HEAVY METAL AND ORGANOCHLORINE POLLUTANTS IN TISSUES OF MARINE FAUNA ALONG THE COAST OF MOMBASA ISLAND - KENYA

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A THESIS SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENT FOR THE AWARD OF THE DEGREE OF MASTER OF SCIENCE IN ZOOLOGY OF KENYATTA UNIVERSITY

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Heavy metal and organochlorine
2002/262436

MARCH, 2000.

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DECLARATION

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

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DEDICATION

This work is dedicated to my parents, especially my late father, Kibor Arap Bariwot, who spared no effort to see us go to school; and to my wife, Alice, and children, Kip, Memoo and Kipkem who missed my presence while I was doing this work.

ACKNOWLEDGEMENTS

May I register my acknowledgements to a number of people and Institutions without which this work could not have been completed this fast.

First, may I sincerely thank all my supervisors, Prof. S. G. Bagalkote (who left the country shortly before the completion of this work), Dr.(Mrs.) J.A. Simbauni (who took over from Prof. Bagalkote), Dr. W. M. Njue, Prof. S. C. Chhabra, all of Kenyatta University, and Dr. A. M. Kinyua of the Institue of Nuclear Science, University of Nairobi for their invaluable advice, guidance and support throughout this work.

Secondly, I wish to thank Dr. Ezekiel Okemwa, Director Kenya Marine and Fisheries Research Institute - KEMFRI, for allowing me to conduct some of my analytical work at the Institute. Through him I also wish to acknowledge his entire staff, notably Mr. Ogega and his team for facilitating this research work both in the field and in the laboratory. On the same note, I also wish to thank the staff of the Institute of Nuclear Science, especially Mr. Bartilol, for their co-operation and total support.

Lastly, many thanks go to Dr. Ole Ntaiya of KARI - Nairobi, not only for his very valuable guidance on the use of the GLC but also for facilitation of the use the facility at the Pesticide Chemistry Laboratory. Finally, I will not forget to appreciate the assistance and co-operation of those good friends who assisted in one way or another, and to Ms. Rose Kerich who typed the bulk of this thesis.

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ABSTRACT

Marine pollution is increasingly becoming a problem along the Kenyan coast. Heavy metals and organochlorine pollutants have the potential to damage the delicate marine ecosystem with the result that the country's important foreign exchange earner - tourism - could seriously be affected. This study aimed at assessing the levels of cadmium, lead, copper, zinc, manganese, iron and titanium using Energy Dispersive X-ray Fluorescene (EDXRF) and Atomic Absorption Spectroscopy (AAS) in selected marine fauna. It further assessed the levels of lindane, aldrin, dieldrin, endosulfan (α-, ß-), DDT and its metabolites using Gas-Liquid Chromatographic (GLC) techniques.

Certified reference material (Mussel Tissue, MA-M-2/TM, IAEA) was analyzed by, both AAS and EDXRF techniques, for quality assurance and control. The two methods are in good agreement and the results are within 10% of the certified values (Appendix III). For statistical analysis, regression analysis was used to calculate the concentration of samples and relationship between pollutant concentrations. Some of the calculations refer to the dry weight of soft tissues. One-way analysis of variance (ANOVA) was applied with the aid of a computer programme to investicate the differences in pollutant concentrations between animal samples and between locations. The level of statistical significance was set at $p \leq 0.05$, unless otherwise stated. Tukey's studentized range test was used to separete the means when ANOVA indicated significant differences.

Marine animals used for the study were chosen from molluscs, echinoderms, crustaceans and chordates sampled mainly along the

coast of Mombasa Island. Some samples were also collected from Vanga in the South Coast, Nyali Beach and Marine Park in the north.

The four groups of animals were all found to have accumulated heavy metals and pesticides to some considerable extent. Concentrations of lead and cadmium ranged from 3.68 - 5.70 ppm and 0.47 - 1.45 ppm respectively. Pesticide levels were, however, relatively low (0.227 ± 0.026 ppm). Lindane which was found in 64% of all the animals studied, ranged from the detection limit (0.01ppm) - 0.561 ppm.

Marine fauna sampled near the Mombasa showground (English Point) contained higher than average (4.25±0.37 ppm against a mean value of 2.295±0.22 ppm) levels of the heavy metals studied. Pesticide concentraion had a similar pattern with a level of 0.383±0.039 ppm against a mean value of 0.235±0.039 ppm.

Vanga was another place where marine animals were found to have accumulated the heavy metals and pesticides to a significant ($p = 0.0481$) extent (4.07±0.25 ppm and 0.242±0.01 ppm respectively).

The highest concentration of lead (14.80 ± 0.42 ppm), recorded in this study was found in *Crassostrea sp.* sampled from Vanga. Cadmium registered a concentration of 3.49 ± 0.31 ppm in *Uca vocans* collected from Mbaraki. The same species registered the highest concentration of lindane (0.561±0.5 ppm).

Although this study has confirmed that marine fauna from the Kenyan Coast have accumulated both the heavy metals and pesticides studied, the levels are generally low compared to the results from a similar study by Windom (1991). However, unless the pollutants are monitored continuously, the levels are set to increase, with serious implications.

CHAPTER ONE

1.0 INTRODUCTION AND LITERATURE REVIEW

1.1 Introduction

Seas and oceans are a natural resource for man's food, energy and minerals. They are also a habitat for a vast array of plants and animals (Sharma, 1990). It is estimated that 50% of people in developing countries obtain 30% of their protein directly from marine fishes. This is excluding that which they get from other marine fauna such as oysters, crabs and lobsters.

Over very long geological periods, the volume and composition of oceans have remained remarkably stable (United Nations Environmental Programme *et al.*, 1984). However, human activities in the production of manufactured industrial goods, foods, and services have led to the production of wastes that must be discarded (United Nations Environmental Programme *et al.*, 1984). Added to the waste disposal problem is the carelessness, indifference and ignorance of the consumers and authorities. This has led to the deterioration of the environment by the waste products in quantities that vary in composition and which are difficult to be naturally assimilated (Sharma, 1990). This results in pollution, which may biologically be

defined as the introduction of any factor or factors, quantitative or qualitative, that may stop, alter or control biological activity.

Significant evidence abounds that some heavy metals and organochlorine pesticides at the levels recorded in the environment may be harmful to health and life of both man and other animals (Mason, 1991). Both these pollutants are persistent in the environment since their rate of biodegradation is so slow that they effectively become permanent additions to the aquatic environment. The pollutants accumulate in the organisms while some may biomagnify in food chains such that carnivores at the top of the food chains will be found to have accumulated them to a high level (Mason, 1991).

1.2 Literature review

1.2.1 Heavy metal pollutants

The term "heavy metals" usually refers to those metals with atomic numbers between 22 to 92, inclusive, in all Groups from Period 3-7 of the Periodic Table (Vernberg and Vernberg, 1974). This is only a guideline and there is really no satisfactory grouping by which they can be identified. Adriana *et al.* (1996), has proposed that the term "heavy metal" be utilized as synonymous to environmental pollutant whenever it is used in the context of

environmental studies. Kinyua (1997) has classified heavy metals into common essential elements (CEE), common essential trace elements (CETE), and potential toxic elements (PTE).

Metals react with electron-pair donors by being electron-pair acceptors to form various chemical groups such as ion-pairs, metal complexes, coordination compounds, or donor-acceptor complexes (Connell and Miller, 1984). They are poisonous to living organisms mainly because they inactivate enzymes by attaching themselves to the thiol or -SH groups thus distorting the enzymes' geometry (Landis and Ming- Ho Yu, 1995). The equation below shows the reaction between lead and an - SH group enzyme.

Eqn. 1 $2\ Enz\text{-}SH_{(aq)} + Pb_{(aq)}^{2+} \longrightarrow Enz\text{-}S\text{-}Pb\text{-}S\text{-}Enz_{(aq)} + 2H^{+}_{(aq)}$

Some metals cause metal shifts from one organ to another. Vanadium for example causes iron to move out of the liver and spleen when fed to rats at 250 ppm (Landis and Ming-Ho Yu, 1995). Higher doses of this metal completely deplete iron from the spleen and liver.

The most severe problems of non-occupational environmental poisoning by heavy metals are caused by mercury, lead and to some extent cadmium

(Muigai *et al.*, 1996). Nriagu (1988) has suggested that over one billion people are currently exposed to elevated concentrations of toxic metals and metalloids in the environment and several may already be suffering from sub-clinical metal poisoning.

The importance of metals in the marine environment emerged from studies of radionuclides resulting from fallout in the oceans during the 1950s and the 1960s (Vernberg and Vernberg, 1974). It became apparent that certain nuclides were being accumulated by organisms in large concentrations, particularly in certain organs. The giant clam, *Tridacna,* for example concentrates cobalt-60 in the kidney (Mason, 1991). Wenzel *et al.* (1996) found out that mercury concentrates more in the liver of kittiwake, *Rossa tridactyla,* nestlings than in their kidneys.

Metals in their pure state present little hazard, except those having a high vapour pressure like mercury and those present in particulate form in the atmosphere (Vernberg and Vernberg, 1974). After all, people have been preparing their food with tools made from metals, cooking it in metal pots and even eating it with metallic forks and spoons! It is their soluble compounds, which create problems in the aquatic environment. Amongst the

most dangerous compounds of metals are the metallo-organic ones such as methyl mercury and tetraethyl lead (GESAMP *et al.*, 1988).

Certain metals are required in life processes and therefore most organisms have, so to speak, "learned" to cope with them. This ability is enhanced by certain feeding and metabolic processes, which can lead to enormously high concentration factors (Mason, 1991). Invertebrates appear to have a particularly high capacity for concentrating metals, along with other foreign materials found in the environment when they filter plankton during feeding (United Nations Environmental Programme *et al.*, 1984). Many metals have the ability to form complexes with organic substances, and therefore there is a tendency for them to be fixed in the tissues rather than be excreted (United Nations Environmental Programme *et al.*, 1984).

1.2.1.1 Lead

Lead is possibly the first metal discovered and worked on (GESAMP *et al.*, 1985) and it is the heaviest element in the periodic table group IVa. It has two oxidation states Pb^{2+} and $Pb4^{+}$ where Pb^{2+} predominates in the aquatic environment (GESAMP *et al.*, 1985).

Rocks containing small amounts of lead are common and widespread, with typical concentrations ranging from 10 to 20 $\mu g\ g^{-1}$ in many igneous and metamorphic rocks; from 10 to 70 $\mu g\ g^{-1}$ in carbonaceous shales to about 100 $\mu g\ g^{-1}$ in some phosphate rocks (GESAMP *et al.*, 1988). There is a wide range of lead concentrations in the soil (2-200 $\mu g\ g^{-1}$) with considerable areal homogeneity. Some geologically unusual soils from diverse countries contain up to 30,000 $\mu g\ g^{-1}$ (Nriagu, 1978).

Other sources of lead stem from their uses as in fuel additives and paints. Vehicular exhaust is a major source of lead pollution in this category. Lead is extensively used in pipes, battery cases, cable sheathing and alloys (Mason, 1991).

Chronic concentrations of lead in aquatic ecosystems mostly affect waterfowls (Mason, 1991). In Great Britain, some 8,000 mallard (*Anas platyrhynche*) are estimated to die each year due to lead poisoning (Mason, 1991). Many others suffer from sub-lethal effects, such as vulnerability to disease and predators.

Exposure to relatively low levels of lead in man has been associated with metabolic and neuropsychological disorders such as significant impairment of

the fine motor, perceptual and visual skills and lower performance intelligent quotient (GESAMP *et al.*, 1988). Elevated exposure affects haemopoietic tissues where biosynthesis of the haem is disturbed (Connell and Miller, 1984). High doses cause encephalopathy whose symptoms are ataxia, coma, and convulsions. Occupationally lead-exposed women have higher frequency of stillbirths and miscarriages (Rom, 1976). Lead passes the placental barrier and causes central nervous system damage to the exposed fetus. The threshold for possible medical intervention in the United States has been set at a concentration of lead in blood (PbB) of 250-300 μg per 100 ml of blood (Sharma, 1990).

1.2.1.2 Cadmium

Cadmium is released slowly into the environment from widespread sources, chief among them being Ni-Cd rechargeable batteries, volcanic eruptions, power generating facilities and burning of agricultural and municipal wastes (GESAMP *et al.*, 1985). Sewage sludge applied to land and phosphate fertilizers are also significant sources (Mason, 1991).

Cadmium is highly toxic to some forms of life, cladocerans being especially sensitive (Olsson, 1986). Sub-lethal effects of cadmium toxicity have been reported from wild populations of fish. Perch (*Persa fluviatilis)* from Swedish

rivers contaminated with cadmium had a markedly increased lymphocyte count, anaemia and changes in the concentration of K^+ and Mg^{2+} in their blood (Larsson, 1985).

A long-term exposure of cadmium in food is associated with kidney damage in humans (Nriagu, 1988). The author estimates that more than 500.000 people worldwide may be at risk from cadmium-induced kidney damage.

1.2.1.3 Copper, Zinc and Manganese

Strictly speaking these three metals may not be a pollution problem to living organisms. In fact they are essential dietary elements. Copper is a prosthetic group of the enzyme *cytochrome oxidase*, zinc is a co-factor in *dehydrogenases* and DNA- *polymerases* while manganese is a co-factor in *arginase* and other enzymes (Goodhart and Shils, 1974; Schmidt-Nielsen, 1990). However, when ingested in large amounts they become a pollution problem. As little as 2 ppm of copper causes a tallowy flavor in milk and butter, hence impairing their storage qualities. Copper also promotes the destruction of vitamin C in fruits and vegetables. Statutory limits prescribed for copper in tomato ketchup is 20 ppm (Pradyot, 1992).

