isAN ASSESSMENT OF HEAVY METALS IN WATER, SEDIMENTS, AND FAUNA OF SELECTED AREAS ALONG THE KENYAN COASTLINE

BY

SALIM MWATSAHU (B.Sc)
REG. NO.: I56/CE/10486/04

A THESIS SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE AWARD OF THE DEGREE OF MASTER OF SCIENCE IN APPLIED ANALYTICAL CHEMISTY IN THE SCHOOL OF PURE AND APPLIED SCIENCE OF KENYATTAUNIVERSITY

FEBRUARY 2013

DECLARATION

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

________________________________ Date:_____________________

Salim Hassan Mwatsahu
Department of Chemistry

This thesis has been submitted with our approval as the University supervisors.

________________________________ Date:_____________________

Dr. Ruth Wanjau
Department of Chemistry
KenyattaUniversity

________________________________ Date:_____________________

Prof. Mwakio Tole
Department of Environmental Sciences
Pwani University

________________________________ Date:_____________________

Dr. Daniel Munga
Technical University of Mombasa
Mombasa

DEDICATION

I dedicate this work to my wife, Fatuma and my sons, Khalil, Rahim and Shebe.

ACKNOWLEDGEMENTS

First I wish to thank Prof. Mwakio Tole for letting me participate in the UNEP-GEF WIO-Lab project, 2007 which enabled me to undertake this research. Secondly my thanks go to my supervisors Prof. Mwakio Tole of Pwani University, Dr. Ruth Wanjau of KenyattaUniversity and Dr. Daniel Munga of Technical University of Mombasa for their advice, guidance and encouragement.

I wish to express my appreciation to Prof. Mohamed Rajab of Pwani University for the assistance and support he gave me and to Dr. David Maina of Institute of Nuclear Science, University of Nairobi for allowing me to use their XRF instrument. My appreciation also to Mr. Simon Bartilol of Institute of Nuclear Science, University of Nairobi for his assistance with the XRF instrument.

I wish to thank Kenya Marine and Fisheries Research Institute for the assistance they extended to me in transportation and sampling for this research project. Also I wish to thank the Institute of Nuclear Science, University of Nairobi for allowing me to do some of the analysis at the institute. My deep appreciation goes to Kenyatta University, Department of Chemistry for according me the chance to do my M.Sc, and to all my colleagues and friends in the department who continuously encouraged me through out the course.

Finally, I greatly appreciate the support from my family towards the successful complexion of my studies. Above all, I thank Allah for giving me the energy, positive attitude and good health that enabled me to undertake this study.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

ABBREVIATIONS AND ACRONYMS

SHO	-	Shirazi Oyster
BOD	-	Biological Oxygen Demand
EEC	-	European Economic Community
ANZECC	-	Australian and New Zealand Environmental and Conservation Council

ABSTRACT

Every year millions of tones of industrial wastes and municipal sewage are dumped into the world oceans as rivers carrying agricultural wastes discharge their waters into the ocean. The Mombasa inshore (Kilindini and Portreiz) waters and Sabaki/Malindi bay complex are characterized by rapid urbanization, industrial activities including shipping, agriculture and tourism. As a result, the coastal fauna, sediments and sea water are polluted with heavy metals, raw sewage and organochlorine pesticides. Heavy metals such as Cadmium (Cd), Copper (Cu), Chromium (Cr), Lead (Pb), Iron (Fe), Manganese (Mn), Mercury (Hg), and Zinc (Zn) have threshold limits (USEPA) above which they are toxic. The aim of this study was to assess the levels of heavy metals Cd, Cu, Cr, Fe, Mn, Hg and Zn at selected areas along the Kenyan Coastline. The analysis was done, during the dry and wet seasons. The levels of the heavy metals were determined using Atomic Absorption spectro-photometry flameless Atomic Absorption Spectrophotometry (Mercury cold vapour) and Energy Dispersive X-ray fluorescence. The levels of the metals were as follows: In sediments Hg: nd, Cr: nd, Cu: 9.912- 40.412-µg/g, Fe: 3,195.667-35,435.981 µg/g, Mn: 135.467-228.780 µg/g, Zn: 54.700 -181.725 µg/g. Biota: Hg: nd, Cr: nd, Cu: 43.963-229843 µg/g, Mn: 29.770-486.611 µg/g, Fe: 379.853-35,277.752 µg/g, Zn: 99.476-872.852 µg/g, Cd: nd, Pb: 135.407-833.111 µg/g. Sea water: Cr: 0.015-0.026 µg/ml, Fe: 0.062-16.524 µg/ml, Cu: 0.010-0.033 µg/ml, Zn: 0.028-0.066 µg/ml, Pb: 0.006-0.010 µg/ml. Cd and Hg levels were not detected in seawater, sediments, and fauna while Cr was not detected in sediments and fauna but had levels above USEPA guidelines at sites at Kilindini, at Malindi Bay and at Sabaki estuary. Cu had levels above USEPA guideline at Sabaki in the water and in sediments at most sites. Pb levels were above USEPA guidelines at most sites of the Kenyan Coastline while Zn levels indicated moderate pollution in seawater, sediments and fauna. These findings indicated that sea water sediments and fauna from the Kenyan Coastline are moderately polluted with Cu, Pb and Zn according to USEPA guidelines. It is recommended that regular assessments of pollution levels be done and measures be put in place to prevent increased pollution of the Kenyan Coastline.

CHAPTER ONE

INTRODUCTION

1.1 Background information

Human beings have a great impact on the environment since they manipulate it for their benefit. The components of the ecosystem, namely air, water and soil are greatly affected through pollution. Pollution in the world is a major health and environmental concern. This concern is priority for action since environmental pollution affects the well being of all organisms in their habitats (Magothe, 2009). Marine pollution has been defined as the introduction of substances or energy into the marine environment resulting in such deleterious effects as to harm living resources, hazards to human health and hindrance to marine activities, and reduction of amenities (Explain that stuff, 2009). Further point source pollution is contamination that enters the environment through any discernible, confined and discrete conveyance, (Advameg, Inc., 2011). Non point sources on the other side are those that spread over a large area and have no specific outlet or discharge point. (NOAA, 2011).

Heavy metals enter the atmosphere from natural sources including volcanic eruptions which throw debris and particulate matter into the air and weathering of soil and rocks. The detrital metals are washed by rain into rivers and eventually into the ocean (Sheik *et al*., 2007). Sub marine volcanic activities and leaching of the ocean floor are also among the natural processes that have caused the enrichments of these elements. (Hashim, 2001).

Since industrialization in the late 1940s and 1950s, the amount of contaminants and toxic substances put into the oceans has greatly increased (USEPA, 2006). These contaminants include heavy metals such as Hg, Pb, Cd, Zn, Cr and Cu and synthetic (man-made) organic compounds such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), pesticides (for example dichlorodiphenyl trichloroethane (DDT)), and human sewage (USEPA, 2006).

Mombasa is the largest coastal city, an island surrounded by Kenyan coastal waters and has an estimated population of 939,370 people (Kenya National Bureau of Statistics 2009). As such it is a source of large quantities of domestic sewage which contribute loads of Biological Oxygen Demand (BOD), nutrients and microbial contaminants to surface and groundwater including coastal waters (Mwaguni and Munga, 1997). The city's water run offs is a significant source of pollution to the marine environment. Inefficient collection, inadequate treatment and disposal of solid waste is a potential source of pollution of groundwater and coastal waters (Munga *et al*., 2005).

In an effort to increase food productivity in farms, sewage sludge and agricultural chemicals such as inorganic fertilizers, herbicides and pesticides have been used on crops and soils (Magothe, 2009). Commercial phosphate fertilizers and sewage sludge contain small amounts of heavy metals which may accumulate in soil with repeated fertiliser applications thus contaminating the soil. Some of these elements such as Cu, Zn, and Mo are essential for plant growth (Greaney, 2005). At the Kenyan coastal region farming along Athi-Galana – Sabaki river basin and on steep slopes enhance soil erosion and result in transportation of high loads of suspended sediments downriver which discharge into the Sabaki estuary and Malindi Bay. The heavy loads of sediments eventually discharge into the Indian Ocean and are a potential source of nutrients, pesticides, residues and heavy metals (Kithiia, 2006).

Tourism is also one of the factors that significantly contribute to marine pollution. The cruise ships carrying tourists produce hazardous waste (toxic) from a number of on-board activities and processes, including silver, mercury, lead and cadmium through dry cleaning, photographic processing, print shops, painting activities, equipment cleaning and other sources (Smart Guide to World Cruise ship, 2011).

Kenya Coastal tourism is estimated to account for about 60% of the national tourism industry, with some of the urban centres attributing their rapid development to tourism, namely Malindi, Watamu and Diani.

Tourism development and activities have led to impacts on wetlands, contributed to beach erosion, are directly responsible for over exploitation of marine resources, while poor waste management practices at tourist establishments and tourist satellite centres are responsible for declining water quality and loss of aesthetic value of some destinations (Mwaguni and Munga, 1997).

Ships too pollute oceans and sea waters through oil spills and these are extremely difficult to clean up. They kill many marine animals, and their effects last for many years (Haluzau, 2011). Toxic chemicals used to keep ship hulls free of fouling marine organisms have contaminated the marine environment and even humans. Small proportions of copper enter during the removal of antifouling paints, which occurs mostly by water blasting. The concentrated nature of the biocide in scrapings and cleaning residues may cause localised environmental problems (Ukmarine SAC, 2011).

1.2 The study Area

The study area covered the Kenyan coastal area between Malindi Bay in the North and Funzi Bay in the South Coast (Figure 1.1). Figure 1.1 (a) shows the whole length of the study area while figure 1.1 (b), 1.1 (c) and 1.1 (d) show the sampling sites of Sabaki estuary/Malindi Bay complex, Kilindini harbor/port reitz creek and Shirazi respectively.Figure 1.2 is an enlarged map of Kilindini/Port reitz Creek, showing sampling sites.

Maps of Kenyan coastline showing sampling sites.

Figure 1.1 (a)

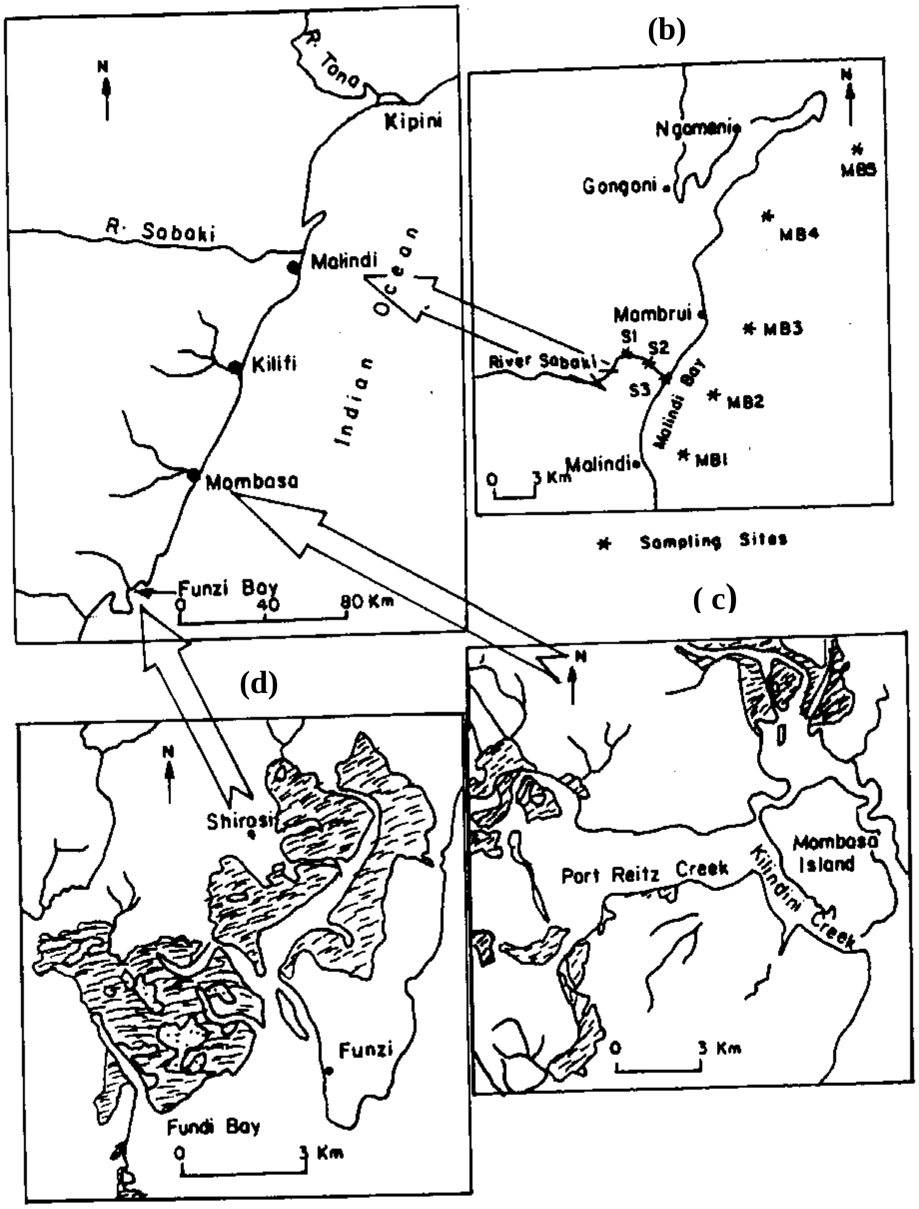
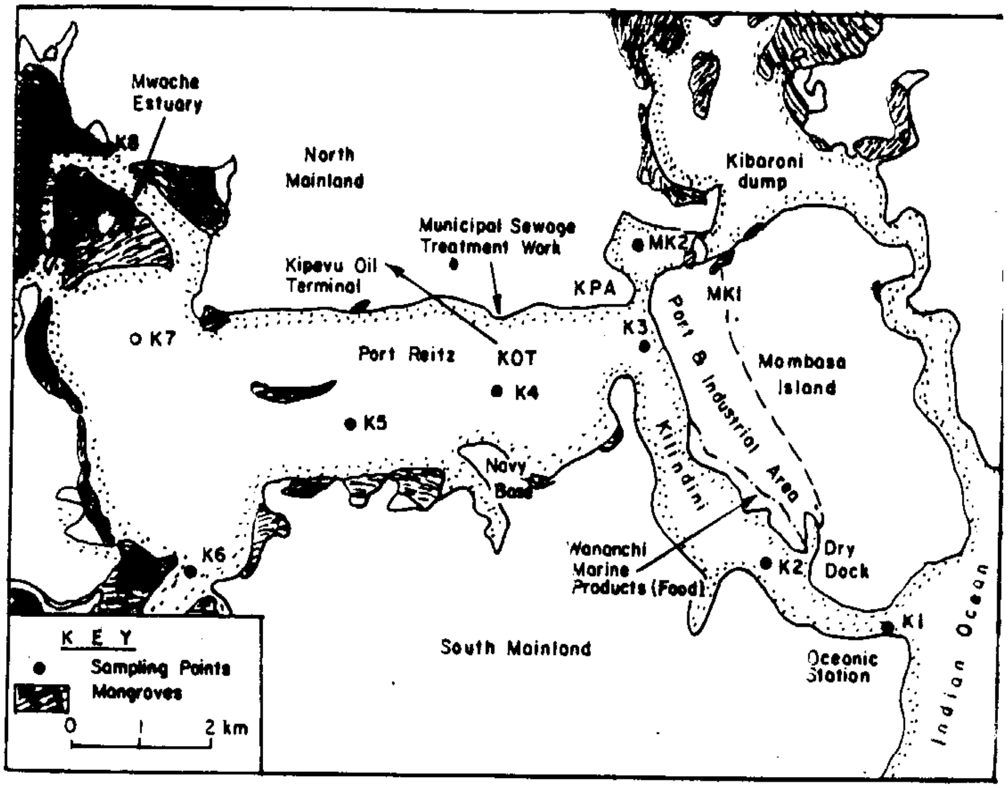


Figure 1.2: Map of Kilindini harbor/ port reitz creek showing sampling Sites



1.3 Problem statement and Justification

Urbanization, industrialization, tourism, shipping (harbour) and agricultural run-offs are key and feared to cause pollution of the marine environment. Sabaki estuary, Malindi Bay and Kilindini harbour are some of the areas along the Kenyan Coastline that are at risk of having high levels of heavy metal pollutants due to surrounding activities. Through the food chain heavy metals including Pb, Cd, Zn, Mn, Cr, Cu and Hg in sea water, sediments, fish and other marine fauna affect the health of human beings. There is therefore the need to assess these heavy metals in the Kenyan coastline.

1.4 Hypothesis

Water, sediments and fauna from the Kenyan coastal line have levels of heavy metals above USEPA guidelines.

1.5 Objectives

1.5.1 General objective

To determine levels of heavy metals in water, sediments and fauna in Mombasa inshore areas (Kilindini and PortReitz), the Sabaki estuary and Malindi Bay complex.

1.5.2 Specific objectives

i. To determine the levels of Pb, Cd, Zn, Mn, Cr, Cu, Fe and Hg in Mombasa inshore areas and Sabaki estuary/Malindi Bay complex during wet and dry seasons in sea water.

ii. To determine the levels of Pb, Cd, Zn, Mn, Cr, Cu, Fe and Hg in Mombasa inshore areas and Sabaki estuary/Malindi Bay complex during wet and dry seasons in marine sediments.

iii. To determine the levels of Pb, Cd, Zn, Mn, Cr, Cu, Fe and Hg in Mombasa inshore areas and Sabaki estuary/Malindi Bay complex during wet and dry seasons in marine fauna.

1.6 Significance of study

In view of the potential risks to man through the food chain and the surrounding activities at the Kenyan Coastal line, it is important to constantly assess the pollution status of the marine ecosystem. This study provides information that is useful towards the status of the Kenyan Coastline. Dissemination of these findings will be helpful to stake holders or agencies that monitor environmental pollution such as UNEP and NEMA.

