remaining in solution at a fixed temperature at equilibrium. Langmuir and Freundlich models were used to fit adsorption data for lead nitrate concentrations determined.

CHAPTER 5

RESULTS AND DISCUSSION

This chapter summarises the water quality results of the study, discusses the implications of the results on water quality and offers explanations for the presence and concentrations of certain parameters.

5.1 Seasonal Variation of pH and Alkalinity

Results of pH and alkalinity showing seasonal variations across the four sampling sites are given in Table 5.1.

Table 5.1: pH and Alkalinity seasonal variations

Seasons	**Parameter**	**Ondiri Swamp**	**Museum Hill Bridge**	**Race Course Bridge**	**Outer Ring Road Bridge**
		Mean ±SD	**Mean ±SD**	**Mean ±SD**	**Mean ±SD**
Dry	pH	6.5 ± 0.45	7.3 ±0.28	6.9 ± 0.31	7.0 ± 0.19
	Alkalinity (mg/l)	213 ± 6.5	461± 13.4	357 ±21.5	300 ± 0.19
Short rains	pH	7.2 ± 0.37	8.3 ± 1.0	7.6 ± 0.29	7.3 ± 0.44
	Alkalinity (mg/l)	215 ± 0.10	505 ± 0.09	450 ± 0.0	490 ± 1.38
Long rains	pH	6.5 ± 0.11	6.7 ± 0.06	6.8 ± 0.27	7.1 ± 0.28
	Alkalinity (mg/l)	226 ± 34.7	388 ± 3.5	460 ± 28.3	405 ± 7.1

ll pH values lie within acceptable WHO (6.0 -8.5), EU (6.0 – 8.5) and KEBS (6.5 – 8.5) limits. The H of the river upstream at Ondiri Swamp was weakly acidic (6.5) in both the dry and long rainy seasons. The same trend was also observed midstream at Race Course Road Bridge. Further downstream at Outer Ring Road Bridge, the river was neutral in the dry season and weakly basic during the seasons of short rains (7.3) and long rains (7.1) tending towards neutral. This would indicate that as the river traverses the city from Museum Hill Bridge, it is neutralized by acidic components introduced midstream at Race Course Bridge by 'Do it yourself' mechanics, the cottage industries at Ngara and street runoff from the Central Business District.

The acidity upstream may be attributed to decaying vegetation beneath the swamp that results in the formation of peat and humic acid. The basic pH during the short rainy season is perhaps due to agricultural run off. Some agrochemicals including fertilizers are basic in nature due to phosphates and reduced nitrogenous compounds. At Museum Hill, the pH increased to basic during the dry and wet seasons. This increase can be attributed to organic pollution and domestic waste discharge draining into he river from the neighbouring residential areas.

The Alkalinity values at all sampling points were relatively high indicating that the concentration of basic compounds in the river was quite high. This would indicate that the river had a high buffering apacity and would not be susceptible to alterations in pH. Possible sources of basic compounds nclude phosphate fertilizers and detergent washings which are phosphate based.

earson's correlation between pH and alkalinity does not show significant interdependence. The two arameters with a correlation coefficient ($r = 0.598$) at confidence level ($p > 0.05$ (0.402)) during the hort rainy season, while during the long rainy season the correlation coefficient was 0.688 with a onfidence level of $p > 0.05$ (0.312). The data shows that the two variables are not significant, and ence not linearly related.

5.2 Seasonal Variation of Conductivity and TDS

The season variation of conductivity and TDS is given in table 5.2

Table 5.2: Conductivity and TDS seasonal variations

Season	Parameter	Ondiri Swamp	Museum Hill Bridge	Race Course Bridge	Outer Ring Road Bridge
		Mean ±SD	**Mean ±SD**	**Mean ±SD**	**Mean ±SD**
Dry	Conductivity (μS/cm)	270 ± 1.38	588 ± 12.3	562 ± 11.7	688 ± 12.3
	TDS (mg/l)	101 ± 0.3	270 ± 1.4	333 ± 5.6	314 ± 4.0
Short rains	Conductivity (μS/cm)	196 ± 1.4	549 ± 2.0	592 ± 1.5	562 ± 1.0
	TDS (mg/l)	99 ± 1.2	273 ±1.5	295 ± 1.0	273 ±1.5
Long rains	Conductivity (μS/cm)	202 ± 0.0	603 ± 1.2	681± 6.4	630 ±2.0
	TDS (mg/l)	100 ± 0.6	300 ± 0.6	339 ±3.9	314 ±1.0

Conductivity is a measure of ions present in water. From results given in Table 2 (Appendix V), conductivity increases with the concentration of dissolved ions in water. This trend was observed from upstream at Ondiri Swamp to midstream at Race Course Bridge, and then there was a sudden drop in conductivity downstream at Outer Ring Road Bridge for all the seasons cited in the table. The same rend is observed with TDS.

The water samples analysed had concentrations that were well above WHO guidelines for conductivity 250 μ s cm $^{-1}$), apart from samples collected from Ondiri Swamp during the short and long rainy easons. The conductivity values recorded at Ondiri Swamp were 196 μS cm $^{-1}$ during the short rainy season and 202 µS cm $^{-1}$ during the long rainy season. The low values could be attributed to the dilution effect when the volume of river water was higher, flow rate faster washing away most of the dissolved solids and resulting in lower conductivity values. The highest conductivity value was recorded downstream at Outer Ring Road Bridge (688 µS cm $^{-1}$). This is because at this site the solid wastes in the water reduces the flow rate making resident time for most pollutants high at this site

Total dissolved solids values in the dry months showed a variation of 101 mg/L to 333 mg/L, with a mean of 254.5 mg/L. During the month of short rains a variation of 98.7 mg/L to 295 mg/L with a mean of 235 mg/L was observed, and during the month of long rains the range was 100.3 mg/L to 339 mg/L with a mean of 263.5 mg/L. All the values recorded were below the allowable standards of WHO (<1500 mg/L), KEBS (1000 mg/L) and EU (360 mg/L). The highest values were recorded at Race Course sampling site for all seasons. This captures activities from the Central Business District and cottage industries in Ngara.

Conductivity and TDS values during the dry season indicate that the two variables are not linearly related very well, the value of $r = 0.925$ at a significance of $p > 0.05$ (0.075). During the short rainy season the correlation was ($r = 0.999$) with a very small significance of $p < 0.001$, indicating that the correlation is significant and that the two variables are linearly related during this season. In the long rainy season the association between the two variables was extremely high ($r = 1.0$) and the correlation coefficient was highly significant and different from zero ($p < 0.01$). This indicated that a linear equation described the relationship between TDS and conductivity with all data points lying on a line for which conductivity increases as TDS increases. Hence the linear relationship between the two parameters is strong.

5.3 Seasonal Variation of Total Suspended Solids

The bar chart (Figure 5.4) indicated below gives seasonal variations of total suspended solids across the four sampling sites of the study.

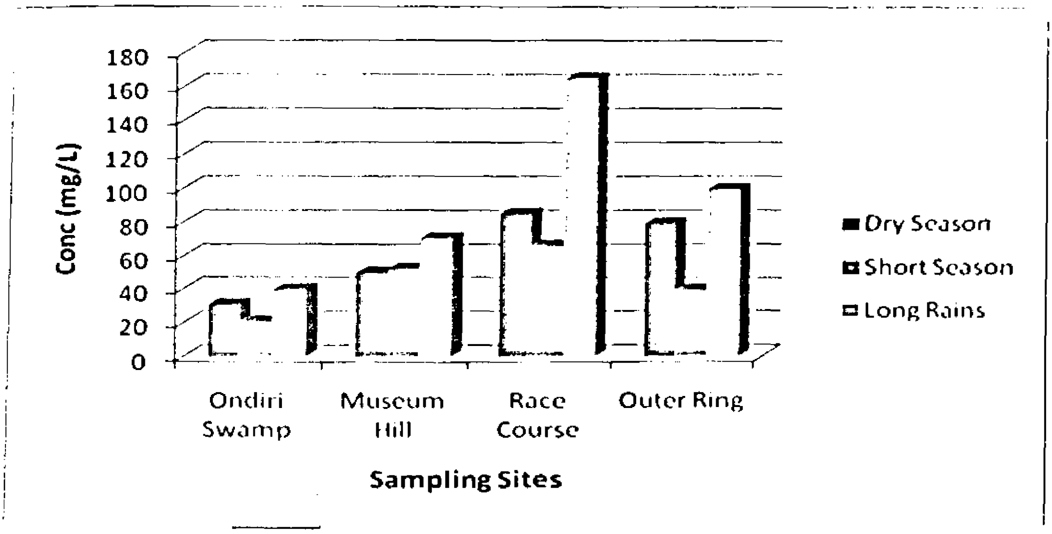


Figure 5.4: Total Suspended solids variation during the dry season, short and long rains

The general trend across the four sampling sites indicates concentration of TSS increasing from upstream at Ondiri Swamp to midstream at Race Course Bridge, then suddenly decreasing downstream at Outer Ring Road Bridge. This trend is observed in all the three seasons.

The highest values of TSS were recorded at Race Course sampling site. This is attributed to human activity around this site. There is burning of solid wastes and a lot of loose soil that result in erosion effects that increase the amounts of TSS in the water. This will also contribute to turbidity that will in effect compromise the quality of water. TSS values range from 39.7 mg/L to 164.7 mg/L during the long rains, 20.7 mg/L to 66 mg/L during the short rains and 30.6 mg/L to 84 mg/L during the long rains. All values were above the WHO allowable standards of 30 mg/L, indicating that the water is polluted.

5.4. Seasonal Variation of Temperature

Figure 5.2 shows a plot of temperature against sampling sites, it also indicates seasonal temperature variations.

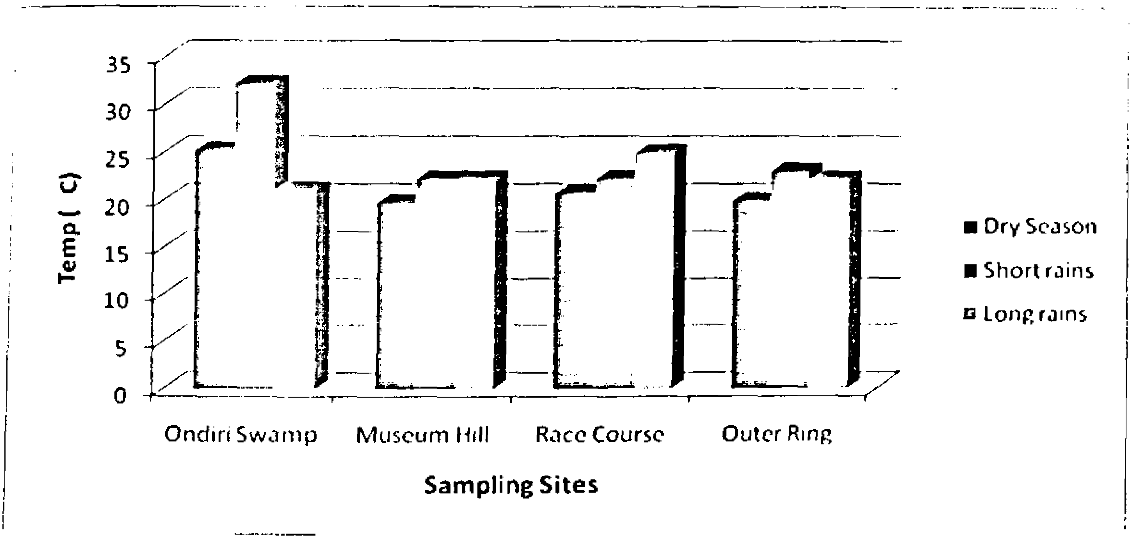


Figure 5.2: Temperature variation during the dry season, short and long rains

Temperature is an important physical parameter in that it will affect aquatic life; affect chemical reactions and reaction rates within wastewater. The temperature values (Appendix V, Tables 1, 2 and 3) ranged from 19.7 ° C to 32.2 ° C. across the three seasons. This is within the range for most biological activity. Other than the abnormally high value of 32.2 ° C which could be attributed to time of sampling, the values reported indicate that temperature profile along the river had no major problem. There was minimal thermal pollution along the river indicating that the industrial effluents entering the river system was not of 'HOT' type e.g. organic solvents. One may also not rule out that there were no industrial wastes discharged into the river at night. It is also possible that at the time of sampling the temperatures recorded were within acceptable ranges.