Copper is biocidal to a number of lower organisms for example fungi, molluscs and insects (Nriagu, 1979), The statutory limit for zinc in food

products is set at 50 ppm (Pradyot, 1992). Toxic effects of zinc poisoning include diarrhoea, central nervous system depression, reproductive impairment, and anaemia (Pradyot, 1992). Manganese poisoning is associated with mining activities and dry-cell battery industries. Manahan (1992) has advanced that neurological and psychological disturbances can result from excessive ingestion of the metal.

1.2.2 Organochlorine pesticides

Natural pesticides, such as derris dust, sulphur, nicotine and pyrethrins have been in use for a considerable period of time but have not been highly successful due to lack of potency, lack of specificity and high cost (Connell and Miller, 1984). In the last 50 years therefore, there has been a steady growth in the use of synthetic organic chemicals and pesticides.

The use of synthetic chemicals, which are potent, selective and comparatively cheap to control pests, principally insects, weeds, fungi and nematodes, has enormously improved production of food (Khan, 1980). Residues of pesticides occur in biological and physical components of the coastal and oceanic environments. Some of these residues have been implicated in degradation of portions of the environments (Connell and Miller, 1984). The environment's impact of pesticides use is related to

several fundamental properties essential to their effectiveness as pesticides. First, pesticides are toxicants capable of affecting all taxonomic groups of biota, including non-target organisms, to varying degrees dependent on physiological and ecological factors (Landis and Ming- Ho Yu, 1995). Secondly, pesticides need to be resistant to environmental degradation so that they can persist in the treated areas and thus enhance their effectiveness. This same property unfortunately also promotes the long-term effects in natural ecosystems. Organochlorine pesticides are hydrophobic, fat-soluble and biologically stable (United Nations Environmental Programme *et al.*, 1988). They therefore accumulate in body fat of living organisms. They also biomagnify along food chains and concentration factors from water to top predators like dolphins, may be as high as 10^7 (Larsson, 1985).

In the developed world restrictions have been placed on the use of organochlorine pesticides and polychlorinated biphenyls (PCBs) because of their long life. The situation is different in the developing countries. In fact developed countries have resorted to selling harmful pesticides very cheaply and dumping them in the developing countries (Maina, 1998). But even if the developing countries were to impose a ban on organochlorines, concentrations from historical and current uses are still sufficiently high to pose problems to sensitive species (Sharma, 1990).

Pesticides enter the aquatic ecosystem by way of run-off from farmlands, besides being applied directly. Sewage and industrial effluents are a further source of pesticides, while atmospheric transport, followed by precipitation in rainfall is also a major route of entry (Haines, 1983; Larsson, 1985).

1.2.2.1 Toxicology

Toxicicity of organochlorine pesticides to fish can be quite high. For example, the 96-hour LC_{50} (median lethal concentration) of DDT to various species ranges from 1-30 mg L^{-1}, while values for invertebrates are similar (Mason, 1991). At sublethal concentrations organochlorine pesticides result in impaired learning, slowed reflexes and a reduction in reproductive success (GESAMP *et al.*, 1988). Two of Europe's leading reproductive researchers have hypothesized that increasing exposure to environmental organochlorine compounds is likely to be responsible not only for lowered sperm counts, but also for genital defects, testicular cancer, and other male reproductive abnormalities (Word Wildlife Fund, 1999).

The human population is widely contaminated with organochlorine pesticides (Mason, 1991). In samples of breast milk from Hong Kong for example, Dichlorodiphenyltrichloroethane (DDT) and Dichlorodiphenylethane (DDE)

concentrations ranged from 0.67-4.04 and 4.07-22.96 mg kg^{-1} fat weight respectively (Mason, 1991). These are some of the highest values reported in the literature and may be due to the importance of seafood in the diet of ethnic Chinese. Mean concentration of DDT in the breast milk (mg kg^{-1} fat) ranged from 1.7 (Australia) to 19.5 (India), with means from seven countries in a study of twenty countries, exceeding 10 mg kg^{-1} (Ip and Philips, 1989). The maximum allowable concentration of DDT in human foodstuff is 0.74 mg kg^{-1} (Mason, 1991). Thus the lowest mean of 1.7 mg kg^{-1} cited in the study above is more than twice this standard.

1.2.3 Brief review of previous work done

Previous work on marine pollution studies in Kenya is scanty. Some work has however been done on a number of our lakes, but these studies have tended to concentrate on trace elements analysis using one analytical method - the AAS. Previous studies have also heavily leaned on sediments and water at the expense of the biota (Muigai *et al.*, 1996). Munga *et al.*, (1994) did a quick assessment on the land-based sources of marine pollution along the Kenyan coast. Their assessment was mainly based on organic pollutants. According to their findings Mombasa District has the highest concentration of major sources of pollution.

A number of studies on heavy metals and organochlorines have been done. Tayel (1995) studied the contamination of trace metals in the muscle tissue of fish (by means of atomic absorption spectrometer) in Au-Qir Bay, Egypt. He found the ranges for lead and cadmium to be 0.16-0.47 ppm and 0.01-0.09 ppm, respectively. The extent of accumulation of heavy metals on fresh water snails has also been assessed in Southern Nigeria by Adewunmi *et al.*, (1996) using flameless AAS (Flameless Perkin-Elmer Model 5000). The latter recorded a mean concentration of cadmium and lead of 2.2 ppm and 10.6 ppm respectively. Similar studies have been done (Vetter *et al.*, 1996) on organochlorine residues in marine mammals from the Northern hemisphere. Vetter *et al.* found different species of marine mammals to have accumulated organochlorines to different levels. Distribution and age-related changes in trace elements in *Rissa tridactyla* was investigated by Wenzel *et al.* (1996) in the German Bight, North Sea. Bremle and Larsson (1998) looked at the concentration of Polychlorinatedbiphenyls (PCBs) in fish from a river system in Sweden. Other works include those of Wagemann *et al.* (1996) who surveyed the regional and temporal differences of heavy metals in Arctic whales and Skaare (1996) who investigated organochlorines (OCs) in marine mammals in Norway.

1.3 Justification of the study

Whereas a significant amount of work has been done on heavy metal pollution of the Kenyan lakes (Muigai *et al.*, 1996), little has been done along the Kenyan coast. Heavy metals and organochlorines are hazardous pollutants that are not only injurious to marine fauna but also to man as exemplified by the Minamata disaster and the "itai - itai" disease witnessed in Japan in the 1950s (Mason, 1991). "Itai - itai" (ouch-ouch) is due to cadmium poisoning and is a disease characterized by severe back and joint pains, a duck-like gait, kidney lesions, protein and sugar in urine and decalcification of bones that often lead to fractures.

1.3.1 Famine

The countrywide famine of 1997 is still very fresh in the minds of Kenyans. The lesson learned was that traditional agricultural practices as modes for food production are unreliable and inadequate due to their dependency on the weather conditions. There is need therefore to diversify to other means of food production. One such means which can be introduced is mariculture along the coast. It is therefore important to know the level of pollutants in tissues of marine organisms intended for harvesting.

1.3.2 Tourism

Tourism remains one of the largest foreign exchange earner to Kenya. The coastal strip continues to be a tourist attraction area. But pollutants have the potential to damage the delicate marine ecosystem. By assessing the levels of pollutants in marine animals one can use them as pollution indicators and thus providing advice on which places are polluted and what can be done to enhance the tourism industry.

1.4 Objectives of the study

The aim of this was work to assess the levels of some heavy metals and organochlorine pollutants in tissues of selected marine organisms. The specific objectives were:

1. To determine by atomic absorption spectroscopy (AAS) the concentration of lead, cadmium, copper, zinc and iron in tissues of selected echinoderms, crustaceans, molluscs and chordates.

2. To quantify by Energy Dispersive X-Ray Fluorescence (EDXRF) the levels of lead,zinc,copper, iron, manganese and titanium in the marine fauna listed above.

3. To assess the levels of the following organochlorine pesticides by Gas-liquid chromatography: Hexachlorocyclohexane (Lindane), Aldrin, Dieldrin, Endosulfan, DDT and its metabolites in tissues of the marine organisms listed above.

CHAPTER TWO

2.0 MATERIAL AND METHODS

2.1 Study area

In this study the phrase "along the coast of Mombasa Island" has been used to include the coastline area between Vanga in Kwale District (latitude 4.5° S) and Marine Park in Kilifi District (latitude 4° S) and the coastline of Mombasa Island itself. **Figure 1** is a sketch map of the study area.

Fig 1: Sketch Map of the Study Area

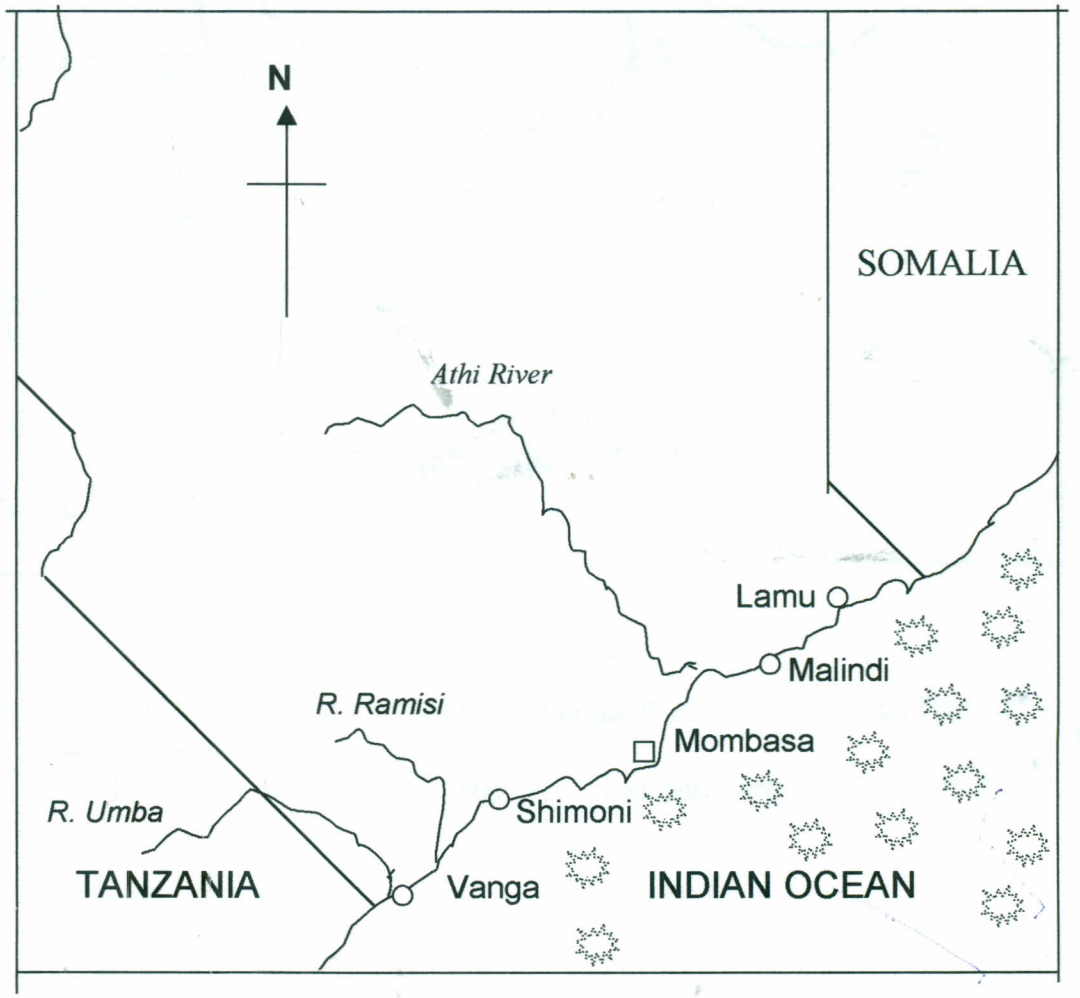
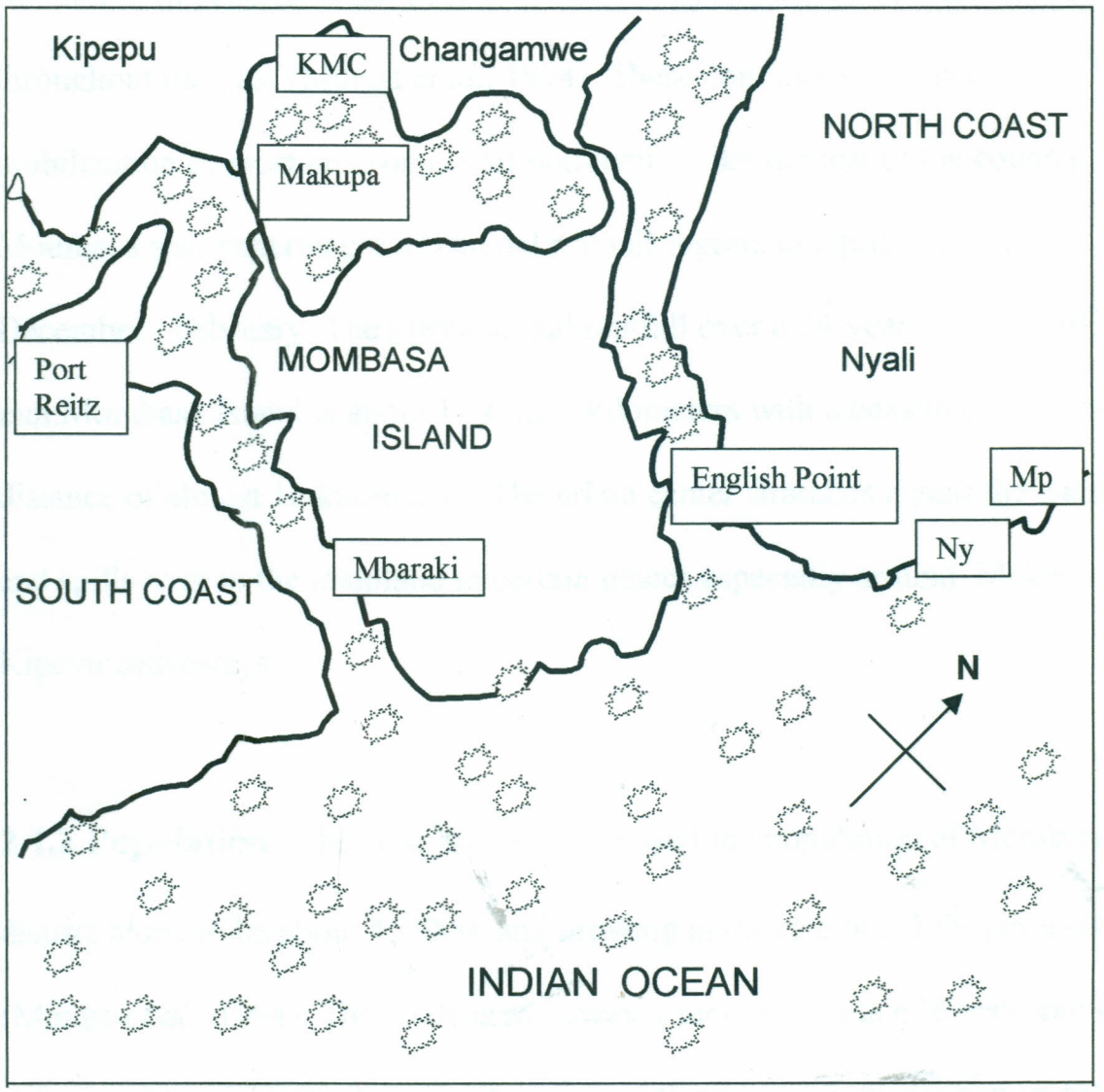