1.7 Scope and limitations

Samples were taken during the dry season and wet season from selected sites along the Kenyan Coastal line namely, Sabaki estuary, Malindi Bay, Kilindini harbour, and PortReizt, and Shirazi at the south coast. Despite a number of heavy metals could pollute the environment, eight heavy metals, namely; Pb, Cd, Cr, Cu, Hg, Zn, Fe and Mn were considered . Water samples were collected without considering tides, while only two fauna (Oysters and Nyangui) were sampled due to their availability.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Heavy metals

Heavy metals such as zinc, copper, chromium, cadmium and manganese are important in small quantities for biological processes in plants and animals and occur naturally in soil, water and the atmosphere. However, when they are discharged in large quantities from sewage, industrial and agricultural run-offs, and they ultimately find their way into water bodies including oceans, they constitute an increasing hazard to humans through the food chain. (Tay *et al*., 2011).

2.1.1 Cadmium

Cadmium (Cd) is mainly found in the earth's crust in combination with zinc (LENNTECH, 2009). No cadmium ore is mined for the metal, because more than enough is produced as a by product of the smelting of zinc from sphelerite (ZnS) in which CdS is a significant impurity (LENNTECH, 2009). Cd is released into the environment during mining and smelting of zinc, lead and copper (Hill, 2007).

The most significant use of Cd is in Ni/Cd batteries, as rechargeable or secondary power sources exhibiting high output, long life, low maintenance and high tolerance to physical and electrical stress. Cd coatings provide good corrosion resistance coating to vessels and other vehicles, particularly in high stress environments such as marine and aerospace. Other uses of Cd are as pigments, stabilizers for Poly Vinly Chloride, in alloys and electronic compounds. Cd is also present as an impurity in several products, including phosphate fertilizers, detergents and refined petroleum products (Greaney, 2005).

Inhalation of Cd can cause respiratory toxicity after a latent period of several hours, including a mild, self-limited illness of fever, cough, malaise, headaches and abdominal pain similar to metal fever. At higher doses, chemical pneumonitis may occur, with laboured breathing, chest pain, and sometimes fatal hemorrhagic pulmonary odema (Kegley*et al*., 2010). Ingested Cd can cause nausea, vomiting, diarrhea, abdominal pain and tenesmus. Chronic symptoms may include: Kidney damage (proteinuria and azotemia) anaemia, liver injury (jaundice) and defective bone structure (Kegley*et al*., 2010). In Japan Itai-Itai disease was found in Cd polluted Jinzu river basin in Toyona prefecture in the 1950's. It was officially recognized in 1968 as the first disease induced by environmental pollution (Kanazawa – Med, 2011). Pollution was noted to have resulted from disposal of cadmium to the aquatic environment (Kanazawa-Med, 2001). The mean concentration of cadmium in surface sea water is in the range of 0.001 to 0.1 µg/g (Neff 2002). Cadmium concentrations in uncontaminated marine sediments usually are in the range of 0.1 to 0.6 µg/g dry wt (Neff, 2002). Safety limits criteria set by USEPA for heavy metals in sea water for Cd is 8.8 µg/l, and in sediments 4.21 µg/g. (Gidarakos and Hahladakis, 2012).

A study by Soualili *et al* (2008) at Algiers in the Mediterranean region reported Cd levels of 0.76 µg/g in sediments. The level was within the background concentrations reported in the literature for the Mediterranean Sea, implying that there was no Cd pollution of the sediments. Mwashote (2003) determined levels of cadmium and lead in seawater, sediments and selected fish species in Mombasa. Cadmium levels in seawater were below ditection limit, while in sediments and fish samples, they ranged from nd to 1.0 µg/g and nd to 3.7 µg/g respectively. These levels were below the USEPA criterion of continuous concentration (ccc) of 8.8 µg/l for seawater and 4.21 µg/g dry wt for sediments. (Gidarakos and Hahladakis, 2012).

2.1.2 Chromium

The earth's crust contains an average of 125 ppm chromium. Trivalent and hexavalent chromium are both found in nature, but chromium (III) predominates. Chromite, $FeOCr_2O_3$, is the only important chromium ore mineral (Carson *et al.*, 1986).

Chromium is a vital trace element, which is essential for carbohydrate metabolism in animals (Hutchicon Encyclopedia, 2001). Unlike many other heavy metals, Cr can exist in a trivalent (chromite) and a hexavatent form (chromate). The Cr (VI) form is more phytotoxic than the Cr (III) form. Hence the redox conditions in the environment are very important. The Cr (VI) form is toxic to many species of marine animals, algae and microorganisms (Langard, 1980). Hexavalent chromium compounds are genetoxic carcinogens. Chronic inhalation of hexavalent chromium compounds increases the risk of lung cancers(Wikipedia, (2012).

Seawater chromium levels is usually between 0.2 and 0.6 ppb. Oyster tissue contain approximately 0.7 µg/g chromium (LENNTECH, 2011). The USEPA guidelines for Cr in sea water is 50.0 µg/l and in sediments is 16 µg/g.

A study by Mubiana and Blust (2006) reported Cr concentrations of 1.0 – 2.0 µg/g in mussels in Western Scheldt estuary in the Netherlands, while Siddique*et al*. (2009) reported Cr concentrations of up to 571.0 µg/g in beach sediments at Karachi, Pakistan. The levels at Karachi were higher than the level recommended by USEPA.

2.1.3 Copper

Copper was the first metal used by man. Although it can be found in pure form, copper is generally locked together with other minerals such as gold, lead, zinc and silver (Australian Mines Atlas, 1999). Copper is a reddish metal that occurs naturally in rock, soil, water, sediment and air. Its average concentration in the earth's crust is about 50 µg/g. Copper also occurs naturally in plants and animals. It is an essential element for all known living organisms including humans and other animals (Habeck, 2010).

There are many industrial uses of copper, due to its high ductility, malleability, thermal conductivity and resistance to corrosion (Baxamusa, 2010). It is alloyed with nickel and used for shipping. It is the main component of coins in many countries. Copper is used for plumbing, roofing and cladding. About 65% of copper that is produced is used for electrical applications. These include uses in power generation and transmission of electricity and in wiring for electrical equipments (Baxamusa, 2010).

Copper deficiency in the human body can lead to gray hair, skin wrinkles, crow’s feet, varicose veins and saggy skin. Copper is often compared to the “Fountain of youth” because it helps in improving the elastic fibre in skin, increasing the skin flexibility, and helps reduce pre-mature grayness of hair (Baxamusa, 2010). Inordinately large amounts of orally ingested copper become toxic. The exposure limit is 1 µg/g for man (Manahan, 1992). Inhalation causes irritation of mucous membrane, nasal perforation, cough, dry throat, muscle ache, chills and metal fever. Skin contact can result in dermatitis. Diseases caused by high concentrations of copper include anaemia, hefechromatiosis, cirrhosis, and yellow atrophy of the liver and tuberculosis (Pradyot, 1992). Copper in water is exceedingly toxic to aquatic fauna. For example, at levels as low as 0.0025to 0.005 µg/g, copper is lethal to fish and other aquatic invertebrates (Manahan, 1992) the USEPA guidelines for Cu in seawater is 3.1 µg/l and in sediments is 108 µg/g.

A study by Siddique *et al*, (2009) reported Cu concentrations of 272. 00 µg/g in sediments in the Gizri creek area in Karachi, Pakistan; they concluded that the high metal concentrations including Cu, were mainly attributed to industrial waste carried by rivers Saleem and Kazi. Morillo *et al* (2009) in a study of the Southwest Coast of Spain reported Cu concentration of 336 µg/g in marine sediments. In another study, Mubiana and Blust, (2006) reported Cu concentrations of 5 to 22 µg/g in mussels from Western Scheldt estuary in the Netherlands. The above concentrations are above the USEPA guidelines which are Cu in seawater 3.1 µg/g and in sediments 108 µg/g.

2.1.4 Iron

Iron is the most abundant metal, and is believed to be the tenth most abundant element in the universe. Iron is a metal extracted from iron ore, and is hardly ever found in the free (elemental) state. Iron is the most used of all the metals, comprising 95 percent of all the metal tonnage produced worldwide. Its combination of low cost and high strength make it indispensable, especially in applications like automobiles, the hulls of large ships, and structural components for buildings. Steel is the best known alloy of iron (Greaney, 2005).

Iron is essential to all organisms, except for a few bacteria (Greaney, 2005). Iron is known as an essential mineral, one that is often supplemented to make sure we are obtaining enough of this vital element. Less known is that iron can be toxic and that iron toxicity is not as rare as might be imagined (Eck and Wilson, 1989), moderate intoxication occurs when ingestion of elemental iron exceeds 40 µg/g. Excess iron in the body (iron overload) causes liver and kidney damage (haemochromatosis) when total iron in the human body is more than 6 g (Spanieman, 2010).

The study by Fatoki and Mathabatha (2001) reported a maximum Fe levels of 15,185. µg/g at Port Elizabeth, South Africa . The results of Fe levels and other heavy metals were indicative of pollution from storm water drains, and streams which carry runoff from industrial, urban and residential sources. There is no iron levels limit set by USEPA.

2.1.5 Lead

Native lead rarely occurs in nature. It is usually associated with ores of Zn, Ag and Cu and is extracted together with these metals. Lead is primarily extracted from the sulphide ore galena (PbS) which has 86.6% lead content. Other minerals commercially mined for lead are cerusite ($PbCO_3$) and anglesite ($PbSO_4$) (Gravita, 2009).

Lead malleability and corrosion resistance makes it useful for roof flashings and cladding. The density of lead provides unrivalled protection from radiation and is used by staff working in hospitals, dental surgeries, laboratories and nuclear installations. Lead stabilizers are added to some Poly Vinly Chloride products to improve durability, and the metal protects underwater power and communication cables. Lead acid batteries are the mainstay of storage technologies for renewable energy sources, such as solar cell and wind turbines and are used to power cars, trucks, buses, motorbikes, electric vehicles and hybrid vehicles (International Lead Association, 2011).

Human beings are exposed to enhanced levels of lead in food and drink and in the air they breathe. Lead is a poison, and once taken into the human body enters the blood from where it is redistributed to soft tissue and the skeleton. The biological half-life of lead in human bone is estimated to be 10 years (UNEP, 1984). Lead intoxication affects the nervous system, blood and vessels, inhibits the enzymic processes of converting porphyrins and iron incorporation into protoporphyrins (Carson *et al*, 1986). The first sign of physiological impairment due to lead, is inhibition of enzyme catalyzing formation of haem. The clinical manifestation of lead poisoning are: abdominal colic, anaemia, renal damage, neuropathy and rarely, encephalopathy. Toxic effects of lead have been reported on the human foetus, and this has prompted restrictions in employment of females in lead using industries (UNEP, 1984). Acute toxicity is quite unusual, since lead is relatively insoluble and cumulative poison. Reported signs are fatigue, disturbance of sleep and constipation, followed by colic, anaemia, and neurocis. Occasionally acute lead encephalopathy, characterized by vomiting, apathy, drowsiness, stupor, ataxia, hyperactivity, seizures, and other neurological signs and symptoms is seen (Carson *et al*., 1986).

A study of heavy metals in sediments of the Western part of Egyptian Mediterranean Sea by Ahdy and Khaled, (2009), reported Pb levels ranges of

2.672-35.624 µg/g. These levels were lower than the USEPA guidelines. The study of Mwashote, (2003), reported levels of Pb in seawater at Mombasa of nd during the dry season and ranging from 0.001 µg/l- 0.006 µg/l in the wet season. In sediments, levels reported were ranging from 1.0 µg/g.-26.9 µg/g. in the dry season and 2.5 µg/g.to 33.3 in the wet season.

These Pb levels were lower than USEPA guidelines levels of 8.1 µg/l in seawater and 112 µg/g. in sediments.

2.1.6 Manganese

Manganese is found in many, widely scattered minerals. It is about 0.1% of the earth's crust. Manganese occurs mainly as the mineral pryrolusite (MnO_2) and to a lesser extent as rhodochrosite ($MnCO_3$) (LENNTECH, 2011). Manganese chemicals are used in fertilizer formulations, pharmaceutical products and in animal feeds (Onyari,*et al* 2003). Uses in medicine include antiseptics and germicides (Onyari, *et al* 2003).

Manganese is a key component of low-cost stainless steel formulations and widely used aluminium alloys. Manganese oxide is also used as a catalyst. Manganese is used to decolorize glass and make violet coloured glass. Potassium permanganate is a potent oxidizer and is used as a disinfectant (LENNTECH, 2011).

Concentrations of Mn in open seawater range from 0 .4 to 10 µg/gl. In the North sea, the North –East Atlantic ocean, the English channel and the Indian Ocean, Mn content was reported to range from 0.3 to 4.0 µg/gl. Howe et al, (2004). The WHO recommended limit of Manganese in river water is 0.4 µg/l.(WHO, 2000).

A study by Ravelonabdra, *et al* (2010) sought to determine levels of heavy metals in coastal sediments in North-Western cities of Madagascar. The level of Mn of sediments at Nosy-Be was 36.02-to 119.1 µg/g. In another study by Nasir et al, (2006), done to evaluate the contamination by heavy metals of the Aden Port sediments in Yemen, reported levels of Mn ranges from 138.23 to 658.87 µg/g. In the study by Howe, (2004), reported mean Mn levels in mussels from the North-West Pacific Ocean as ranging from 2.8 to 9.3 µg/g dry weight. Mn concentrations in barnacles from Xiamen habour and Hong Kong Coastal waters ranged from 5.9 to 277 µg/g dry weight.

2.1.7 Mercury

Mercury is found throughout the earth's crust, primarily as various sulfides (Carson, 1986). The chief source of mercury is the mineral cinnabar (HgS), but it sometimes occurs in nature as free metal (Hutchinson Encyclopedia, 2001). An important source of air pollution is the chlor-alkali process for the production of Cl_2 and NaOH from brine where 0.1 to 0.2 kg Hg are lost into the environment with every 1000 kg Cl_2 produced (Alloway and Ayres, 1997).

The major uses of Hg are in electrical equipment and in chlor-alkali industry for production of chlorine. Other uses include as a catalyst in polyurethane foams, industrial and control instruments (Carson, 1986). A silver-mercury amalgam is used in dentistry for filling cavities in teeth. Also other industrial uses include, mercury-vapour lamps, arc rectifier, power control switches, barometers and thermometers (Hutchinson Encyclopedia, 2001).

Mercury is a non-essential element. Acute mercury poisoning is usually by the soluble inorganic salts. Early signs and symptoms include pharyngitis, dysphagia, abdominal pain, nausea and vomiting, bloody diarrhea and shock. Later, swelling of the salivary glands, stomatitis, loosening of the teeth, nephritis, anuria, and hepatitis occur. Death results from the effects on the gastrointestinal tract ulcerations, bleeding and shock (Stokinger, 1981). Mercurialism, chronic intoxication by elemental mercury vapour or mercury salts, is much more frequently seen than acute toxicity, due to its cumulative nature. The classic syndrome begins with psychic and emotional disturbances. The victim becomes excitable especially when criticized. He can no longer concentrate mentally, and becomes depressed. He may complain of headache, fatigue and weakness, loss of memory, drowsiness or insomnia. He will show a fine muscular tremor, usually beginning in the hands, which soon interferes with handwriting and other precision work. There are “intension tremors”, absent during sleep, most pronounced when under stress. The victim may develop paresthesias and neuralgia. Other systems are sometimes affected, renal disease, chronic nasal catarrh and epitaxis are common (Stokinger, 1981).

In the Minamata Bay in Japan, $HgSO_4$ in effluents reaching the Bay was first of all precipitated as insoluble HgS, which later underwent biomethylation through action of bacteria in the sediments to form CH_3Hg^+ (Alloways and Ayres, 1977; Hill, 2007). This methylated form is very volatile and lipophylic and accumulated in the food chain of fish catches in the bay having high concentrations of mercury which were harmful to humans eating them, leaving people severely affected by the CH_3Hg^+ poisoning (Alloway and Ayres, 1977). Methylmercury (and other alkylmercury compounds) produce "Minamata Disease," which has the clinical appearance of enphalitis. The earliest signs are gradual decreases in the senses of touch, vision, hearing and taste. The skin becomes less and less sensitive, numbness in the fingers, toes, lips and tongue interferes with normal activities, including walking, working, speaking, eating and drinking. Tunnel vision occurs and may lead to complete blindness. Hearing loss is over the entire frequency range. The motor system is affected by progressive loss of balance, tremors and in coordination. Mood changes like those observed in mercurialism occur (USEPA, 1980).

There is no known nutritional requirement for mercury in humans and plants, and most of the Hg present in foods results from environmental contamination (Rana, 2006). Concentration of total mercury in uncontaminated estuarine and marine sediments generally are 0.2µg/g dry wt. or lower. Neff (2002).The USEPA guideline levels in seawater for Hg is 0.94 µg/gl and in sediments is 0.3 µg/g. dry weight. (Gidarakos and Hahladakis, 2012).

2.1.8 Zinc

Zinc is a chalcophilic element like copper and lead, and a trace constituent in most rocks. Zinc rarely occurs naturally in its metallic state, but many minerals contain zinc as a major component from which the metal may be economically recovered. Sphalerite (ZnS) is the most important ore mineral and the principal source for zinc production. (Environmental Health Criteria 221, 2001).

Zinc is the fourth most widely used metal in the world after iron, aluminum and copper. Zinc is mainly used as a protective coating of other metals, such as iron and steel. Because the metal lacks strength, it is often alloyed with other metals, for example, aluminium, copper, titanium and magnesium, to impart a variety of properties. Zinc is an essential element that is important for immune function, wound healing, normal taste and smell and is needed for DNA synthesis. Zinc also supports normal growth and development during pregnancy, childhood and adolescence (Tidy, 2010).