5.6 Seasonal Variation of Oil and Grease

Results of oil and grease variations are given in Figure 5.6.

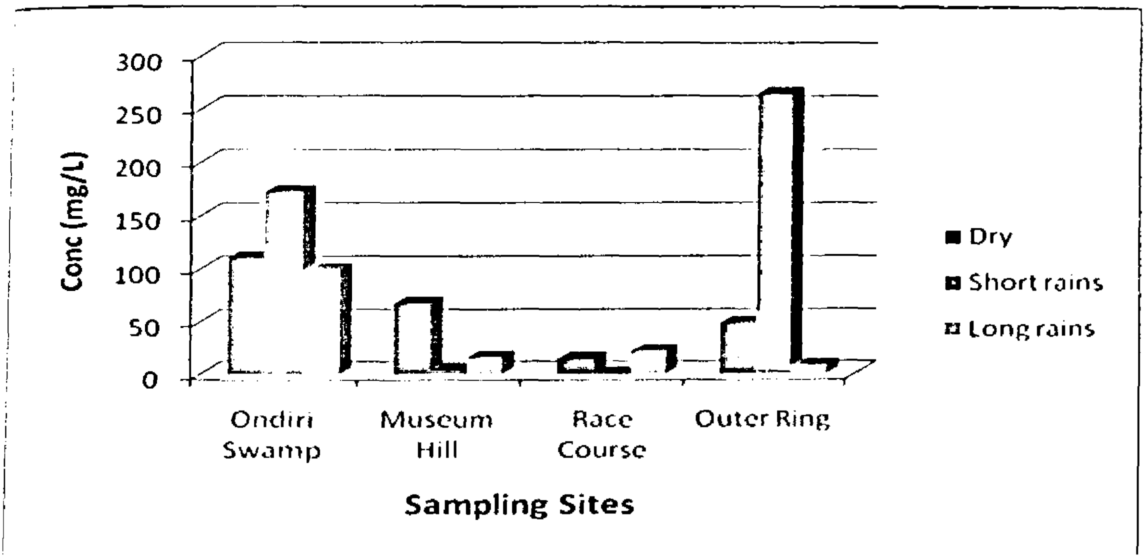


Figure 5.6: Oil and grease variation during the dry season, short and long rains

Oil and grease analysis is a rough estimate for determining the organic content in water. From the matrix spike prepared in section 4.8.2.2.1 of page 56 of the study, there was 90% recovery. This would indicate that concentrations obtained do not actually depict the real picture on the exact amount of oil and grease pollution.

Generally, the levels of oil and grease (Figure 5.6) are highest at Ondiri Swamp. This is because at this sampling site portable water pumps are placed strategically by the swamp to water vegetables grown nearby. The water pumps contaminate the water with oil and grease. During the short rains, the levels of oil and grease drastically drop from 172.2 mg/L at Ondiri Swamp to 3.8 mg/L at museum hill and 0.6mg/L at Race Course Bridge then reaching a maximum of 264 mg/L at Outer Ring Road Bridge. The relatively high values at Outer Ring sampling site could be attributed to industrial effluents from industries that may be located along the river run off from car wash facilities, domestic effluents and improper disposal of used oil by mechanics from the 'Jua Kali' sector.

The oil and grease from these sources are washed downstream to Outer Ring which records relatively high concentrations.Results obtained from this study showed that correlations do not exist between oil and grease and other organic parameters such as COD and BOD. In the dry season, both BOD and COD show strong inverse correlation with oil and grease according to correlation values. With BOD a correlation of $r = -0.863$ with a significance of $p > 0.05$ (0.137), while COD posted a correlation of $r = -0.808$ with a significance of $p > 0.05$ (0.192). However, the p values indicate that there is no correlation. The same trend is observed during the rainy season, during the season of short rains the correlations are (BOD) $r = 0.492$, $p > 0.05$ (0.508); (COD) $r = 0.634$, $p > 0.05$ (0.366); long rains (BOD) $r = -0.569$, $p > 0.05$ (0.431). During the long rainy season COD and oil and grease were linearly related (COD) $r = -0.960$, $p<0.05$, and the correlation was significant.

5.7 Seasonal Variation of Chemical Oxygen Demand

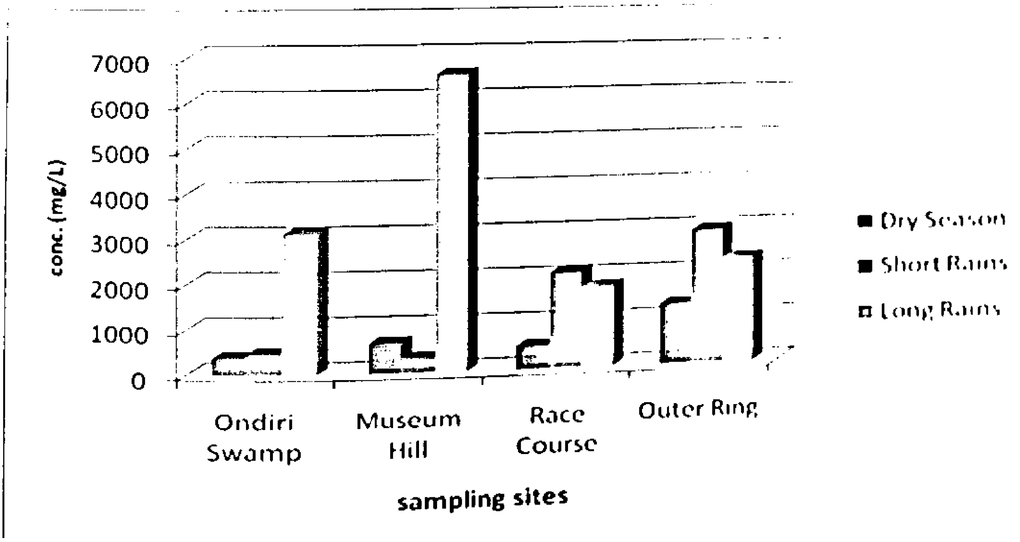


Figure 5.7: Chemical Oxygen Demand variation during the dry season, short and long rains

The concentration levels of COD are indicated in Figure 5.7. In the dry months, the concentration ranged from 372.6 mg/L to 1353 mg/L with a mean of 901.5 mg/L. There was a general increase of COD values downstream indicating that amount of organic matter was increasing.

During the month of short rains, the values ranged from 200 mg/L to 3000 mg/L. At Ondiri swamp concentration was 466.2 mg/L, this was relatively high and could be attributed to decaying vegetation, peat and humic acid formed in the water. The concentration then drastically drops to 200 mg/L at Museum Hill then increases to 2133 mg/L at Race Course Bridge reaching maximum concentration of 3000 mg/L at Outer Ring sampling site. At this site a lot of domestic wastes in sacks are thrown into the river, sewage is also directly discharged and burning of car tyres and plastics by the river. During the season of long rains that did not take place, concentration values in all sites were high. The water volume was small; flow rate was slow, so most organic wastes discarded hardly moved hence the high concentrations [Ondiri (3110 mg/L, Museum (660 mg/L, Race Course (1798 mg/L) and Outer Ring (2353.3 mg/L)]. The amount of rainfall recorded at this time was low; refer to Table 6.1 page 86.

5.8 Seasonal Variation of Biochemical Oxygen Demand

The results of seasonal variation of BOD in the Nairobi River water samples are presented in Figure 5.8.

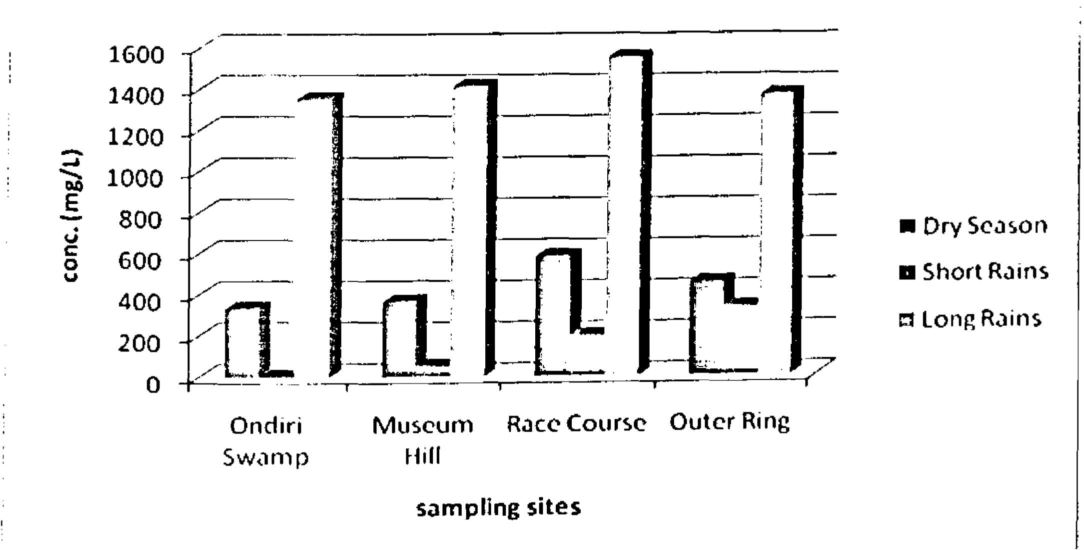


Figure 5.8: Biochemical Oxygen Demand variation during the dry season, short and long rains

The BOD data obtained (Figure 5.8) ranged from 333 mg/L to 583.3 mg/L with a mean of 434.5 ± 4.7 mg/L in the dry season, 4.4 mg/L to 333.3 mg/L with a mean of 148.2 ± 30.2 mg/L during the short rains and 1350 mg/L to 1549 mg/L with a mean of 1419 ± 25.8 mg/L during the season of long rains. The highest values in all the seasons were recorded at Race Course. KEBS allowable limit for BOD is 30 mg/L. The concentrations obtained at all sampling points clearly indicate that they exceed the allowable limits, indicating that the water is polluted, lacks oxygen and has a lot of micro organisms and organic matter.

5.9 Seasonal Variation of Chloride ions

The bar chart indicated below gives seasonal variations of chloride ions across the indicated sampling sites.

