OCCURRENCE OF HEAVY METALS IN SEDIMENTS, FISH AND OYSTERS FROM MTWAPA, PORT REITZ, MAKUPA AND SHIRAZI CREEKS ALONG THE KENYAN COAST

By

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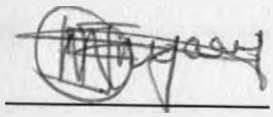
DECLARATION

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

Muohi A Wairimu

This thesis has been submitted with our approval as the university supervisors



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DEDICATION

To My Family

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LIST OF ABBREVIATIONS

AAS = Atomic Absorption Spectroscopy.

Ag = Silver.

Al = Aluminium.

Al_2O_3 = Aluminium oxide.

AMF = Anthropogenic Mobilisation Factors.

As = Arsenic.

ATSDR = Agency for Toxic Substances and Disease Registry.

Br = Bromine.

Cs = Caesium.

Cd = Cadmium.

$Cd(NO_3)_2.4H_2O$ = Cadmium nitrate.

CdS = Cadmium sulphide.

Co = Cobalt.

Cr = Chromium.

CRC = Chemical Rubber Company.

Cu = Copper

$CuSO_4.5\ H_2O$ = Copper sulphate.

DNA = Deoxyribonucleic acid.

EDTA = Ethylenediaminetetraacetic.

ED-XRF = Energy dispersive x=ray fluorescence.

FDA = Food and Drug Administration.

Fe = Iron

FSC = Food Standards Committee.

HCl = Hydrochloric acid.

Hg = Mercury

HNO_3 = Nitric acid.

H_2O_2 = Hydrogen peroxide.

H_2SO_4 = Sulphuric acid.

HWS = High Water Spring.

IAEA = International Atomic Energy Agency.

ICES = International Council for the Exploration of the Sea.

IMCO = Inter-Governmental Maritime Consultative Organisation.

K = Potassium.

KMFRI = Kenya Marine and Fisheries Research Institute.

Li = Lithium.

LWS = Low Water Spring.

MAFF = Ministry of Agriculture Fisheries and Food.

MCM = Municipal council of Mombasa.

Mn = Manganese.

Mo = Molybdenum.

Na = Sodium.

NAS = National Academy of Science.

Nb = Niobium.

NEM = NorthEast Monsoons.

NHMRC = National Health Medical Research Council.

Ni = Nickel.

NTA = Nitrilotriacetic acid.

OECD = Organisation for Economic Co-operation and Development.

OSPAR = Oslo and Paris Commission.

Per Comm: = Personal Communication.

Pb = Lead

$Pb(NO_3)_2$ = Lead nitrate.

PVC = Polyvinylcarbon.

Ra = Radium

Rb = Rubidium.

RECOSCIX=WIO = Regional Co-operation in Scientific Information Exchange in the Western Indian Ocean

Se = Selenium

SEM = SouthEast Monsoons.

SPM = Suspended Particulate Matter.

Sr = Strontium.

Ti = Titanium.

TiO_2 = Titanium oxide.

TPHR = Tasmania Public Health Regulation.

Turkey-HSD test = Turkey Honest Significant Difference test.

U. K. = United Kingdom.

U. S. A. = United States of America.

VLIR-IUC-UON = Vlaamse Inter-universitare Raad (Flemish Inter-University Council)-University of Nairobi.

V = Vanadium.

WHO = World Health Organisation.

WPM = Working Party of the Monitoring of Foodstuffs for Heavy Metals.

WTW = Wissenschaftlich-Technische-Werkstätten.

Y = Yttrium.

Zn = Zinc.

ZnS = Sphalerite (Zinc sulphide).

Zr = Zirconium.

ABSTRACT

Prior to the present study, the Reitz-Kilindini Creek complex situated on the westerly and southwesterly boundaries of Mombasa Island (4.05^0S, 39.65^0E), was presumed to be contaminated with both inorganic and organic anthropogenic inputs from industrial and domestic effluents. Mtwapa Creek located about 20 km north of Mombasa town, was presumed contaminated mainly with organic inputs while Shirazi Creek situated 70 km south of Mombasa, was presumed to be relatively unpolluted.

A comparative survey of the occurrence of heavy metals in the selected creeks was carried out to assess a possible anthropogenic activity influence in those ecosystems with respect to the trace element levels. Sediments, fish and oyster samples from various stations within the three sites were collected and analysed between the months of January and July 2001. A total of 106 sediment samples were digested using hydrochloric acid and hydrogen peroxide. Fish muscle from 158 individuals of 13 fish species were digested using nitric and sulphuric acids plus hydrogen peroxide. 81 groups, each of 1-12 oysters (*Saccostrea cucullata*) were digested in the same manner as fish muscle. Copper, zinc, lead and cadmium elemental concentrations in the digests were assessed by atomic absorption spectrophotometry (AAS). The method of analysis was validated using SOIL-7, MA-M-2 (Mussel tissue) and MA-A-2 (Fish homogenate) International Atomic Energy Agency (IAEA) certified reference materials. These and a few experimental samples were also analysed using Energy dispersive X-ray fluorescence (ED-XRF) spectrometry. The data collected was analysed using Statistica and Excel software.

The results showed that in Mtwapa Creek sediments, Cu concentrations (μg g^{-1}, dry wt) ranged from 6.5 to 80.6, (Mean±Standard deviation = 37.5±15.9), Zn, 17.2 to 185.4, (71.8±31.5), Pb, 29.5 to 94.6 (58.1±17.2) and Cd, 0.6 to 83.4, (6.7±18.0). In Port Reitz Creek sediments concentrations were Cu, 11.3 to 45.1 (21.6±7.1), Zn, 30.7 to 92.9 (57.1±17.9), Pb, 15.7 to 71.2, (26.2±11.6) and Cd, 0.55 to 3.24, (1.4±0.7). In Makupa Creek sediments concentrations were, Cu, 50.9 to 228.9, (101.7±46.0), Zn, 275.9 to 3193.2, (1017.2±840.4), Pb, 54.6 to 164.5, (103.4±35.8) and Cd, 31.0 to 81.9, (51.0 ± 14.3). In Shirazi Creek sediments concentrations were, Cu, 2.2 to 19.9, (7.1±4.0), Zn, 9.1 to 26.2, (17.1±4.4), Pb, 8.5 to 45.9, (19.4±11.9) and Cd, 0.3 to 4.7, (1.3±1.2). In fish (7 spp) collected from Mwapa Creek, Cu concentrations (μg g^{-1}, wet wt) ranged from 0.14 to 0.95, (0.44±0.27) Zn, 2.7 to 8.5, (5.7±2.3) Pb, 0.025 to 1.9. (1.03±0.63) and Cd, 0.05 to 0.33, (0.16±0.10). In fish (5 spp) from Port Reitz creek, concentrations were Cu, 0.14 to 0.60, (0.33±0.17), Zn, 4.12 to 6.70, (5.67±1.32), Pb, ≤0.005 to 1.65, (0.56±0.67) and Cd, 0.04 to 0.30, (0.15±0.11). In fish (1 spp) from Makupa Creek, concentrations were, Cu, (Mean = 0.341), Zn, (11.4), Pb, (0.443) and Cd, (0.614). In fish (9 spp) from Shirazi Creek, concentrations were, Cu, 0.12 to 0.45, (0.25±0.13), Zn, 2.7 to 4.6, (3.4±0.57), Pb, 1.2 to1.7, (1.45±0.17) and Cd, 0.003 to 0.29, (0.097±0.093). In oysters collected from Mtwapa Creek, Cu concentrations (μg g^{-1}, wet wt) ranged from 9.3 to 44.7, (21.0±9.2), Zn, 166.1 to 393.2, (247.5±63.7), Pb, ≤0.005 to 3.9, (1.4±1.1) and Cd, ≤0.02 to 5.6 (1.9±1.6). In oysters from Port Reitz Creek, concentrations were, Cu, 15.2 to 35.4, (20.3±6.1), Zn, 171.5 to 736.5, (315.3±207.1). Pb, 0.54 to 3.1, (1.8±0.9) and Cd ≤0.002 to 0.9, (0.54±0.28). In oysters from Makupa creek, concentrations were, Cu, 310.6 to