Zinc toxicity has been seen in both acute and chronic forms. Toxicity from chronic ingestion of zinc usually presents with the features of copper deficiency. Prolonged intake of zinc ranging from 100 – 150 µg/g interferes with copper metabolism and causes low copper status, reduced iron function, red blood cell microcytosis, neutropenia, reduced immune function and reduced levels of high-density lipoproteins. Ingesting 200 to 800 mg/day of zinc can cause abdominal pain, nausea, vomiting and diarrhea. Other reported effects include gastric irritation, headache, irritability, lethargy, anaemia and dizziness (Tidy, 2010).

Zinc concentrations in ocean waters are much higher in highly polluted industrialized coastal areas like the North sea (up to 70 µg/g) than in open ocean (0.1 µg/g) (Marine Biodiversity Wiki, 2009). Zinc tends to be bio accumulated by bivalves. Oysters especially contain large amounts of zinc; in the highly contaminated English Restrongnet Creek which contain zinc concentrations above 10,000 µg/g dry weight (Marine Biodiversity Wiki, 2009).

USEPA guidelines in seawater for Zn is 81.0 µg/l and in sediments is 271 µg/g dry weight. A study of an assessment of heavy metal pollution in East London and Port Elizabeth harbours, (Fatoki and Mathabatha, 2001) reported Zn levels of 0.5-27.6 µg/l in seawater and 26.1-332. µg/g in sediments at East London harbor and Zn levels of 0.7-16.2 µg/l in seawater and 18.8 – 1260. µg/g in sediments at Port Elizabeth. The results were indicative of the contribution of heavy metal pollution from storm water drains and streams which carry run off from industrial, urban and residential sources. (Fatoki and Mathabatha, 2001)

2.2 Methods of analysis

A number of sensitive and reliable analytical techniques for analysis of heavy metals are known. They include Inductively Coupled Plasma Atomic emission Spectroscopy (ICP - AES) (Wanjau*et al.*, 2004), Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) (Horwitz, 2001), Atomic Absorption

Spectrophotometry (AAS) (Miregi *et al*., 2007; Magothe, 2009), Energy Dispersive X-ray Fluorescence (EDXRF) (Oyugi, *et al* 2000; Wanjala, 2009). In this study the AAS and EDXRF techniques were used.

2.2.1 Atomic absorption specteophotometry (AAS)

The AAS is an analytical method for the quantitative determination of elements in small qualities. The method is largely free from spectral or radiation interference because each metal has its own characteristic absorption wavelength and the source lamp is composed of the element being determined (Skoog*et al*., 2004). It is based on the absorption of radiation energy by free atoms (Lajuuen, 1991). The sample solution is aspirated into a flame as in flame emission spectrometry and the sample element is converted to atomic vapor. The flame then contains atoms of that element. Some atoms are thermally excited by the flame, but most remain in the ground state. These ground state atoms can absorb radiation given off by a special source made from the element being determined (Hollow cathode lamp). The wavelengths of radiation given off by the source are the same as those absorbed by the atoms in the flame (Christian, 2004). The amount of radiation absorbed depends on the number of atoms that depend on concentration of the element in the sample. In the present study AAS was used for quantitative analysis of marine sediments and marine fauna.

2.2.1.1 Principles

Atomic absorption is a viable analytical technique for determining trace elements because of its high specificity and relatively high sensitivity and has been used for trace elements analysis of environmental samples (Slavian, 1978). The determination of elements by AAS is based on the principle of absorption or emission of radiation by free atoms, for the excitation of ground state atom, *R* to R* as shown in Equation 2.1.

$$R + hv = R^* \qquad \text{Eq 2.1}$$

Where *h* is Plank's constant and *v* is the frequency of the absorption or emission of atoms associated with the process of transition of atoms from one steady state to the other. For the steady state m and n with energies Em and En, respectively, absorption of light will take place when $E_n > E_m$, following the transition from m to n, while the transition n to m, results in the emission of radiation. The frequency v_{mn} for m to n transition will be inversely proportional to the Plank's constant, given by Equation 2.2.

$$v_{mn} = \frac{E_n - E_m}{h} \qquad \text{Eq 2.2}$$

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

i). Emission (n →m), transition from an excited state to a lower energy state due to external radiation of the same frequency n_{nm}.

ii). Spontaneous emission ($n \rightarrow m$), transmission from the excited state to a lower energy state, and iii). Absorption ($m \rightarrow n$), transition from a lower energy state to a higher one due to external radiation with frequency υ_{mn}. This forms the basis of AAS.

Absorption involving ground state atoms result in the production of resonance lines characteristic of the element. However, the population of excited atoms to ground state atoms at a given temperature is governed by Boltzmann distribution (Tertian *et al*.,1982), given by Equation 2.3.

$$\frac{N_n}{N_m} = \left\{ \frac{g_n}{g_m} \right\} \exp\left[\frac{E_n - E_m}{KT} \right] \qquad \text{Eq 2.3}$$

Where;

N_n= number of atoms in excited state

N_m= number of atoms in ground state

g_n and g_m= statistical weights of excited and ground states respectively.

$E_n$and E_m= energies of excited and ground states respectively

E_n –E_m= excitation energy

K = Boltzmann's constant 1.38 x 10^{-23}

T = absolute temperature

At a fixed value of g_n/g_m, the ratio N_n/N_m increases with temperature for a particular element at particular spectral line. For an atomic gas consisting of atoms in thermal equilibrium capable of absorbing a quantum of energy $h\upsilon$, containing a radiation of frequency υ and intensity I_o, passing through the atomic gas, the absorption of the incident radiation by neutral atoms is given by Equation 2.4.

$$A = \log\left(I_o / I\right) \qquad \text{Eq 2.4}$$

The resulting emission I does not compensate the absorption I_o because it is unidirectional. The absorption can be measured by classical spectrophotometric procedures. It permits the quantitative determination of the elements introduced into the atomizing source. A relation exists between I_o and I that depends on the absorption (Slavian, 1978) as shown in Equation 2.5.

$$I = I_o.\exp - (K_n N_o L) \qquad \text{Eq 2.5}$$

Where;

I_o = intensity of the incident beam

I = intensity of transmitted beam

K_n = absorption coefficient of the frequency, γ

N_o = atomic population with concentration of number of atoms per cm^3 in path

L = length of sample cell

2.2.1.2 Instrumentation

A schematic diagram of an atomic absorption spectrophotometer is shown in Figure 2.1.

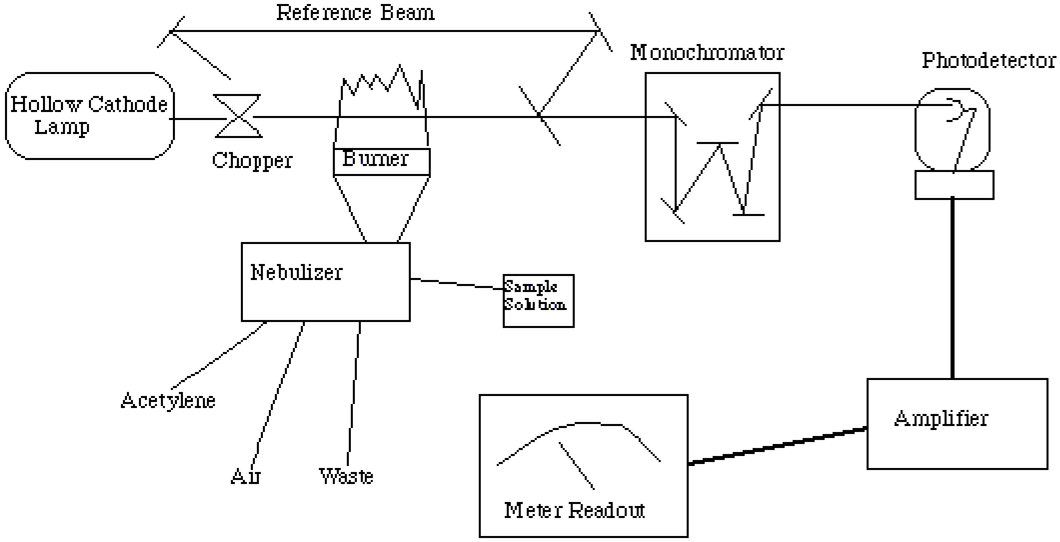


Figure 2.1: Sketch of an atomic absorption spectrophotometer
Source: (Chatwal and Anand, 1994).

This is a double- beam instrument that measures the ratio of P_o/P. The source beam is alternately sent through the flame and around the flame by a chopper. The detector measures these alternately and the logarithm of the ratio is displayed. The detector amplifier is tuned to receive only radiation modulated at the frequency of the chopper, and so dc radiation emitted by the flame is discriminated against (Christian, 2004).

The most important components of a typical AAS are the hollow cathode lamp is the spectral source which emits the radiation spectrum of the element of interest.

The light source emits narrow resonance line profile with little background noise and stable and reproducible output of sufficient intensity to ensure high signal to noise ratios. The atom cell, is a flame furnace or graphite furnace, where the atoms of the sample are formed by thermal dissociation. Atom cells produce atomic vapour of the metal to be determined. Commonly used atom cell atomizer for AAS is flame, the electrically heated graphite atomizer is also used in significant amount of analytical work. A monochromator for the spectral dispersion of the source radiation and an exit slit for selection of the wavelength of the analyte resonance line. The monochromator is a wavelength selector that isolates the resonance line from the non-absorbing lines situated close to it in the spectrum. The detector, normally a photo multiplier tube, measures the radiation intensity at the resonance line. The photo multiplier having cathodes coated with photosensitive materials amplify optical signals received from the monochromators. The photons received strike the photosensitive material and eject electrons. Each electron produced repeats the process until an amplification factor of 10^6 or greater is achieved. The amplifier and display unit records the absorption values, where the signal is read out on an analogues or digital display. In modern instruments, read-out facilities may be handled by an inbuilt microprocessor (Skoog *et al*. 2004).

2.2.1.3 Cold Vapour Atomic Absorption (CVAA)

Since atoms for most elements cannot exist in the free, ground state at room temperature, heat must be applied to the sample to break the bonds combining atoms into molecules. The only notable exception to this is mercury. Free mercury atoms can exist at room temperature and, therefore, mercury can be measured by atomic absorption without a heated sample cell.

In the cold vapour mercury technique, mercury is chemically reduced to the free atomic states by reacting sample with a strong reducing agent like stannous chloride or sodium borohydride in a closed reaction system. The volatile free mercury is then driven from the reaction flask by bubbling air or argon through the solution. Mercury atoms are carried in the gas stream through tubing connected to an absorption cell, which is placed in the light path of the AA spectrometer.

As the mercury atoms pass into the sampling cell, measured absorbance rises indicating the increasing concentration of mercury atoms in the light path. Some systems allow the mercury vapour to pass from the absorption tube to waste, in which case the absorbance peaks and then falls as the mercury is depleted. The highest absorbance observed during the measurement will be taken as the analytical signal. The procedure is based on the absorption of radiation at 253.7mm by mercury vapour. The absorbance is measured as a function of Hg concentration and recorded in the usual manner. (Galbraith Laboratories Inc., 2011).

A schematic diagram of the apparatus for flameless Hg determination is shown in Figure 2.2

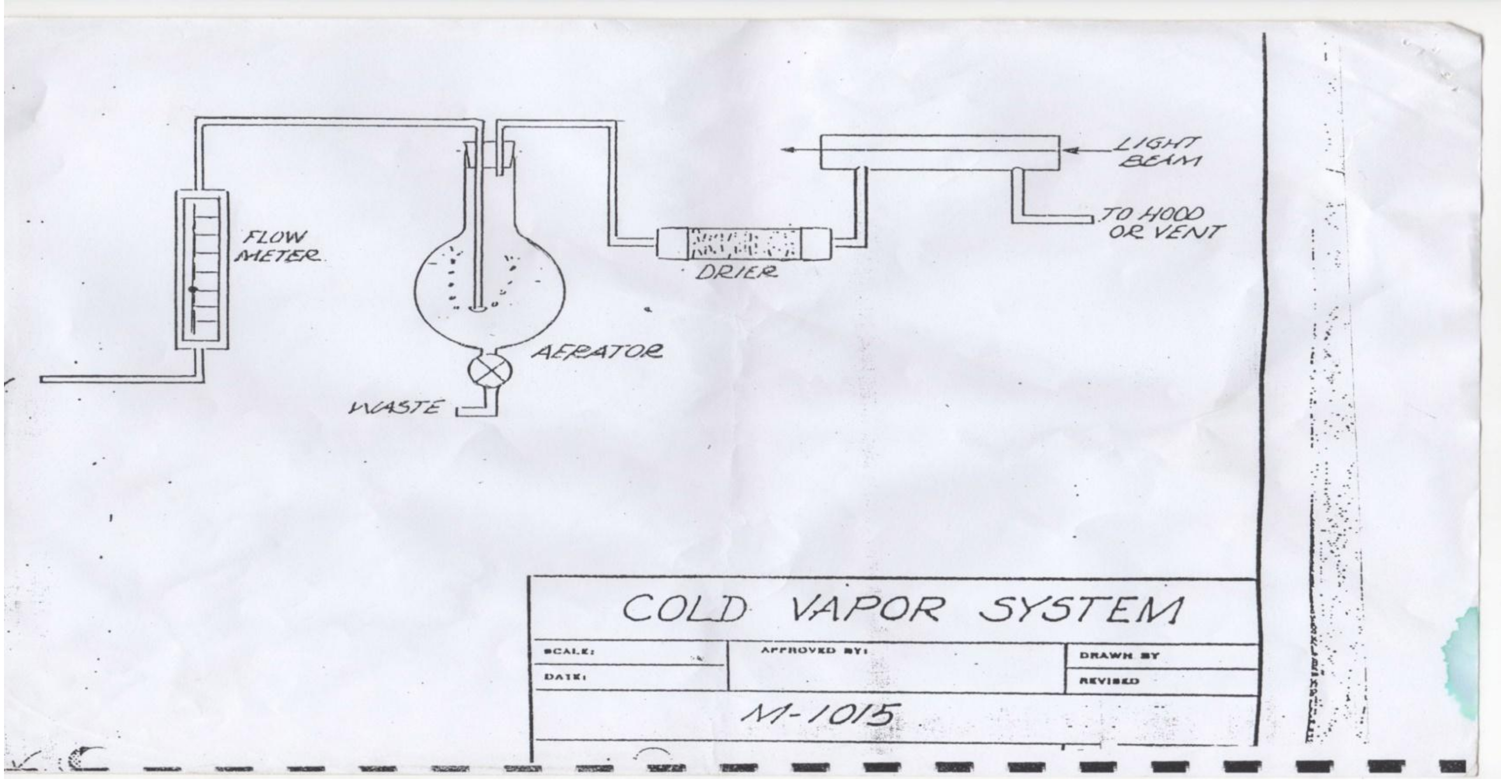


Figure 2.2: A sketch of the cold vapour apparatus. (Buck Scientific, Arsenic/Selenium/Mercury manual Mode’ls 1015, 1016 and 1017).

2.2.2 The Energy Dispersive X-Ray Fluorescence (EDXRF)

2.2.2.1 Principle

In X-ray analysis, the atoms in the sample are bombarded with energetic primary X-rays, to produce a positive ion with a valency in an inner electron shell. The ionized atoms return to the ground state by transition of electrons from an outer shell to the inner shell. As a result, there is emission of fluorescence X-rays equal in energy to the difference in electron energy levels. The energy of this fluorescence X-ray emissions is a function of the atomic number of the element and therefore characteristic of that element. This relationship serves as the basis for the quantitative analysis by XRF (Magothe, 2009). X-rays interact with the atom of the material through processes such as photoelectric absorption, incoherent scattering and coherent scattering effects (Michette *et al*., 1993). Each interaction has a certain probability of occurring, referred to as a cross-section. The fractions of the photons that pass through the material after the interaction is given by Equation 2.6.

$$I = I_o e^{-\mu\rho d} \qquad \text{Eq 2.6}$$

Where

I = Intensity of the photon beam after traversing an absorbing material

I_o = Initial intensity of the photon beam

ρ = Density of the absorbing material

d = Thickness of material

μ = Total mass absorption coefficient (sum of the scattering coefficients and the photoelectric absorption coefficient)

For photoelectric absorption effect, the incident photon energy is completely absorbed by the electron leading to ejection of the electron from the sub-shell. The ejected electron is called a photoelectron. The incident photon must have enough energy, *hv* to overcome its binding energy in a given shell for ejection to occur, “a hole” is created in the energy level from which electron is ejected. To restore stability, the atom must rearrange its electrons in the various electron shells. When an electron is transferred from a higher level to a lower energy level, the atom loses energy by emitting a characteristic X-ray radiation (Kump, 1993).

Incoherent scattering effect involves a photon of primary energy *hv* colliding with a weakly bound electron assumed to be at rest. Thus, a part of the incident photon energy is converted into the kinetic energy of the struck electron with the original direction of the photon changing. Coherent scattering occurs when the low energy photons are scattered by elements with high atomic numbers, as more tightly bound atomic electrons are involved. The mass of the atomic nucleus is much higher than that of the incident photon, hence the photons do not undergo change in energy (Leyden, 1984).