Fig 2: Sketch Map of Mombasa Island showing the sampling points



KEY: Sampling Station

Mp. ⇒ Marine Park Ny. ⇒ Nyali Beach

(**Nb**: Ny. and Mp. are in Kilifi District)

2.1.1 Climate

Mombasa, in general, is hot (23.4 ^{o}C - 30.1 ^{o}C) and humid (67%R.H.) almost throughout the year (Munga *et al.*, 1994). These conditions enhance mobilization of most environmental pollutants. Like the rest of the country, Mombasa also experiences a bimodal rainfall regime in April / May and December / February. The mean annual rainfall over a 24-year period is 1038 mm.Mombasa Island is about 13 square kilometers with a coastline spanning a distance of almost 16 kilometers. The urban center straddles across the island and spills over to the mainland in certain places especially around Makupa and Kipevu causeways.

2.1.2 Population. The census of 1989 showed the population of Mombasa district alone to be about 467000 and growing at the rate of 3.14% per annum (Munga *et al.*, 1994). The study area however included parts of Kwale and Kilifi districts. Assuming the then population growth rate of 3.14% per annum then the estimated population in 1999 was therefore 636,192 people for Mombasa District alone.

2.1.3 Sampling stations

In Kwale District two sampling stations, Vanga and Ramisi were selected. These sites receive land-based pollutants from rivers

Umba and Ramisi respectively. However, no samples targeted for this work were found in Ramisi. Mombasa District had the largest number of sampling points, many of them along the coast of Mombasa Island. They included the following:

English Point
Makupa
Kenya Meat Commission (KMC)
Mbaraki
Port Reitz

There were two sampling points in Kilifi district- Nyali Beach and Marine Park. There are a chain of tourist hotels along Nyali beach, that dump various wastes, including raw sewage, into the adjacent sea water. Marine Park is a popular tourist spot and includes the Kenyatta public beach where there is a lot of human activity. Waste products such as plastics and food remains are found strewn all over.

2.1.4 Industries

Mombasa Island boasts of a numbers of industries, chief among them being shipping, fish processing, Bamburi cement works, and Changamwe oil refinery. All these may actually be discharging effluents into the sea.

2.2 Study material (Biota)

In this study, the following adult marine organisms were used:

Astichopus multifidus	-	Sea cucumbers
Oreaster reticulatus	-	Sea stars
Tripneuster esculantis	-	Sea urchins
Uca lactea	-	Fiddler crabs
Uca vocans	-	Fiddler crabs
Thalamita crenata	-	Swimming crabs
Scylla serrate	-	Mangroove crabs
Crassostrea gigas	-	Oyster
Crassostrea sp	-	Oyster
Gerres oyearia	-	Bony fish
Therapon theraps	-	Bony fish

These organisms came from four main phyla namely:

-Echinodermata	(sea urchins, sea stars, sea cucumbers)
-Crustacea	(crabs)
- Mollusca	(oysters)
- Chordata	(fishes)

2.3 Sampling procedure

The sampling procedure used was stratified random sampling which minimizes sample variation due to different micro-habitats. Animals were collected by hand, with nylon-lined gloves to avoid contamination, at low

tide and immediately packed into sterilized plastic containers kept in ice-boxes for transportation to the laboratory. Once in the laboratory, they were kept in deep freezers to await sample preparation and analysis. For pesticide analysis, samples were wrapped in aluminium foils and packed into glass jars. Marine fauna were collected from all the ten sampling stations chosen except for Mtwapa and Ramisi. Sampling was done during both the wet (April-May) and the dry (July-September) seasons in order to minimize seasonal variation.

2.4 Preparation of Samples

2.4.1 Sample Preparation for AAS Analysis

Soft tissues of the whole animal were separated from the skeletons, using stainless steel dissecting equipment. They were then thoroughly homogenized in a high-speed tissue homogenizer (Janke & Kunkel, ultra-turrax T25 model). Sub-samples between 0.5 g and 1.0 g of the fresh homogenized tissue of each animal species were digested in 16 ml of a mixture of concentrated ultra-pure nitric and perchloric acids in the ratio of 3:1 v/v.(Muigai *et al.*, 1996). The digestions were carried out in teflon beakers maintained at 150 ^{o}C. The digest was then cooled, brought to 50 ml with double-distilled water and stabilized with a little HCl.

For quality control a certified animal reference material - lyophilised mussel tissue, MA-M-2/TM-IAEA (**Table IIIa**) - was digested along with the test samples. The mean and standard deviation of the certified standard were then calculated. Homogeneity of the working matrix was also checked periodically by analyzing 5 sub-samples for the heavy metals of interest, where coefficient of variation was ensured to be less than 10%.

2.4.2 Sample Preparation for EDXRF Analysis

For XRF analysis 5 g of fresh homogenized tissue were dried at 80 ^{o}C for three days. The dried samples were ground into fine powder, sieved and pelletized. Pellets of between 0.2 and 0.8 g were made with a hydraulic pelletizer at a pressure of 20 tons/square inch. The pellets were then analyzed for trace metals. For quality control, certified biological (mussel tissue, fish flesh) and geological (Soil-7) reference materials were pelletized and irradiated for the same period as those of the samples.

2.4.3 Sample Preparation for GLC Analysis

5 g of fresh homogenized tissue were dried with 15 g of anhydrous sodium sulphate and sohxlet-extracted with analar grade n- hexane for 8 hrs (United Nations Environmental Programme *et al.*, 1982). The extract was then concentrated to 10 ml with a rotatory evaporator maintained at 30 ^{o}C, and

then dried with sodium sulphate and transferred to a Kud erna Danish concentrator to reduce the volume to about 5 ml (United Nations Environmental Programme *et al.*, 1982).

For clean-up 5 ml of the extract was passed through a micro-scale fluorosil and eluted with 6% of hexane in diethyl ether (F_1), followed by 15% of the same eluent to yield the second fraction (F_2) (United Nations Environmental Programme *et al.*, 1988). Fraction one (F_1) contains less polar pollutants than fraction 2 (F_2). 2 μl of each fraction was then injected into the GLC. For quality control certified standard solutions of lindane, aldrin, dieldrin, endosulfan and DDT were used to calibrates the GLC system as well as for peak identification and quantification.

2.5 Analysis of Samples

For statistical analysis, regression analysis was used to calculate the concentration of samples and relationship between pollutant concentrations. Some of the calculations refer to the dry weight of soft tissues. One way analysis of variance (ANOVA) was applied with the aid of a computer programme to investigate the differences in pollutant concentrations between animal samples and between locations. The level of statistical significance was set at $p \leq 0.05$, unless otherwise

stated. Tukey's studentized range test was used to separate the means when ANOVA indicated significant differences.

2.5.1 Sample Analysis by AAS

Atomic Absorption Spectroscopy (AAS) is a versatile analytical technique for elemental analysis. It has the following advantages over other similar techniques such as flame emission.

- It has high specificity that allows the analysis of individual elements even in a complex mixture.
- Has a fairly good sensitivity and thus suitable for the analysis of substances of low concentrations.
- It is free from spectral interferences because each metal has its own characteristic wavelength for absorption.

The technique is based on the absorption of light (characteristic wavelength) sourced from a suitable cathode lamp. The flame dissociates the metal salt (sample) into a vapour of metal atoms which then absorb the monochromatic light from the cathode lamp at the characteristic wavelength (Lucky and Venugopal, 1977). The absorption is proportional to concentration of the absorbing atoms. The decrease in the intensity of the monochromatic light is

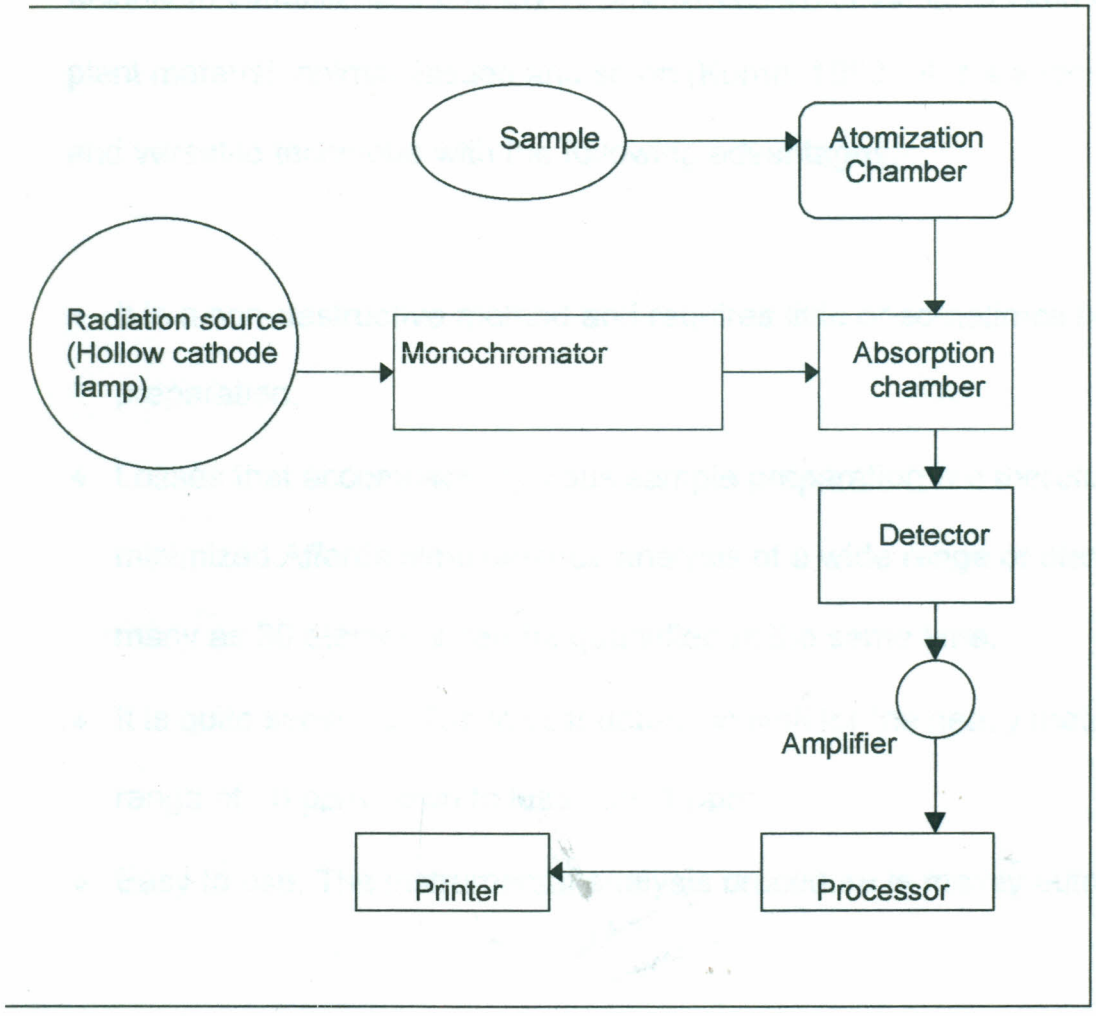
detected, amplified and recorded by suitable electronics system. The monochromator is designed to produce a spectrum of light that is in the absorption range of the metal under test. Most have absorption line in the range of 190 nm and 850 nm. In this study AAS Model: Varian SpectrAA-10 was used. The machines' operational parameters are given in Table I below.