1090.7, (744.3±192.5), Zn, 635.7 to 1538.7, (1146.5±262.5), Pb, 12.2 to 97.6, (45.8±23.3) and Cd, 6.1 to 19.6, (14.8±3.3). In oysters from Shirazi Creek, concentrations were, Cu, 3.3 to 17.7, (9.5±4.3), Zn, 46.8 to 404.8, (196.8±90.8), Pb, ≤0.005 to3.8, (1.01±1.07) and Cd, 0.01 to 4.2, (1.07±1.04)

Analysis of variance tests revealed that, in general, there was significant variation in the elemental concentrations in sediments between and within sites. In fish there was significant variation in elemental concentration between sites, species and individuals. Similarly, in oysters there was significant variation in elemental concentration between and within sites and between groups. All p-values with respect to these variations were < 0.05. Notably higher elemental concentrations which, in some cases exceeded the World Health Organisation limit guidelines were observed in sediment and oyster samples from Makupa creek. On average, elemental concentrations observed in each fish species did not exceed the World Health Organisation (WHO) limits. From the present study results, in order of most to least influenced, the creeks under investigation may be graded as follows, Makupa>Mtwapa>Port Reitz>Shirazi. However, further research into actual sources and fates of the elements investigated among others is warranted.

1.0. INTRODUCTION

Heavy metals may be regarded as those having an atomic number of 22 to 92. Thus, they include many of the transition metals as well as metals and metalloids in groups, IIB, IVB, VB and VIB in the Periodic Table (Sterrit and Lester 1980). In terms of specific gravity or density, Burell (1974) classifies them as those with specific gravity of over 4.5 (Titanium (Ti)). The Encyclopaedia of Chemical Science (Van Nostrand, 1964) uses a specific gravity of 4.0, whereas Lapedes (1974) in the Dictionary of Scientific and Technical Terms uses 5.0. This excludes Ti and Selenium (Se) (4.8). Nieboer and Richardson (1980) disagree with the above because the parameters include lanthanides and actinides, as well as Yttrium (Y) and Radium (Ra), whose chemistry generally excludes them from the category. Heavy metal classification encompasses a heterogeneous array of elements with diverse chemical and biological properties. Consequently, a classification based on the relationship between atomic properties and the solution chemistry of metal ions was proposed (Nieboer and Richardson, 1980). This separates the heavy metals into three categories as, (1) oxygen seeking, (2), nitrogen or sulphur seeking and (3), intermediate. This is of value in interpreting the biochemical basis for metal ion toxicity.

The problem of heavy metal environmental pollution is generally associated with industrial, agricultural and other economic activities. The abiotic and biotic components of water, land and air are media used for the cycling of waste heavy metal pollutants. These components act as both sinks and sources of trace elements. Their non-biodegradable nature distinguishes them from other toxic pollutants and often the physical or chemical form of a particular metal is a more important criterion than total

concentration in assessing toxicity. In addition once in the environment their potential toxicity is controlled largely by biological and geochemical factors (Sterrit and Lester, 1980). Thus, the presence of one or more, toxic or nontoxic metals will influence toxicity, suppressively, additively or synergistically.

However, metals have certain properties, which render them amenable to treatment and/or removal from waste waters. Metals can be removed with cation exchangers. Generally, the metals form highly insoluble sulphides and can be precipitated from solution. Due to their propensity towards the formation of complexes, metals can be chelated by chelating agents such as Ethylenediaminetetraacetic acid (EDTA) and the sodium salt of Nitrilotriacetic acid (NTA). These agents appear to render the heavy metals less toxic (Sprague, 1968). In nature, the organic substances found in waters of high humic acid content appear to perform to some extent the same function. Even organic substances in sewage may render heavy metals less toxic than they would be in pure, uncontaminated water (Lewis *et al.*, 1972).

Though most heavy metals are generally micronutrients, distinction needs to be made between those often actually required in substantial amounts by organisms (e.g. Cu, Fe, Mo, Mn and Zn) and for which the organism has a wide range of tolerance, (with a deficiency threshold as well as a toxicity threshold) and those required only in small amounts (e.g. Se and Br), as well as those not required at all (e.g. Pb and Hg), for which the organism has a narrow tolerance range.

One of the major problems that metals pose with respect to their effects on aquatic organisms, is their long biological half-life. That is, due to their ability to form complexes with organic substances, there is a tendency for them to get fixed in the tissue and not to

be excreted. The capability of most organisms to concentrate certain metals required in life processes may be enhanced by certain feeding and metabolic processes. This can lead to enormously high concentration factors. The invertebrates appear to have a particularly high capability for concentrating metals, along with other foreign materials found in their environment, when they filter plankton during feeding.

Metals may affect organisms directly, for instance by attacking nervous tissues where enzymatic blocking of critical biochemical reactions occurs. More frequently, heavy metals act indirectly through the destruction of detoxifying and excreting organs, such as liver and kidneys. Therefore metals not only biomagnify or bioaccumulate through the trophic levels of a food web but also accumulate differentially in tissues and this differentiation varies between species.

The contamination of seafood by heavy metals represents a potential hazard to consumers and the ecosystem. Marine organisms have been shown to accumulate most heavy metals to concentrations several times those present in seawater. Vinogradov (1953) compiled some of the earliest studies of the bioaccumulation of trace elements in the sea, where many marine organisms were noted to be capable of highly concentrating the metals present in seawater. In commercial fishing terms, metals have had a devastating economic impact, particularly on the freshwater fisheries in Canada and the United States, arising out of the uncovered mercury contamination episode of the 1970-71 period. When the Food and Drug Directorate of Canada and the United States Food and Drug Administration placed a maximum acceptable level for mercury in food at 0.5 ppm, a large part of the freshwater fisheries catch had to be confiscated. Later, there was also great concern about mercury in marine fishes, tuna and swordfish bearing the brunt

of this ban, although mercury in dogfish and Pacific halibut did not go unnoticed (Environment Canada, 1973).

A comprehensive account of trace elements in biotic and abiotic compartments of aquatic ecosystems along the Kenyan Coast is lacking. This study was therefore initiated to survey concentration levels of some metals in marine tidal Creek biota (biological compartment) as well as in the environmental compartments particularly bottom substrates in the selected creeks. An attempt was also made to compare these measurements in presumed polluted and unpolluted Creeks.

1.1 Justification

There are a limited number of studies reported on the status of heavy metal levels in environmental and biological compartments in aquatic ecosystems along the Kenyan Coast. For instance, studies on heavy metal levels in sediments from the Kenyan Coast include those by Oteko (1987); Nyatebe (1990); Nguta (1993); Everaarts and Neuwenhuize 1995; and Williams et al 1996. There is only one study reported on heavy metals in fish probably from the Kenyan Coast and that is the study by Wandiga and Onyari (1987) who assessed heavy metal levels in fish bought from Mombasa markets. No studies have been reported on heavy metals in oysters from the Kenyan Coast except for one pertinent study by O'omolo (1987) who measured cadmium, copper and mercury toxicity in *Crassostrea cucullata.*

Results thus obtained from the present study will provide a useful database on the status of heavy metal levels in the evaluated environmental and biological compartments of the investigated creeks. The database will also be useful for instance in identification of priority areas in Environmental Impact Assessment plans where necessary.

1.2 Hypothesis

The creeks under investigation are contaminated with potential heavy metal pollutants at varying degrees due to the differential influence of anthropogenic activities in and around those creeks.

1.3 Objectives

1. To collect and preserve (where necessary) sediment, fish and oyster samples from various stations (where applicable) within the creeks.
2. To prepare and digest replicate subsamples and analyse them for selected heavy metals particularly copper, zinc, lead and cadmium.
3. To statistically compare the elemental levels within and between creeks and compartments.
4. To compare observed elemental concentrations with stipulated quality criteria guidelines and recommend appropriate prospective and/or retrospective conservation measures where necessary.