2.2.2.2 Instrumentation

A typical X-ray tube based EDXRF spectrometer is shown in Figure 2.3

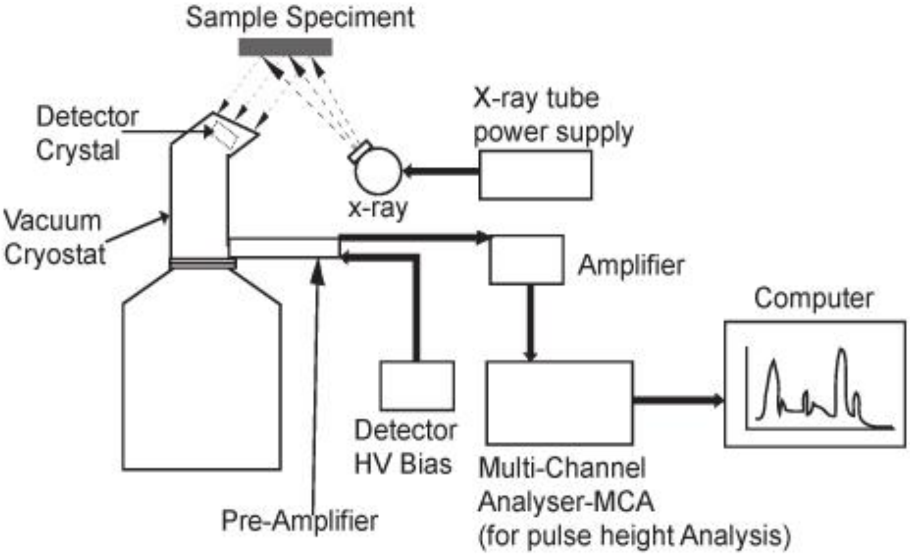


Figure 2.3: Typical X-ray EDXRF spectrometer (Guthrie, 2011)

The basic concept for all spectrometer is a source, a sample, and a detection system. The source irradiates a sample and a detector measures the radiation coming from the sample. EDXRF spectrometers have a detector that is able to measure the different energies of the characteristic radiation coming directly from the sample. The detector can separate the radiation from the sample into the radiation from the elements in the sample. This separation is called dispersion. A typical X-ray tube based EDXRF spectrometer is shown in Figure 2.2.

2.2.2.3 Basic EDXRF intensity equations

In EDXRF analysis, low energy X-ray photons from ^{55}Fe, ^{109}Cd, ^{241}Am and X-ray tubes are used to excite the atoms in the sample material. The fluorescence radiation from the sample are separated and analysed on the basis of their respective photon energies. The intensity of the fluorescence radiation can be evaluated from the fundamental parameter equation developed by Criss and Birks (1968). In this technique, an incident beam, of intensity I_0 excites the elements in sample material of mass thickness ρd in the geometry shown in Figure 2.3.

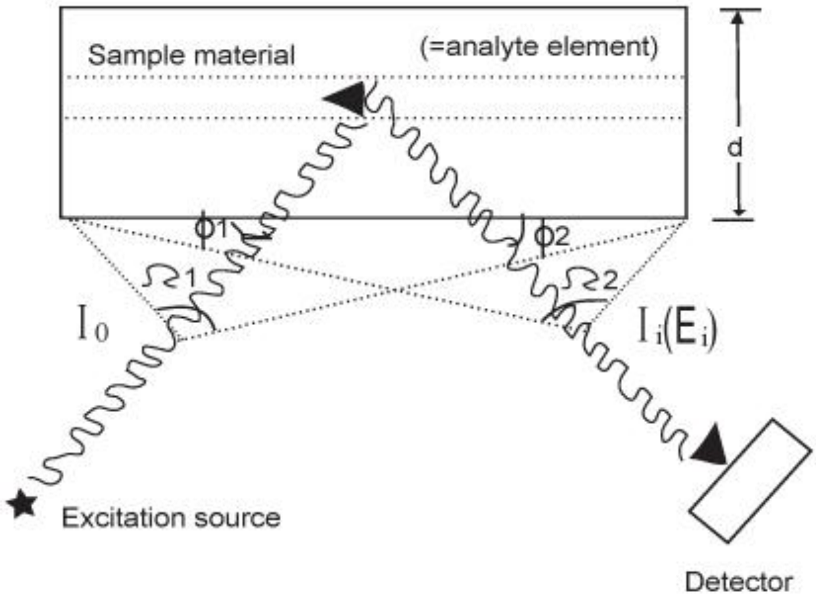


Figure 2.4: Geometry for calculation of fluorescence intensity

Source: (Criss and Birks, 1968).

The elemental concentrations are evaluated using the equation for the fluorescence intensity, I_i, of the analyte element '*i*' (Criss and Birks, 1968) as given by Equation 2.7.

$$I_i = G_0 k_i \rho_i d \left[\frac{1-e^{-(a\rho d)}}{(a\rho d)} \right] \qquad \text{Eq 2.7}$$

Where,

I_i =Fluorescence intensity (counts/s)

G_0 = Geometric constant (Counts/s)

K_i =Relative excitation detection efficiency (cm^2/g)

d = Thickness of material (cm)

ρ = Density of the sample g/cm^3

ρ_i= Partial density of element i within the sample (g/cm^3)

a = Combined absorption coefficient for primary and fluorescent x-rays in the sample

The background was calculated by the analysis of X-ray spectra by Iterative Least square fitting (AXIL) program that fits a polynomial function to the actual spectra (Epsen *et al* 1993). Net areas of the elements of interest present in the sample were calculated after spectrum deconvolution.

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Research design

Quantitative research design was used in this study. Quantitative research design, where an environmental phenomenon namely marine pollution, was accurately converted into numerical data. Samples of water, sediments, and fauna were collected from various points along the Kenyan coastline for analysis of heavy metals (Cd, Cu, Mn, Fe, Cr, Pb, Zn and Hg).

3.2 Sampling design

Sampling was done during wet and dry seasons. Samples of marine sediments, fauna and ocean water were collected from three sites along the Kenyan coast, namely; Sabaki estuary/Malindi bay complex, Kilindini and Port Reitz creek system while Funzi bay/Shirazi, served as the reference site. The sampling and sample analyses were conducted as in the scheme shown on Figure 3.1.

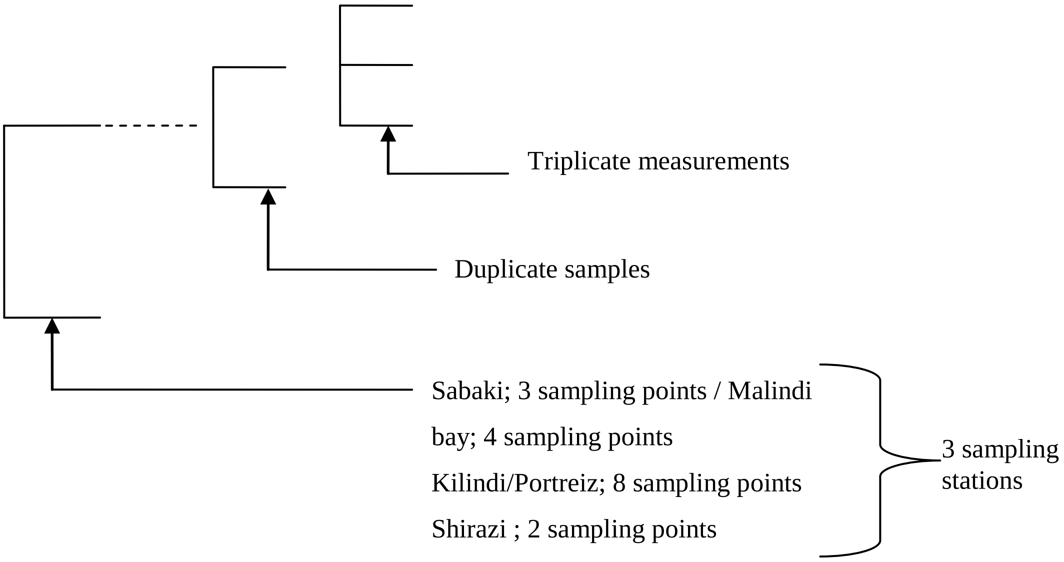


Figure 3.1: Sampling and sample analysis scheme used in this study

3.3 Description of sampling sites

Sampling points in the Sabaki estuary/Malindi bay complex were selected in the inshore/nearshore and 2 kms from the shore. Four sampling points were selected within the bay and along the shoreline, and another 3 points were selected within the Sabaki estuary (Figures 2).

Sampling points at Mombasa were on the Kilindini harbour and Port Reitz creek, were shipping activities including bunkering and discharging crude oil take place. There are also industries,Kipevu oil terminal and the Kenya Naval base (Figure 3.2). The reference site was located in the Funzi bay at Shirazi 70 Km south of Mombasa where the only activities at the site were subsistence farming with low levels of agrochemicals used, artisanal fishing and little tourist activities; hence having no heavy metal pollution.

3.4 Cleaning

Teflon vessels, glass ware and plastic ware (including sampling bottles) were soaked in a soap solution overnight in a plastic bucket. The apparatus were then first rinsed in tap water then with distilled de-ionized water. They were put and left to stand for six days in 10% (v/v) concentrated HNO_3 solution at room temperature. They were then rinsed thoroughly with distilled deionized water and allowed to dry in open air. The dried apparatus were put in closed plastic polythene bags and stored.

3.5 Collection of samples

Water samples were collected from the ocean surface directly into plastic bottles by sub-merging the sample bottle just below the water surface. Samples were immediately acidified with 1 ml concentrated HNO_3 and stored at a temperature of 4 °C. Surface sediments were collected using a Van Veen grab sampler and put into plastic bags, labeled, and transported to the laboratory. The sediments were dried at 50 ^oC and stored. Fauna were picked manually, put in plastic bags, labeled, kept in ice during transport and stored at temperature below 0 ^oC. Then they were dried at 50 ^oC. The flesh inside the shell was used for the heavy metal determination.

3.6 Chemicals, reagents and solvents

Chemicals, reagents and solvents used were of Suprapur, analytical grade.

3.7 Sample Preparation

3.7.1 Digestion of sediment for AAS analysis

0.2000 g portion of dry sample was weighed accurately (Adam Equipment Co. Ltd, Model AAA 160/L, AE04876108) in labeled Teflon vessels. 1 ml aliquot of aqua regia (HNO_3: HCl, 1:3 v/v) was added slowly followed by 6 ml of concentrated Hf and left to stand at room temperature for 1 hour. The Teflon vessels were closed and placed on a hot plate and heated at 120 ^oC for 2 hours and 30 minutes. Samples were allowed to cool to room temperature then the teflon vessels were opened. Separately, 2.7000 g portions of boric acid were weighed and put in labeled volumetric flasks and dissolved in 20 ml distilled deionised water. The sediment samples above were then transferred into the flasks and put in a water bath for 30 minutes until all boric acid was dissolved. They were then allowed to cool to room temperature and put in plastic containers (Azemard *et al*., 2006), labeled and stored.

3.7.2 Digestion of fauna for AAS analysis

Portions of 0.2000g of dry fauna samples were weighed accurately in labeled Teflon vessel. A 5 ml aliquot of concentrated HNO_3 was added and then left at room temperature for 1 hour. The vessel were then closed and heated on a hot plate at 90 ^oC for 3 hours. They were allowed to cool to room temperature and then transferred to 50 ml volumetric flask and volume adjusted to mark with distilled deionised water (Azemard *et al*., 2006).

3.7.3 Calculation of concentrations of sediment and Fauna Samples

The concentrations calculations were carried out using the calibration curve method, and worked out as follows:

$$\mu g/g = \frac{\text{measured concentration (ppm)} \times \text{Dilution} \times \text{Sample Volume (ml)}}{\text{Dry Weight of Sample (g)}}$$

3.7.4 Preparation of water samples for EDXRF analysis

Sea water samples were analyzed by EDXRF technique. Preconcentration procedure with the use of ammonium pyrolidine dithio carbonate (APDC) and analysis was done as follows: The sea water samples (100 ml of sample) was acidified with 5 ml dilute HNO_3 and pH adjusted to between 3.5-4.0 using dilute ammonia solution. 10 ml of freshly prepared 1% APDC solution was added followed by 0.2000 g of Cd solution added as a carrier prior to precipitation. They were thoroughly mixed by manually agitating after every 10 minutes for 40 minutes at room temperature forming a suspension. The suspension was then filtered through a Nucleopore filter (0.45 µm pore size). The Nucleopore filter was air dried and irradiated for determination of the elements (IAEA, 1997).

3.7.5 Preparation of stock and standard solutions

Commercial standards of 1000 µg/g strength were diluted using the formula $V_1C_1=V_2C_2$, and standards of concentrations of 0 - 10.0 µg/g were prepared.

3.7.6 Preparation of reference standard and blank

Reference material IAEA- 433 was used. The reference material solutions were prepared using the same procedure as the sediment samples. The blank was prepared using distilled/deionized water instead of sample.

3.8 Analysis of samples by FAAS

The FAAS instrument used was Buck Scientific 210VGP Atomic Absorption Spectrophotometer. The machine operational parameters for the analysis are given in Table 3.1.

Table 3.1 Operational parameters of the AAS

Operational parameters	**Elements**						
	Cu	Cd	Cr	Ni	Pb	Zn	Mn
Wavelength	324.7	324.8	357.9	232.0	283.3	213.9	279.5
Slit width (nm)	0.7	0.7	0.7	0.2	0.7	0.7	0.7
Lamp current (ma)	3-8	5-10	5-10	7-15	3-7.5	3-10	5 -15
Detection limit (µg/ml)	0.02	0.005	0.05	0.04	0.1	0.005	0.01
Flame	Air - acetylene						
Flame temperature	2300 °C						

The standards were first aspirated and the absorbance recorded. A calibration curve was obtained for each element analysed. The sediments and fauna samples and the reference materials were then aspirated and the absorbances recorded. The concentrations of the samples were calculated by extrapolation of absorbances of the individual samples on the graphs of the elements.

3.8.1 Analysis of samples by HGAAS

The cold vapour technique was used for analysis of Hg. A mercury hollow cathode lamp was placed in holder and allowed to warm up for about 15 minutes. The burner head of the AAS was removed and the absorption cell and holder was positioned. The lamp current (6.5 MA) and wavelength (253.6 nm) were optimized and 50 ml of sample solution were pipetted into the reaction flask and 5 ml of mixed acid solution (3:1HCl:H_2SO_4) was added.

A 10.0000 g portion of analytical grade stannous chloride was put in an empty acid- cleaned 100 ml plastic bottle and then 20 ml concentrated HCl, 2 grams tin metal and 75 ml distilled dionised water were added. The bottle was swirled gently to dissolve the solids. 5 ml of the 10 % stannous chloride reductant solution prepared as above, was injected into the septum of the flask stopper assembly with a syringe.

The argon gas was switched on and the highest signal reading on the machine was taken. The reading was allowed to get back to zero then the Argon bubbles flow was turned off and the reaction flask removed. The flask was rinsed with 5% HCl / 5% H_2O_2solution, and also the bubbler tube was soaked in the same solution to remove traces of the $SnCl_2$. It was reassembled for the next run. The analysis was started first with the reagent blank run, then the standards and lastly the samples.

3.9 Method validation

The methods used in this study, that is the AAS and EDXRF were validated by the use of reference materials and commercial standards.

3.10 Data analysis

The data was analysed using the student t-test and the Standard Statistical Package for Social Sciences (SPSS)Version 17.

CHAPTER FOUR

4.0 RESULTS, DISCUSSION AND CONCLUSION

4.1 Method validation

4.1.1 The EDXRF validation

The EDXRF level of accuracy and quality control comprised of the measurement of ICP Multi-element standard solution 1 CertiPUR (Certified reference material). The results are presented in Table 4.3.

Table 4.1: The EDXRF results for ICP Multi-element Standard Solution 1CertiPUR

Element	**Concentration in µg/g (*n* = 3)**		***t-test***
	Certified (mean ± SE)	**Measured (mean ± SE)**	**tcal**
Cr	25.3 ± 0.50	19.754±6.03	0.92
Fe	15.2 ± 0.50	15.336±3.85	0.03
Cu	20.3 ± 0.50	19.444±3.25	0.26
Zn	20.0 ± 0.50	20.525±3.48	0.15
Pb	203 ± 4.00	182.902±31.76	0.63
Mn	5.1 ± 0.20	5.00 ± 0.20	0.50
Cd	20.8 ± 0.50	20.40 ± 0.50	0.80

Measured values were not significantly different from certified values since *t* - calculated values were less than the *t* - critical value (*tcrit* = 4.303, df = 2, α = 0.05). Therefore the EDXRF method and hence the results presented in this study are accurate and reliable.

4.1.2 The AAS validation

The AAS level of accuracy and quality control was determined by certified reference material "IAEA 433", for trace elements and methyl mercury in marine sediments, and certified reference material "IAEA 436" for Trace elements in the fauna. The comparison of means between the levels in the certified reference material and measured values are presented in tables 4.1 and 4.2.

Table 4.2: Comparison of mean levels of heavy metals in CRM IAEA 433, and measured values.

Element	**Concentration in µg/g(n = 3)**		***t-test***
	Certified (mean ± SE)	**Measured (mean ± SE)**	**tcal**
Cu	30.8 ± 2.60	30.3 ± 2.60	0.19
Pb	26.0 ± 2.70	25.5 ± 2.50	0.20
Zn	101 ± 8.00	103.37 ± 8.20	0.28
Mn	316 ± 16.00	315.5 ± 15.90	0.03
Cr	136 ± 10.00	135 ± 9.50	0.10
MeHg	0.17 ± 0.07	0.14 ± 0.06	0.50
Cd	0.153 ± 0.03	0.140 ± 0.03	0.43

tcal = t calculated

Table 4.3: Comparison of mean levels of heavy metals in CRM IAEA 436, and measured values.

Element	**Concentration in µg/g (n = 3)**		***t-test***
	Certified (mean ± SE)	**Measured (mean ± SE)**	**tcal**
Cu	1.73 ± 0.19	1.70 ± 0.18	0.17
Zn	19.0 ± 1.30	19.0 ± 1.40	< 0.001
Mn	0.238 ± 0.04	0.250 ± 0.04	0.30
MeHg	3.67 ± 0.42	3.55 ± 0.04	3.00
Cd	0.052 ± 0.01	0.050 ± 0.01	0.20
Cr	0.194 ± 0.06	0.193 ± 0.06	0.02

tcal = t calculated

Measured values were not significantly different from certified values since *t* - calculated values were less than the *t* - critical value (*tcrit* = 4.303, df = 2, α = 0.05). Therefore the AAS results presented in this study are accurate and reliable.