Table I: Operational parameters of the AAS used.

Parameter	**Description**
Lamp Type	Hollow cathode lamp
Flame Temperature	2200^{o}C
Fuel	Air/Acetylene mixture
Monochromator	Grating 1200 lines/mm and a Blaze angle of 250 nm
Radiation Detector.	Photomultiplier tube, spectral Range of 190 nm - 780 nm.
Monochromator	Zeruy - Turner design
Slit width	Adjustable depending on Element

Figure 3: Block diagram for a typical AAS set-up

(Source: Godden, 1996)



2.5.1.1 Calibration of the AAS

Before analysis was commenced the AAS was first calibrated. Standards of Pb, Cd, Cu, Zn and Fe were prepared from 1000 ppm analar grade stock solutions

2.5.2 Sample Analysis by EDXRF

The Energy Dispersive X-ray Fluorescence (EDXRF) is an analytical technique suitable for the analysis of environmental samples such as soils, plant material, animal tissues and so on (Kump, 1993). It is a sophisticated and versatile technique with the following advantages:-

- It is a non-destructive method and requires little or sometimes no sample preparation.
- Losses that accompany rigorous sample preparation are therefore minimized.Affords simultaneous analysis of a wide range of elements. As many as 30 elements can be quantified at the same time.
- It is quite sensitive. The lowest detection limit for the heavy metals is in the range of 10 ppm down to less than 1 ppm.
- Easy to use. The instrumental analysis procedure is mainly automated.

A typical EDXRF electronic set-up is given in Figure 4

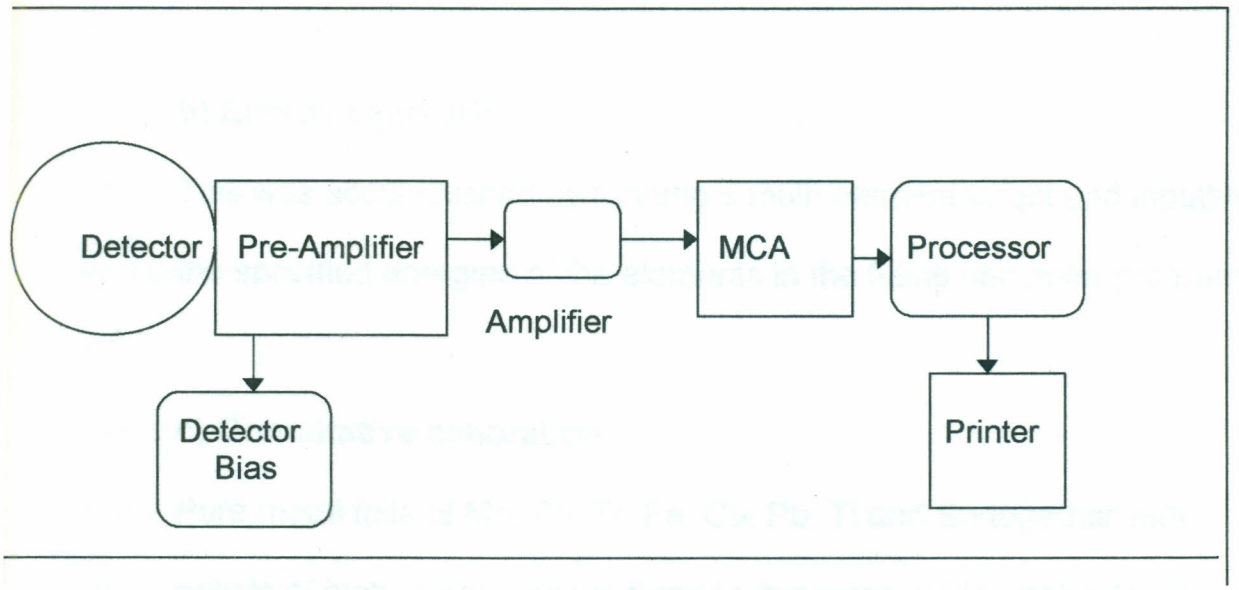


Fig: 4 EDXRF electronic set-up **(Source:** Kinyua, 1982)

2.5.2.1 Calibration and optimization of EDXRF

Calibration and optimization of instruments for quantitative analysis is necessary before any analysis is done. The EDXRF system used in this analysis was ensured to be working efficiently by carrying out the following:

a) Electronic system adjustment for maximum signal output.

The shaping time, polarity and gain were adjusted, according to the manufacturer's specifications, for the amplifier. The power supply

output was biased to -500V, while the gain/range was adjusted to 4K on the Analog-Digital Converter (ADC).

b) Energy calibration

This was accomplished by running a multi-element target and inputting the specified energies of the elements in the fitting computer program.

c) Quantitative calibration.

Pure metal foils of Mo, Zn, Zr, Fe, Cu, Pb, Ti and Sn together with pellets of high purity uranium fluoride, tungsten oxide, molybdenum oxide and dysprosium fluoride were used as standards for calibration. In addition the following certified reference materials were also used:

Mussel Tissue (Table IIIa)

Soil-7 (Table IIIb)

Fish flesh homogenate (Table IIIc)

2.5.2.2 Theoretical principles

Atoms of the sample are bombarded with energetic primary X-rays sourced from an appropriate radioactive element such as Cadmium-109 or Iron-55. The rays remove electrons from the K-shell of the atoms under test and

excite them to higher energy levels such as L,M, and N (Kinyua,1982). De-excitation of these excited atoms to the ground state results in the emission of energy in the form of characteristic fluorescent x-rays. The energy of the fluorescent x-rays is a function of the atomic number of the atom emitting it and is characteristic of the given element. Thus it forms the basis for identification and quantification of the element. De-excitation to the K-shell constitutes K-lines while to the L-shell constitutes L-lines and so forth. A computer programme - AXIL is designed to fit spectra, calibrate, distinguish between K and L lines; and even resolve K-lines into K_α and K_β. This allows recognition of an elemental peak from a multi-element display of the sample.

2.5.2.3 Analysis

Pellets weighing 0.5 g were made without any binder and hence no dilution. The pellets were irradiated for 1000 seconds. Spectral data were collected and stored on computer. Spectral conversion was done by a computer program called QAES (Quantitative Analysis of Environmental Samples) (Kump, 1993), while curve fitting was done by AXIL program (Analysis of X-ray spectra by Iterative Least squares fit program) (IAEA, 1996). The EDXRF System used in this study consists of 28 mm^2 x 5 mm thick ORTEC Si (Li) detector with beryllium window of thickness 25 μm, a Canberra amplifier/pulse processor with pile-up rejector Model 2020, and a Canberra

S100 PC based multichannel analyzer system (Kinyua *et al.*, 1999). The detector resolution (full width at half maximum - FWHM) was 190 eV at Mn K-α line at 5.9 keV, while the pulse shaping time constant was 6 μs. The excitation source used was ^{109}Cd (20mCi)

2.5.3 Sample Analysis by Gas-Liquid-Chromatography (GLC)

Chromatography is a technique used in separating individual compounds in a complex heterogeneous mixture. It utilizes the compounds' adsorptive properties to some suitable surface (United Nations Environmental Programme *et al.*,1988).

High resolution gas-liquid-chromatography is suitable for qualitative and quantitative analysis of a wide range of environmental samples including aerosols, water, particulates and biota. However, required are appropriate cleaned-up extracts dissolved in n-hexane for injection into the GLC system (United Nations Environmental Programme *et al.*,1988). Halogenated pesticides and other electron-capturing compounds may appropriately be analysed using this method.

The GLC used in this analysis utilizes an open tubular ("capillary") column that is advantageous over packed columns. With capillary columns it is

possible to identify and quantify many compounds in the complex mixtures occurring in environmental samples. For instance, it is possible to separate the 209 possible congeners of PCBs from interfering compounds and determine them as individual compounds, using one capillary column only. Capillary columns eliminate the ambiguities associated with the use of packed columns.

2.5.3.1 The Electron-capture Detector (ECD)

The electron capture detector is an extremely sensitive tool for analysis of organochlorine compounds. It is about five orders of magnitude more sensitive than for hydrocarbons (United Nations Environmental Programme *et al.*, 1988). An equilibrium concentration of thermal electrons is supplied by repeated collisions of high-energy electrons emitted by a radioactive source (Ni-63) within the detector with carrier gas molecules (United Nations Environmental Programme *et al.*, 1988).The thermal electrons are captured by the sample molecules and the resulting reduction in the cell current provides the signal.

2.5.3.2 Analysis

Standards of lindane, aldrin, dieldrin, endosulfan, DDT and its metabolites were used for both peak identification and quantification as well as to

establish optimum chromatographic performance. The retention times and peak areas in the sample chromatogram were compared to those of corresponding standards and concentrations of particular components calculated using equation 2 below (United Nations Environmental Programme *et al.*, 1988)

Eqn. 2: $$C_{S.} = \frac{C_{std.} \times A_{S.} \times Dl. \times V_{S.}}{W_{S.} \times A_{std.}}$$

$C_{S.}$ = Concentration in ppm of sample

$C_{std.}$ = Concentration (ppm) of standard

$A_{S.}$ = Peak area of sample

$A_{std.}$ = Peak area of standard

Dl. = Dilution factor

$V_{S.}$ = Final volume of sample

$W_{S.}$ = Weight of sample.

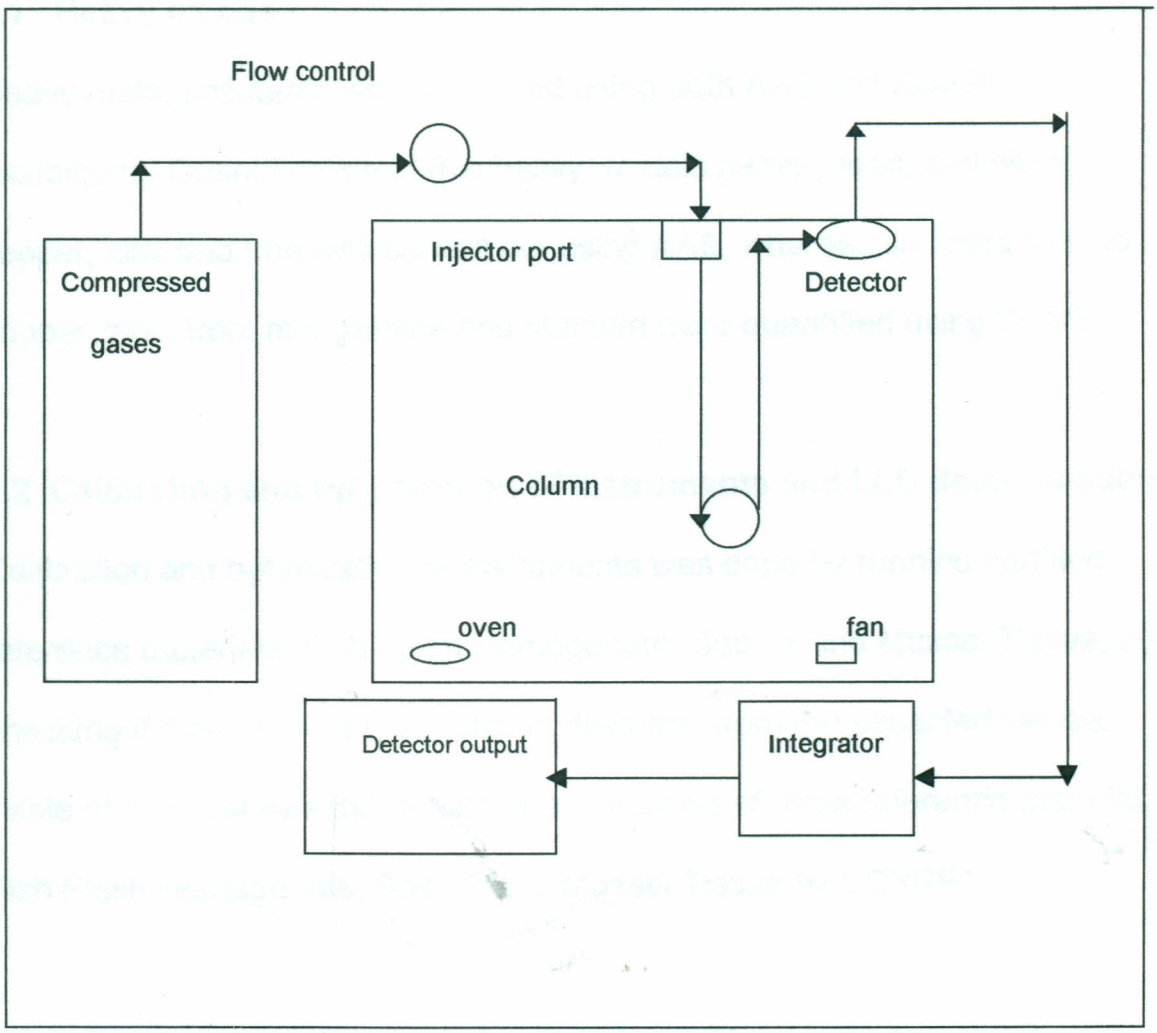
The GLC Model used for this analysis (**Fig.5**) was Varian 3400 equipped with a short response-time (0.25 seconds) integrator Model Varian 4400 (United Nations Environmental Programme *et al.*,1988). Other operation parameters of the GLC are given in Table II below.