1.4 Regional Setting

The Indian Ocean coast of Kenya is centred on latitude 4.05°S and longitude 39.65°E. (See Figure 1).

Mombasa district has a coastline of about 32 Km and covers an area of approximately 275 km^2, composed of the Island (13 km^2), mainland areas (197 km^2) and the Tudor, Kilindini/Port Reitz (Figure 2) and Makupa (Figure 2 and 3) Creeks (65 km^2). A causeway bridge (Makupa causeway) connects the island to the west mainland, and in effect prevents mixing of the Makupa Creek with Tudor Creek waters.

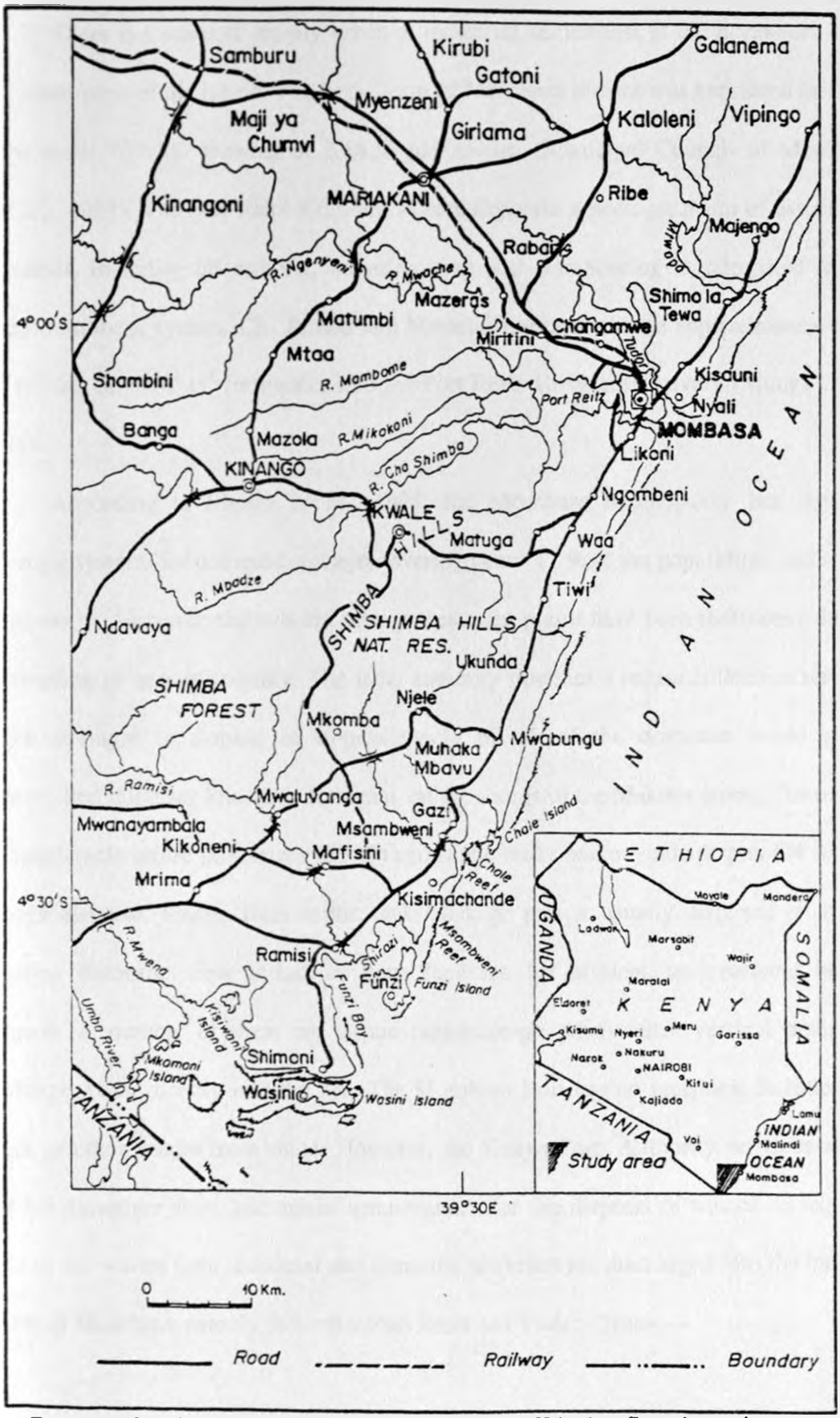


Figure 1. Map showing the location of Mtwapa, Reitz-Kilindini Complex and Shirazi Creeks in relation to Mombasa Island. (Source: Survey of Kenya 1989)

There is a series of mainly urban or industrial settlements to the north-east, west and south-west of the Island. The population of Mombasa district was estimated in 1989 to be about 467,000 growing at 3.14 % per annum (Municipal Council of Mombasa (MCM), 1991). The Port Reitz-Kilindini system supports a wide spectrum of associated industries, including oil refining, manufacturing and warehousing as compared to the Tudor-Mombasa system. Cha Simba and Mwache rivers discharge approximately 40 x 10^6 m^3 and 50 x 10^6 m^3 freshwater into the Port Reitz Creek respectively (Munga *et al.*, 1993).

According to Munga *et al.*, 1993, the Mombasa municipality has separate sewerage systems for domestic sewage, covering about 17 % of the population, and storm water runoff. However, the two old sewage treatment plants have been ineffective due to overloading or unserviceability. The local authority operates a refuse collection service, which manages to dispose of approximately 60 % of the domestic waste at an uncontrolled dumpsite known as Kibarani, on the shores of the Makupa creek. The rest of the inhabitants utilise pit-latrines (59 %) and septic tanks and/or soakage pits (24 %) for sewage disposal. Sludge from septic tanks/soakage pits is usually disposed of at the Kibarani dumpsite. Few industries have facilities for effluent pre-treatment before disposal. A number of them use septic tank/soakage pit systems, vertical drains or discharge waste directly into the sea. The Mombasa Port has no reception facilities for bilges or other wastes from ships. However, the Kenya Ports Authority provides waste bins for passenger ships and makes arrangements for the disposal of wastes on request. Most of the wastes from industrial and domestic activities are discharged into the inshore waters of Mombasa, namely, Kilindini/Port Reitz and Tudor Creeks.