4.2 Levels of heavy metals in sea water

The levels of Pb, Cd, Zn, Mn, Cr, Cu, Fe and Hg in sea water were determined using EDXR and are presented in Tables 4.4 and 4.5 for wet and dry season respectively. Site abbreviations are expounded in Appendix I.

Table 4.4: Mean levels of heavy metals in sea water during the dry season

	Concentration μg/ml±SE (n=3)					
SITE	Pb	Zn	Mn	Cr	Fe	Cu
K1	0.007±0.001^{bc}	0.072±0.029^{b}	0.010±0.001^{abc}	0.014±0.000	0.174±0.013^{a}	0.006±0.001^{a}
K2	0.007±0.000^{bc}	0.044±0.014a^{b}	0.008±0.004^{ab}	0.015±0.003	0.260±0.068^{a}	0.015±0.004^{ab}
K3	0.008±0.001^{bc}	0.013±0.000^{a}	0.011±0.002^{abc}	0.013±0.002	0.171±0.056^{a}	0.011±0.001^{ab}
K4	0.010±0.002^{bc}	0.031±0.001^{ab}	0.013±0.000^{abc}	0.014±0.002	0.159±0.005^{a}	0.013±0.002^{ab}
K5	0.009±0.001^{bc}	0.013±0.002^{a}	0.011±0.001^{abc}	0.012±0.001	0.220± 0.013^{a}	0.014±0.002^{ab}
K6	0.012±0.001^{bc}	0.029±0.000^{ab}	0.011±0.000^{abc}	0.056±0.042	0.339±0.035^{a}	0.011±0.001^{ab}
K7	0.008±0.001^{bc}	0.024±0.002^{ab}	0.016±0.002^{bc}	0.013±0.002	0.459±0.017^{a}	0.016±0.001^{b}
K8	0.009±0.000^{bc}	0.023±0.000^{ab}	0.019±0.003^{c}	0.019±0.001^{b}	0.787±0.021^{b}	0.010±0.001^{ab}
MB1	0.000±0.000^{a}	0.025±0.004^{ab}	0.010±0.000^{abc}	0.060±0.049	0.079±0.013^{a}	0.012±0.002^{ab}
MB2	0.006±0.003^{bc}	0.034±0.009^{ab}	0.005±0.003^{a}	0.009±0.005	0.430±0.255^{a}	0.017±0.004^{b}
MB3	0.013±0.003^{c}	0.033±0.006^{ab}	0.008±0.004^{ab}	0.017±0.001	0.196±0.070^{a}	0.013±0.000^{ab}
MB4	0.005±0.002^{b}	0.021±0.001^{ab}	0.014±0.003^{abc}	0.008±0.004	0.343±0.293^{a}	0.015±0.003^{b}
S1	0.011±0.000^{bc}	0.072±0.000^{ab}	0.089±0.000^{d}	0.013±0.013	17.613±0.006^{d}	0.036±0.000^{ab}
S2	0.009±0.000^{bc}	0.070±0.000^{b}	0.036±0. 000^{e}	0.032±0.000	20.351±0.014^{e}	0.036±0.000^{d}
S3	0.010±0.001^{bc}	0.057±0.000^{b}	0.045±0.000^{abc}	0.033±0.001	11.609±0.003^{a}	0.027±0.001^{d}
SH1	0.007±0.000^{bc}	0.054±0.028^{ab}	0.013±0.001^{abc}	0.017±0.002	0.063±0.003^{a}	0.009±0.000^{ab}
SH2	0.009±0.001^{bc}	0.034±0.001^{ab}	0.015±0.001^{abbc}	0.013±0.002	0.061±0.004^{a}	0.011±0.001^{ab}
p.value						

Mean values followed by the same letter(s) within the same column are not significantly different. (Oneway ANOVA, SNK-test, $\alpha = 0.05$)

Table 4.5 Mean levels of heavy metals in sea water during the wet season

	Concentration µg/ml ±SE (n=3)					
SITE	Pb	Zn	Mn	Cr	Fe	Cu
K1	0.005±0.001^{ab}	0.044±0.005^{abc}	0.012±0.001^{a}	0.012±0.000^{a}	0.068±0.007^{a}	0.011±0.001
K2	0.006±0.000^{ab}	0.040±0.002^{ab}	0.011±0.002^{a}	0.022±0.002^{a}	0.061±0.002^{a}	0.012±0.001
K3	0.006±0.000^{ab}	0.040±0.002^{ab}	0.011±0.002^{a}	0.022±0.002^{a}	0.061±0.002^{a}	0.012±0.001
K4	0.006±0.000^{a}	0.040±0.002^{ab}	0.011±0.002^{a}	0.022±0.002^{a}	0.061±0.002d^{e}	0.012±0.001
K5	0.005±0.001^{ab}	0.045±0.000^{abc}	0.009±0.000^{a}	0.011±0.001^{a}	0.094±0.006^{bcd}	0.008±0.000
K6	0.007±0.001^{ab}	0.042±0.001^{abc}	0.010±0.001^{a}	0.014±0.001^{a}	0.150±0.005^{f}	0.010±0.001
K7	0.008±0.001^{b}	0.023±0.002^{a}	0.009±0.001^{a}	0.019±0.002^{a}	0.098±0.005^{cd}	0.036±0.001
K8	0.006±0.000^{ab}	0.046±0.000^{abc}	0.009±0.000^{a}	0.015±0.000^{a}	0.307±0.000^{h}	0.009±0.000
MB1	0.005±0.000^{a}	0.038±0.000^{ab}	0.010±0.000^{a}	0.012±0.000^{a}	0.082±0.000^{abc}	0.008±0.000
MB2	0.008±0.001^{b}	0.032±0.002^{ab}	0.010±0.001^{a}	0.013±0.001^{a}	0.079±0.005^{abc}	0.010±0.000
MB3	0.005±0.000^{a}	0.041±0.001^{ab}	0.012±0.001^{a}	0.022±0.001^{a}	0.096±0.002^{cd}	0.012±0.000
MB4	0.007±0.001^{ab}	0.064±0.000^{c}	0.013±0.001^{a}	0.117±0.052^{b}	0.093±0.004b^{cd}	0.018±0.000
S1	0.014±0.001^{e}	0.158±0.020^{e}	0.024±0.003^{c}	0.024±0.000^{a}	4.326±0.007^{j}	0.019±0.005
S2	0.014±0.000^{e}	0.177±0.001^{f}	0.027±0.000^{d}	0.023±0.001^{a}	4.323±0.^{006j}	0.024±0.001
S3	0.010±0.000^{c}	0.086±0.000^{d}	0.065±0.001^{e}	0.053±0.001^{a}	15.610±0.002^{k}	0.037±0.000
SH1	0.006±0.000^{ab}	0.027±0.000^{ab}	0.011±0.000^{a}	0.016±0.000^{a}	0.071±0.000^{ab}	0.011±0.000
SH2	0.014±0.000^{a}	0.012±0.000^{d}	0.011±0.000^{a}	0.194±0.000^{g}	0.012±0.000	0.039±0.000^{ab}
p.value						

Mean values followed by the same letter(s) within the same column are not significantly different. (One way ANOVA, SNK-test, $\alpha = 0.05$)

4.2.1 Lead (Pb)

During the dry season, Pb levels ranged from < dl at MB1 at the Malindi marine park to 0.014 µg/g at S1 at Sabaki river, 2 kilometers before the river water enter the sea. These levels were lower than the guide level set by USEPA, implying that the sea water is safe of Pb. However Pb accumulation is known to be dangerous resulting in inhibition of enzyme catalyzing formation of haem (UNEP, 1984). Other studies of the Kenyan coastline also found levels of Pb in sea water to be lower than the USEPA guidelines.(Oyugi *et al* 2000), Mwashote(2003). Oyugi *et al (*2000), reported a range of 0.012 to 0.06 µg/mlwhile Mwashote (2003) reported Pb levels of 0.05 to 0.62 in seawater at Mombasa concluding that there was need for constant monitoring of the region. A comparison of Pb between the dry and the wet seasons showed a difference ($P < 0.05$).

4.2.2 Zinc (Zn)

Zinc levels in seawater in the dry ranged 0.013 µg/ml at sampling point k3 at oceanic sampling at Kilindini harbor to 0.072 µg/ml at K1 next Mombasa industrial area at Kilindini harbor. Zn was also detected at all other sampling points. These ;levels were lower than the guidelines of 81.0 µg/l set by USEPA. This implies that the results show that the seawater was polluted by zinc, except at Sabaki during the wet season.

Previous studies of the Kenyan coastline reported levels lower than the USEPA guidelines (Oyugi, *et al* 2000 Hashim 2000).Oyugi *et al*

(2000)reported the range of 0.03 µg/g at Mombasa to 0.07 at Vanga, while Hashim (2001) reported 0.57 µg/l to 8.10 µg/l at Mombasa. Other water bodies in the world reported levels of 0.5-27.6 µg/l in sea water at Port Elizabeth, South Africa. This was indicative of pollution attributed to run-offs from industrial sources (Fatoki and Mathabatha 2001).In the wet season Zn levels in seawater were higher, that is 0.177µg/l at Sabaki. In non statistical comparison, the Zn levels of Kenyan Coastline seawater is lower than the USEPA guidelines.A comparison between the Zn levels in the dry, and wet seasons showed significant difference ($P < 0.05$).The wet season had higher levels than the dry season.

4.2.3 Manganese (Mn)

Mn levels in seawater in the dry season ranged from 0.005 µg/ml at MB2 infront of Malindi Jetty sampling point at Malindi Bay to 0.89 µg/ml at S1 at Sabaki river. Mn was also detected in all other sampling points. These levels are lower than the WHO recommended levels of 0.4 µg/l for drinking water (WHO, 2000). The Mn levels indicated Mn pollution of the seawater at Sabaki.In the wet season seawater levels ranged from 0.009 µg/ml at K8 at Mwache to 0.065 µg/ml at S3 sampling point at the Sabaki river. These levels are higher than WHO recommended level of 0.4 µg/l. In previous studies of the Kenyan Coastline Hashim (2001) reported a range from 0.24-0.51 µg/ml at Mombasa and 0.12-0.19 µg/g at Malindi. The above levels were indicative of Mn pollution of the seawater of the Kenyan coastline.

Studies from other regions of the world, in the North sea, the north east Atlantic ocean, the English channeled and the Indian Ocean, Mn levels were reported to range from 0.3 to 4.0 µg/l (Howe, et al 2004).

A comparison between the Mn levels in the dry and wet seasons showed no significant difference, $p > 0.05$.

4.2.4 Chromium (Cr)

Chromium levels in seawater in the dry season ranged from 0.008 µg/l at MB4 at Malindi Bay in front of Gongoni to 0.117 µg/ml at MB3 at Malindi Bay in front of Mambrui. The level at NB 3 is higher than the USEPA guidelines of 50 µg/l, for Cr(vi) since the Cr level found was total Cr and not differentiated between Cr (III) and Cr(Vi), the pollution status of Cr pollution could not be inferred from above levels. Crhas not been reported in previous studies of the Kenyan Coast.

4.2.5 Iron (Fe)

Iron levels in sea water in the dry season ranged from 0.061 µg/ml at SH2 at shirazi to 20.351 µg/ml at 52 at Sabaki.Previous studies of the Kenyan Coastline reported comparable Fe levels in seawater. Oyugi *et al* (2000) reported level ranging from 0.11 µg/ml at Mombasa Marine park to 13.5 µg/ml at English point Mombasa, while Hashin (2001) reported iron levels of 0.44-1.33 µg/ml at Mombasa, 6.34 - 44.21 µg/ml at Malindi and 0.67-8.53 µg/ml at Gazi. These two previous studies reported higher levels than this study could be due to that the difference in sampling sites. In unpolluted oceanic waters, levels of iron ranging between 2.8 to 29 µg/l and 224-1228 µg/l have been reported (UK Marine, 2011). USEPA quality criteria does not exist for iron as it is considered a non- priority pollutant.(Uk Marine, 2011).

4.2.6 Copper (Cu)

Copper levels in seawater in the dry season ranged from 0.006 µg/ml at K1 at the oceanic sampling point at Kilindini to 0.037 µg/ml at S1 and S2 at Sabaki river.In other study of the Kenyan coastline, Hashim (2001) reported Cu levels in seawater of 0.05-0.13 µg/ml at Mombasa, 0.05-0.11 µg/ml at Malindi and 0.04-0.08 µg/ml at gazi. These figures are higher than those reported in this study. This could be due to difference of sampling points. The levels also show a reduction in Cu indicative of reduction in Cu pollution of the Kenyan coastline.

In the wet season levels of Cu in seawater ranged from 0.011 µg/ml at KI at the oceanic sampling station at Kilindini to .037 µg/ml at S1 at Sabaki river. There is no significant difference in the levels during the dry and wet seasons. The levels of Cu in seawater in this study are higher the USEPA guidelines of 3.1 µg/l in seawater, indicating that there was Cu pollution in the Kenyan coastline seawater.

4.3 Levels of heavy metals in marine sediments

The levels of Pb, Cd, Zn, Mn, Cr, Cu and Fe in sediments were determined using AAS. The Hg levels in sediments were determined using cold vapor method. AAS calibration curve for Pb is shown in figure 4.1 below. Culibration curves for other metals are in Appendix II. The results for dry and wet seasons are presented in Table 4.6 and 4.7. Site abbreviations are explained in abbreviations and acronyms list. Cd, Cr and Hg however were not detected in marine sediment samples.

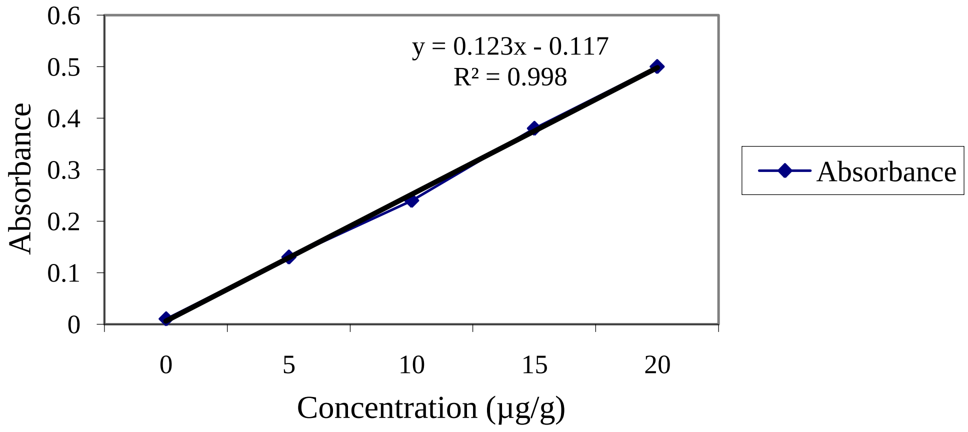


Figure 4.1 calibration curve for lead

Table 4.6 Mean levels of heavy metals in sediments during the dry season

	Concentration in µg/g ± SE (*n* = 3)				
SITE	Pb	Zn	Mn	Fe	Cu
K1	170.769±0.116^{g}	140.859±0.335^{k}	460.674±0.163^{g}	46314.705±0.103^{l}	43.034±0.034^{g}
K2	170.769±0.116^{g}	141.093±0.052^{i}	460.840±0.160^{g}	46315.705±0.103^{m}	41.064±0.032^{f}
K3	133.400±0.100^{b}	145.169±0.037^{m}	400.917±0.220^{c}	40554.153±0.078^{j}	43.034±0.034^{g}
K4	133.400±0.100^{b}	145.093±0.001^{m}	400.917±0.220^{c}	40554.153±0.078^{h}	43.034±0.034^{g}
K5	134.417±0.209^{c}	137.288±0.006^{j}	450.075±0.038^{e}	35129.710±0.095^{k}	44.077±0.033^{i}
K6	160.673±0.163^{e}	145.077±0.038^{m}	455.717±0.148^{f}	41500.185±0.094^{i}	32.902±0.004^{e}
K7	230.556±0.067^{j}	332.507±0.004^{o}	420.979±0.226^{d}	35203.435±0.219^{f}	28.027±0.002^{d}
K8	185.700±0.153^{h}	137.281±0.000^{j}	450.323±0.007^{e}	33351.784±0.045^{c}	28.027±0.001^{d}
MB1	290.800±0.115^{k}	83.592±0.001^{g}	130.117±0.060^{a}	9351.835±0.017^{c}	10.133±0.002^{b}
MB2	290.833±0.120^{k}	83.104±0.058^{f}	130.450±0.275^{ab}	9351.835±0.017^{g}	10.134±0.001^{b}
MB3	230.667±0.176^{j}	101.495±0.005^{h}	750.547±0.227^{k}	33425.595±0.298	27.018±0.009^{c}
MB4	165.700±0.153^{f}	101.495±0.005^{h}	1050.853±0.07^{4i}	83425.609±0.304	94.595±0.003^{k}
MB5	165.900±0.208^{f}	102.496±0.004^{i}	1051.187±0.29^{2i}	83425.275±0.327^{p}	94.597±0.007^{k}
MK	220.509±0.065^{i}	311.154±0.001^{n}	460.261±0.069^{g}	52520.900±0.153^{o}	60.510±0.006^{j}
S1	131.167±0.083^{a}	52.343±0.001^{a}	520.670±0.165^{i}	12231.387±0.202^{d}	43.916±0.003^{h}
S2	135.445±0.028^{d}	58.208±0.004^{e}	540.677±0.162^{j}	14907.500±0.323^{e}	43.903±0.009^{h}
S3	135.445±0.028^{d}	56.308±0.00a4^{d}	480.393±0.018^{h}	48240.730±0.015^{n}	43.916±0.003^{h}
SH1	135.497±0.088^{d}	55.250±0.000^{c}	130.677±0.162^{ab}	3250.533±0.291^{b}	9.912±0.006^{a}
SH2	135.467±0.067^{d}	54.147±0.013b	131.038±0.221^{b}	3140.800±0.416^{a}	9.912±0.006^{a}
p.value					