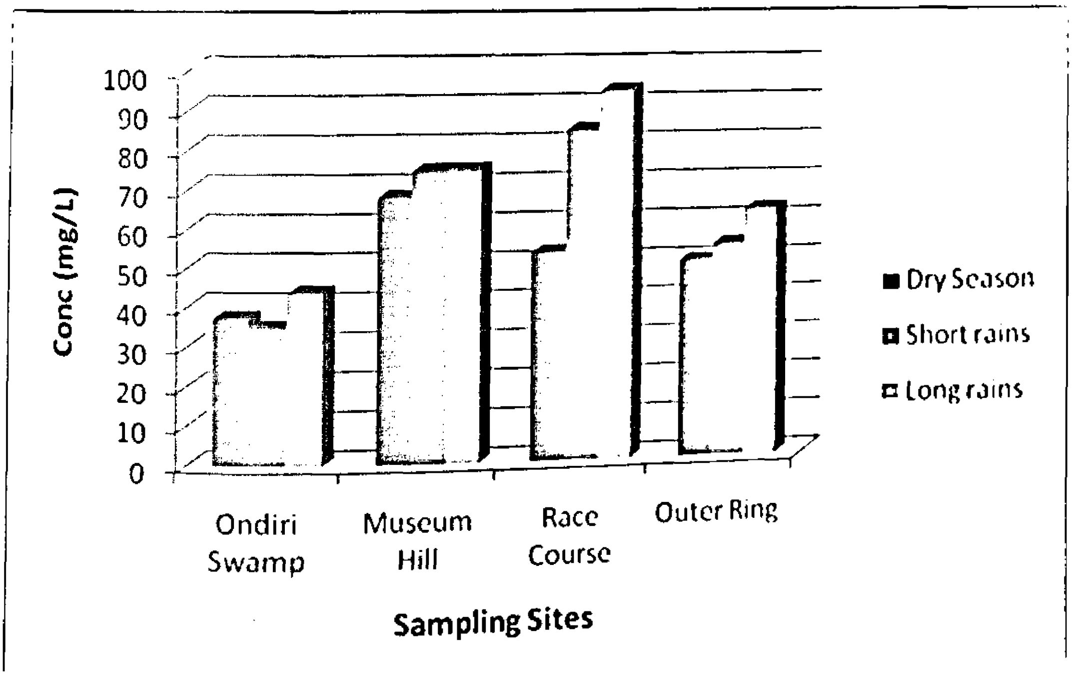


Figure 5.9: Chloride ion variation during the dry season, short and long rains.

The general trend for all seasons (Figure 5.9) indicate a general increase in concentration of chloride ions from Ondiri Swamp (37.3 ±4.95 mg/L) to Museum Hill (67.9 ±27.8 mg/L), then a slight drop at

Race Course (53.3 ±14.2 mg/L) and a further drop at Outer Ring (50.5 ±4.88 mg/L) in the dry season. Similarly during the season of short rains and long rains the chloride ion concentration increased from Ondiri Swamp to Race Course then dropped at Outer Ring sampling site. The drop in concentration at the last sampling site clearly indicates that some kind of reaction may have taken place that reduces the concentration of chloride ions. This could be addition of certain components that may precipitate out the chloride ions. Sources of chloride contamination include fertilizers e.g. use of potash (KCl), treatment of domestic water and geochemical processes. The normal range for river surface water is 45mg/L to 155 mg/L. WHO and KEBS indicate allowable limits of 250 mg/L. Results from the study indicate that the water is not polluted with regard to the amount of chloride ions found.

5.10 Seasonal Variation of Total Phosphorus

Figure 5.10 is plot indicating concentration of total phosphorus versus sampling sites.

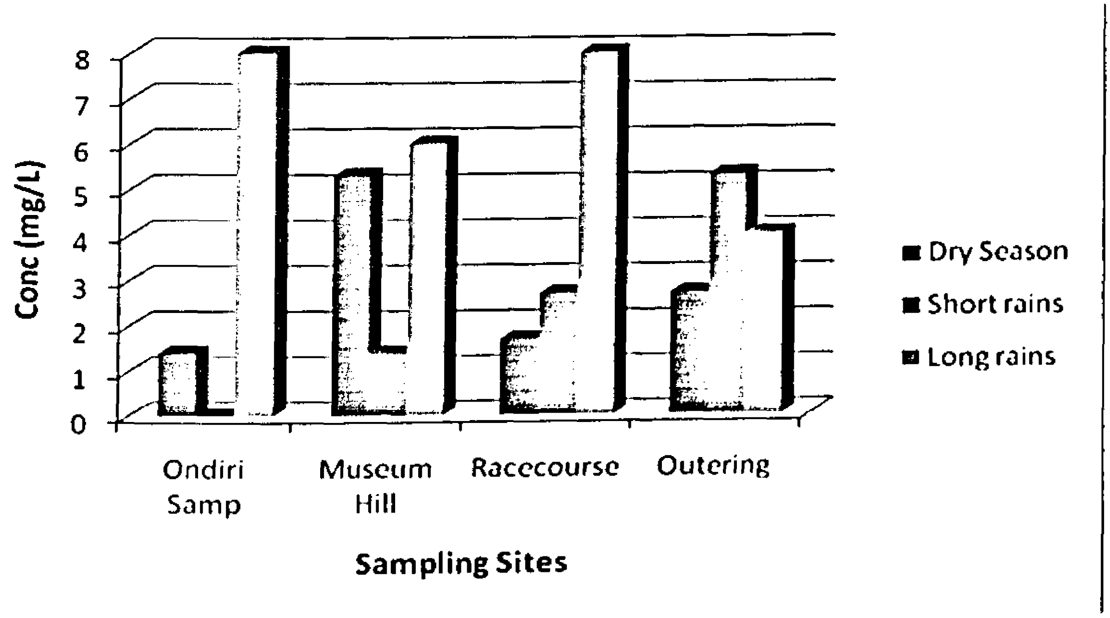


Figure 5.10: Phosphate ion variation during the dry season, short and long rains

Phosphorus is a nutrient that is essential to the growth of plants and other biological organisms but when concentrations in water are too high, noxious algal blooms can occur. Municipal waters may contain between 4 and 16 mg/L of phosphorus (Metcalf and Eddy, 2003). According to KEBS the limit of phosphorus levels in wastewater is (30 mg/L) and EU (0.1 mg/L). The concentrations recorded are within allowable limits. However, the long rainy season recorded an increase in concentrations when compared with the dry and short rainy season. During the short rainy season, the general profile showed an increasing trend downstream, possibly due to the dilution effect from upstream to downstream.

Possible sources of phosphate pollution are agricultural run off of fertilizers around Ondiri Swamp since there was a lot of agricultural activity around the site, seepage of water from the headwaters of Ondiri Swamp (rich in nutrients and cowdung), domestic waste rich in soap and detergents from residential areas (kileleshwa, Lavington and Riverside) and Chiromo hostels, beautification around Museum Hill Bridge may introduce phosphorus into the river through fertilizer or manure run off. Faecal coliforms and urine contamination under Race Course Bridge, soapy domestic wastes from food kiosks and restaurants in the central business district and wastewater from carwash and garages located before the Race Course sampling site.

According to data obtained from Kenya Meteorology Department an average of 80.7mm of rainfall was recorded in April [long rains] with a standard deviation of 3.9, while in November [short rains] an average of 188.6 mm of rainfall was recorded with a standard deviation of 68.3. The levels of phosphate ions in the month of April ranged from 4ppm to 8 ppm, while in November the levels of phosphate ions ranged from 0-5.3 ppm.

5.11 Seasonal Variation of Heavy Metals in Sediment

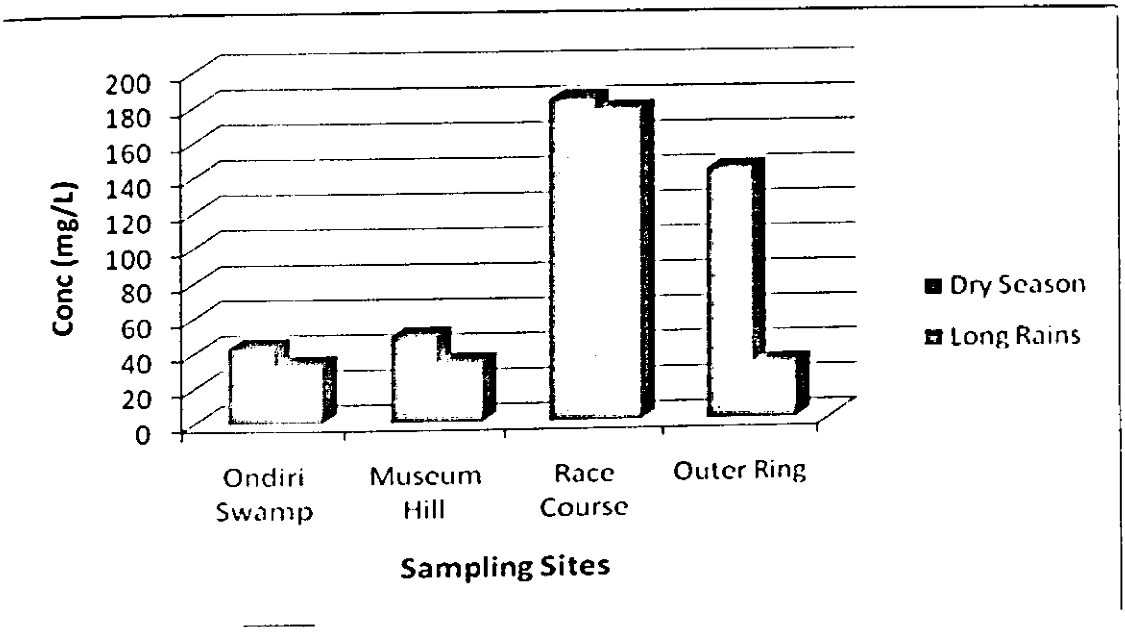


Figure 5.11: Variation of lead in sediment using XRF

Only Lead was detected in all the sampling sites (Figure 5.11, Tables 7 and 8). During the dry season concentration was highest at Race course bridge i .e 189 ±19.9 ppm. The range for the dry season was between 42.6 to 189 ppm. The relatively high values could be attributed to the numerous cottage industries in the 'Jua Kali' sector before the Race course site. This sector uses paints that may have lead. From Ondiri Swamp, the concentration progressively increases from 42.6 ±6.6 ppm, reaching its peak at Race Course then dropping to 142.5 ±15.5 ppm at Outer Ring site. Concentrations of lead in the wet season in the same sampling sites show lower values, possibly due to the dilution effect. The wet season also follows the same pattern at Ondiri Swamp concentration is 32.95 ±5.7 ppm, progressively increasing and reaching a peak of 176 ±18.5 ppm at Race Course then drastically dropping to 35.95 ±6.5 ppm at Outer Ring site.

5.12 Analysis using the atomic absorption spectrophotometer [AAS]

In the analysis of heavy metals, the operating conditions employed are summarized in Table 4.1 in chapter 4. Only lead was detected in the four sampling sites. Cadmium and chromium were not detected because of lack of nitrous oxide/acetylene which would have provided a hotter flame which allows for sensitive analysis. However, previous studies carried out by the Nairobi River Basin Programme phase III, recorded concentrations of 0.14 ppm of cadmium and 0.015 ppm of chromium at Naivasha Bridge at Mwiki sampling site.