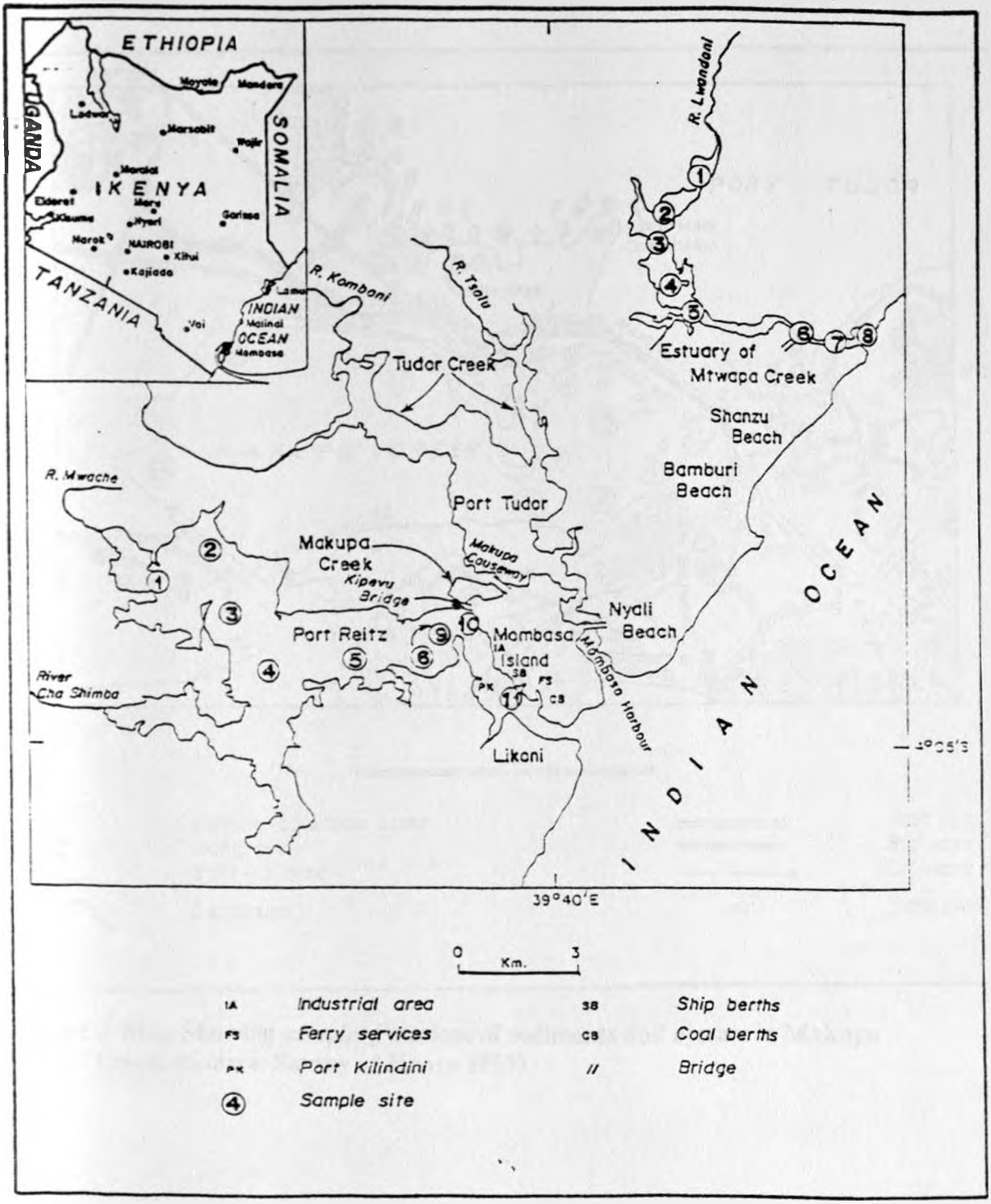


Figure 2. Map showing sampling stations of sediments and oysters in Port Reitz and Mtwapa Creeks, and the location of Makupa Creek in relation to the Reitz-Kilindini Complex Creek System. (Source: Williams *et al.*, 1995)

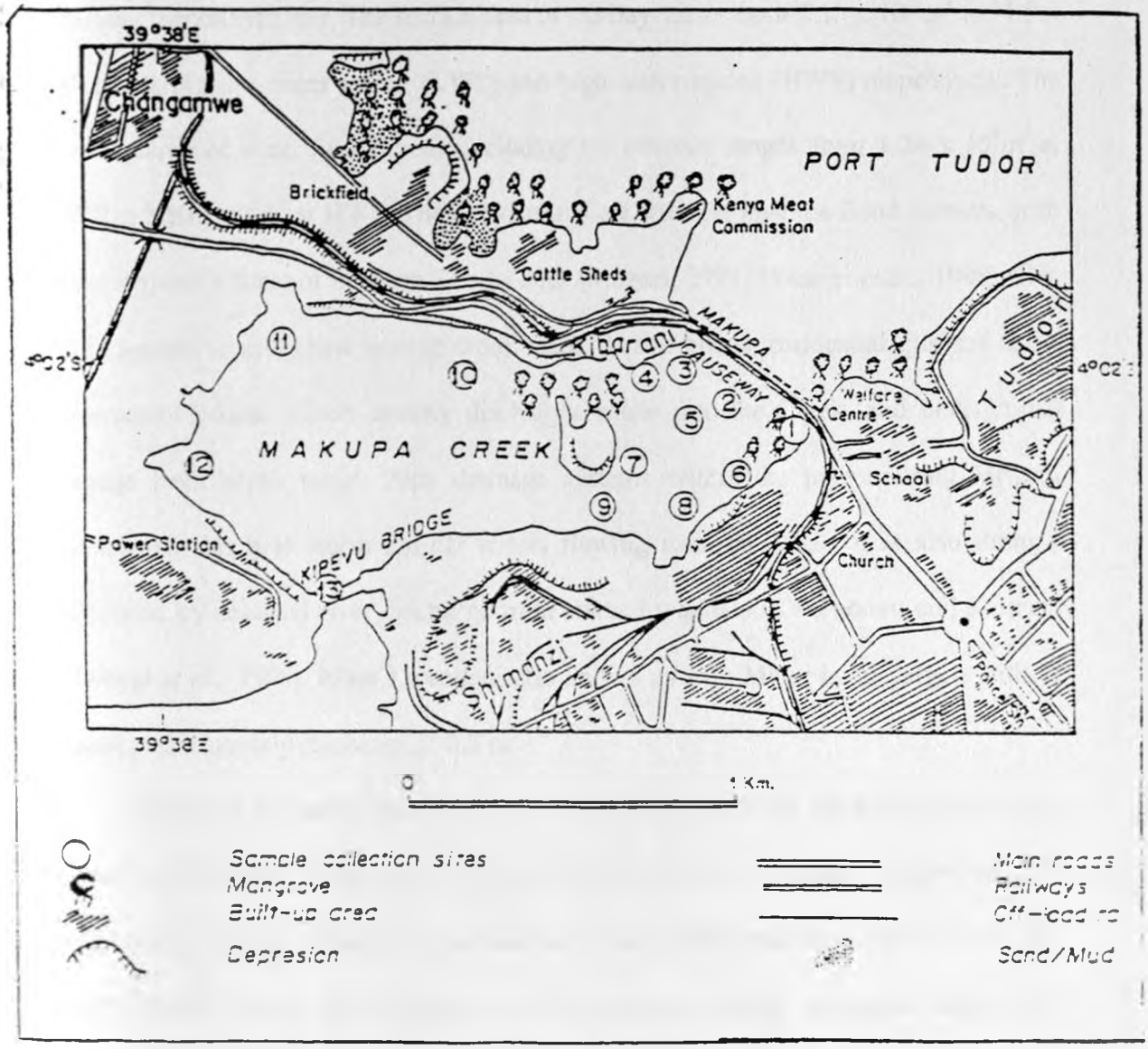


Figure 3. Map Showing sampling stations of sediments and oysters in Makupa Creek. (Source: Survey of Kenya 1959)

Mtwapa Creek is located about 20 km north of Mombasa town (Figure 1 and 2). According to Magori (1997), Mtwapa Creek is connected to the ocean through a long narrow channel. There are reef linings at the entrance. Inward from the channel is a shallow, lagoon type bay. The surface area of the bay varies from 2.15 x 10^6 m^2 to 11.8 x 10^6 m^2 during low water spring (LWS) and high water spring (HWS) respectively. The total volume of water in the creek including the channel ranges from 1.24 x $10^7 m^2$ at LWS to 3.80 x $10^7 m^2$ at HWS. The ebb currents are stronger than the flood currents, with water residence times of between 3 to 14 days (Magori, 1997; Mwangi *et al.*, 1998). This creek system receives raw sewage from nearby beach hotels, residential quarters and a government prison, which directly discharges waste into the Creek, and underground seepage from septic tanks. Poor drainage systems within the neighbouring Mtwapa municipality leads to storm run-off waters flowing into the Creek. It is also strongly influenced by seasonal river discharge from rivers Lwandani, Kwa ndovu and Kidutani (Mwangi *et al.*, 1998). River Lwandani also known as Mto Mkuu is the largest with an annual mean monthly discharge of 0.3 $m^3 s^{-1}$

Funzi bay is situated about 70 km south of Mombasa along the Kenyan coast (See Figure 1). Funzi bay connects to Shirazi Creek and Ramisi estuary (Figure 4). The neighbouring Shirazi village has a population of about 800 inhabitants (Per Comm: Sub Chief Shirazi village, 2001). Main activities include fishing, mangrove cutting and cultivation of crops on the former grounds of the sugar factory. Funzi bay and its associated Creeks are relatively unpolluted. Although tourism activities and urbanisation is slowly on the increase, there are not many human settlements around this area.