Mean values followed by the same letter(s) within the same column are not significantly different. (One way ANOVA, SNK-test, α = 0.05)

Table 4.7 Mean levels of heavy metals in sediments during the wet season

		Concentration in μg/g ± SE (*n* = 3)			
SITE	Pb	Zn	Mn	Fe	Cu
K1	187.767±0.145^{c}	142.192±0.004^{j}	471.813±0.094^{h}	47314.705±0.103^{l}	43.913±0.006i
K2	187.667±0.167^{c}	142.164±0.033^{j}	471.810±0.146^{h}	47315.705±0.103^{m}	40.810±0.005^{h}
K3	135.646±0.180^{b}	146.093±0.001^{k}	442.718±0.034^{d}	41754.153±0.078^{i}	43.913±0.006^{i}
K4	135.646±0.180^{b}	146.093±0.001^{k}	443.051±0.351^{d}	41754.153±0.078^{i}	43.913±0.006^{i}
K5	135.639±0.182^{b}	138.288±0.006^{i}	464.664±0.168^{g}	37129.710±0.095^{g}	43.913±0.006^{i}
K6	187.820±0.160^{c}	146.077±0.038^{k}	462.756±0.172^{f}	41759.185±0.094^{j}	33.309±0.004^{g}
K7	239.789±0.120^{e}	333.507±0.004^{m}	428.177±0.089^{c}	36203.435±0.219^{f}	27.028±0.001^{d}
K8	239.789±0.120^{e}	138.281±0.000^{i}	457.197±0.103^{e}	34351.784±0.045^{e}	28.024±0.002^{e}
MB1	291.778±0.111^{f}	84.110±0.006^{f}	138.269±0.134^{a}	19400.407±0.348^{c}	11.215±0.010^{c}
MB2	291.778±0.111^{f}	84.110±0.006^{f}	139.035±0.201^{b}	19500.407±0.348^{d}	10.896±0.017^{b}
MB3	231.721±0.140^{d}	100.497±0.004^{g}	725.254±0.127^{i}	53300.373±0.190^{o}	30.167±0.017^{f}
MB4	187.700±0.153^{c}	101.495±0.005^{h}	1210.890±0.059^{k}	95420.100±0.058^{q}	95.204±0.004^{k}
MB5	187.667±0.167^{c}	101.495±0.005^{h}	1210.890±0.059^{k}	95422.100±0.058^{r}	95.204±0.004^{k}
MK	239.563±0.054^{e}	310.153±0.002l	464.698±0.201^{g}	53796.092±0.099^{p}	60.808±0.004^{j}
S1	239.589±0.006^{e}	65.700±0.005^{c}	1710.890±0.059^{l}	40833.144±0.099^{h}	43.912±0.006^{i}
S2	187.671±0.165^{c}	67.972±0.008^{e}	1783.198±0.117^{l}	45462.908±0.030^{k}	43.613±0.306^{i}
S3	187.873±0.127^{c}	66.937±0.022^{d}	1015.216±0.009^{j}	51943.400±1.224^{n}	43.870±0.035^{i}
SH1	130.493±0.194^{a}	56.250±0.000^{b}	138.272±0.136^{a}	6582.777±0.400^{b}	10.134±0.001^{a}
SH2	130.340±0.070^{a}	54.240±0.020^{a}	138.185±0.093^{a}	6500.252±0.144^{a}	10.134±0.001^{a}
p.value					

Mean values followed by the same letter(s) within the same column are not significantly different. (One way ANOVA, SNK-test, $\alpha = 0.05$)

4.3.1 Cadmium, Chromium and Mercury(Cd, Cr, Hg)

Cd, Cr and Hgconcentrations in the marine sediments were below detection limits in all stations sampled during both the dry and the wet seasons. Oyugi *et al*(2000) had the same observations. However Kamau (2002), and Mwashote (2003) reported concentrations of 1.0 µg/g and 0.08 µg/g of Cd in Makupa and Kilindini harbor respectively. The difference could be due to sampling points, time of sampling and activities taking place. For chromium and mercury no reports are available. Cadmium levels are lower than those reported earlier by Oyugi (2000) and Kamau (2002) and Mwashote (2003) who studied cadmium in Kilindini Creek.

A study in Algiers in the Mediterranean region (Soualili et *al* 2008) reported sediment cadmium levels of 0.76µg/g. USEPA guidelines (PEL Indicators) for cd is 4.21 µg/g, for Cr is 160 µg/g and for Fg is 0.7 µg/g (Gidarakos and Hahladakis, 2012).

4.3.2 Lead (Pb)

The results for Pb levels in marine sediments are given in tables 4.6 and 4.7. Pb levels in marine sediments in the dry season ranged from 135.47 µg/g at S2 at Shirazi to 290.83 µg/g at MB 2 at Malindi Bay. In the wet season Pb levels ranged from 13.4 µg/g at S2 at Shirazi to 291.78 µg/g at MB1 in Malindi Bay. There was a significant difference in the Pb levels during the dry and the wet seasons, (P-value > 0.05).

In earlier studies on Pb pollution in the Kenyan Coastline, Oyugi *et al*(2000) and Hashim (2001) reported Pb levels of 7.76±0.96 and 52.22±7.92 µg/g respectively. In a study to the south, Sheikh *et al* (2007) reported lead levels of 228 – 1150 µg/g for Zanzibar port. These high lead levels may be due to discharge of effluents from a tannery in the city.

USEPA guidelines (PEL Indicators) for Pb is 8.1 µg/g (Gidarakos and Hahladakis, 2012).

Within the Sabaki estuary/Malindi bay complex, the concentrations of lead increased from the Sabaki River (S1) towards the ocean at S3. At Malindi bay there was an increase from MB1 at Malindi marine park toward M4 where the Sabaki River enters the ocean. The high concentrations could be due to pelagic activities bringing some pollutant from the open sea. In Kilindini the high concentrations of lead could be due to the shipping activities taking place at the port and the domestic and industrial wastes from the municipal treatment works and the Kipevu oil terminal and other industries. Concentrations at Shirazi are due to terrigeneus activities of the region. There was no relationship of the concentrations at Malindi/Sabaki complex and Kilindini due to their geographical separation.

4.3.3 Zinc

The Zn levels in sediments in the dry season ranged from 52.34 µg/g at SH2 at Shirazi to 332.51 µg/g at K7 at Kiindini harbor. In the wet season the Zn levels ranged from 54.24 µg/g at SH2 at Shirazi to 333.51 µg/g at K7 at Kilindini harbor.

There was no significant difference in concentrations during the dry season and the wet season, p-value >0.000. The high concentrations could have been due to industrial activities around the Kilindini creek. These levels were comparable with levels obtained by Oyugi*et al* (2000), at the range of 27.68 µg/g at English Point Mombasa to 347.73 µg/g at Makupa creek. Another study by Hashim (2001) reported levels ranging from 60.97±5.38 µg/g at Malindi to 320.17 ±76.31 µg/g at Mombasa. In a study to the south, Sheikh *et al*. (2007) reported Zn levels of 339 – 3600 µg/g for Zanzibar port and 107 – 3190 µg/g for Dar es Salaam port. Zinc concentrations in the Sabaki river had no variations from S1 to S3. There were increase in the Malindi Bay from 83.59±0.01 µg/g at the Malindi marine park (MB1) to 102.50±0.04 µg/g at the mouth of the Sabaki river (MB5). This rise could be due to pelagic activities at MB5. At Kilindini the significantly high level was at K7 with a concentration of 332.51±0.04 µg/g. This concentration could be due to local geochemical background.

USEPA guidelines (PEL indicators) for Zn is 81.0 µg/g (Gidatakos and Hahladakis, 2012), hence the Zn levels of the Kenyan coastline are indicative of Zn pollution.

4.3.4 Manganese (Mn)

The Mn levels in sediments in the dry season ranged from 130.68 µg/g at SH1 at Shirazi to 1051.19 µg/g at MB5 in Malindi Bay.In the wet season Mn levels ranged from 138.19 µg/g at SH2 at Shirazi to 1783.20 µg/g at S2 at Sabaki river.

In earlier studies, Oyugi,*et al* (2000) reported Mn levels which were lower than those of this study, ranging from nd at Diani Beach to 1,100.02 µg/g at Vanga. Hashim (2001) found even lower Mn levels, from 97.54±19.33 µg/gat Gazi to 550.83±52.55 µg/g at Malindi. In their study Sheikh *et al*. (2007), reported levels of 537 –812 µg/g for Zanzibar harbor and 277-725 µg/g - for Dar es Salaam port.

No trend in the sediment manganese concentrations were observed along the Sabaki and at Kilindini. But at Malindi Bay there was an increase from at MB5. This could be due to pelagic activities in the open sea showing highest levels at MB5 since the monsoons were strongest at that point. There was significant difference in sediment manganese concentrations between the dry and the wet seasons (P value > 0.05) this could be due to siltation.

According to USEPA guidelines sediment Mn level > 500 µg/g are indicative of heavy Mn pollution (Ahdy and Khaled, 2009). The Kenyan coastline could be considered to be heavily polluted with Mn.

4.3.5 Iron (Fe)

The Fe levels in sediments in the dry season ranged from 3,14.80 µg/g at SH2 at Shirazi to 83,425.61 µg/g MB4 in Malin di Bay. In the wet season, Fe levels ranged from 6,500.25 µg/g at SH2 at Shirazi to 95,422.1 µg/g at MB 5 in Malindi Bay. Fe levels at Kilindini harbor ranged from 34,351.78 et al K8 to 47,314.70 µg/g at K1. In earlier studies, Oyugi *et al*(2000) reported iron levels ranging from 800.19 µg/g to 19,312.05 µg/g along south coast to Mombasa area. Kamau (2002) reported iron concentrations ranging from 4,268 µg/g to 42,660 µg/g at Port-Reiz creek, Mombasa.

A none-statistical comparison shows lower levels in Oyugi et al (2000) and Kamau's studies than this study. This could be due to difference in time and sampling points.Studies done in Zanzibar and Dar es Salaam ports by Sheikh *et al*. (2007) reported levels in the range of 67,500 – 12,400 µg/g and 43,300 – 7,040 µg/g respectively. There was a trend in the Fe levels as seen from Tables 4.6 and 4.7 that the iron sediment concentrations increased from 12,231.39±0.20 µg/g at S1 to 48,240.73±0.02 µg/g. Also at Malindi Bay theFe concentrations increased from 9,351.84±0.0.02 µg/g at MB1 at the Malindi Marine Park to 83,425.28±0.33 µg/g at MB5. This could be effects of pelagic activities at open sea. Pollution being transported towards the East African Coastal zone by the very strong currents of which the South East monsoon is the driving force (Everaats and Nieuwenhuize, 1995). No trend was observed on the iron concentrations at Kilindini.

4.3.6 Copper (Cu)

Tables 4.6 and 4.7 indicate Cu levels in Marine sediments in the dry season ranged from 9.91 µg/g at SH1 and SH2 at Shirazi to 94.6 µg/g at MB4 and MB5 in Malindi Bay. In the wet season Cu levels ranged from 10.13 µg/g at SH1 and SH2 at Shirazi to 95.2 µg/g at MB4 and MB5 at Malindi Bay. These figures are comparable to those of an earlier study by Hashim (2001) with levels of 47.68±4.83 µg/g for Mombasa area and 13.96±1.47 µg/g for Gazi area which is near Shirazi. Oyugi*et al* (2000) also reported concentrations ranging from 18.70 µg/g at Mombasa Marine Park to 49.97 µg/g at Diani. Kamau (2002) reported concentrations ranging from 2.30 µg/g to 32.30 µg/g at Kilindini creek. Individual differences could be due to difference in sampling points. In studies for other water bodies, Sheikh *et al*. (2007) reported levels of 4 - 75 µg/g for Zanzibar port and nd - 36 µg/g for Dar es Salaam harbour.

The sediment copper concentrations were the same along the Sabaki (43.92±0.03 µg/g). In the Malindi Bay an increasing trend from 10.13±0.02 µg/g at MB1 to 94.60±0.07 µg/g at MB5. This could be due to effects of the strong currents of the South East monsoon. There was no trend of sediment copper concentrations at Kilindini. USEPA guidelines (PEL indicators0 for Cu sediments is µg/g (Gidarakos and Haliladakis, 2012). Therefore the Kenyan coastline is free of sediments Cu pollution.

4.4 Levels of heavy metals in marine Fauna

The levels of Pb, Cd, Zn, Mn, Cr and Cu analysed in the fauna are shown in Tables 4.8 and 4.9.

Table 4.8 levels of heavy metals in Fauna during dry season

		Concentration (µg/g)± SE (*n* = 3)				
	Sample	Mn	Fe	Cu	Zn	Pb
Shirazi	Cerithium decollata	37.002±0.049^{b}	565.576±0.289^{c}	145.323±0.039^{c}	380.480±0.010^{c}	135.407±0.007^{a}
Shirazi	Saccostrea cucullata	210.920±0.040^{c}	564.909±0.053^{b}	43.963±0.024^{a}	872.852±0.174^{e}	135.412±0.006^{a}
malindi	Saccostrea cucullata	334.286±0.162^{d}	8342.698±0.154^{d}	229.843±0.081^{d}	446.882±0.009^{d}	831.778±0.969^{c}
Sabaki	Cerithium decollata	29.770±0.119^{a}	379.853±0.176^{a}	128.382±0.009^{ab}	99.476±0.262^{a}	135.663±0.169^{a}
Kilindini	Cerithium decollata	486.611±0.222^{e}	35277.753±0.037^{e}	43.970±0.025^{a}	157.909±0.054^{b}	236.485±3.143^{b}
p.value						

Mean values followed by the same letter(s) within the same column are not significantly different. (One way ANOVA, SNK-test, α = 0.05)

Table 4.9 levels of heavy metals in Fauna during wet season

		Concentration (µg/g)± SE (*n* = 3)				
site	Sample	Mn	Fe	Cu	Zn	Pb
Shirazi	Cerithium decollata	35.669±0.285^{b}	565.909±0.524^{b}	145.474±0.074^{c}	381.480±0.010^{c}	135.507±0.058^{a}
Shirazi	Saccostrea cucullata	211.413±0.322^{c}	565.242±0.287^{b}	43.990±0.010^{a}	873.067±0.186^{e}	135.407±0.007^{a}
malindi	Saccostrea cucullata	333.200±1.604^{d}	8343.031±0.316^{c}	230.177±0.283^{d}	446.948±0.040^{d}	833.111±0.676^{c}
Sabaki	Cerithium decollata	29.867±0.133^{a}	380.187±0.260^{a}	128.546±0.023^{b}	99.737±0.263^{a}	135.997±0.274^{a}
Kilindini	Cerithium decollata	485.611±0.812^{e}	35278.086±0.348^{d}	44.037±0.042^{a}	158.038±0.085^{b}	236.624±3.214^{b}
p.value						

Mean values followed by the same letter(s) within the same column are not significantly different. (One way ANOVA, SNK-test, α = 0.05)

4.4.1 Cadmium, mercury and chromium (Cd, Hg, Cr)

Cd, Hg and Crlevels in the fauna samples were below detection level, both in the wet and dry seasons. These levels are lower than those found by Bor (2000) who reported levels at Mombasa ranging from 0.29±0.01 µg/g to 2.36±0.70 µg/g for cadmium chromium and mercury levels in fauna have not been reported in previous studies of the Kenyan coastline.

4.4.2 Lead (Pb)

Tables 4.8 and 4.9, show lead concentration levels for cerithidea decollate (Nyambua) ranged from 135.41±0.07 µg/g at Shirazi during the dry season to 236.62±3.21 µg/g at Kilindini during the wet season. For saccostrea cucullata (rock oyster) the levels ranged from 135.507±0.058 µg/g to 833.11±0.68 µg/g at Malindi Bay during the wet season. These levels are significantly higher than those found in another study (Bor, 2000), who recorded levels for pearl oysters at Mombasa ranging from 2.35±0.11 µg/g to 121±0.02 µg/g.

The present study was done ten years after that of Bor, so it can be suggested that lead pollution has taken place in the subsequent period and that the sea animals have accumulated lead over time. T statistics for temporal variations, showed *p*-value > 0.05 meaning that there was no significant difference in lead concentrations of fauna between dry and wet seasons at the Kenyan coastline.

A study done in the Middle East (Fowler *et al*. 1993) recorded levels for rock oysters ranging from 0.08 µg/g to 2.1 µg/g. Mostafa et al., (2009) reported lead concentrations of rock oysters in Yemen of the range 2.6 – 15.4 µg/g.

4.4.3 Zinc (Zn)

Zinc levels for cerithidea decollate ranged from 99.48±0.26 µg/g at Sabaki to 381.48±0.01 µg/g at Shirazi during the wet season. Zinc levels for saccostrea cucullata ranged from 446.88±0.09 µg/g at Malindi during dry season to 873.07±0.19 µg/g at Shirazi during the wet season (Table 4.9). Bor (2000) reported zinc levels at Mombasa ranging from 30.1±1.81 µg/g to 119±1.4 µg/g. These are much lower levels of zinc than those found in this study. The high lead levels could be due to boating activities at Malindi which is a busy tourist resort and shipping activities at Kilindini harbor. The high zinc concentrations in oysters at Shirazi could be due to the biogeochemical environment. The zinc concentrations in the Kenyan Coast are high. The Australian National Health and Medical Research council recommended level is 1000 µg/g (Brown and McPherson, 2003).

Zinc tends to be bioaccumulated by bivalves. Especially oysters contain large amounts of zinc. In the highly contaminated English Restrongnet Creek oysters contain zinc concentrations above 10,000 µg/g dry weight. However, like most heavy metals zinc does not tend to biomagnify, so that it causes little harm to sea birds or marine mammals (Marine Biodiversity Wiki, 2009).