5.13 Seasonal Variation of Heavy metals in water

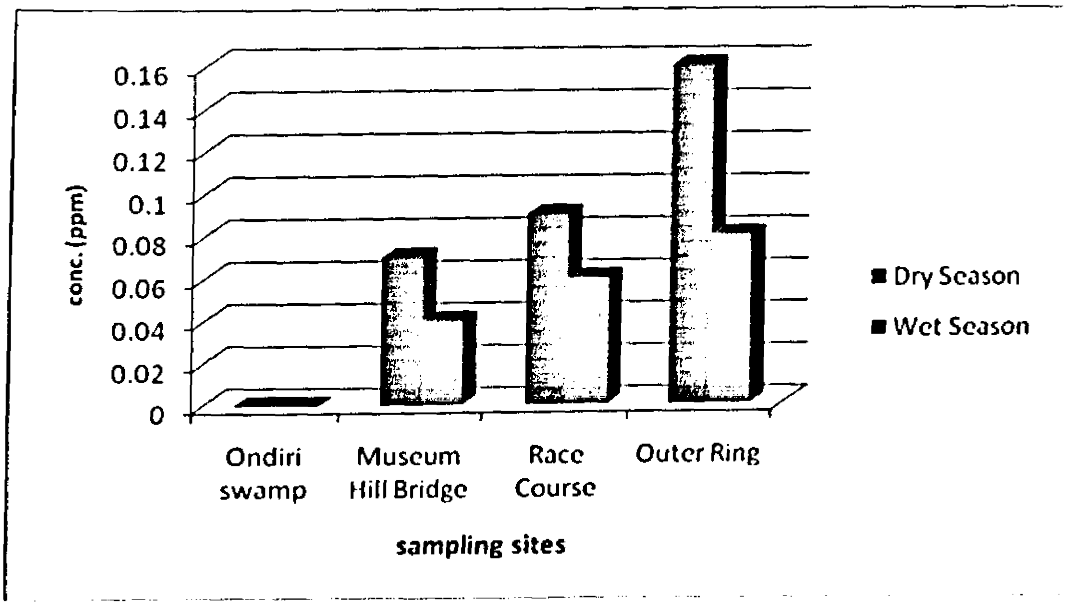


Figure 5.12: Seasonal variation of lead in water using AAS

Figure 5.12 and tables 9 and 10 (Appendix VIII) clearly indicate that lead was detected in three sampling sites during analysis. Concentrations of lead show a consistent trend of increase from upstream to downstream.

In both wet and dry seasons, no lead was detected at Ondiri Swamp, possibly because all other sampling sites are situated on busy traffic roads where there is a lot of traffic which contribute to lead pollution by the roadside which eventually reach water systems.

The cottage industries along Ngara and industrial area may release effluents that contain lead. The concentrations of Lead found are above the allowable WHO standards for potable water [0.05 ppm]. The concentration of lead in both the dry and wet season ranged from 0.07 to 0.16ppm and 0.04 to 0.08ppm.

5.14 Comparing levels of heavy metals using AAS and XRF

Table 11 (Appendix IX) indicates that lead concentrations determined using AAS are much lower than those of XRF. This would indicate that analysis using XRF is more sensitive to the analysis of lead than AAS. No cadmium was detected using XRF possibly concentrations present are minute and below the detection limit. Analysis using AAS detected a higher concentration of chromium during the dry season and it ranged from 0.06 ±0.01 ppm upstream at Ondiri Swamp to 0.24 ±0.02 ppm downstream at Outer Ring Road Bridge. During the wet season, concentrations of chromium dropped with a range of 0.01-0.21ppm. In both seasons, high levels of chromium were found at Race Course Bridge, probable sources are the cottage industries which may be using paint which is a source of chromium or those who may be tanning leather.

5.15 Factors affecting adsorption of lead ions in solution using ground fish bones

Several experiments were carried out to determine factors that would enhance the rate of adsorption using fish bone. Figures 5.1, 5.2, 5.3 and 5.4 are graphical plots of concentration of lead ions adsorbed versus factor being investigated. Experimental data for the plots can be found in Tables 13, 14, 15 and 16 in Appendix IX.

5.15.1 Effect of Contact Time on Adsorption by Fish Bones

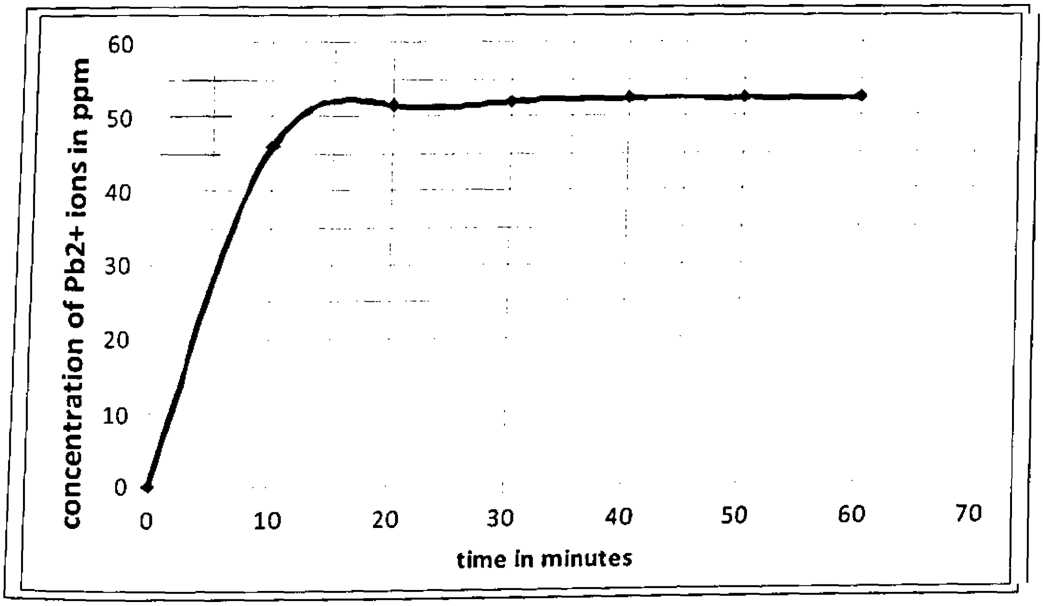


Figure 5.13 Effect of contact time on amount of lead adsorbed

Figure 5.13 (Table 13 in the Appendix IX) shows that the adsorption rate increases for the first 10 minutes, then between the 10th and 20th minute the adsorption rate increased slightly reaching maximum adsorption of 52.5 ±0.15 ppm at 40 minutes. Increase in time of contact increases number of cations adsorbed. No more adsorption takes place either because all the adsorption sites have been saturated with lead or all the lead ions in solution have been adsorbed.

5.15.2 Effect of Temperature on Adsorption by Fish Bones

The effect of temperature on the amount of lead ions adsorbed by fish bones is given in Figure 5.2.

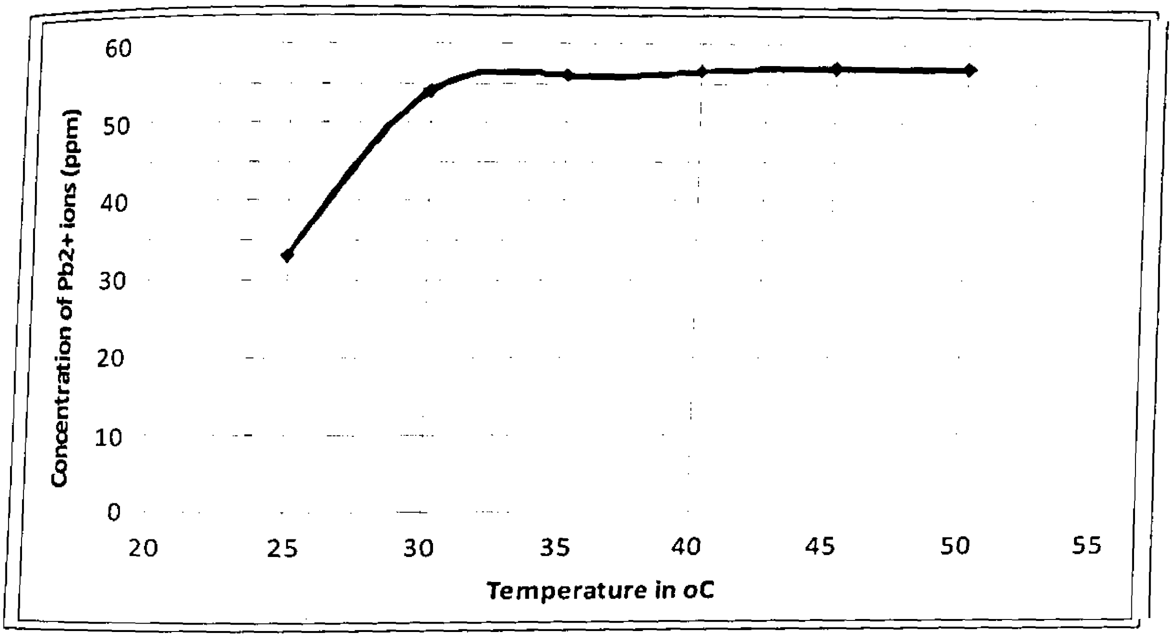


Figure 5.14 Effect of temperature on adsorption

Figure 5.14 (Table 14 appendix IX) shows rate of adsorption increasing with increase in temperature. The rate reached maximum at 45 °C at a concentration of 57 ±0.58 ppm. The experimental values clearly indicate that adsorption is an endothermic process. Increase in temperature will activate the available adsorption sites, lowers the activation energy and provides the lead ions in solution with sufficient energy to overcome the energy barrier and increasing rate of adsorption.

5.15.3 Effect of Particle Size on Adsorption by Fish bones.

Figure 5.3 shows a graphical plot of effect of particle size on adsorption fish bones.

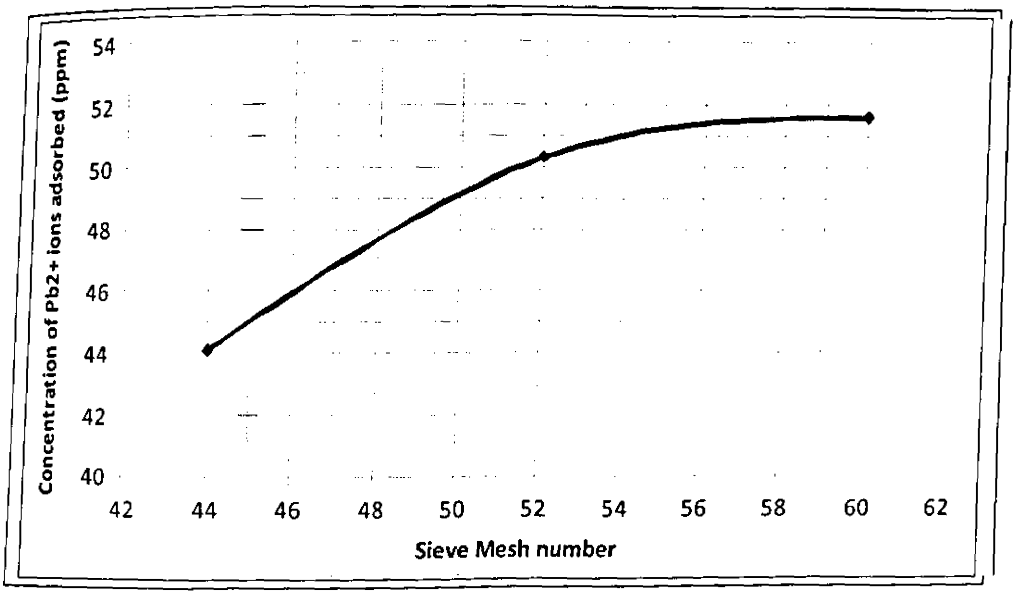


Figure 5.15 Effect of surface area on adsorption

Figure 5.15 and table 15 (see appendix IX) indicate that with increase in mesh number, particle size decreases, this in effect increases surface area hence increasing rate of adsorption. This indicates that surface area plays a crucial role in the adsorption process. Adsorption was greatest with mesh number 60 which corresponds to mesh size 250 microns.