Table II: Operation Parameters of the GLC used

Parameter	**Description**
Column	Temp-programmed capillary column
Detector	Electron-capture (ECD) with ^{63}Ni radioactive source operated at 300^0C.
Carrier gas	N_2, flow rate, 5 ml/min. Make-up gas flow rate of 25 ml/min
Temp-program	100^0C hold 5 min, then 4^0C/min to 220^0C, followed by a 15 min hold at 220^0C.

Figure **5** is a schematic diagram of a typical GLC system

(Source: UNEP *et al.* 1988)



CHAPTER THREE

3.0 RESULTS

3.1 Heavy metals

Heavy metal pollutants were analyzed using both AAS and EDXRF techniques. Quantification of five heavy metals namely lead, cadmium, copper, zinc and iron was carried out using AAS, whereas six metals - lead, copper, zinc, iron, mangenese and titanium were quantified using EDXRF.

3.2 Calibration and optimization of Instruments and LLD determination

Calibration and optimization of instruments was done by running certified reference materials, Fish Flesh Homogenate, Soil - 7 and Mussel Tissue, and checking if there were any significant deviation from the expected values. Table III below shows the results of the analysis of three reference material, Fish Flesh Homogenate, Soil - 7 and Mussel Tissue by EDXRF.

Table III (a) : EDXRF Results for Fish Flesh Homogenate

	Concentration (ppm $\pm \delta$)	
Element.	Experimental	Expected (Control)
Fe	58 $\pm$ 5.0	54 $\pm$1.0
Zn	35.1$\pm$ 2.5	33 $\pm$1.0

Table III: (b) EDXRF Results for Soil - 7.

	Concentration (ppm or as stated $\pm\delta$). Confidence interval in brackets	
Element	Experimental	Expected (control)
Ca	16.96%$\pm$0.81	16.30 % (1570 - 1740)
Mn	655.2$\pm$52.1	631 (604 - 650)
Fe	2.40% $\pm$ 1.1	2.57% (252 - 263)
Zn	101.7$\pm$ 8.0	104 (101 - 113)
Br	6.8$\pm$1.4	7 (3 - 10)
Rb	47.3$\pm$3.5	51 (47 - 56)
Sr	106.0$\pm$5.0	108 (103 - 114)
Y	21.5 $\pm$1.6	21 (15 - 27)
Zr	182.3$\pm$8.7	185 (180 - 206)

Table III: (c) EDXRF Results for Mussel Tissue

	Concentration (ppm or as stated $\pm\delta$). Confidence interval in brackets	
Element	Experimental	Expected (control)
Br	331.4 ± 15.0	357.8 (304.1 - 416.7)
As	11.7 ± 2.2	11.8 (11.8 - 14.4)
Fe	286.1 ± 20.1	256.2 (229.2 - 268.2)
Zn	159.2 ± 8.9	159.5 (152.8 - 166.7)
Mn	70.0 ± 11.8	67.1 (60.7 - 75.3)
Rb	5.7 ± 1.8	6.96 (5.30 - 7.80)

The lowest limit of detection (LLD) was determined from the results of a certified reference material (Mussel Tissue) using the equation:

Eqn. 3: $LLD = \frac{3\sqrt{Rb}\,(conc.)}{P_a}$ Where:

R_b = Background count rate

Conc. = Concentration

P_a = Peak area

A graph of the variation of the detection limit and atomic number of the element is given in appendix IV.

3.3 Intercomparison of Analytical Techniques

Table IV shows an intercomparison of the analytical results of the analysis by AAS and EDXRF techniques. The results were quite comparable. The differences observed in some cases, particularly for iron, may mainly be due to contamination during transport and storage Moreover, there was considerable loss of elements during preparation for AAS (recoveries were about 83%).

Table IV: Comparison of AAS and EDXRF results for two animal species *Gerres oyearia* (fish) and *Tripneuster esculentis* (sea urchin).

	Concentration (ppm $\pm\delta$)		
Species	Element	AAS	EDXRF
Gerres oyearia (fish)	Pb	2.95 $\pm$ 0.05	6.38 $\pm$ 0.45
	Zn	47.2 $\pm$ 2.5	63.05 $\pm$ 2.76
	Fe	242.0 $\pm$ 14.5	497 $\pm$ 2.83
	Cu	5.90 $\pm$ 0.12	6.29 $\pm$ 0.57
Tripneuster esculentis (Sea urchin.)	Pb	3.33 $\pm$ 0.11	6.68 $\pm$ 0.04
	Zn	19.31 $\pm$ 1.64	27.65 $\pm$ 0.35
	Fe	196.0 $\pm$ 2.2	209.5 $\pm$ 2.12
	Cu	6.66 $\pm$ 0.47	6.26 $\pm$ 0.62

3.4 AAS and EDXRF Results

Table V(a) and V(b) respectively shows AAS and EDXRF results in parts per million (ppm). Three samples from each animal species were analyzed and results given as mean $\pm$ one standard deviation of the mean.

Table V(a): AAS results of Concentration of Pb, Cd, Cu, Zn, and Fe (in ppm) in tissues of marine fauna along the coast of Mombasa Island

		Concentration (ppm $\pm\delta$				
Site	**Species (n=3)**	Pb	Cd	Cu	Zn	Fe
English	Sea star	7.80 ± 0.86	2.36 ± 0.07	19.6 ± 0.39	119 ± 1.4	137 ± 2.88
Point	Sea cucumber	5.70 ± 0.51	1.14 ± 0.03	3.68 ± 0.33	48.4 ± 1.5	125 ± 5.13
Makupa creek	Fish	2.95 ± 0.05	0.29 ± 0.01	5.90 ± 0.12	47.2 ± 2.5	242 ± 14.5
KMC	Fiddler crab	1.21 ± 0.02	0.65 ± 0.01	0.06 ± 0.05	30.1 ± 1.81	25.6 ± 0.90
(Kenya Meat	Oyster	6.03 ± 2.11	1.00 ± 0.06	4.01 ± 0.01	61.4 ± 0.86	64.2 ± 0.94
Commission)	Fish	4.40 ± 0.12	0.66 ± 0.01	6.61 ± 0.07	51.1 ± 0.81	84.7 ± 0.76
Mbaraki	Fiddler crab	3.21 ± 0.05	3.49 ± 0.31	2.34 ± 0.16	40.1± 0.41	23.5 ± 1.65
Port Reitz	Fidddler crab	5.56± 0.42	0.92 ± 0.01	11.2 ± 0.89	71.6 ± 3.72	170 ± 3.06
Vanga	Oyster	2.35 ± 0.11	0.74± 0.01	5.01± 0.35	30.2 ± 1.57	43.4 ± 0.56
	"Shell"	14.80 ± 1.09	0.92 ± 0.02	9.19 ± 0.19	63.3 ± 4.56	177 ± 6.34
	Swimming crab	5.31 ± 0.26	0.25 ± 0.01	21.1 ± 0.97	40.0 ± 1.87	33.5 ± 0.81
Nyali Beach	Fish	2.90 ± 0.23	0.29 ± 0.02	5.80 ± 0.05	99.2 ± 1.08	155 ± 10.6
	Swimming crab	3.72 ± 0.04	0.93 ± 0.00	31.8 ± 0.47	30.1 ± 0.28	121 ± 7.02
Marine Park I	Sea star	5.84 ± 0.11	3.22 ± 0.25	8.73 ± 0.65	57.4 ± 1.44	132 ± 2.38
	Sea urchin	10.7 ± 0.48	1.87 ± 0.83	5.33 ± 0.08	23.5 ± 1.86	163 ± 2.76
	Sea cucumber	1.86 ± 0.15	0.37 ± 0.00	6.10 ± 0.07	14.9 ± 1.19	94.4 ± 1.78
Marine Park II	Sea cucumber	1.73 ± 0.12	0.52 ± 0.03	5.19 ± 0.38	28.7 ± 0.52	100 ± 3.51
	Sea urchin	3.33 ± 0.11	0.67 ± 0.02	6.66 ± 0.47	19.3± 1.64	196± 2.15

Table V(b): EDXRF Results (ppm) of Pb, Cu, Zn, Fe, Mn, and Ti in tissues of Marine Fauna

		Concentration (ppm $\pm\delta$					
Site	**Species** (n=3)	Pb	Cu	Zn	Fe	Mn	Ti
English	Sea star	10.5 ± .28	6.68 ± 0.11	3487±73	4685±21	248.5±51	LLD*
Point	S/cucumber	LLD	5.54±0.48	25.7±1.6	467.5±0.7	55.3±0.12	LLD
Makupa	Fish	6.38±0.45	6.29±0.57	63.1±2.8	497±3	LLD	LLD
Kenya	Fiddler crab	6.54±0.06	51.9±0.6	1385±35	9580±240	317±11	1620±99
Meat	Oyster	8.03±0.11	42.6±2.6	1165±7	6745±50	234±14	1485±120
Commiss.	Fish	6.74±0.5	4.49±0.08	754±3	345±21	68.5±3.4	LLD
Mbaraki	Fiddler crab	6.68±0.39	51.5±0.6	1230±14	7450±184	293±18	1560±0
P/Reitz	Fiddler crab	7.56±0	65.6±3.8	1720±28	11500±70	480±28	2350±27
Vanga	Oyster	LLD	2.14±0.17	10.5±0.88	174±7	LLD	LLD
	S/crab**	27.4±0.3	6.17±0.35	2640±70	2885±21	175±4	641±49
	"Shell"	12.05±0.4	5.05±0.44	45.9±3.9	1235±7	385±55	LLD
Nyali	Fish	2.7±0.3	3.38±0.27	131±5.5	153±8	LLD	LLD
Beach	S/crab	LLD	6.64±0.28	16.8±0.7	467±7	LLD	LLD
Marine	Sea star	15.3±1.1	7.33±0.3	42±0.42	280.5±8	61.8±1.1	409±3
Park I	Sea urchin	2.11±0.04	3.47±0.02	6.86±0.06	300±12	LLD	LLD
	S/cucumber	8.35±0.48	6.63±0.47	42.2±0.71	251±1	LLD	LLD
Marine	S/cucumber	5.23±0.06	5.9±0.19	52.9±1.3	101±3.7	42.3±2.7	LLD
Park II	Sea urchin	6.68±0.04	6.26±0.62	27.7±0.35	209±2.1	LLD	LLD

LLD* = Lowest Limit of Detection **S/crab = Swimming crab

AAS and EDXRF results are comparable except for a few elements like iron where the difference has already been explained elsewhere in this thesis. Correlation tests confirm that there is no significant difference between the two results (r = 0.9451) (Appendix V).

3.5 Results of Pesticide Analysis

From each animal species three samples were analyzed and three readings for each sample recorded. The following pesticides were analyzed.

Aldrin	α - Endosulphan
Dieldrin	ß - Endosulphan
Lindane (HCH)	p,p'-DDE
o,p'-DDT	

Results are tabulated below.

Table VI: Concentrations in ppm of Organochlorine Pesticides in Marine Fauna along the coast of Mombasa Island. (LLD* - Lowest Limit of Detection)

	Organochlorine pesticides						
Station and Species	Lindane	DDE	DDT	Aldrin	Dieldrin	α– Endosulfan	β- Endosulfan
English Point							
A. multifidus	0.054± 0.001	0.949± 0.006	0.146± 0.11	LLD*	LLD	LLD	LLD
Makupa creek							
Gerres oyearia	LLD	LLD	LLD	LLD	LLD	LLD	LLD
KMC							
Crassostrea sp	0.189± 0.021	LLD	LLD	LLD	0.458± 0.41	LLD	0.061± 0.005
A. multifidus	0.039± 0.002	LLD	LLD	LLD	LLD	LLD	LLD
Mbaraki							
Uca vocans	0.561± 0.5	LLD	LLD	0.414± 0.31	LLD	0.503± 0.061	LLD
Port Reitz							
Crassostrea gigas	0.409± 0.31	0.122± 0.101	0.268± 0.032	0.017± 0.006	LLD	LLD	LLD
Uca lactea	0.432± 0.035	LLD	LLD	LLD	LLD	0.087± 0.007	LLD
Vanga	LLD	LLD	0.354± 0.032	LLD	LLD	LLD	LLD
Scylla serrate							
Crassostrea sp.	0.129± 0.012	LLD	LLD	LLD	LLD	LLD	LLD
Nyali Beach							
Thalamita Crenata	0.202± 0.010	0.193±. 0.17	LLD	LLD	0.063± 0.007	LLD	0.048± 0.004
Therapon theraps	0.119± 0.016	LLD	LLD	0.040±. 0.003	LLD	LLD	LLD
Marine Park							
A. multifidus	0.200± 0.011	LLD	LLD	0.018± 0.001	LLD	LLD	LLD
Oreaster reticulatus	LLD	LLD	LLD	LLD	LLD	LLD	LLD
Tripneuster esculentis	LLD	LLD	LLD	0.116± 0.012	LLD	LLD	LLD

CHAPTER FOUR

4.0 DISCUSSION AND CONCLUSIONS

4.1 Discussion

4.1.1 Heavy metals

The single organism that repeatedly recorded the highest concentration of heavy metals in this study was the crab. It is noted that the crab was present in almost all the sampling stations - even those suspected to be the most polluted. Crabs are marine scavengers that feed on almost anything available in their environment. They in the process ingest lots of pollutants. A rather high concentration of lead (significantly higher than the mean at $p \leq 0.01$) was recorded in *Crassotrea sp.* (oyster) found in Vanga. Oysters are filter feeders and are thus prime targets for a wide variety of pollutants. Vanga from which the oyster was collected is a small town bordering Kenya and Tanzania. Old automobile parts could be seen strewn all over the place and might have contributed to high levels of lead in water and consequently organisms residing in the waters. Moreover, River Umba, emanating from Tanzania, discharge its pollution load into the sea just close to Vanga.