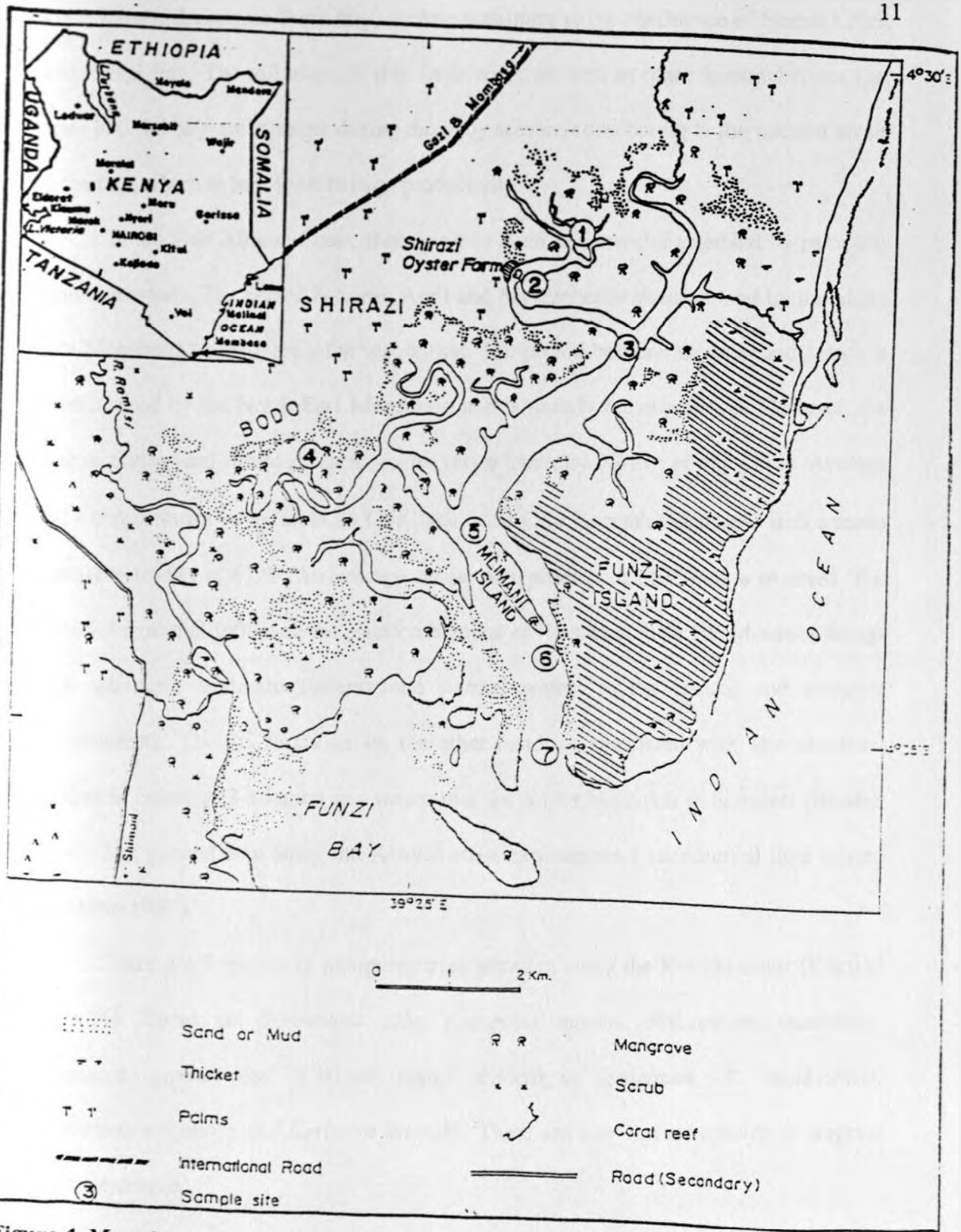


Figure 4. Map showing sampling stations of sediments and oysters in Shirazi Creek. (Source: Anyango *et al.*, 2000)

River Ramisi drains into Funzi bay, at close proximity to the confluence of Shirazi Creek with Funzi bay. The influence of this fresh water as well as other seasonal rivers that drain into the bay, are stronger during the rainy season, contributing to the nutrient levels in the bay, which in turn leads to high productivity.

In the East African Coast, there are two main seasons characterised by particular monsoon winds. The period between April and September is characterised by the South East Monsoons and is mainly the wet season. The period between October and March is characterised by the North East Monsoons, and is mainly the dry season. However, the precise timing and extent of each season varies annually (Grove *et al.*, 1985). Average daily temperatures range from 23 °C in June to 31 °C in December-January, with a mean relative humidity of 67 %. An average annual precipitation of 1100 mm is received. The periods of rainfall influence the physicochemical environment. The NE Monsoon brings high salinities, minimum currents and warmer waters to the coastal and estuarine environments. The SE Monsoon on the other hand, is associated with low salinities, maximum currents (3-4 knots) and waters that are colder but richer in nutrients (Brusher 1974). The general area along the Kenyan coast experiences a semidiurnal tidal pattern (Okemwa 1989).

There are 9 species of mangrove trees growing along the Kenyan coast (Kairo *et al* 2001). These are *Sonneratia alba, Avicennia marina, Rhizophora mucronata, Bruguiera gymnorrhiza, Ceriops tagal, Xylocarpus granatum, X. mollucensis, Lumnitzera racemosa and Heritiera littoralis*. There are also various species of seagrass and macroalgae.

2.0. LITERATURE REVIEW

2.1. Sources, Uses and Effects of Heavy Metals (Cu, Zn, Pb and Cd)

Trace metals are ubiquitous by-products of industrialisation and urbanisation. Although used by humans since pre-historic times, the large quantities of these elements presently mobilised by modern civilisation, has resulted in increased concentration in many natural environments. This has exposed the biota to toxic levels of these pollutants leading to reduction in biodiversity and in the quality of many natural renewable resources. Consequently, significant effects on human health have been reported in many regions of the world (Lacerda and Vannucci, 1998).

Table 1 summarises the most recent estimates of the quantities of selected trace metals mobilised annually by industrial process and natural weathering and their respective anthropogenic mobilisation factors defined as the ratio between these two variables.

Table 1. Global mobilisation of selected trace metals due to industrial processes and natural weathering and respective anthropogenic mobilisation factors (AMF) (Thousands of tons per year).

Metal	Hg	Cd	As	Cr	Cu	Pb	Mn	Zn
Industrial mobilisation	11	24	105	1010	1048	565	1894	1427
Natural weathering	1	5	90	810	375	180	4800	540
AMF's	11	4.8	1.2	1.2	2.8	3.1	0.4	2.6

Based on Bowen (1979); Salomons and Forstner (1984) and Nriagu (1990).

The importance of metals in the marine environment emerged from studies of radionuclides resulting from fallout in the oceans during the 50's and 60's (National Academy of Science (NAS), 1971a). These workers observed that certain nuclides, for

example cobalt-60 accumulated in organisms in large concentrations, particularly in the kidney of the giant clam *Tridacna* sp. They further found that the non-radioactive metals behave in much the same way as the radioactive group in their uptake in organisms. It was suspected that the stable metals were accumulating in marine organisms to high concentrations than in seawater. This was the case, for the high concentrations of zinc and copper found in oysters dwelling in waters receiving effluents containing these metals. In view of these findings, the high concentrations of heavy metals in shellfish are now used to trace movements of metal-containing pollutants (Environment Canada, 1973), and to generally identify the presence of heavy metal pollution (Huggett *et al.*, 1973).