5.15.4 Effect of Mass on Adsorption by Fish Bones

The graph indicated in Figure 5.4 shows the effect of mass on amount of lead adsorbed by fish bones.

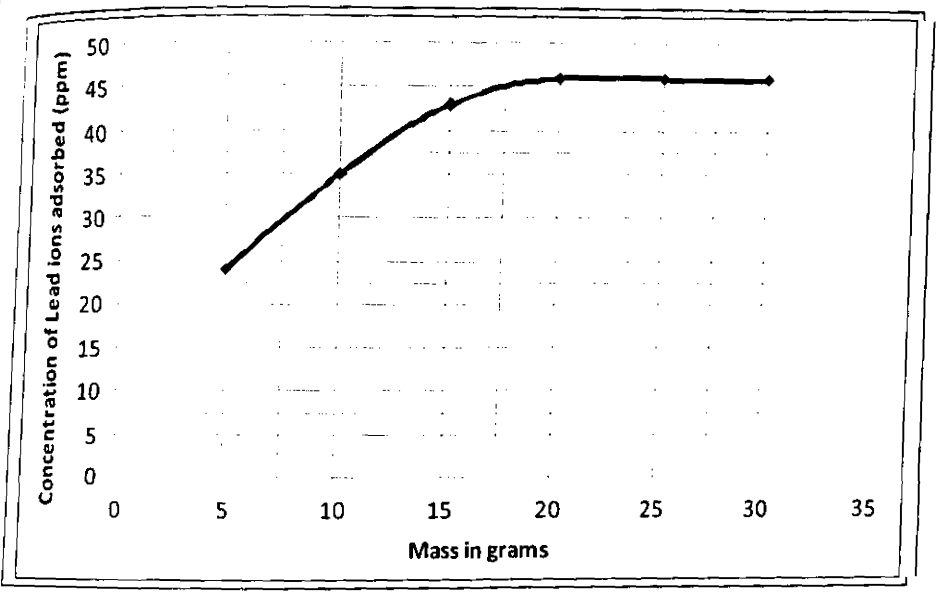


Figure 5.16 Effect of mass on adsorption

Figure 5.16 (Table 16 in Appendix IX) shows an increase in lead ions adsorbed with increase in mass of fish bone reaching a maximum adsorption rate of 46 ±0.31 ppm at 20 g. Adsorption increases with increase in weight of the fish bones. Increase in mass provides more adsorption sites, hence more ions are adsorbed. This would imply that the ratio of weight of fish bone to concentration of lead ions in solution plays a significant role in the adsorption process.

5.16 Isothermal Studies

Equilibrium relationship between the adsorbent and adsorbate can be described by adsorption isotherms. This is the ratio of quantity of metal ions adsorbed and those remaining in solution at equilibrium. Langmuir and Freundlich models were used to fit adsorption data for lead ion concentrations determined. The models have certain constants whose values when determined express surface properties and affinities of the adsorbent.

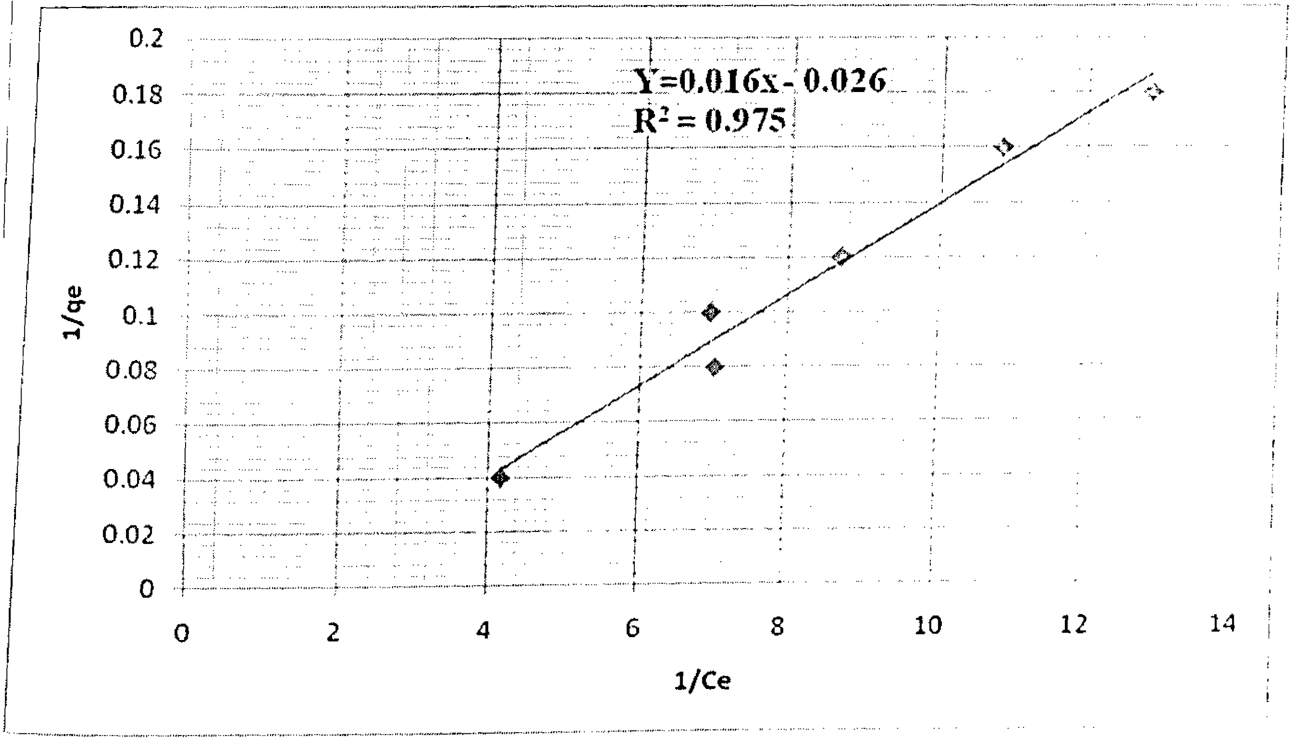


Figure 5.17: Linearised Langmuir isotherm for adsorption of lead

Langmuir isotherm equation (Langmuir, 1906):-

$$\frac{1}{q_e} = \frac{1}{Q_0 b C_e} - \frac{1}{Q_0}$$

C_e= Equilibrium concentration (mg/L)

q_e = Amount adsorbed per unit mass of adsorbent at equilibrium (mg/L)

$Q_o b$ = Langmuir constants relating to the maximum adsorption capacity and adsorption energy respectively

The y-intercept of the graph plotted in figure 5.18 is 0.026, therefore 1/Qo = 0.026, therefore Q_o will be

38.5 mg/g. The slope of the Langmuir curve is 0.016, therefore 1/ (bCe) Qo = 0.016 implying that the adsorption energy, b = 1.625.L/mg.

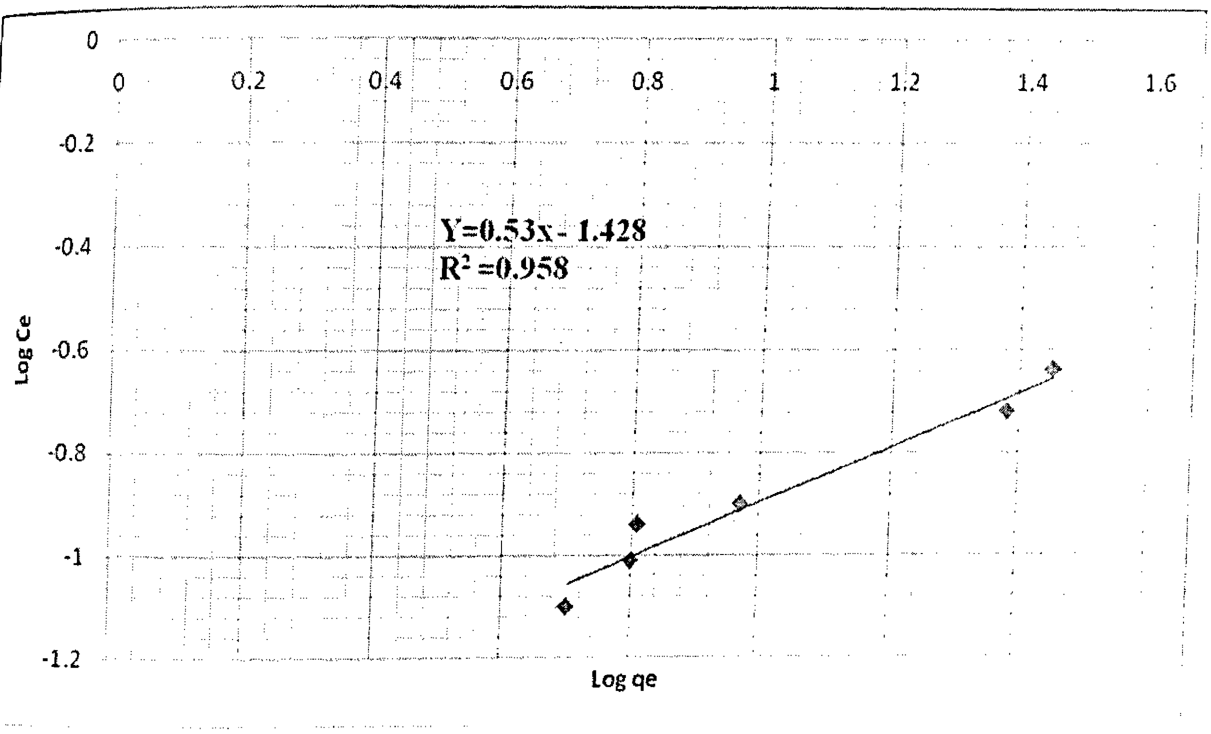


Figure 5.18 Linearised Freundlich isotherm for adsorption of lead.

Freundlich isotherm equation (Freundlich, 1916) is expressed;

$$\log q_e = \log K_f + \frac{1}{n}\log C_e$$

Where,

C_e = the Concentration of adsorbate in solution at equilibrium (mg/L).

q_e = Amount of metal adsorbed per unit weight of adsorbent (mg/gm)

K_f = equilibrium constant indicative of adsorption capacity;

n = adsorption equilibrium coefficient.

Using figure 5.19 and Freundlich isotherm, the y-intercept is given as Log K_f= -1.428 therefore K_f = 37.33 mg/g. The slope of the Freundlich curve is 0.53, therefore 1/n = 0.53 hence n = 2.