It is also evident from Tables **V(a)** and **V(b)** that Port Reitz has shown high levels of heavy metal pollutants. This could be attributed to the fact that

Port Reitz is a favourite fishing ground for fishermen and was once a busy port for boats and smaller sea vessels.

Another notable observation from the tables is that different organisms show widely diverse tolerance to heavy metal pollution. Animal proteins called methallothioneins are believed to sequester heavy metals and thereby reduce their toxic effects (Landis and Ming-Ho Yu, 1995; and Mendieta *et al.*, 1999). It is possible that different marine organisms posses different capabilities of synthesizing these proteins and hence the differing metal tolerance.

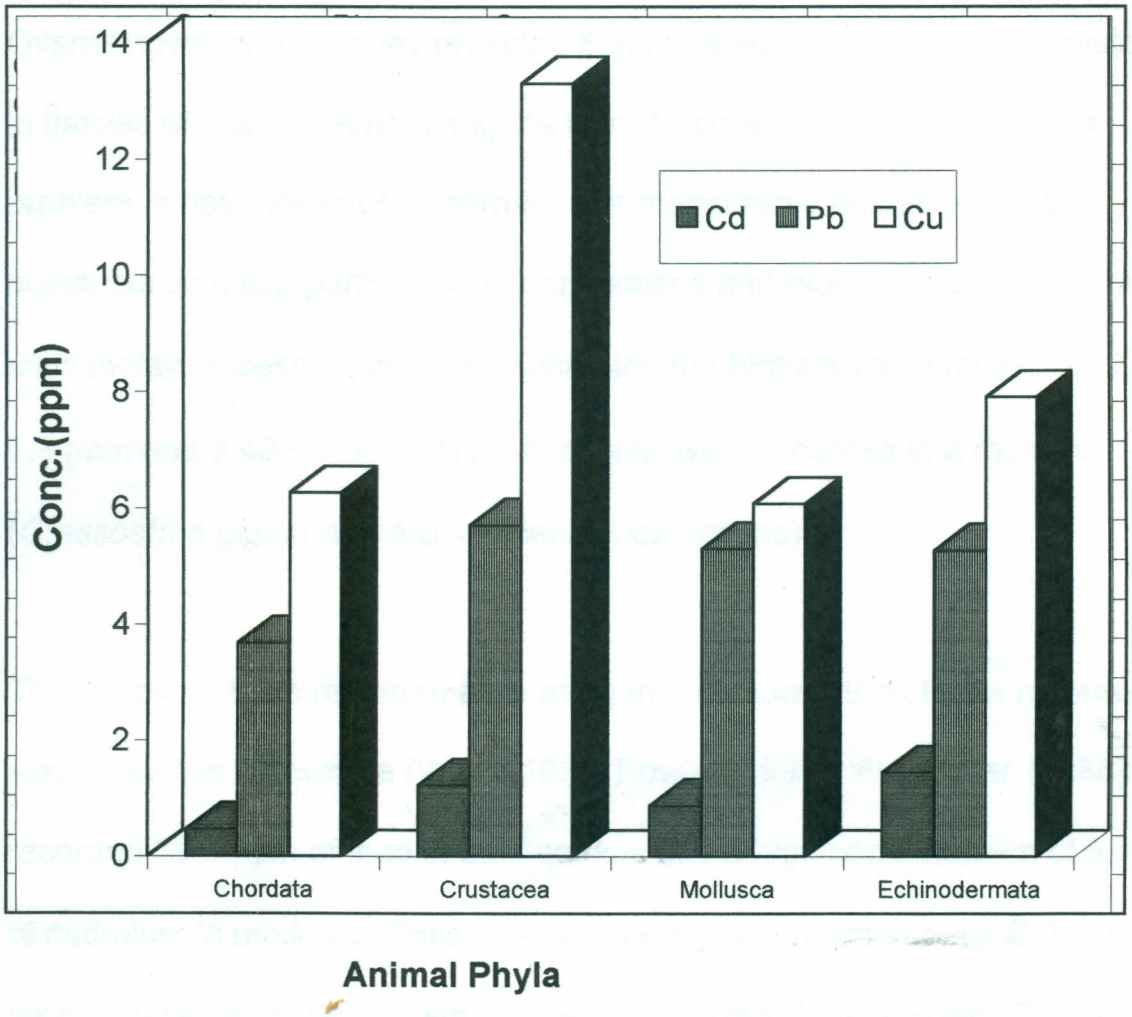
It is interesting to note that heavy metal pollution differ from phylum to phylum. In this study animals from four phyla were assessed. Table VI summarizes the concentration of Pb, Cd, Cu, Zn, Fe and Mn in the four phyla.

Table VII: A Summary of the concentration in ppm of Pb, Cd, Cu, Zn, Fe Mn, and Ti

	Concentration (ppm)						
Phylum	Pb	Cd	Cu	Zn	Fe	Mn	Ti
Chordata	3.68	0.47	6.26	73.2	159	22.8	LLD
Crustacea	5.7	1.23	13.3	42.4	74.7	295	1106
Mollusca	5.3	0.88	6.07	51.6	93.9	136	708
Echinodermata	5.27	1.45	7.91	44.6	135	58.3	58.4

Figure 6 is a graph showing the results of Lead Cadmium, and Copper from Table VI.

Fig. 6: Conc. of Heavy Metals Vs. Animal Phyla



The highest concentration of Pb (5.7ppm), and Cu (13.3 ppm) were recorded in the phylum crustacea, while that of Cd (1.45 ppm) was recorded in echinoderms. Its notable that chordates registered the lowest concentration of both Pb (3.68 ppm) and Cd (0.47 ppm). For the two most toxic metals in

this study, lead and cadmium, it may be deduced that among the four phyla, crustaceans (the crabs) had the highest amount of Pb (5.7 ppm) and Cd (1.23 ppm).

Overall however, this study revealed that the levels of heavy metal pollutants in tissues of marine fauna along the Kenyan coast is yet to be a serious problem. It has, however, confirmed that measurable amounts of the pollutants do exist, particularly in crustaceans and molluscs. Of the two most toxic metals assessed, lead and cadmium, the highest concentration of 27.4 ± 0.3 ppm and 3.49 ± 0.31 ppm respectively, were recorded in a mollusc (*Crassostrea gigas*) and a crustacean (*Uca vocans*).

The concentrations recorded here are generally lower than those recorded in similar studies elsewhere (Ward, 1996; Fowler, 1993). Ward *et al.* (1986) had recorded 29.4 ppm of lead in crustaceans and a high concentration of 5.1 ppm of cadmium in molluscs. These values are significantly higher ($p \leq 0.01$) than for the same marine organisms analyzed from the Kenyan coast. Fowler *et al.* (1993), did extensive work on heavy metal pollutants in oysters from the Gulf Region after the 1991 Gulf war and recorded the following concentration as quoted hereunder:

Table VIII: Selected Heavy Metals in Oysters from the Gulf Region (µg/g dry weight) (From Fowler *et al.*,1993)

Location.	**Sample**	Cd	Cu	Pb	Fe	Zn.
Saudi Arabia	Pearl oyster	0.66	16	0.43	266	1618
Bahrain	Pearl oyster	17.9	2.7	2.1	180	898
Oman	Rock oyster	15.3	20	0.13	179	157
Salalah	Rock oyster.	12.9	50	0.08	11	275

Again these concentrations are comparatively higher ($p \leq 0.01$) than what is reported in this study.

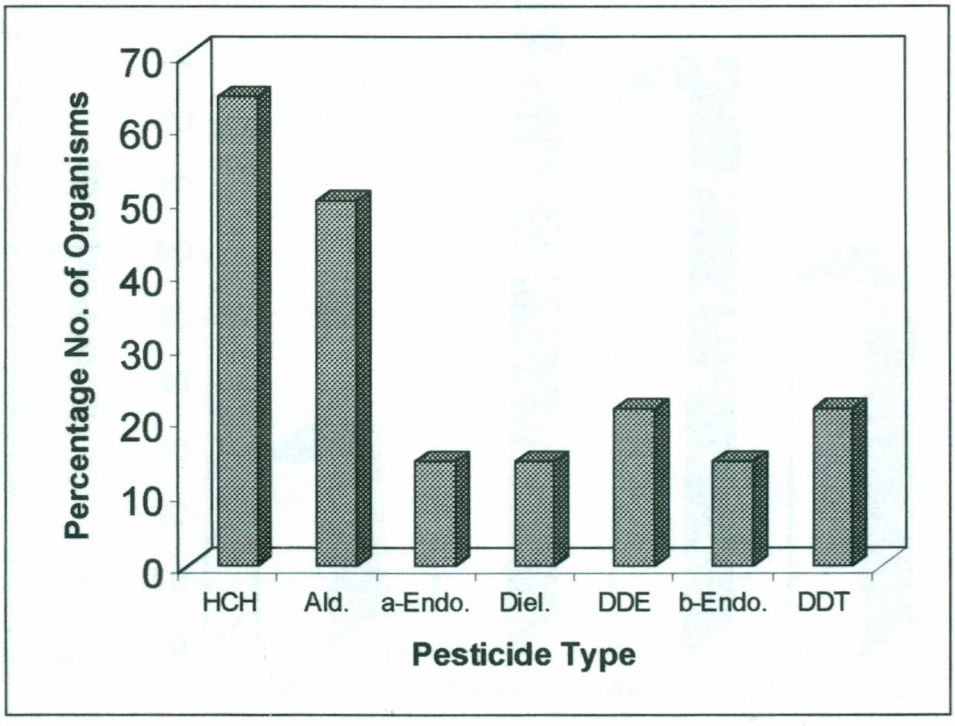
4.1.2. Pesticides

From the results tabulated in Table VI, it may be stated that pesticide pollution is, at the moment, generally low (<1 ppm) at the Kenyan Coast. Westgate *et al.* (1997) recorded a mean concentration of 3.1±1.4 ppm of p,p'-DDE in the blubber of harbour porpoises from the coast of Newfoundland. For the same pesticide (pp'-DDE), only 0.949±0.006 ppm was recorded in a sea cucumber in Mombasa. In the same study he reported a range of 0.86- 3.46 pmm of dieldrin while the highest concentration of dieldrin in the present study is only 0.458 ppm in an oyster found at the

KMC sampling site. Other studies on organochlorine pesticides by Berhoft *et al.* (1997) Tulonen and Vuorinen (1996), Weihe *et al.* (1996) and Skaare (1996) show the concentration of most organochlorine pesticides to be greater than 1 ppm.

However, these comparatively lower pesticide concentrations at the Kenyan Coast may increase to serious levels in future. Some marine organisms seem to have accumulated many pesticides. Figure 7 is a graph showing the percentage (%) number of organisms studied versus the pesticide detected. Lindane (HCH) and aldrin have been accumulated by the largest number of the organisms studied. It is possible that these two pesticides are more persistent than the others. DDT and its metabolite DDE, are the two other pesticides accumulated by well over 25% of the organisms studied.