2.1.1. Copper

Copper is a trace element essential for the health of plants and animals including humans. The natural sources of copper exposure include windblown dust, volcanoes, decaying vegetation, forest fires and sea spray. Available statistics (WHO 1998) show that, average background concentrations of copper in air in rural areas range from 5 to 50 ng m^{-3}. Copper levels in seawater of 0.15 µg L^{-1} and in fresh water of 1–20 µg L^{-1} are found in uncontaminated areas. Sediment is an important sink and reservoir for copper. Background levels of copper in natural freshwater sediments range from 16 to 5000 mg kg^{-1} (dry weight). Copper levels in marine sediments range from 2 to 740 mg kg^{-1} (dry weight). In anoxic sediments, copper is bound strongly by sulphide and therefore not bioavailable. Median copper concentrations in uncontaminated soil are about 30 mg kg^{-1} (range 2–250 mg kg^{-1}) (WHO 1998).

Copper ores are mined, smelted and refined to produce many industrial and commercial products. Copper is widely used in cooking utensils and water distribution systems, as well as fertilizers, bactericides, fungicides, algaecides and antifouling paints. It is also used in animal feed additives and growth promoters, as well as for disease control in livestock and poultry. Copper is used in industry as an activator in froth flotation of sulphide ores, production of wood preservatives, electroplating, azo-dye manufacture, as a mordant for textile dyes, in petroleum refining and the manufacture of copper compounds.

Copper is an essential element and therefore adverse health effects are related to deficiency as well as excess. The adult body contains between 1.4 and 2.1 mg of copper per kilogram of body weight. To maintain this concentration, it is recommended that the daily intake of copper should be 0.4 mg day^{-1} for children aged 1-3 years and 1.2 mg day^{-1} for adults (Benjamin, 1978). Copper deficiency is associated with anaemia, neutropenia and bone abnormalities but clinically evident deficiency is relatively infrequent in humans. Balanced dietary intake data may be used to anticipate clinical effects, whereas serum copper and ceruloplasmin levels are useful measures of moderate to severe deficiency but less sensitive measures of marginal deficiency (Benjamin, 1978). Wilson's disease (hepatolenticular degeneration), a hereditary metabolic disorder in humans is manifested by accumulation of potentially toxic concentrations of copper, characterised by increased liver copper concentrations, leading to Cirrhosis, neurological symptoms due to elevated brain levels, renal tubular damage in kidneys and in the cornea it leads to a characteristic "Kayser-Fleischer ring"(brown or green) (Goyer and Mehlan, 1977).

Plants, invertebrates and fish among others accumulate copper. For instance, its bioaccumulation in oysters and other invertebrates has been known for a long time. Copper tends to give the oysters not only a green colour, but also a rather unpleasant metallic taste. The concentration of copper in seafood has never been considered a serious threat to human health because the colour and flavour imparted to such items as oysters usually deter consumers before the concentration of copper is high enough to cause harm. However, the marketing of such seafood is seriously affected. In regulations for controlling noxious substances other than oil transported by ships developed in the new convention on prevention of pollution from ships (Inter-Governmental Maritime Consultative Organisation (IMCO), 1973), close control must be maintained over those substances which bioaccumulate and produce a taint or discoloration in aquatic organisms.

2.1.2. Zinc

Zinc is one of the most common elements in the earth's crust. It is found in the air, soil, and water and is present in all foods. The average natural level of zinc in the earth's crust is 70 mg kg^{-1} (dry weight), ranging between 10 and 300 mg kg^{-1} (Malle 1992).
At some locations, zinc has been concentrated to much higher levels by natural geological and geochemical processes. Such concentrations, found at the earth's surface and underground, are being exploited as ore bodies. The most commonly found zinc mineral is sphalerite (ZnS). Zinc metal is produced both from ores and from recycled zinc products. Thirty percent of the world zinc supply today comes from recycled zinc. In other words, 2 millions tonnes of zinc are recycled every year (European Zinc Institute, 1990). Due to natural erosion processes like the weathering and abrasion of rock, soils

and sediments by wind and water, a small but significant fraction of natural zinc is continuously being mobilised and transported in the environment. Volcanic eruptions, forest fires and aerosol formation above seas also contributes to the natural transport of zinc. These processes cause cycling of zinc in the environment, resulting in natural background levels in the air, surface waters and soil.

Zinc provides the most cost-effective and environmentally efficient method of protecting steel from corrosion. Besides, it has many other uses for instance in making brass and other alloys, automotive equipment and household appliances, fittings, tools, pharmaceuticals, medical equipment and cosmetics, tyres and all rubber goods, fertilisers and animal feed.

According to Benjamin (1978), zinc plays a vital role in human metabolism. For example, zinc is required for the proper functioning of more than 200 enzymes, for the stabilisation of DNA and the expression of genes, and for the transfer of nervous signals. Zinc is fairly non-toxic, especially in amounts of less than 100-150 mg of elemental zinc daily. The recommended dietary allowance for zinc in adults is 15 mg with additional amounts needed during pregnancy and lactation (up to 25 mg) (Benjamin 1978). Clinical symptoms of zinc deficiency include anorexia, pica, impaired taste acuity and menstrual lethargy. Chronic deficiency in paediatric and adolescent age groups causes growth retardation and delayed sexual maturation (Casey and Hambridge, 1980). "Metal fever" exhibited by pulmonary manifestations, fever, chills and gastro-enteritis has been reported among industrial workers exposed to fumes containing zinc (Murphy, 1970). Acute zinc toxicity has been observed in a renal failure patient, following hemodialysis, characterised by nausea, vomiting, fever and severe anaemia (Galley *et al* 1972).

However, though zinc is one of the essential elements for bacteria, plant, mammals and fish (Bowen, 1966), elevated levels in the aquatic system has been shown to be toxic. Waldichuk in Vernberg and Vernberg (1974) observed zinc in oysters at concentrations as high as 17,000 ppm (dry weight) in some zinc contaminated waters of the Malaspian strait, British Columbia. So far, that had apparently not produced overt symptoms of poisoning in normal consumers of oysters. The high concentration of zinc-65 in oysters exposed to radionuclides released from nuclear reactors (Seymour and Lewis, 1964) indicated that molluscs accumulated this neutron-induced radionuclide. More studies of uptake by the mussel, *Mytilus edulis*, of ^{65}Zn, ^{54}Mn, ^{58}Co and ^{59}Fe showed that the principal accumulation of these metal radionuclides occurs through the food and that the transfer directly from the water is relatively minor (Pentreath, 1973a). A further study on the accumulation and retention of ^{65}Zn and ^{54}Mn by the plaice *Pleuronectes platessa*, led to the same conclusion (Pentreath, 1973b). However, the uptake of metals may differ between species because of the differences in the feeding behaviour. For instance gastropods and molluscs in general may accumulate metals from solution, suspended particles, sediments or from their diet of seaweeds and phytoplankton (Bryan *et al.*, 1983).

2.1.3. Lead

Present when the earth was formed, lead is a naturally occurring element. It is usually associated with other minerals, notably zinc, silver and copper. Trace amounts of other elements, including gold, are sometimes found with lead ore. The most common lead ore is galena, or lead sulphide. Lead contribution from natural sources amounts to about 25000 ty^{-1} (Nriagu, 1978).

Since lead is easily re-melted and refined, it has the highest recycling rate of all industrial metals in the world. Thus, secondary or recycled lead is now, and has been for years, significantly used in the lead market. For instance, it is used in dozens of important consumer, industrial and defence applications, including batteries for automobiles, industrial lift trucks and other equipment, X-ray and radiation shielding, waterproofing materials, noise and vibration barriers, optics, electronics and computers, sports equipment and many more. Lead has been used as a protective barrier against radon exposure in homes and lead batteries will play an important role in the development and use of electric vehicles.

Pollution of the environment occurs through the smelting and refining of lead, the burning of petroleum fuels containing lead additives and, to a lesser extent, the smelting of other metals and the burning of coal and oil. Metallic lead derived from shotgun cartridges or used as fishing weights is lost in the environment and remains available to organisms. On the other hand, because of the low solubility of most of its salts, lead tends to precipitate out of complex solutions, and besides, lead in the environment is strongly adsorbed onto sediment and soil particles reducing its availability to organisms. However, fish one of the most sensitive aquatic species has been documented, to show symptoms of exposure to 100 ug L^{-1} of lead over long periods, while reproduction of Crustacea such as *Daphnia magna.* stops at around 30 ug L^{-1} lead concentration.