Table 5.3: showing Langmuir and Freundlich Parameters

Langmuir	R^2	Q_0[mg/g]	b[L/mg]
Parameters	**0.975**	**38.5**	**1.625**
Freundlich	R^2	K_f [mg/g]	n
Parameters	**0.958**	**37.33**	**2**

Langmuir explains the monolayer adsorption; Maximum adsorption capacity was 0.29 mg/g and Adsorption energy is 0.08 L/mg. Freundlich Isotherm explains the multi-layer adsorption, the n value from the isotherm is 2, an indicator of a good adsorbent The value of K_f was relatively high 37.33 mg/g hence the fish bones has high affinity for adsorption. The Langmuir model best explains the adsorption process using fish bones. Based on the graphical plot and the value of R^2, the Langmuir model gives the best fit, indicating that the adsorption process is monolayer.

CHAPTER 6

CONCLUSION AND RECOMMENDATIONS

6.1 Conclusion

Water is a basic resource and its sustainable use demands that water should not be interfered with. Yet, the limited available water has deteriorated due to infiltration of pollutants from different human activities. The case in point is the Nairobi River; the study carried out from November, 2008 to April 2009, provides information on the general water quality of the river. This was with reference to physico-chemical characteristics, concentration of pollutants, and aesthetic nature of the water. Results obtained from the study reveal that Nairobi River is polluted.

The analysis showed that pollution sources of the Nairobi River can be divided into point sources and non point sources. The effluents from the industries and the 'jua kali' sector, agriculture, wastes from residential areas and the informal settlements make up the former, while pollutants carried by the run off of earth surface formed the latter.

Concentration of pollutants during the month of long rains was higher than during the month of short rains, which was unexpected. Generally, one would expect concentration of pollutants to decrease due to the dilution effect. However, when one looks at Table 6.1 which gives the amount of rainfall recorded by the Kenya Meteorological Department (KMD) during the period of the study, then one would understand the trend of results obtained for the two rainy seasons.

The average rainfall in November (short rainy season) was 174 ±68.8 mm with a range of between 82.6 to 248.3 mm, while in April (long rainy season) a mean of 81 ± 3.9 mm with a range of 75.7 to 84.5.

Table 6.1 Kenya Meteorological Department – Rainfall in Nairobi Nov.2008 –April, 2009

Nairobi Stations	November 2008	December 2008	January 2009	February 2009	March 2009	April 2009
9136130	248.3	1	59.4	17.0	19.4	83.1
9136164	172.2	0.5	64.5	20.1	137.9	79.3
9136168	82.6	0	52.4	34.1	27.1	84.5
9136208	191.6	5.3	42.8	18.1	76.6	75.7

Source: KMD, (2009) N/B: Rainfall in millimetres (mm)

91360130 - Wilson Airport

91360164 - Dagoretti Corner

91360168 – JKIA Airport

91360208 – Kabete Agrovet Station

These waters showed a pH varying between 6.4 and 8.3 indicating that the water was either acidic, neutral or basic, conductivity varied between 196.2μS and 907.3μS, the high conductivity value may be due to localised pollution sources, temperatures ranged between 17.8° C and 32.2°C this corresponds to seasonal variations and sampling times. TDS varied from 98.7mg/L and 454.7mg/L, while TSS varied between 8mg/L to 174.3mg/L, depending on the activity taking place by the river environs, agricultural activity and burning of wastes by the riverside increases turbidity and concentration of TSS.

The Biochemical Oxygen Demand and Chemical Oxygen Demand content induced due to organic waste disposal and microorganisms within the rivers showed an increasing trend from upstream to downstream. This is attributed to continuous output of organic wastes from domestic activities, industries, the 'jua kali ' sector and direct raw sewage discharge.

Sources of lead contamination are mainly from car battery acids and paints from motor vehicles. Although lead free petrol was in sale during the time of my study, one may not completely rule out leaded petrol in cars from other countries plying Kenyan roads.

Accumulation in water sources is due to run-off which transports spilt car battery acids and paint from garages and the 'jua kali' sector and erosion of large amount of soil contaminated with lead. The study detected levels of lead that exceeded allowable WHO guidelines of 0.05mg/L.

X-Ray Fluorescence Analysis is a useful technique in the determination of heavy metals. The method has several advantages over Atomic Absorption Spectrometry which requires samples to be in solution making them susceptible to contamination. In X-Ray Fluorescence, there is minimum sample preparation and multi element analysis can be done. The deviations may have resulted from inhomogeneity. It is not easy to homogenize an element in a sample if the element is present in very low concentration. This problem is minimized in X-Ray Fluorescence since the sample is finely ground and screened through a very fine mesh size 150μ m.

6.3 Analysis using fish bones

Lead is a contributor to the global water crisis, with significant health problems resulting from drinking water with levels higher than the 0.05 mg/L WHO guidelines and EU standards. This study evaluated ground fish bone as an appropriate adsorbent for lead removal and investigated the factors that would increase and maximize rate of adsorption. Data suggests that fish bone is a viable option for lead removal.

The experiments carried out established that 20g of fish bone ground finely, screened through size 60 mesh sieve (mesh size 250 microns) and agitated in an orbital shaker for thirty (30) minutes at a temperature of 45 °C, registered the highest rate of adsorption. The following results were also obtained when conductivity and pH of water samples from Outer Ring were investigated before and after remediation using ground fish bone. Conductivity of water sample after remediation decreased from 236.8 μs to 102.6 μs while the pH remained fairly constant at 7.14 from 7.10 indicating that fish bones play a buffering role when placed in aqueous solution.

In the analysis using AAS, before remediation the concentration of lead in the water was 0.11ppm. After remediation using fish bones the concentration of lead ion dropped to 0.08 ppm, this represents a 27% reduction in concentration of lead nitrate solution.

The advantage of using fish bones in remediation is that they are inexpensive, readily available, environmentally friendly and an effective metal ion adsorbent from nature as an alternative to existing conventional adsorbents. Other than reducing the amount of fish bones discarded which may pollute the environment, this process will provide an affordable technology for small and medium scale industries and create wealth to local communities by enhancing local entrepreneurship.

6.4 Recommendations

The value of water quality cannot be overestimated. There is need to provide clean reliable water, a resource that is critical to our health and quality of life. Protecting water resources for future sustainable use will require research, financial planning, communication, innovative solutions and sound policy decisions by the Government.

From the discussions carried out, the following recommendations are made:-

1. Funding for training and establishing a monitoring programme to continually monitor levels of pollutants in the Nairobi River so that they do not reach critical levels.
2. Upgrading of slums by installation of a sewage system to reduce domestic effluents being released into the Nairobi river waters.
3. No form of farming or any activity should be allowed within 30 meters of the river vicinity.
4. The water treatment plants could consider the possibility of using fish bone as it offers a low cost treatment of wastewater containing heavy metals.

5. Enforce existing legislations on disposal of wastes by industries, the 'jua kali' sector, central business district and the Kenyan population to control standards to regulate the quantities discharged into water systems.
6. Investigate other forms of bones which are abundant e.g. cattle bones as a possible adsorbent for heavy metals.
7. Investigate whether fish bones adsorb other pollutants other than heavy metals.
8. The nature of the bond in the adsorption process should be studied in detail using x-ray crystallography to provide information on the possibility of recycling fish bones after use.
9. There is also need to study competitive adsorption of the toxic metals with respect to ground fish bones.
10. Investigate fish bone char as a possible adsorbent.