Fig.7: Percentage Number of Organisms Vs. Pesticide Studied

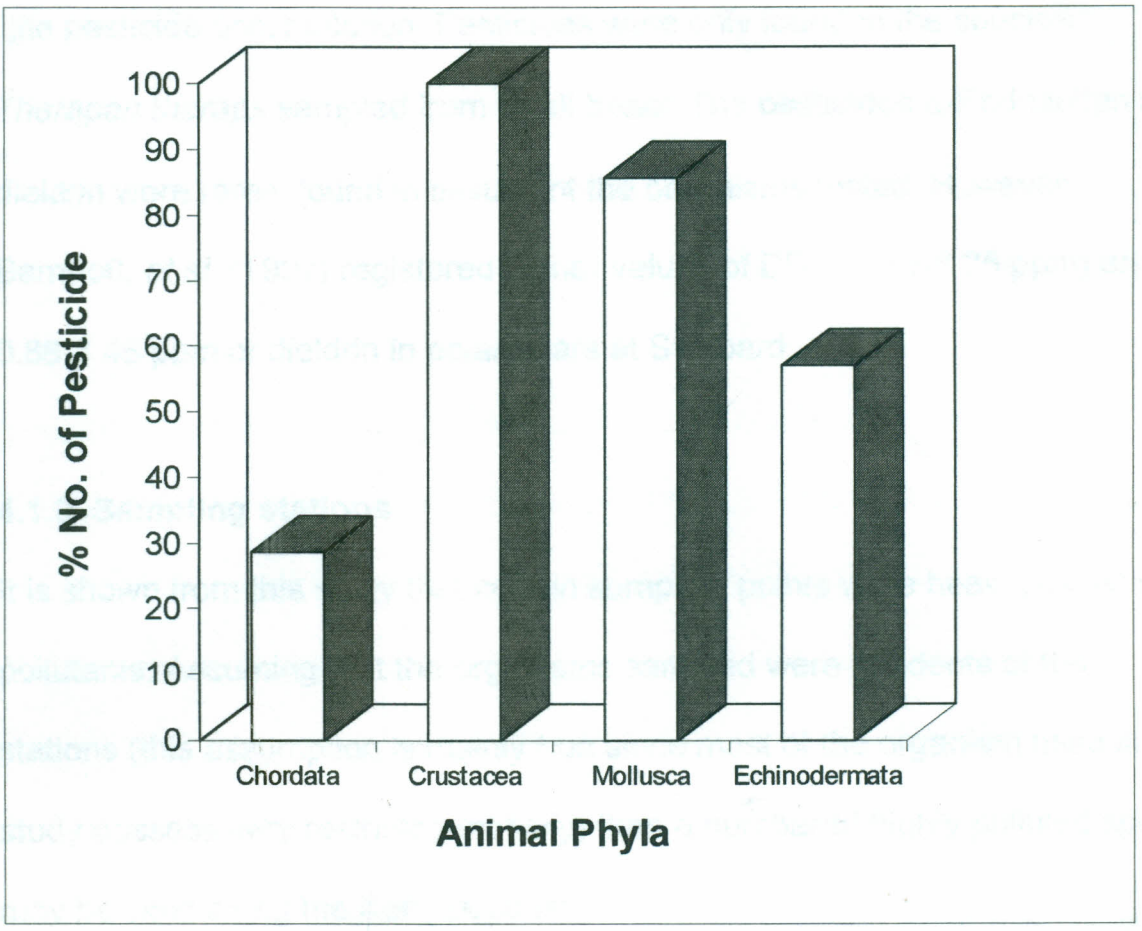


Key; **Ald.** ⇒ Aldrin, **a-Endo** ⇒ α-Endosulfan, **Diel.** ⇒ Dieldrin

b-Endo. ⇒ β-Endosulfan

Figure 8 similarly shows the number of pesticides detected in each of the four phyla studied. Crustaceans have yet again led the others in having accumulated all the seven pesticides analyzed in this study. Molluscs, the filter feeders have, expectedly been the second in having acquired about 86% of all the pesticides quantified.

Fig. 8: Percentage Number of Pesticides Vs. Animal Phyla



Crustaceans are marine scavengers, not only for heavy metal pollutants, but also for organochlorine pesticides. The molluscs are not far behind. Being filter feeders they have, true to type, also accumulated a good number of the pesticides studied.

Organochlorine pesticides levels at the Kenyan coast are generally low (< 1 ppm). It is noted that concentration of hexachlorocyclohexane (HCH) and aldrin were found to be accumulated by the largest number of the organisms studied. Like for heavy metals, crustaceans and molluscs had considerable

amounts of many of the pesticides studied. The phylum chordata recorded little pesticide accumulation. Pesticides were only found in the species *Therapan theraps* sampled from Nyali beach.The pesticides α-Endosulfan and dieldrin were rarely found in tissues of the organisms tested. However Bernhoft, *et al.* (1997) registered higher values of DDE (1.31-8.85 ppm) and 0.86-3.46 ppm of dieldrin in polar bears at Svalbard.

4.1.3 Sampling stations

It is shown from this study that certain sampling points were heavily-laden with pollutants. Assuming that the organisms sampled were residents of the stations (this assumption is mainly true since most of the organism used in the study possess very restricted mobility) then a number of highly polluted spots may be cited along the Kenyan coast.

Vanga: Most organisms found here had higher than average concentration of heavy metals, particularly lead and copper.

English Point: Was home for both pesticides and some heavy metals. This may be due to discharges into the ocean from the adjacent Mombasa show ground.

Nyali Beach: Was another polluted sampling station. The large number of Nyali Beach hotels around the station may probably be contributing a lot to the state of the environment around there. Mombasa residents allege that raw sewage is being let into the ocean waters from some hotels.

4.2 Conclusion

From the results of this study a number of conclusions have been made :

1. Marine organisms sampled along the coast of Mombasa Island were found to have accumulated heavy metals and organochlorine pesticides in their tissues. Of the two pollutants, heavy metals seem to have been concentrated by many of the organisms as compared to organochlorine pesticides. The levels are however low.

For heavy metals, Windom (1992) had commended thus "Heavy metals although perceived by public to be a major constraint of the marine environment pose little threat on a global scale". The results from this study tend not to support this statement.

Although concentrations of the order of 0.26 - 430 mg/g Pb; 0.06 - 11 mg/g Cd; 3.8 - 160 mg/g Cu; and 25 - 140 µg/g Zn; occurring in livers of marine

mammals are considered normal (Law et al; 1991), the same cannot be said of invertebrates.

2. It has emerged from this study that English Point, Vanga and Nyali Beach maybe resident for various pollutants, particularly heavy metals. It has also been noted that crustaceans and molluscs seem to tolerate higher pollution loads than the other phyla involved in this study.

RECOMMENDATIONS FOR FURTHER WORK

According to the above results and discussion the following are recommended for further research:

1. Heavy metals and pesticides have been found in measurable quantities in tissues of crabs and oysters, it is necessary to investigate the physiological effects that these sub-lethal levels may be eliciting in the organisms. For instance the effect of these pollutants on the physiological functioning of their body systems such as reproduction, digestion and so on. It would also be worthwhile to assess the effect of these pollutants on the fragile marine ecosystem.

2. Vanga, English Point, Nyali Beach and to some extent Port Reitz appear to be more polluted than the rest of the sampling stations. There is need to carry out an in-depth study of these locations to find out the possible sources of pollutants.

3. This study was not able to identify the sources of the heavy metals and pesticides studied. There is need to carry out a research project aimed at identifying these sources. This should enable the stake holders in matters environmental to take appropriate measures at controlling the pollutants.

REFERENCES

Adewunmi, C.O., Becker, W., Keuhnast, O., Oluwole, F. and Dorfle, G., (1996). Accumulation of copper, lead and cadmium in freshwater snails in southern Nigeria. *The Science of the Total Environment* **193** p.69-73. Elsevier Science.

Adriana, B., Sergio, H., Rodolfo, N. and Barbara, P. (1996). Mineralogy and Geochemistry of Terra Rossa soils, Western Scicily: Insight into heavy metal fractionation and mobility. *The Science of Total Environment*, **193**, p. 57-67. Elsevier Science.

Bernhoft, A. Wiig, Q. and Skaare J. U. (1997). Organochlorines in Polar Bears (*Ursus maritimus*) at Svalbard. *Environmental Pollution,* Vol. **95** p. 159-175.

Bremle Gudrun and Per Larsson (1998). PCB Concentration in Fish in a River System after Remediation of Contaminated Sediment. *Environmental Science and Technology* **32**, p.3491-3495. Lund Sweden.

Connell, D.W. and Miller, G.J.(1984). Chemistry and Ecotoxicolgy of Pollution. Wiley Interscience Inc. p.237-288.

Fowler, S.W., Readman, J.W., Oregioni, B., Villenenve, J. - P, and Mc Kay, K., (1993). Petroleum Hydrocarbons and Trace Metals in Nearshore Gulf Sediments and Biota before and after the 1991 War. *Marine Pollution Bulletin*. Volume **27** p. 171 -182

GESAMP(IMO/FAO/UNESCO/WHO/IAEA/UN/UNEP) {1985}. Joint Group of Experts on the scientific Aspects of Marine Pollution): Aluminium lead and tin in the marine environment. UNEP Regional Seas, *Reports and Studies* No. 56. UNEP, 1985.

GESAMP(IMO/FAO/UNESCO/WHO/IAEA/UN/UNEP) (1988). Joint Group of Experts on the Scientific Aspects of Marine Pollution): arsenic, mercury, and selenium in the marine environment. UNEP Regional Seas, *Reports and Studies* No. 92. UNEP, 1988.

Godden, R.G. (1996). An Introduction to the Principle and Application of Atomic Absorption Spectroscopy. CTA 2000 ChemTech Analytical. Cambridge, March 1996, p. 1-20.

Goodhart, S.R. and Shils, E.M. (1974). Modern Nutrition in Health and Disease. Henry Kimpton Publishers, London. p. 362-399.

Haines, T.A.(1983). Chlorine residue in brook trout from remote lakes in northern United States. *Water Soil Pollution*. **31** p. 605-629.

International Atomic Energy Agency (IAEA-TECDOC, 1996). Operation guide on sampling and sample preparation procedures of XRF analysis of environmental samples.p.45-46.

Ip, H.M.H. and Philips, D.J.H. (1989). Organochlorine chemicals in human milk in Hong Kong. *Environmental Contamination Toxicology.* **18** p.490-494.

Khan, S.U. (1980). Pesticides in the Soil Environment. Elsevier Science, Amsterdam. p.184-206.

Kinyua, A.M. (1982). Multi-element analysis of liquids and solids samples by x-Ray Fluorescence (XRF). M.Sc. Thesis, University of Nairobi, Kenya.

Kinyua, A.M. (1997). Traditional Medicines in Anticonvulsant Therapy: Implication of Trace Elements in Heath and Disease. PhD Thesis, University of Nairobi.

Kinyua, A.M., Gatebe, C.K., Mangala, M.J., Maina, D.M., Korir,A.K., Odhiambo G.O., Kwach R., Bartilol S., Njau L.N. and Mukolwe E.A. (1999). Enviromental and Industrial Applications of XRFand related techniques at the Institute of Nuclear Science, University of Nairobi, Kenya. International Atomic Energy Agency (IAEA-TECDOC-1121). p.51-66.

Kump, P. (1993). Quantitative analysis of Environmental Samples (QAES), Ljubljana, Slovenia.

Landis, G.W. and Ming - Ho Yu. (1995). Introduction to Environmental Toxicology. CRC Press Inc. p.285-296

Larsson, L.A. (1985). Fish physiology and metal pollution: results, experience from laboratories and field studies. *Ecotoxicology and Environmental Safety*. **9** p.250-281.

Law, R.J., Fileman, C.F., Hopkins, A.D., Baker, J.R., Harwood, J., Jacson, D.B., Kennedy, S., Martin, A.R. and Moris, R.J. (1991). Concentrations of trace metals in the livers of marine mammals (Sea

porpoises and dolphins) from waters around the British Isles. *Marine Pollution Bulletin.* **22** p.183-191.

Lucky, T.D. and Venugopal, B. (1977). Physiology and Chemical Basis for Metal Toxicity. Plenum Publishing Corporation New York. p. 28-39

Maina, P. (1998). East African Standard Newspapers, July 29th. 1998 p. A-D Dangerous Chemicals (News Supplement)

Manahan, S.E. (1992). Toxicological Chemistry. 2nd. Edition. Lewis Publishers Inc. Chelsea, Michigan, p. 249-257.

Mason, C.F. (1991). Biology of Freshwater pollution. British Library Cataloguing, Publication, 2nd Edition, p.168-186.

Mendieta, J., Diazcruz, MS., Monjonell, A., Tauler, R., and Esteban, M. (1999). Complexation of cadmium by the C-terminal hexapeptide Lys-Cys-Thr-Cys-Cys-Ala from mouse metallothionein: study by differential pulse polarography and circular dichroism spectroscopy with multivariate curve resolution analysis. *Analytica Chimica Acta 1-3,* p.390.

Muigai, P.G., Kinyua A.M. and Kamau G.N. (1996). Optimization of the Parameters for effective analysis of metals in Biological samples. *Internationa Journal of Biochemiphysics* vol. **5** (1-2), p.19-23.

Munga, D., Yobe,A.C. and Mwanguni, S.M. (1994). Assessment of Land-based Sources of Pollution along the Kenyan Coast, p. 1-140. Kenya Marine and Fisheries Research Institute (KEMFI),Mombasa (Internal Report).

Nriagu, J.O. (1978). Lead in soils sediments and major rock types. The biochemistry of lead in the environment. Elsevier Scientific Publishing Co. Ltd., New York, p.15-72.

Nriagu, J.O. (1979). Copper in the environment. Part 1. Health effects. John Wiley and Sons, New York, p.2-13.

Nriagu, J.O. (1988). A silent epidemic of environmental metal poisoning. *Evironmental Pollution* Elsevier Science, New York, **50** p.139-161.

Olsson, M. (1986). PCBs in the Baltic Sea Environment. PCBs and the environment. Press Boca. Raton. vol.3, p.181-208.

Pradyot, P. (1992). A Comprehensive Guide to the Hazardous Properties of Chemical substances. Van Nostrand Reinhold Publishers, New York, p.499-508.

Rom, W.N. (1976). Effects of lead on the female reproduction. A review. *Mt. Sinai Journal of Medicine*; *43* : p.542-552.

Schmidt-Nielsen, K. (1990). Animal Physiology. Cambridge University Press p. 154-158.

Sharma, P.D. (1990). Ecology and Environment. Rastogi Publications. Shivaji Road, Meerut, India, p.305-359

Skaare Janneche Utne, (1996). Environmental pollutants in marine mammals from the Norwegian coast and Arctic. *The Science of the Total Environment* **186,** p. 25-27. Elsevier Science.