Lead poisoning arises from excessive exposure of lead in the human body. After the body is exposed to lead through inhalation, dermal absorption, or ingestion, it enters the bloodstream and attaches to proteins that carry it to different tissues and organs. Since the human body cannot utilise this lead, even small amounts can lead to serious problems.

Lead doses eventually accumulate increasing the possibility of health risks. When in the body, it replaces iron, calcium, and other minerals in the blood, which are extremely important during the critical stages of growth and development. Since young children require more minerals to grow and develop, they are thus more vulnerable to lead poisoning. Some symptoms may have serious effects on specific body systems. For instance, acute lead encephalopathy is the swelling of the brain, which increases pressure within the skull and severely limits proper functioning (Agency for Toxic Substances and Disease Registry (ATSDR), 1992). The early symptoms of lead posoning include changes in red blood cells (reticulocytosis and erythrocytic basophilia). Other reported clinical manifestations of lead poisoning include "psychoorganic syndrome", emotional and sleep disturbances, psychosensory disorders and distorted perception (visual, auditory and tactile hallucinations (Kirikebji and Piven, 1971).

2.1.4. Cadmium

Cadmium is a natural element in the earth's crust. It is usually found as a mineral combined with other elements such as oxygen (cadmium oxide), chlorine (cadmium chloride), or sulphur (cadmium sulphate, cadmium sulphide). All soils and rocks, including coal and mineral fertilizers, contain some cadmium. However, even though the average cadmium concentration in the earth's crust is generally placed between 0.1 and 0.5 ppm, much higher levels, from 0.1 to 25 ppm may accumulate in sedimentary rocks, and marine phosphates and phosphorites have been reported to contain levels as high as 500 ppm (Cook and Morrow 1995, WHO 1992). Igneous and metamorphic rocks tend to show lower values, from 0.02 to 0.2 ppm. Naturally, zinc, lead and copper ores, which are mainly sulphides and oxides, contain even higher levels, 200 to 14,000 ppm for zinc

ores and around 500 ppm for typical lead and copper ores. The raw materials for iron and steel production contain approximately 0.1 to 5.0 ppm, while those for cement production contain about 2 ppm. Fossil fuels contain 0.5 to 1.5 ppm cadmium, but phosphate fertilisers contain from 10 to 200 ppm cadmium (Cook and Morrow 1995).

Weathering and erosion of parent rocks result in the transport by rivers of large quantities, recently estimated at 15,000 tonnes per annum, of cadmium to the world's oceans (WHO 1992, Organisation for Economic Co-operation and Development (OECD), 1994). Volcanic activity is also a major natural source of cadmium release to the atmosphere, and estimates on the amount have been placed as high as 820 tonnes per year (WHO 1992, OECD 1994, Nriagu 1980, Nriagu 1989). Forest fires have also been reported as a natural source of cadmium air emissions, with estimates from 1 to 70 tonnes emitted to the atmosphere each year (Nriagu 1980). Cadmium also enters air from mining, industry, and burning coal and household wastes. Cadmium particles in air can travel long distances before falling to the ground or water.

The average cadmium content in the world's oceans has variously been reported as low as <5 ng L^{-1} (WHO 1992) and 5-20 ng L^{-1} (OECD 1994, Jensen and Bro-Rasmussen 1992) to as high as 110 ng L^{-1} (Chemical Rubber Company (CRC) 1996), 100 ng L^{-1} (Cook and Morrow 1995) and 10 to 100 ng L^{-1} (Elinder 1985). Higher levels have been noted around certain coastal areas (Elinder 1985) and variations of cadmium concentration with the ocean depth, presumably due to patterns of nutrient concentrations, have also been measured (WHO 1992, OECD 1994).

Just like zinc, cadmium is used to a small extent as coatings (often achieved by electroplating) to protect metals such as iron. Its use is however, restricted because of

environmental concerns. The metal is a component of some specialist alloys including solders and alloys with low coefficients of friction and good fatigue resistance. Cadmium is a component of nickel-cadmium (Ni-Cd) batteries. It is used in some control rods and shields within nuclear reactors. Cadmium is also used in black and white television phosphors and in blue and green phosphors for colour television tubes. Some semiconductors contain cadmium. The sulphide (CdS) is used as a yellow pigment. Some compounds are used as stabilisers for Polyvinylcarbon (PVC) (CRC 1996).

Waste disposal and spills or leaks at hazardous waste sites do contribute to entry of some cadmium into water and soil. Though it binds strongly to soil particles, some cadmium does dissolve in water. However, it doesn't break down in the environment, but can change forms. Fish, plants, and animals take up cadmium from the environment. Cadmium stays in the body a very long time and can easily bioaccumulate from many years of exposure to low levels.

It has been shown that cadmium has acute and long-term toxicity to mammals and that there is a positive correlation between cadmium poisoning and hypertension (Ramade, 1987). Cadmium toxicity in humans may aggravate atherosclerosis and heart disease and produce complications of stroke. Zinc therapy can reduce cadmium toxicity from cadmium in water or foods or from any other source of pollution. Chronic cadmium poisoning involves kidney damage and obstructive lung disease. Occupational exposure to cadmium has been reported as likely to increase the risk of prostate cancer and possibly lung cancer (Niosh 1976). An epidemic of cadmium poisoning (through prolonged consumption of rice grown in areas containing elevated levels of cadmium) was reported in Japan in 1955 and was described as "Itai-itai disease". Symptoms of this

disease include renal dysfunction, lumbar pains and leg myalgia, waddling gait and bone deformation leading to multiple fractures (Piotrowski and Coleman, 1980).

Cadmium in fish is usually of low biological value (Fergusson, 1990) and is usually located in low molecular weight in form of metalloprotein and metallothionein. Cadmium levels in fish are usually below instrumental detection limits with values rarely exceeding 0.2 $\mu g\ g^{-1}$ wet weight in muscle. The values are however higher in the liver and kidney (Furness and Rainbow, 1990). Preston (1973) summed up that concern about human intake of cadmium, is restricted to a few "hot spots" in coastal waters and that the main items that exhibit high concentrations of cadmium are molluscan shellfish and brown meat of crabs. However, the United Kingdom Working Party on the Monitoring of Foodstuffs in their Fourth Report concluded that the average human diet contains an insignificant amount of cadmium from these sources (United Kingdom., Working Party of the Monitoring of Foodstuffs for Heavy Metals (WPM), 1973). However, the situation has certainly since changed and there is need for continuous surveillance on foodstuffs.

2.2. Previous Research on Heavy Metal Occurrence in Marine Biotic and Abiotic Compartments

2.2.1. Biotic Compartments

Wandiga and Onyari (1987) observed that concentrations of trace elements in marine fish were slightly higher than fresh water fish. However, all those concentrations of Mn, Fe, Cu, Zn, Cd and Pb in $\mu g\ g^{-1}$ wet wt, obtained in fish muscle from Lake Victoria (0.12-0.74, 0.53-4.64, 0.15-0.53, 2.21-7.02, 0.04-0.12 and 0.39-1.08) and from Mombasa Markets (0.12-4.58, 3.42-28.9, 0.36-2.0, 4.67-40.8, 0.04-0.38, and 1.22-6.48) respectively, were below maximum recommended values. Therefore it was deduced that the levels posed no potential danger to the consumers.