4.4.4 Manganese (Mn)

Manganese levels for cerithium decollate ranged from 29.77±0.12 µg/g at Sabaki during the wet season to 486.61±0.22 µg/g at Kilindini during the dry season. For saccostrea cucullata the manganese levels ranged from 210.92±0.04 µg/g at Shirazi during the dry season to 334.29±0.16 µg/g at Malindi during the dry season.

4.4.5 Iron (Fe)

Iron levels for cerithium decollate, ranged from 379.85±0.18 µg/g at Sabaki during the dry season to 35,278.09±0.35 µg/g at Kilindini during the wet season. For Saccostrea cucullata, the levels ranged from 564.91±0.05 µg/g at Shirazi during the dry season to 8343.03±0.32 µg/g at Malindi during the wet season (Table 4.9). Bor (2000) recorded much lower levels ranging from 25.60±0.90 µg/g to 242.00±14.50 µg/g at Mombasa. Elsewhere, in the Middle East, Fowler *et al*. (1993), recorded Fe levels for rock oysters, ranging from 11 to 266 µg/g.

The high iron concentrations could be due to regional geochemical environment. Marine organisms accumulate iron (UK Marine, 2011). Normally, tissue concentrations of iron are related to the water and sediment concentrations, but there can be considerable variability (UK Marine, 2011).

4.4.6 Copper (Cu)

Copper levels for cerithium decollate ranged from 43.97±0.03 µg/g at Kilindini during the dry season to 145.47±0.07 µg/g at Shirazi during the wet season. Copper levels saccostrea cucullata, ranged from 43.96±0.02 µg/g at Shirazi during the dry season to 230.18±0.28 µg/g at Malindi during the wet season (Tables 4.9). The study by Bor (2000) reported a much lower Cu level for pearl oyster of 4.01±0.01 µg/g at Mombasa.

Copper is an essential element for marine animals, especially decapods, gastropods and cephalopods need copper in their respiratory pigment hemocyanin. Homecyanin is a protein which (like haemoglobin) binds oxygen to transport it to the tissues (Media Wiki 2011).Oysters appear to accumulate large amounts of copper in their leucocytes (a type of blood cell), where they do little harm. Copper like most other metals, doesn't show biomagnifying characteristics (Media Wiki, 2011).

4.5 Conclusions

From the findings of this study the following conclusions were made:

i) The Kenyan coastline e is polluted with heavy metals. In particular Cu, Pb, Zn and Mn levels were found to be higher than the USEPA guidelines.

ii) Marine fauna had the highest levels of heavy metals due to bioaccumulation of the metals. Exceptions were found in Fe and Mn which were higher in sediments attributed to the local biogeochemical environment.

iii) There was no significant differences in the levels of heavy metals the wet and the dry seasons, in the sediments and in the marine Fauna.

4.6 Recommendation

4.6.1 Recommendations from this work

Regular monitoring of heavy metals on seawater, marine sediments and biodata of the Kenyan coastline should be carried out regularly. This will act as a whistle blowing activity should safe limits of heavy metals be exceeded due to increasing activities (agricultural, industrial and port).

4.6.2 Recommendations for further work

i) Further research needs to be carried out to determine point sources that contribute to the pollution of the marine ecosystem.

ii) Speciation studies should be carried out to determine the intra and inter-relations of the different metal and effect on pollution of the Kenyan coastline.

REFERENCES

Advameg, Inc, (2011) pollution issues-point source http://www.pollutionissues.com/p1-Re/Point-source.html accessed: 11/04/2011

Australian Mines Atlas (1999) Coper http:// www.australianminesatlas.gov.all//education/rockfile/copper.jsp.accessed on 12.06.2011.

Alloway, B. J and Ayres, D. C. (1997).Chemical Principles of Environmental Pollution.Blackie Academic & Professional.London.

Azenard, S., Wyse, E., Demora, S. J. (2006). Laboratory Procedure Book.Training Workshop on the analysis of Trace Metals in Biological and Sediment Samples.International Atomic Energy Agency.Marine environmental Laboratory. B. P 800, MC – 98012 Monaco. pp 3 – 13.

Baxamusa, B. N. (2010). Copper: Uses of copper. Buzzle.com. http://www.buzzle.com/articles/copper-uses-of-copper.html. Accessed on 01.06.2011.

Bor, S. K. (2000). Heavy metal and Organic pollutants in tissues of marine fauna along the coast of Mombasa Island.Kenya. MSc. Thesis, KenyattaUniversity 50 – 51.

Brown, R. R. and McPherson, R. G., (2003). Concentrations of copper, zinc and lead in the Sydney rock oyster, saccostrea commerciahs (Iredale and Rough ley) from the Georges River, New south Wales. *Science of the Total Environment* 126:1 – 2, 27 - 33. http://www.sciencedirect.com/science/artical/p/0048969792904817. Accessed on 21.02.2012.

Buck Scientific (1996). Arsenic/Selenium/Mercury Manual Models 1015, 1016 and 1017.

Carson, b. L., Ellis 111, H. V., McCann, J. L. (1986).Toxicology and Biological Monitoring of metals in Humans. Lewis Publisher Inc. 121 South Main Street, Chelsea, Michigan48118.

CCREM, (1987).Canadian Water Quality Guidelines.Canadian Council of Resource and Environmental Ministers.Inland waters Directorate, Environmental Canada.Ottawa.

Chatwal G. and Anand S. (1994).Instrumental Methods of Chemical Analysis.Himalaya Publishing House Bombay.Nagpur. Delhi.

Christian, G. D (2004) Analytical Chemistry.6th Ed.John Wiley & Sons Inc New Yolk.

Criss, J. W. and Birks, L. S. (1968).Calculation Methods Flourescent X-ray spectrometry. Analytical Chemistry, 40 pp 1080 - 1086.

Eck, P. C. and Wilson, L. (1989). Iron Toxicity. The Eck Institute of Applied Nutrition and Bioenergetics Ltd.http://www.arltma.com/IronToxdoc.html. Accessed on 05.03.2011.

Environmental Health Criteria 221; (2001).Zinc.World Heath Organization Geneva.

Explain that stuff, (2011). Water pollution: an introduction. http://www.explainthatstuff.ccom/waterpollution.html viewed 11/04/2011.

Everaarts, J.M and Nieuwenhuize (1995).Heavy metals in surface sediments and Epibenthic macroinvertebrates from the Coastal zone and continental slope of Kenya. Marine pollution Bulletin, 31: 4,281-289.

Fatoki, O. S. and Mathabatha, S. (2001). An assessment of heavy metal pollution in the East London and Port Elizabeth.*Water S. A.* 27, 2.

Fowler, S. W., Reading, J. N., Oregioni, B., Villenerve, J. P. and Mckay, K. (1993). Petroleum hydrocarbons and trace metals in nearshore gulf sediments and biota before and after the 1991 war. *Marine Pollution Bulletin*. 27, 171 – 182.

Gidarakos, E. and Hahladakis, J. (2012) Assessment of released heavy metals from the Ms “Sea Diamond shipwreck. Technical University of Crete.Department of Environmental Engineering.

Gravita India Limited (2009). Lead, metal http://www.gravitaindia.com/lead-metal.html Accessed on 09.06.2011.

Greaney, K. M. (2005). An Assessment of heavy metal contamination in the marine sediments of Las Perlas Achipelago.Submitted as part assessment for the degree of Master of Science in Marine Resource Development and Protection.School of life Sciences.Heriot – Watt University.Edinburgh.

Guthrie, J. M. (2011). Overview of X-ray Fluorescence. Archeometry Laboratory. University of Missouri, archaeomtry.missouri.edu/xrf-overview.html accessed on 15.11.2011.

Habeck, M. (2010).Copper eco-usa.net http://www.eco-usa.net/toxics/chemicals Accessed on 12.06.2011.

Haluzan N, (2011). Marine pollution from ships.Pollution articles.http://pollutionarticles.blog.spot.com/2011/ marine-pollution-from ships-guide facts.html viewed 28/0003/2011.

Hashim, N. O., (2001). The levels of radionuclides and trace elements in selected Kenyan coastal ecosystems. A thesis submitted in partial fulfillment for the requirement of the degree of Masters of Science in Physics of Kenyatta University.

Hill, M.K. (2007). Understanding Environmental Pollution: A primer.Cambidge University Press.

Hoda, H. H., H and Khaled Ahdy (2009).Heavy metals contamination in sediments of the Western part of Egyptian Mediterranean Sea.*Australian Journal of Basic and Applied Sciences* 3 (4) 3330 – 3336.

Horwitz, Official methods of analysis, 17th Edition.Association of Official Analytical Chemist (AOAC) International (2001).

Howe, P. D., Malcohm, H. M., Dobson, S., (2004).Manganese and its compound.Environmental aspects. World Health Organization, Geneva. http://www.inchem.org/documents/cicads/cicads/cicads63.htm. Accessed on 21.02.2012.

Hutchison Encyclopedia, (2001). Helicon Publishing Ltd. Oxford. 26.

IAEA (1997).Sampling, storage and sample preparation procedures in X-ray Fluorescence.Analysis of Environmental materials. IAEA-TECH-DOC-950, International Atomic Energy Agency, Vienna, Austria 55.

International Lead Association (2011). Lead uses. http://www/daint.org/lead-information/head-uses Accessed on 09.06.2011.

Jeetu-1220889, (2009) Marine pollution, its effects and causes.http://churmura.com/general/marine-pollutionts-effect-and-causes/1899949/.

Kamau, J. N. (2002). Heavy metal distribution and Enrichment at Port-Reitz creek, Mombasa.*Western Indian Ocean Journal of Marine Science* 1, 1, 65 - 70.

Kanazawa – Med. (2011). Itai – Itai disease.http://www.kanazawa-med.ac.jp/publichealth/cadmium2/itaiitai/itaiO/html. Accessed on 10.04.2011.

Kegley, S. E., Hill, B. R., Orme S., Choi, A. H. (2010). Cadmium: Identification, toxicity, use, water pollution potential, ecological toxicity and regulatory information. PAN Pesticide Database, Pesticide Action Network. San Francisco, North America.

Kenya National Bureau of statistics (2009) population and housing census.
www.knbs.or.ke/census%20results/KNBS%bronchure.pdf accessed 20.11.2011.

Kithiia, S.M, (2006). The effects of land use types on the hydrology and water quality of the upper-Athi river basin, Kenya. PhD Thesis.University of Nairobi, Kenya.

Kump, P. (1993). Quantitative Analysis of Environmental Samples by X-ray Spectroscopy.Ljubliana, Slovenia. 164 – 173.

Lajuuen L.H.J, (1991) Spectrochemical Analysis by Atomic Absorption and Emission. The Royal Society of Chemistry. Thomas Graham House, TheSciencePark, Cambridge CB4 4 WF.

Langard, S. (1980).In metals in the Environment.Academic Press.London. Chapter 4.

LENNTECH (2011) Chromium LENNETECH BV Rotterdamseweg 402M 2629HH Delft.The Netherlands.http://www./euntech.com/periodic/elements/mn.htm . Accessed on 07.04.2011.

LENNTECH (2011).Manganese.LENNETECH BV Rotterdamseweg 402M 2629HH Delft.The Netherlands.http://www./euntech.com/periodic/elements/mn.htm . Accessed on 07.04.2011.

Leyden D. E. (1984).Fundamentals of X-Ray Spectroscopy. Tracor x-ray Inc. 345E Mindlefictf Road, California.

Magothe, J. K. (2009). Analysis of Lead, Zinc and Copper levels of roadside soil and plants across Thika – Nairobi highway, Kenya. A Thesis submitted in partial fulfillment for the requirements of the award of the Degree of Master of Science in Applied Analytical Chemistry in the School of Pure and Applied Sciences of Kenyatta University.

Manaham, S. E., (1992). Toxicological Chemistry.2nd Edition. Lewis Publishes Inc. Chelsea Michigan. 249 – 257.

Marine Biodiversity Wiki, (2009). Zinc Marine Biodiversity Wiki. http://www.marbef.org/wiki/zinc Accessed on 01.06.2011.
Media Wiki (2011).Copper.Media wiki.
http://www.theseusproject.en/wiki/copper. Accessed on 23.2.2012.

Michette, A. G., Buckley, C. J. (1993). X-Ray Science and Technology. Pleum OP Publishing, Bristol.

Mildred P. (Oyugi, Sumesh C. Chhabra, Wilson M. Njue and Antony M. Kinyua(2003) *Journal of Trace and Microprobe Techniques*. 21 (1) pp 147-159

Mileukovic N, Damjonovic M. and Ristic M, (2005).Study of heavy metal pollution in sediments from the Iron Gate (Danube River), Serbia and Montenegro. Polish Journal of environment studies Vol.144 No. pp 781-787.

Mireji, P. O., Keating, J., Hassanali, A., Mbogo, C. M., Nyambaka, H., Kahindi, S., Beie, J. C. (2007). Heavy metals in mosquito larval habitats in urban Kisumu and Malindi Kenya and their impact.*Toxicology and Environmental Safety*.Doc: 10.1016/j. ecoenv. 2007.03.012.

Morillo, J., Usero, j. Gracio, I (2004). Heavy metal distribution in marine sediments from the Southwestern coast of spain. Chemisphere Volume 55 Issue 3 pp 431 – 442 http://www.science/direct.com/science?-ob=Articlelist PPURL method list and Articlelist ID = 17600688905 – sort = u. Accessed on 24.05.2011.

Mortvedt J.J, (2005). Heavy metal contaminants in inorganic and organic fertilizers.Nutrient cycling in Agro ecosystems Volume 43, No.1-3. Pp 55-61.

Mostafa, A. R., Al-Alimi, A. K. A., Barakat, A. O., (2009). Metals in surface sediments and marine bivalves of the Hadhramout coastal area, Gulf of Aden. Yemen. *Marine Pollution Bulletin*, 58, (2009) 209 - 311. Elsevies Ltd.

Mubiana, V. K., Blust, R. (2006). Metal content of marine mussels from Western shceldt Estuary and nearby protected marine bay, Netherlands; impact of past and present contamination.*Bulletin of environmental contamination and Toxicology*. 77 (2); 203 – 210.

Munga, D., Mwangi, S., Ong’anda, H., Kitheka, J. V., Mwanguni, S. M., Barongo, J., Massa, H. S., Mdoe, F. and Opello, G. (2005). Assessment of vulnerability and Pollution of Groundwater in Kisauni, Mombasa, Kenya.Final report.UNEP/UNESCO/UN-HABITAT/ECA.Project on Assessment of Pollution status and vulneranilty of water supply aquifer in African cities. Project No. CP/1000-02-03. 34.

Mwaguni, S and Munga, D. (1997). Land based sources and activities affecting the quality and uses of the marine, coastal and associated fresh water environments along the KenyaCoast. Coast Development Authority, Mombasa, Kenya.

Mwashote, B. M. (2003). Level of Cadmuim and lead in water, sediments and selected fish species in Mombasa, Kenya.*Western Indian Ocean Journal of Marine Science*. 2 (1), 25 – 34.

Nasir, S. M., Okbah, M. A. Kasen, S. M. (2006). Environmental Assessment of Heavy metal Pollution in bottom sediments of Aden Port, Yemen. International Journal of oceans and Oceanography 1, 99 – 109. Research India publications. http://www.ripublication.com/ijoo.htm. Accessed on 24.05.2011.

National Oceanic and Atmospheric Administration (NOAA).National Ocean Service, (2011).http://oceanservice,noaa.gov/facts/pollution.html

Neff J.N (2002) Cadmium in marine sediments.Bioaccumulation in Marine Organisms.Elsevier Ltd 84 Theobalds road London WCIX 8RR UK.

Neff J.N (2002) Mercury in marine sediments.Bioaccumulation in Marine Organisms.Effect of contaminants from oil well.Elsevier Ltd 84 Theobalds road London WCIX 8RR UK.

Neff J.N (2002) The ANZEE and ARMCANZ water Quality Toxicants. Books.goggle Co.ke/books?Isbn = 00806527841 accessed on 16.02.2013.

Onyari, M.J, Muohi, A.W, Omondi, C and Maveti, K.M (2003) Heavymetals in sediments from Makupa and port reitz Creek system, Kenya Coast. *Environment International* 28(7) pp 637-647.

Pradyot, (P.(1992). A comprehensive Guide to the Hazardous Properties of chemical substances. Van Nostrand Reinhold Publisher, New York 499-508.

Rana, S.V.S. (2006). Environmental Pollution Health and Toxicology. Alpha Science International Ltd. Oxford, U.K.

Ravelonabdra, P.H., Rajoelisoa, A., Mong, Y., Rajaonarivony, M., Ravonizafy, C. and Niricalaina, A. (2010).Assessment of heavy metals concentrations in coastal sediments in north-western cities of Madagascar.*African Journal of environmental Sciences and Technology* 4 (2), 051 – 060.

Richmond, M.D (2002) Afield guide to the seashores of eastern Africa and the Wesern Indian Ocean islands.Sida department for research and cooperation, SAREC and University of Dar es Salaam.Dar es Salaam Tanzania.

Sheik, M.A, Noah, N.M, Tsuha, K, and Oomari, T. (2007) Occurrence of Vibytylin Compounds and characteristics of heavy metals.*International Journal of Environmental Science and Technology*, Vol.4.No.1.

Siddique, A., Munitaz, M., Zaigham, N. A., Mallick, K. A., Sailed, S., Zahir, E., Khwaja, H. A. (2009). Heavy metal toxicity levels in the coastal sedimenst of the Arabian Seal along the urban Karachi, (Pakistan) region. Marine Pollution Bulletin 58, 1406 – 1419.

Smart Guide to World Cruise Ships, (2011). Ocean pollution, “Floating Cities” are polluting the water. http://www.smart-guide-to-world-cruise-ship.com/ocean-pollution.html

Skoog, D., West, M. D., Holler J. (2004).Fundamentals of Analytical Chemistry. Brooks Cole.

Slavian, W. (1978).Atomic Absorption Spectroscopy.Interscience Publishers, New York. 38 – 56.

Smart Guide to World Cruise Ships (2011).