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Appendix

Appendix Ia: Ondiri Swamp

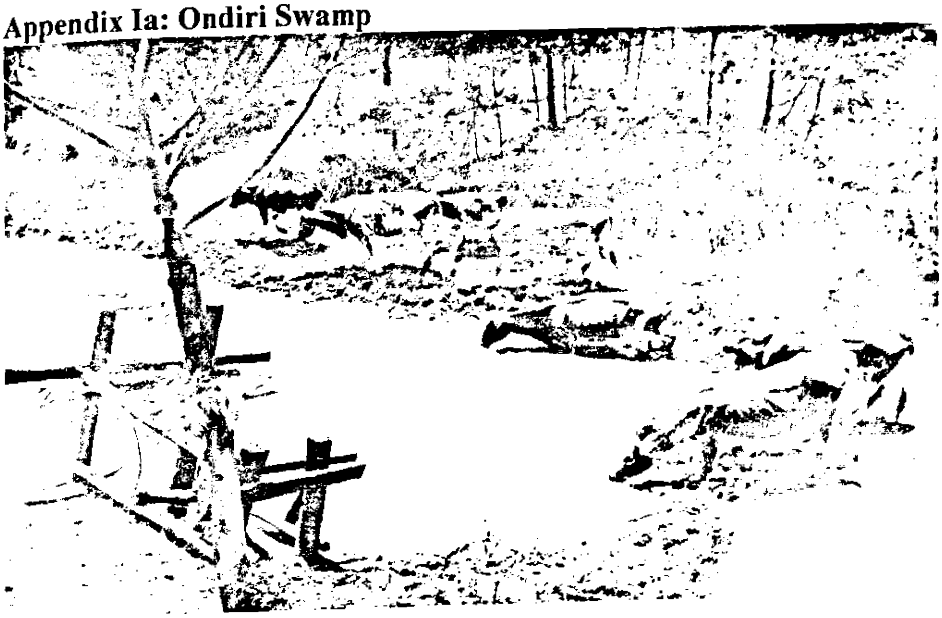

Figure 5.1a: Headwaters of Ondiri Swamp

Appendix Ib: Activities round Ondiri Swamp

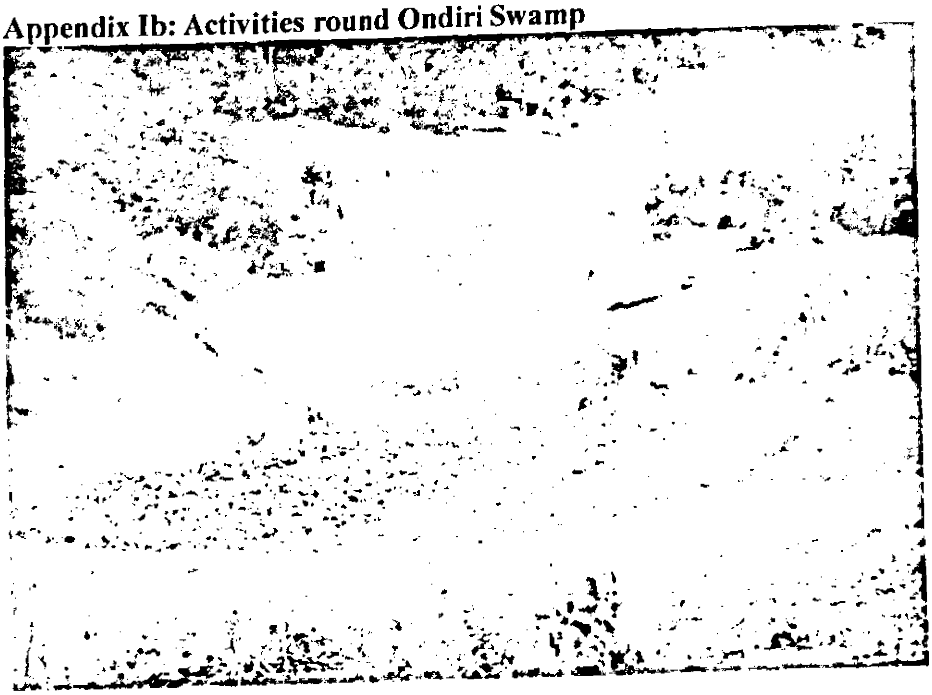

Figure 5.1b: Agricultural activities round Ondiri Swamp

Appendix Ic: The Ondiri Swamp sampling site

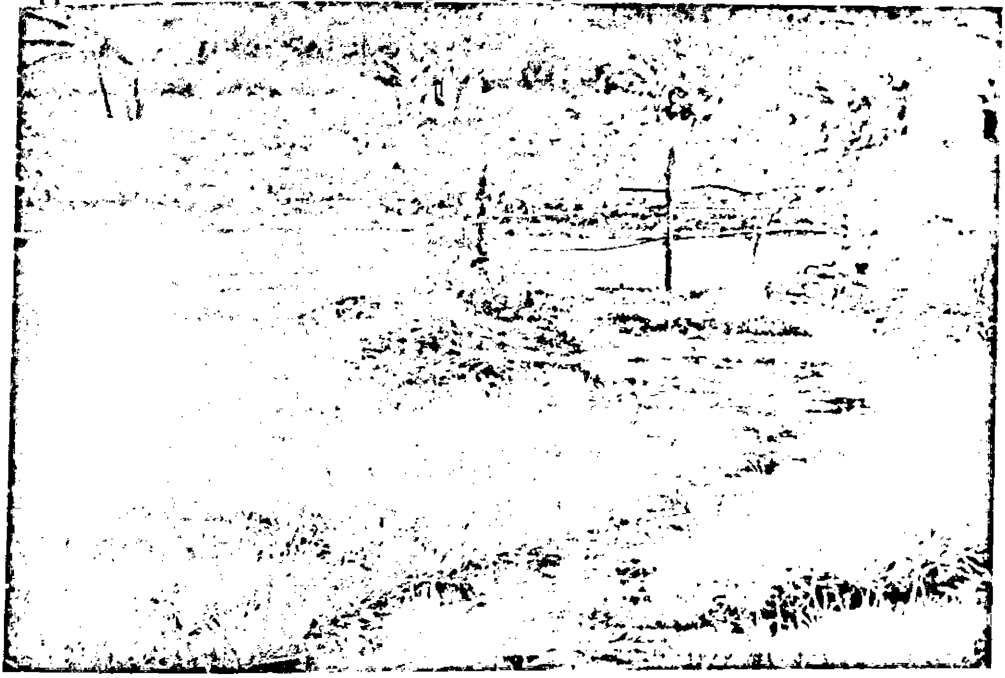

Figure 5.1c: Ondiri Swamp sampling site

Appendix Id: State of water at Ondiri Swamp

Figure 5.1d: Ondiri Swamp sampling site

Appendix IIa: Museum Hill Bridge

Figure 5.2a: Museum Hill Bridge sampling site

Appendix IIb: Activities round Museum Hill Bridge

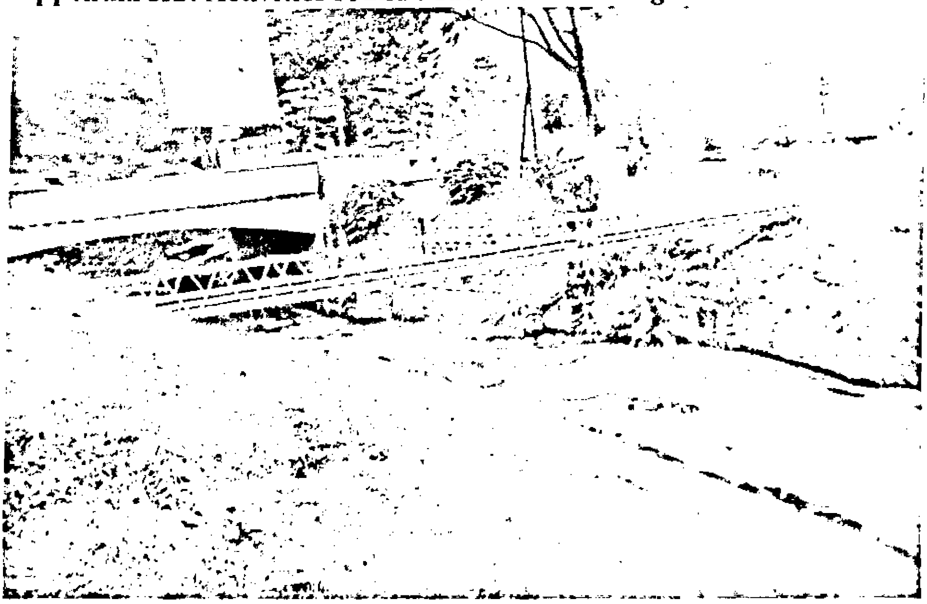

Figure 5.2b: Activities surrounding Museum Hill Bridge

Appendix IIc: Beautification round the Museum Hill Bridge

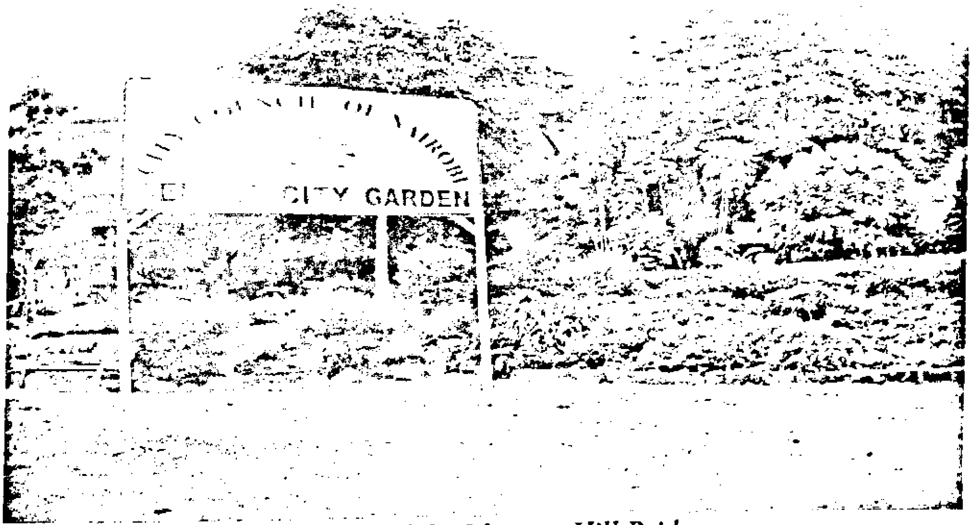

Figure 5.2c: Beautification round the Museum Hill Bridge

Appendix IIIa: Race Course Road Bridge

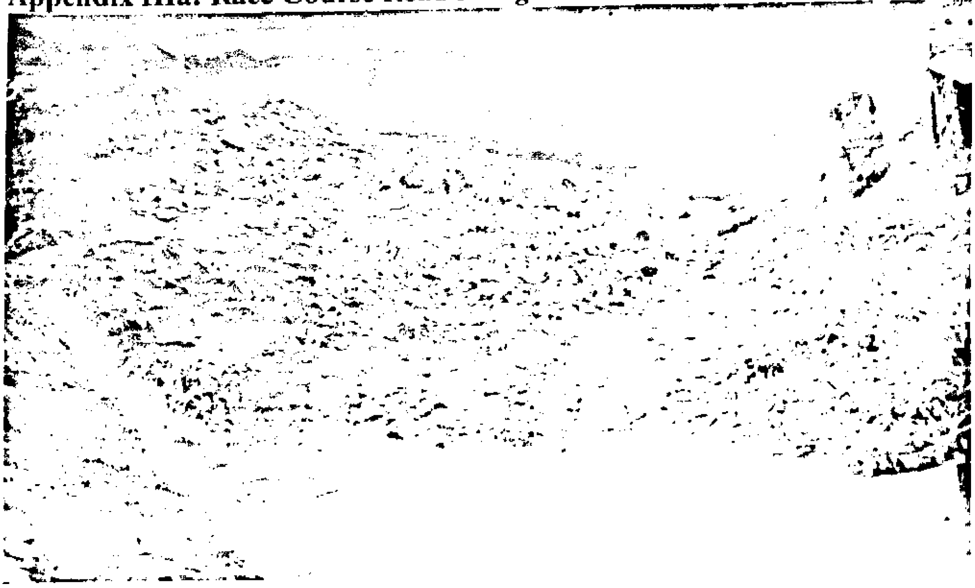

Figure 5.3a: Race Course sampling site

Appendix IIIb: State of water at Race Course

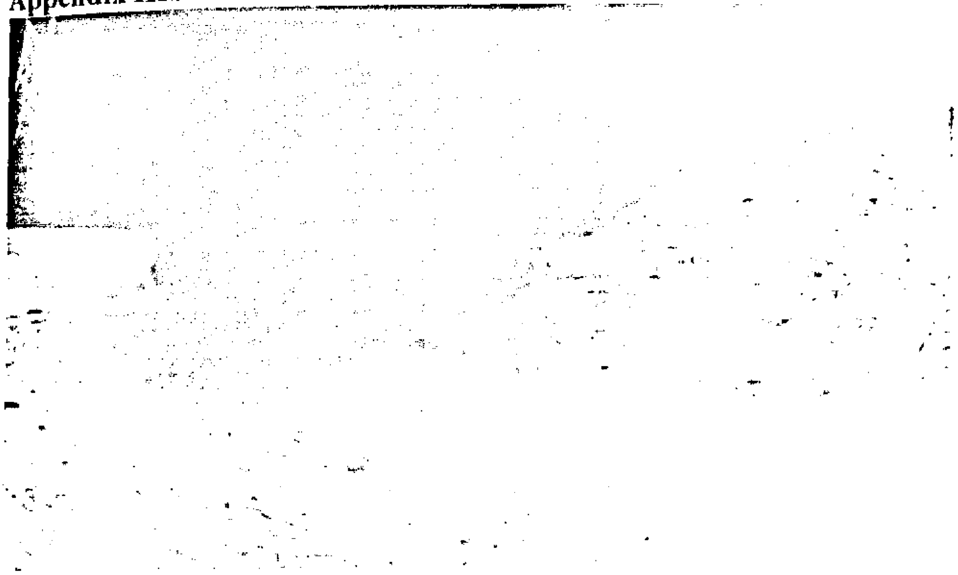

Figure 5.3b: Race Course sampling site

Appendix IVa: Outer Ring Road Bridge

Figure 5.4a: Outer Ring Road Bridge sampling site

Appendix IVb: State of water at Outer Ring sampling site

Figure 5.4b: Outer Ring sampling site

Appendix IVc: Activities that occur near Outer Ring Road Bridge

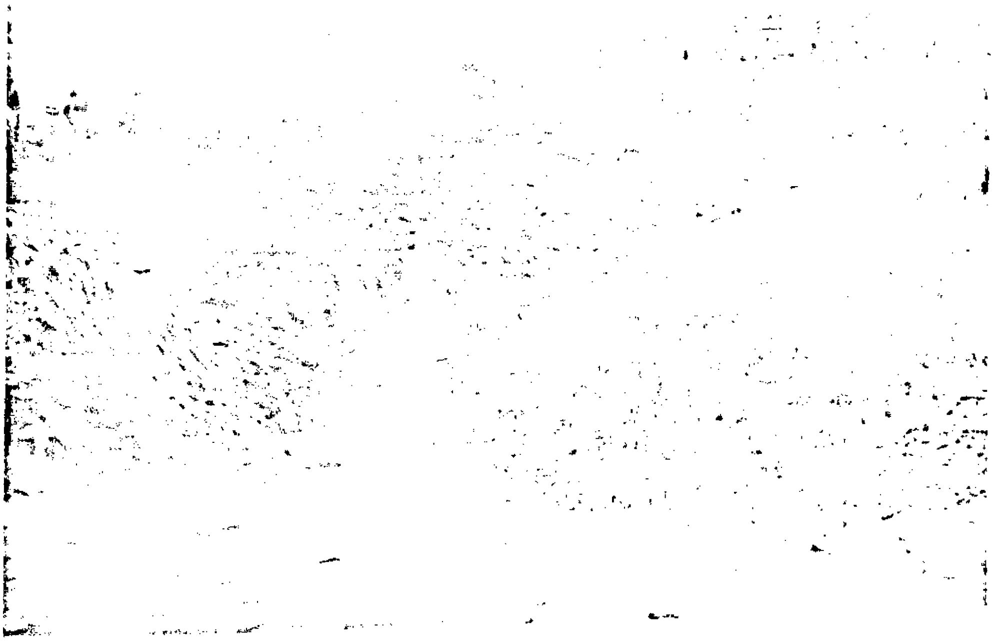

Figure 5.4c: Outer Ring sampling site

Appendix V: Data of physical parameters

Table 1: Physical analysis results – Dry season

Parameters	Ondiri Swamp	Museum Hill	Race Course	Outer Ring
pH	6.48 ± 0.45	7.32 ± 0.28	6.93 ± 0.31	6.99 ± 0.19
Conductivity (mg/L)	270 .0± 1.38	588 .0± 12.3	562 .0 ± 11.7	687.7 ± 12.3
TDS (mg/L)	101.0 ± 0.3	270.0 ± 1.4	333 .0 ± 5.6	313.8 ± 4.0
TSS (mg/L)	30.6 ± 6.8	50.0 ± 6.2	84.0 ± 8.9	79.0 ± 7.1
Temperature (^{0}C)	25.2 ± 5.65	19.7 ± 1.30	20.7 ± 1.82	19.9 ±1.68

Table 2: Physical analysis results – [wet season] Short rains

Parameters	Ondiri Swamp	Museum Hill	Race Course	Outer Ring
pH	7.24 ± 0.37	8.25 ± 1.00	7.57 ± 0.29	7.31± 0.43
Conductivity (mg/L)	196.2 ± 1.40	549.0 ± 2.0	592.3 ±1.53	562.0 ± 1.0
TDS (mg/L)	98.67 ± 1.15	273.33 ± 1.53	295.00 ± 1.00	273.33 ± 1.53
TSS (mg/L)	20.67 ± 12.09	52.33 ± 7.51	66.00 ± 1.73	39.33 ± 0.58
Temperature (^{0} C)	32.2	22.2	22.2	23

Table 3: Physical analysis results – [wet season] long rains

Parameters	Ondiri Swamp	Museum Hill	Race Course	Outer Ring
pH	6.47 ± 0.11	6.70 ± 0.06	6.82 ± 0.27	7.10 ± 0.28
Conductivity (mg/L)	202.0 ± 0.00	602.67 ± 1.15	681.33 ± 6.35	630.00 ± 2.65
TDS (mg/L)	100.33 ± 0.58	300.33 ± 0.58	339.33 ± 2.89	314.00 ± 1.00
TSS (mg/L)	39.67 ± 4.93	70.33 ± 11.37	164.67 ± 6.66	99.33 ± 0.33
Temperature (^{0} C)	21.1	22.2	25	22.2

Appendix VI: Data of chemical parameters

Table 4: Chemical analysis results – dry season

Parameters	Ondiri Swamp	Museum Hill	Race Course	Outer Ring
Oil and grease (mg/L)	132.1 ± 19.7	67.5 ± 3.1	14.5 ± 7.2	6.3 ± 1.6
COD (mg/L)	372.6 ± 0.0	667.0 ± 7.10	525.0 ± 16.3	1353.0 ± 22.3
BOD (mg/L)	333.0 ± 46.7	366.3 ± 57.7	583.3±70.7	455.3± 57.7
Chloride ion [Cl^- (mg/L)	37.3 ± 4.95	67.9 ± 27.8	53.3 ± 14.2	50.5 ± 4.88
Phosphate ion [PO_4^{3-}] (ppm)	1.4 ± 0.0	5.3 ± 0.0	1.7 ± 0.7	2.7 ± 1.8
Alkalinity (mg/L)	213.4 ± 6.53	460.5 ± 13.44	356.7 ± 21.47	300.2 ± 12.75

Table 5: Chemical analysis results -Wet season [short rains]

Parameters	Ondiri Swamp	Museum Hill	Race Course	Outer Ring
Oil and grease (mg/L)	172.2 ± 92.70	3.8 ± 0.28	0.6 ± 0.00	264.2 ± 5.10
COD (mg/L)	466.2± 0.00	333.0± 0.00	2133.0± 0.00	3000 .0± 14.10
BOD (mg/L)	4.4± 0.0	55.3± 4.7	199.9± 0.0	333.0 ±0.0
Chloride ion [Cl^-] (mg/L)	34.8 ± 0.00	74.6 ± 0.00	84.5 ± 0.00	54.7 ± 0.00