Tayel, T. Fathy (1995). Trace metal concentration in the muscle tissue of ten fish species from Abu-Qir Bay, Egypt. *International Journal of Environmental Health Research* **5,** p. 321-328.

Tulonen, J. and Vuorinen, P. J. (1996). Concentration of PCBs and other organochlorine Compounds in eels (*Anguilla anguilla*, L.) of the Vanajavensi Watercourse in Southern Finland, 1990-1993. *The Science of the Total Environment* **187,** p. 11-18.

UNEP/IOC/IAEA (1982). Determination of DDTs and PCBs in selected marine organisms by Gas-Liquid Chromatography. Reference Methods for Marine Pollution Studies No. 14. UNEP, 1982.

UNEP/FAO/ IAEA/IOC (1984). Determination of total zinc,lead and copper in selected marine organisms by Flameless Atomic Absortion Spectrophotometry. *Reference methods for marine pollution studies* No. 11. UNEP, 1984.

UNEP/IOC/IAEA (1988). Determination of DDTs and PCBs by Capillary Gas Chromatography/Electron capture detection. Reference Methods for Marine Pollution Studies No.40. UNEP, 1988.

Vernberg, F.J. and Vernberg B.W. (1974). Pollution and Physiology of Marine Organisms. Academic Press Inc., p.1-223.

Vetter, W., Luckas, B., Heidemann, G. and Skirnisson, K., (1996). Organochlorine residues in marine mammals from the Northen hemisphere - A consideration of the composition of Organochlorine residues in the blubber of marine mammals. *The Science of the Total Environment* **186** (1996) p. 29-39. 27.

Wagemann, R., Innes, S. and Richard, P,R. (1996). Overview and regional and temporal differences of heavy metals in Arctic whales and ringed seals in the Canadian Arctic. *The Science of the Total Environment* **186** (1996) p. 41-66.

Ward, T.J., Correl, B.L. and Anderson, R.B. (!986). Distribution of cadmium, lead, and zinc amongst the marine sediments, sea grasses, and fauna, and the selection of the sentinel accumulators, near a lead smelter in South Australia. *Australian Journal of Marine and Freshwater Research* **5,** p.567-585.

Weihe, P., Grandjean, P., Debes, F., White, R. (1996). Health implications for Faroe Islanders of heavy metals and PCBs from pilot whales. *The Science of the Total Environment* **186** p.141-114.

Wenzel, C., Adelung, D. and Theede, H. (1996). Distribution ofage-related changes of trace elements in kittiwake, *Rossa tridactyla* nestlings from an isolated colony in the German Bight, North Sea. *The Science of the Total Environment* **193** (1996), p.13-26. Elsevier Science.

Westgate, A.S., Muir, D.C.G., Gaskin, D.E. and Kingsley. M.C.S. (1997). Concentrations and accumulation patterns of Organochlorine Contaminants in the Blubber of the Harbour Porpoise, *Phocoena phocoena* from the Coast of New-foundland, the Gulf of St. Lawrence and the Bay of Fundy/Gulf of Maine. *Environmental Pollution,* Vol. **95** No. 1 p. 105-119

Windom, H.L. (1992). Contamination of the marine environment from land-based sources. Marine Pollution Bulletin **25** 1-4, p.32-36.

World Wildlife Fund (1999). Persistent Organic Polluntants: Hand-Me-Down Poisons that threaten wildlife and people. P. 1-19.

APPENDICES

APPENDIX I

Abstract of Research Proposal presented at the 5th. Annual Postgraduate Scientific Conference held at Kenyatta University on 7th. August, 1997.

THE MAGNITUDE OF VARIOUS POLLUTANTS IN TISSUES OF MARINE ORGANISMS ALONG THE COAST OF MOMBASA ISLAND - KENYA

By
Bor samuel Kipkosgei M.Sc. Project.

Coastal and estuarine areas have a tendency of being both heavily populated and highly industrialized. As a result, the majority of the coastal zones of many countries are to some significant extent polluted with a wide variety of toxicants. Man-induced environmental changes are now part and parcel of what has otherwise been a normal environment. While biologists have long known that the resistance adaptations of organisms are a function of many environmental stimuli, it is only recently that much attention has been directed towards the physiological effects of pollutants on marine organisms.

Amongst the most dangerous pollutants being discharged into the coastal areas are heavy metals, raw sewage, organochlorine pesticides and polychlorinated biphenyls (PCBs). Environmental pollution by heavy metals became widely known with the Minamata disaster in Japan, but we ought to be asking ourselves how polluted are the marine organisms in our own coastal waters.

This protocol portends to examine the concentration of pollutants in tissues of a number of marine organisms, especially those that are of economic importance to man.

Heavy metals will be analyzed by Atomic Absorption Spectroscopy (AAS), while organochlorine pesticides will be by Gas-Liquid Chromatography (GLC).

APPENDIX II

Abstract of the Presentation of Research Result held on 7th. May, 1998 at Jomo Kenyatta University of Agriculture and Technology

HEAVY METAL POLLUTION IN TISSUES OF MARINE FAUNA ALONG THE COAST OF MOMBASA ISLAND-KENYA

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ABSTRACT

Coastal and estuarine areas tend to be both highly industrialized and heavily populated. As a result the majority of the coastal zones of many countries are to some significant extent polluted with a wide variety of toxicants. Among the most dangerous pollutants discharged into the coastal areas are heavy metals, raw sewage and organochlorine compounds.

In the present study, heavy metals were analyzed by Atomic Absorption Spectroscopy (AAS) and X-ray Fluorescence (XRF) methods.

A range of heavy metals was analyzed with a strong bias for lead, cadmium and copper. Preliminary results indicate that marine fauna along the coast of Mombasa Island may be contaminated with heavy metals.

APPENDIX III

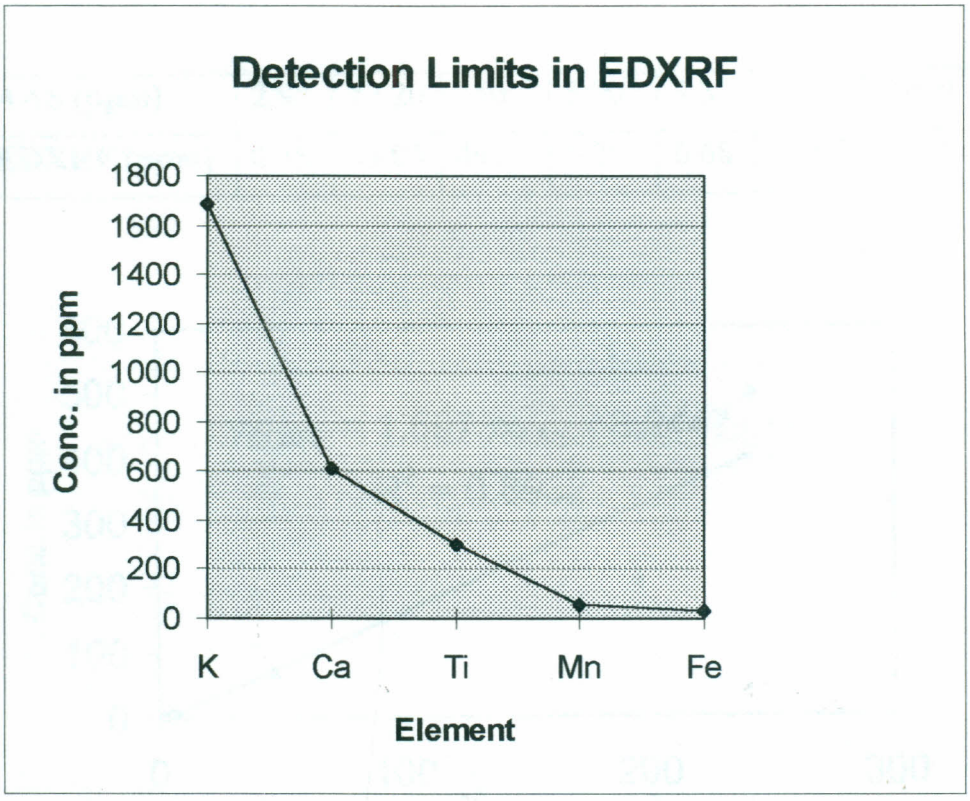
Results of analysis of Certified Reference Material, MA-M-2/TM IAEA, by EDXRF (ppm)

Element	Experimental Values	Certified Values	% Error
Zn	150.1±18.1	156.5	-4.1
Fe	264.3±23.8	256.2	+3.2
Cu	8.61±0.64	7.96	+8.2
Mn	62.6±5.8	67.1	+6.7

Results of analysis of Certified Reference Material, MA-M-2/TM IAEA, by AAS (ppm)

Element	Experimental Values	Certified values	% Error
Zn	148.2±14.5	156.5	-5.3
Fe	273.1±30.5	256.2	+6.6
Cu	8.55±5.2	7.96	+7.4
Mn	59.8±5.4	67.1	-10.1

APPENDIX IV


Detection Limits in EDXRF
Conc. in ppm
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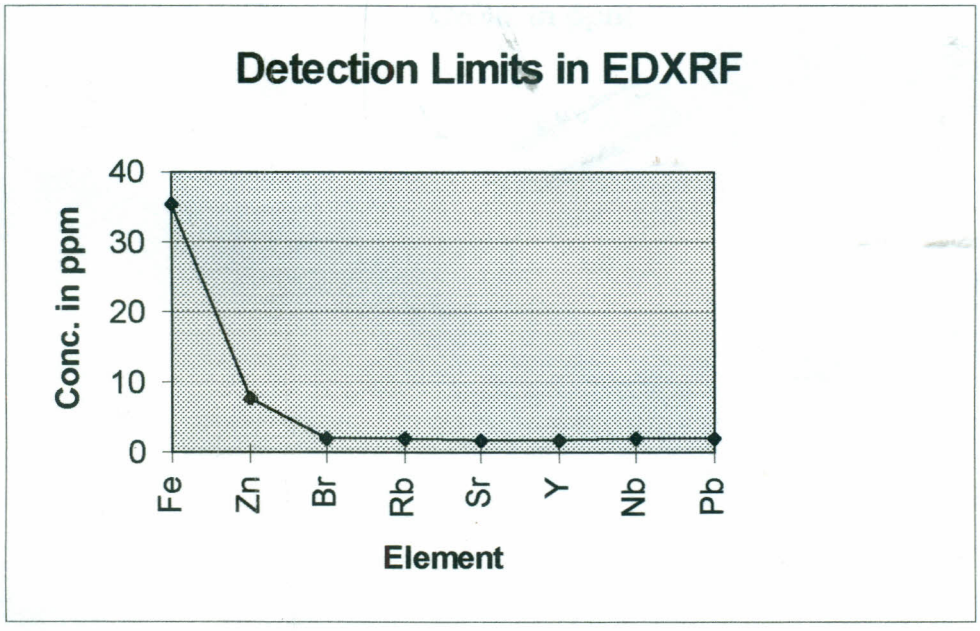
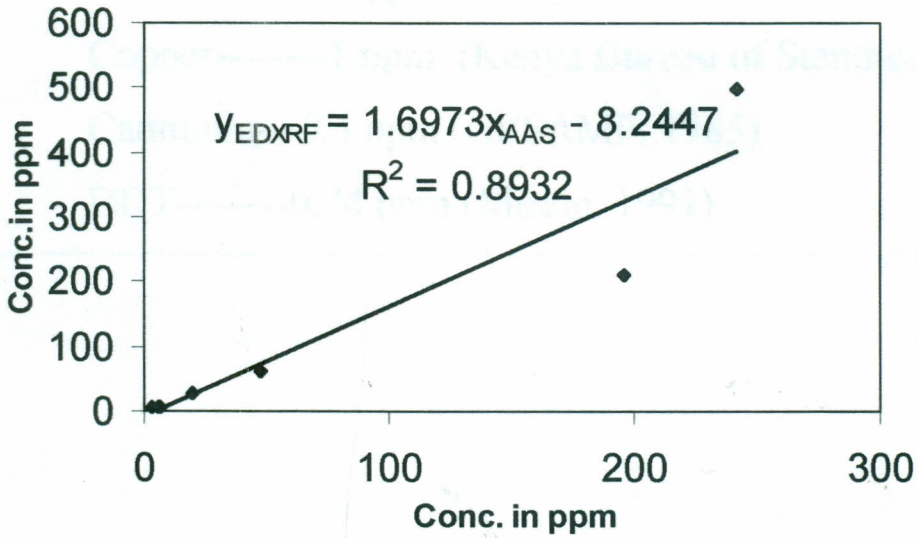
1600
1400
1200
1000
800
600
400
200
0
K
Ca
Ti
Mn
Fe
Element


Detection Limits in EDXRF
Conc. in ppm
40
30
20
10
0
Fe
Zn
Br
Rb
Sr
Y
Nb
Pb
Element

APPENDIX V

Correlation analysis for AAS and EDXRF values.

AAS (ppm)	2.95	47.20	240	5.90	3.33	19.31	196.0	6.66
EDXRF (ppm)	6.38	63.05	497	6.29	6.68	27.65	209.5	6.26



APPENDIX VI

Safety guidelines for some heavy metal and organochlorine pesticides in fish and fish products

Lead---------0.1 ppm (Kenya Bureau of Standards)
Copper--------1 ppm (Kenya Bureau of Standards)
Cadmium---0.4 ppm (GESAMP, 1985)
DDT--------0.74 ppm (Mason, 1991)

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