Soualili D. Dubois P., Gosselin P. Pernet Pand Guillon M(2008).Assesment of seawater pollution by heavy metals in the neighbourhood of Algiers use of the sea Urelium, paracentrotus lividus, as a biondicator. ICES Journal of amrine science. 65 pp 132-139
http:// www.icesjus.oxfordjournals.org/content/65/2/132 fall.pdf accessed on 27/04/2012.

Spanierman, C. S. (2010). Toxicity, Iron.http://emedicine,medsape.com/article/815213-overview. Accessed on 5.03.2011.

Stokinger, H. E. (1981). The Metals Patty's Industrial and Toxicology.3rd Edition 2A.A Wiley Interscience Publication.John Wiley and Sons.

Tay, C., Asmah. R. and Biney, C.A. (2011). Trace metal concentrations in commercial important fishes from some Coastal and inland waters in Ghana. *West African Journal of Applied Ecology* – 13. http:/www.ajol.info/index.php/wajae/article/viewFile/40579/8112 accessed on 29.05.2011.

Tertian, R. and Claisse, F. (1982).Principles of Quantitative X-ray Flourecence Analysis.Heyden and Sons Ltd.London pp 385.

Tidy, C. (2010). Zinc Excesses and Zinc Toxicity. Emis & P.P. Patient U.K. http://www.patient.co.uk/doctorzinc-Excess and Zinc - Toxicity.htm.Accessed on 04.03.2011.

UK Marine Special Areas of Conservation. (2011). TBT-based autofouling paints. http://www.ukwarinesea.org.uk/activities/ports/ph431htm viewed 10/4/2011.

UK Marine Special Areas of Conservation.(2011). Iron. http://www.ukwarinesea.org.uk/activities/water-quality/wq-12.htm. Accessed on 22.02.2012.

UNEP (1984). Determination of total Cadmium, Zinc, Lead and Copper in selected marine organisms by flameless atomic absorption of marine pollution studies. 11 (1).

USEPA (2006).Pollutant Discharge Elimination System.http://www.epa.gov/npdes. Viewed 11/0004/2011.

Wanjala, O. F. (2009). Assessment of heavy metals concentration in soils at selected points on roads and sites around Nairobi using EDXRF spectrophotometer. A Thesis submitted in partial fulfillment of the requirements for the award of the degree of Master of Science in the school of Pure and Applied Sciences of Kenyatta University.

Wanjau, R. Bin H, Jiang Q Y Man, Z H Pei L. (2004). Determination of Trace Metal Impurities in Cerium Oxide by Fluorination-Assisted ETV-ICP-AES after HPLC Separation.*Journal of Rare Earths*. 22: 197-200.

World Health Organization (2000) hazardous Chemical in Human and Environmental Health. WHO Geneva Switzerland.

APPENDIX I

SAMPLING SITES

K1 - Kilindini 1
K2 - Kilindini 2
K3 - Kilindini 3
K4 - Kilindini 4
K5 - Kilindini 5
K6 - Kilindini 6
K7 - Kilindini 7
K8 - Kilindini 8
KG - Kilindini Gastropa
MB1 - MalindiBay 1
MB2 - MalindiBay 2
MB3 - MalindiBay 3
MB4 - MalindiBay 4
MB5 - MalindiBay 5
MK - Makupa
MO - Malindi Oysters
S1 - Sabaki 1
S2 - Sabaki 2
S3 Sabaki 3
SG - Sabaki Gastropa
SH1 - Shirazi 1
SH2 - Shirazi 2

APPENDIX II

CALIBRATION CURVES FOR INVESTIGATED METALS

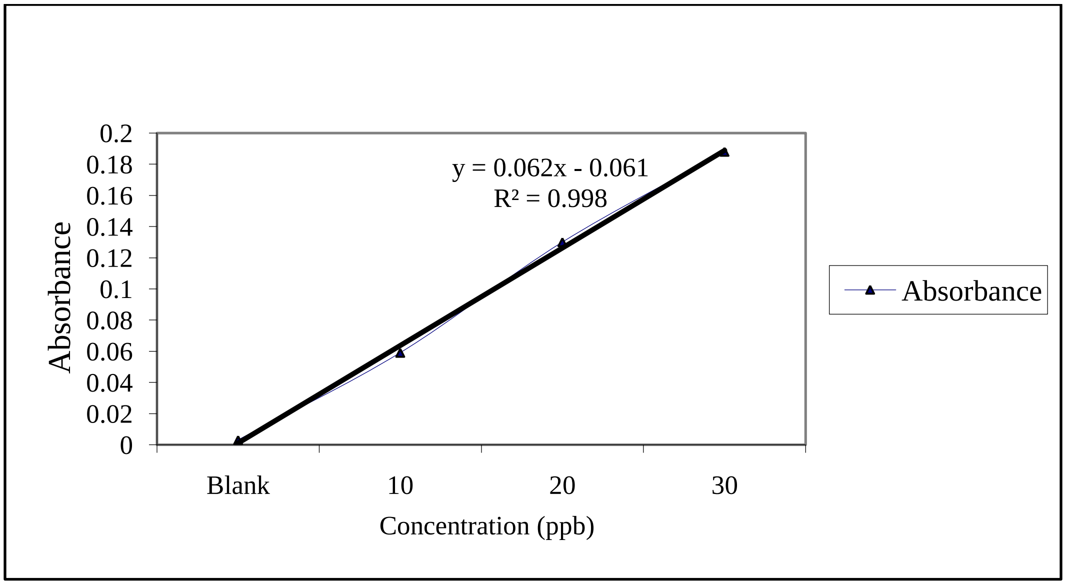


Figure 4.2: Calibration curve for Mercury

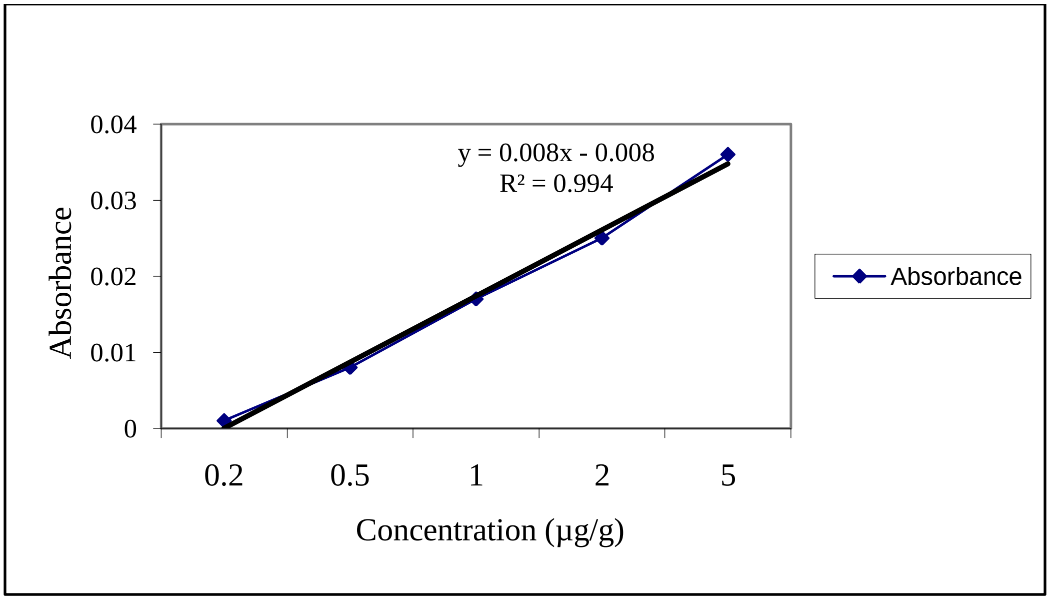


Figure 4.3:Calibration curve for Copper

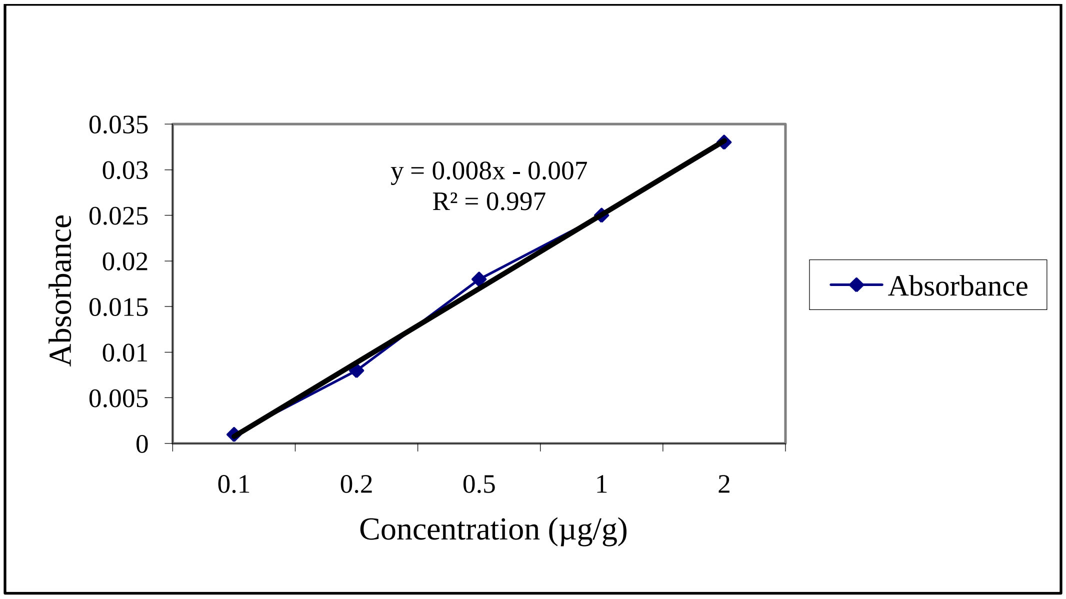


Figure 4.4:Calibration curve for Cadmium

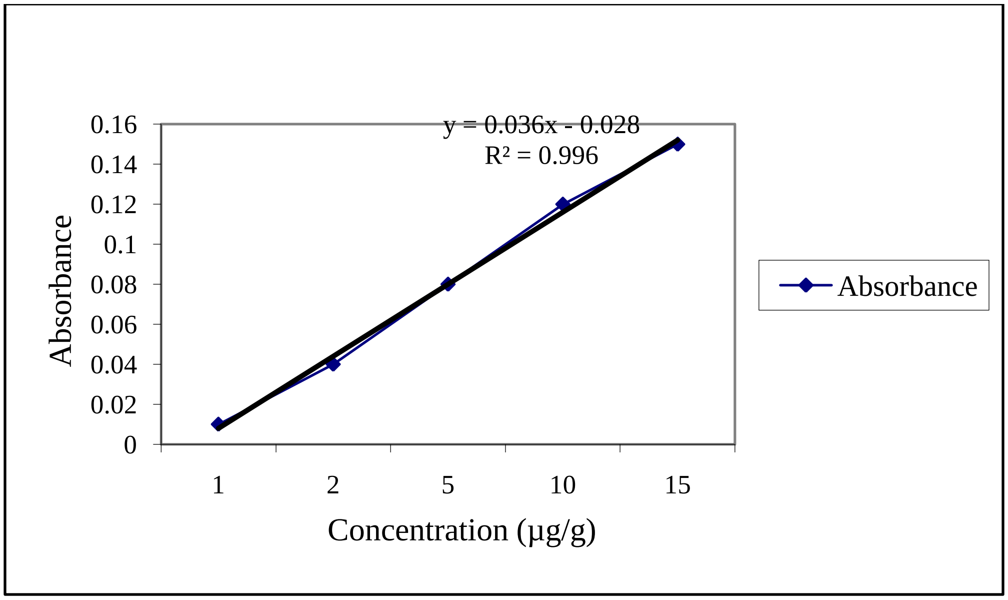


Figure 4.5:Calibration curve for Manganese

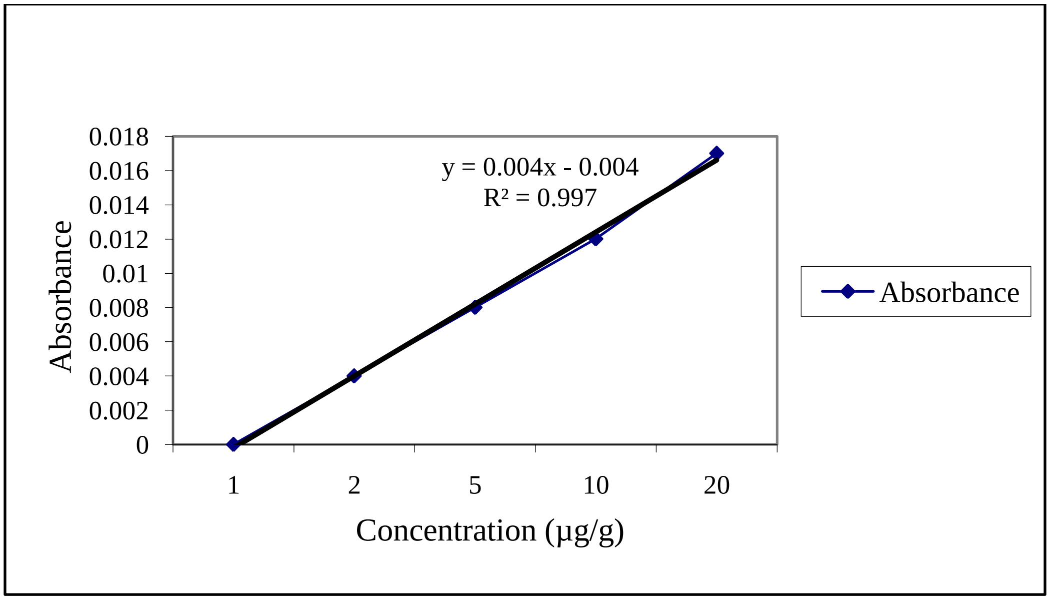


Figure 4.6:Calibration curve for Iron

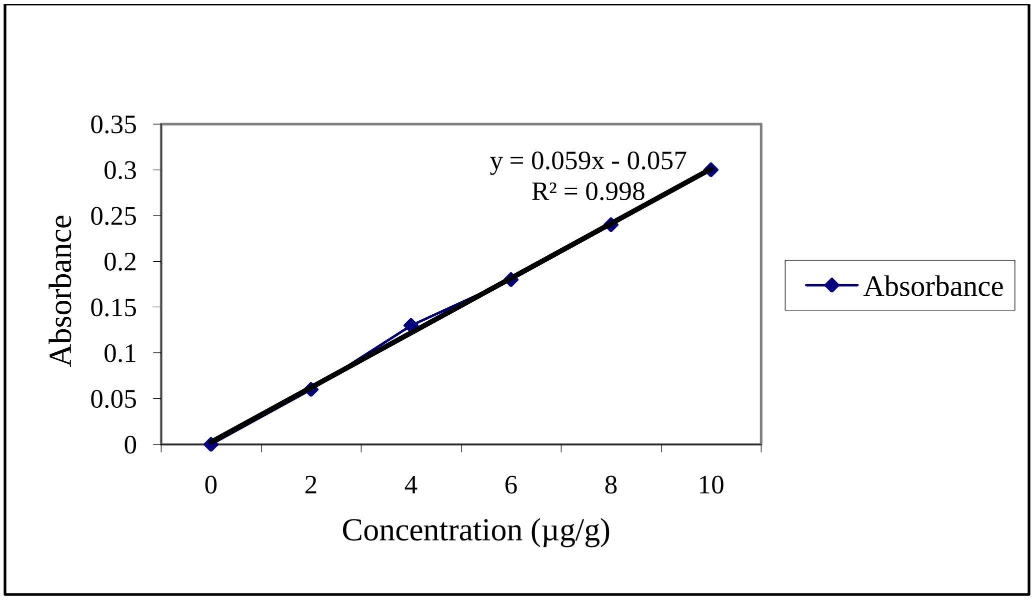


Figure 4.7:Calibration curve for Chromium

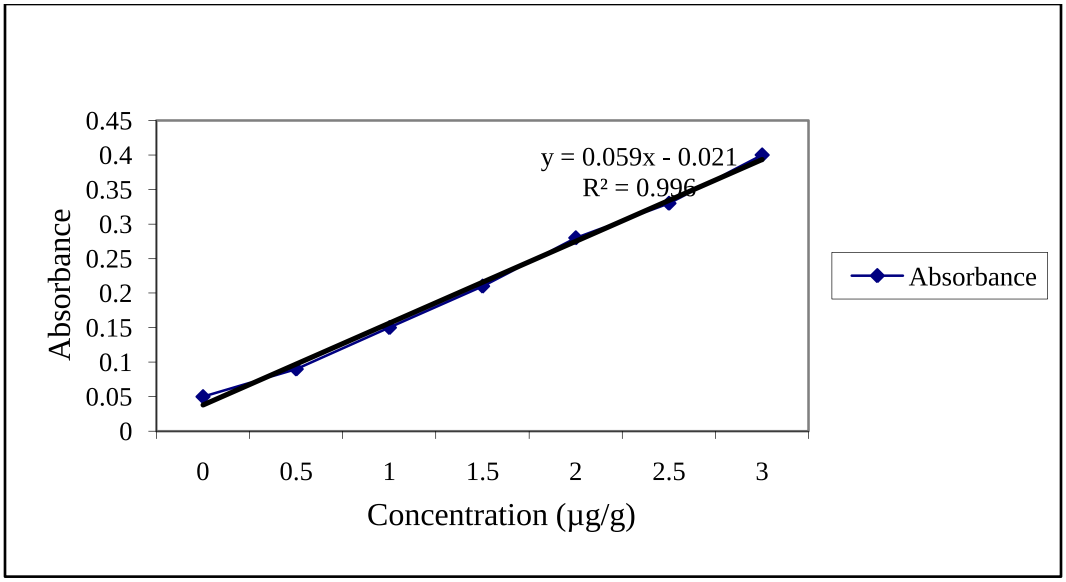


Figure 4.8:Calibration curve for Zinc