Phosphate ion [PO_4^{3-}] (ppm)	0	1.4 ± 0.0	2.7 ± 0.0	5.3 ± 0.0
Alkalinity (mg/L)	215.0 ± 0.10	505.0 ± 0.09	450 .0± 0.00	490.0 ± 1.38

Table 6: Chemical analysis results – wet season [long rains]

Parameters	Ondiri Swamp	Museum Hill	Race Course	Outer Ring
Oil and grease (mg/L)	99.4± 49.5	15.9 ± 5.3	22.0 ± 3.6	8.1 ± 6.7
COD(mg/L)	3110.0 ± 18.9	6600 .0± 28.3	1798.0± 28.3	2353.3± 23.1
BOD (mg/L)	1350.0 ± 10.0	1411.0 ± 58.5	1549.0 ± 0.0	1366.0 ± 15.0
Chloride ion [Cl^-] (mg/L)	43.7 ± 0.00	74.6 ± 0.00	94.4 ± 0.00	63.5± 0.00
Phosphate ion [PO_4^{3-}] (ppm)	8	6	8	4
Alkalinity (mg/L)	225.5 ± 34.7	387.5 ± 3.5	460.0 ± 28.3	405.0 ± 7.1

Appendix VII: Data of heavy metals in sediment

Table 7: Heavy metal content in sediment using XRF – wet season

Element	Ondiri Swamp	Museum Hill	Race Course	Outer Ring
As	LDL	LDL	LDL	LDL
Cd	LDL	LDL	LDL	LDL
Cr	LDL	LDL	LDL	LDL
Pb [ppm]	32.95 ± 5.7	41.1 ± 4.9	176.5 ± 18.5	35.95 ± 6.5

LDL: Low detection limit

Table 8: Heavy metal content in sediment using XRF – dry season

Element	Ondiri Swamp	Museum Hill	Race Course	Outer Ring
As	BDL	BDL	BDL	BDL
Cd	BDL	BDL	BDL	BDL
Cr	BDL	BDL	BDL	BDL
Pb [ppm]	42.6 ± 6.6	46.1 ± 7.5	189.0 ± 19.9	142.5 ± 15.5

BDL: below detection limit

Appendix VIII: Data of heavy metals in water

Table 9: Concentration of heavy metals in the water sample [dry season]

Metal	Ondiri swamp	Museum Hill Bridge	Race Course	Outer Ring
As	ND	ND	ND	ND
Cd	ND	ND	ND	ND
Cr	ND	ND	ND	ND
Pb [ppm]	ND	0.07 ± 0.05	0.09 ± 0.05	0.16 ± 0.05

ND: Not detected

Table 10: Concentration of heavy metals in the water sample -wet season

Metal	Ondiri swamp	Museum Hill Bridge	Race Course	Outer Ring
As	ND	ND	ND	ND
Cd	ND	ND	ND	ND
Cr	ND	ND	ND	ND
Pb [ppm]	ND	0.04 ± 0.02	0.06 ± 0.02	0.08 ± 0.02

ND: Not detected

Appendix IX: Data showing comparisons of heavy metal concentrations using AAS and XRF

Table 11: Comparing concentrations of heavy metals (Pb) in sediment using AAS and XRF

Method of analysis	Seasons	Ondiri Swamp	Museum Hill Bridge	Race Course	Outer Ring
XRF	Wet	32.95 ± 5.7	41.1 ± 4.9	176.5 ± 18.5	35.95 ± 6.5
AAS		0.62	0.39	2.14	1.63
XRF	Dry	42.6 ± 6.6	46.1 ± 7.5	158.0 ± 11.8	142.5 ± 15.5
AAS		0.71	0.33	2.37	1.33

Table 12: Comparing concentrations of heavy metals (Cr) in sediment using AAS and XRF

Method of analysis	Seasons	Ondiri Swamp	Museum Hill Bridge	Race Course	Outer Ring
XRF	Dry	BDL	BDL	BDL	BDL
AAS		0.06	0.06	0.24	0.11
XRF	Wet	BDL	BDL	BDL	BDL
AAS		0.04	0.04	0.21	0.01

BDL: Below Detection Limit

Appendix IX: Data on factors affecting adsorption

Table 13: Effect of contact time on amount of adsorbed Pb^{2+}

Time [minutes]	0	10	20	30	40	50	60
Concentration of lead ions [ppm]	0	46	48	52	52.5	52.5	52.5

Table 14: Effect of temperature on amount of adsorbed Pb^{2+}

Temperature [°C]	25	30	35	40	45	50
Concentration of lead ions [ppm]	33	54	56	56.5	57	57

Table 15: Effect of particle size on amount of lead ions adsorbed.

Sieve mesh number	44	52	60
Concentration of lead ions [ppm]	44.1	50.3	51.6

Table 16: Effect of mass on amount of lead ions adsorbed

Mass of ground fish bones [g]	5	10	15	20	25	30
Concentration of lead ions [ppm]	24	28	43	46	46	46

Appendix XI: Langmuir and Freundlich Model

Table 17: Langmuir and Freundlich Model

$Weight\ of\ fish\ bone\ [m]$	5g	10g	15g	20g	25g	30g
$Co(\frac{mg}{L})$	52.50	52.50	52.50	52.50	52.50	52.50
$Ce\left(\frac{mg}{L}\right)$	28.50	12.50	10.00	8.33	6.28	5.01
$[Co - Ce](\frac{mg}{L})$	24.00	40.00	42.50	44.17	46.22	47.49
$Volume, V(L)$	0.05	0.05	0.05	0.05	0.05	0.05
$qe = \frac{[Co - Ce]V}{m}(\frac{mg}{mg})$	0.23	0.19	0.13	0.12	0.10	0.08
$\frac{1}{qe}(\frac{mg}{mg})$	4.17	7.02	6.95	8.70	10.82	12.82
$\frac{1}{Ce}\left(\frac{L}{mg}\right)$	0.04	0.08	0.10	0.12	0.16	0.18
$Logqe$	-0.64	-0.72	-0.90	-0.94	-1.01	-1.10
$LogCe$	1.45	1.38	0.97	0.81	0.80	0.70