In another study at the Kenyan Coast, Everaarts and Nieuwenhuize (1995) observed that in crustaceans, the concentration of Cu and particularly Cd was significantly above baseline levels, varying from 45 to 90 μg g^{-1} dry wt and 1.0 to 8.5 μg g^{-1} dry wt, respectively. Zinc (49-102 μg g^{-1} dry wt) was at about baseline levels or a little elevated. On the contrary, Pb showed very low concentrations, varying from 0.1 to 0.6 μg g^{-1} dry wt. Other macroinvertebrate species (including Spider-crabs-*Majidae*, Swimming crabs-*Portunidae*, Hermit crabs-*Paguridae*, brittle stars-*Ophiuroidea*, sea urchins-*Regularia* and cuttefish-*Sepia* sp.) in their study showed the same pattern. These workers concluded that the cadmium concentrations did exceed the maximum admissible level of 1.5 μg g^{-1} dry wt in crustaceans, according to the Dutch standards for acceptable intake based on WHO standards.

O'molo (1997) working on measurement of Cd, Cu and Hg toxicity of *Crassostrea cucullata* from the Kenyan coast, reported that cadmium compared to copper and mercury is more toxic to oysters even at low concentrations. Cadmium toxicity effects were evidenced after a short period of exposure, and Cd, Cu and Hg toxicity increased with exposure period. In that experiment, oysters were found to accumulate more copper in their tissues and survived for longer periods. In a previous similar experiment on the kinetics of copper bioaccumulation in *C. Cucullata*, D'silva and Qasim (1979) observed that, the initial uptake of copper was directly related to metal concentration in the medium. The net rate of uptake ranged from 1.76 to 1.97 g/week and the rate of copper loss, measured after transferring the oysters into natural seawater, was dependent on the original copper concentration in the soft parts. These workers also

observed that accumulation occurs in the oyster tissue more rapidly than cleansing can eliminate it.

Kulekana (1997) observed that, concentrations of Zn in *Crassostrea cucullata* were highest followed by Cr, Cu, Co, Pb and Cd, for those oysters collected from a Harbour on Zanzibar Island while in those oysters from Kisakasaka the order was Zn, Cr, Cu, Cd, Co and Pb. The high levels of heavy metal concentrations in oysters collected from the harbour was attributed to pollution from domestic sewage, storm water, small scale industries and garages, shipping as well as ship wrecks. Values obtained for Pb in *C. cucullata* in that study were compared with those obtained from *Mytilus edulis* and *Navajuelas chilenas* in Australia and Chile respectively and were found to be higher. Both organisms recorded values of <0.5 $\mu g\ g^{-1}$. De Wolf *et al.,* (2001) observed that, heavy metals (Cu, Mn, Sr and Zn) in the soft tissues of a mollusc *Littorina scabra* exhibited significant sampling-site difference. Of these elements Cu, Mn and Zn decreased from Msimbazi to Mbweni (Tanzania). Other elements revealed no clear geographical pattern (i.e., Ag, Cd, Cr and Fe), and/or were only detected in Msimbazi (i.e., As, Co, Ni and Pb) or revealed a trend of decreasing concentration towards the less polluted sites (i.e., Sr).

Biney and Beeko (1991) conducted a survey of metals in fish and sediments from the River Wiwi in Kumasi, Ghana and found a positive correlation between mercury concentration and body weight of fish. They also reported higher levels of Cd and Hg in fish than in sediment. Studies on the distribution of Hg, Cd, Pb, Cu, Zn and Fe in water, finfish and shellfish, macrophytes and sediments from Kpong head pond and lower Volta

river by Biney (1991) showed the highest concentrations of Fe and Pb in sediments and of Mn and Cd in macrophytes.

Joiris and Azokwu (1999) working on heavy metals in the bivalve *Anadara* (*Senilia*) *senilis* from Nigeria observed highly significant differences in metal concentrations between stations and years. These differences were, however, explained by differences in the size distribution of the samples: the smaller the cockle, the higher the metal concentration corresponding to a so-called "growth dilution" effect. Boyden (1974); Philips (1976) and Simpson (1979); have established that the trace metal content of most molluscs is related to their size. Williamson (1980) observed similar results with Cd, Pb and Zn in a population of snails and attributed this pattern and its variations to the metabolic activity of the animals. He suggested that the increase in metabolic rate in younger individuals may affect metal uptake and elimination differentially. The absence of actual geographical variation, after correction for size effects, was contrary to expectations for Pb in samples from Okrika, located towards the industrial city of Port Harcourt. However, in comparison with data collected elsewhere in Africa, similar results were obtained for Pb, Cd and Cu, but those of Zn were lower (Joiris and Azokwu 1999). These workers concluded that, taking into account some national guidelines for fisheries products, metal levels detected in Nigerian cockles were not considered a threat to human health, though individual values sometimes approached those limits.

Browne *et al.*, 2000 observed that cockles of the species *Anadara granosa* sampled from Tambak Lorok and Morodemak (Indonesia) had high levels of Cd, Ni, Pb and Zn relative to fish. Bivalve molluscs are efficient accumulators of heavy metals, and concentrations vary widely between locations and species (Rainbow, 1990). Cadmium

content was within the range reported for the green mussel from Jakarta Bay (Hutagalung, 1989). Cadmium concentration in cockles from the Semarang coast was significantly higher than in those from Morodemak. This may indicate greater bioavailability of Cd in Tambak Lorok. These workers also observed that, there was no evidence of increased concentrations of the heavy metals Cd, Ni, Pb or Zn in fish muscle tissue at the Tambak Lorok site versus the Morodemak site.

According to Fisher and Reinfelder (1995), only Cd, and Zn are known to biomagnify beyond the trophic level of zooplankton and would be expected to show inter-site differences due to environmental contamination. No significant inter-site differences in Cd, Ni or Pb concentrations within fish species were found in fish from Tambak Lorok and Mrodemak. Zinc did show significant inter-site variation within catfish, ponyfish and sole; however, the trend was not consistent between sample sites. Ponyfish and sole showed higher levels of Zn at Tambak Lorok while catfish showed lower levels of Zn at Tambak Lorok compared to Morodemak. Plankton and detrital feeding fish (mullet, catfish, ponyfish) were found to have higher levels of Zn than fish preying on invertebrates and other fish (sole and croaker). The observed trend reflected the expected downward shift in Zn concentration with trophic level (Bernhard and Andrea, 1984). Significant differences in length existed between fish samples, however, no clear association between Cd, Ni, Pb and Zn concentrations and fish size were established in literature (Langston and Spence, 1994). Browne *et al.*, (2000) concluded that consumption of seafood did not pose a health risk to residents of the rural community. In the urban community only Cd was concluded to pose a potential risk. The estimated risk from seafood was slight but warranted further more comprehensive study

of the dietary intake of Cd in the urban fishing village of Tambark Lorok, in order to determine if Cd exposure poses a significant health risk to residents.

Mitra and Choudhury (1993) working on heavy metal concentration in *C. cucullata* of Hooghly Estuary, West Bengal, India reported that the oyster accumulated Zn, Cu, Mn and Fe in the adductor muscle, gills and mantle. Similar studies by the same workers Mitra and Choudhury (1994), working on heavy metal concentrations in *C. cucullata* of Henry's Island, India observed that, the concentrations of Zn were higher than other metals analysed (Cu, Mn and Fe). Gill and mantle exhibited higher concentrations of metals than the adductor muscles. Concentration of all metals enhanced in all the body parts during the monsoon months. Krishnakumar *et al.*, (1990) observed that trace metal concentration in the oyster (*C. cucullata),* Mussel (*Perna viridis*) and seaweed (*Sargassum tenerimum*) collected from the vicinity of a caustic soda plant discharge point in Karwar, India, were comparatively high. These workers concluded that oysters were more effective bioaccumulators for Zn, Cu and Cd, while mussels and seaweeds for Pb and Mn.

Krishnakumar *et al.*, (1998) working on heavy metal distribution in the biotic and abiotic matrices along Karnataka Coast, West Coast of India, observed that mean Hg and other toxic heavy metals in the sediment and oysters at Binage, Karwar from a stream originating from the vicinity of a caustic soda factory were relatively high. The Hg concentration in seawater, sediments and oysters collected from that stream varied from 0.05-0.8 $\mu g\ g^{-1}$, 0.07-0.47 $\mu g\ g^{-1}$ and 0.18-0.54 $\mu g\ g^{-1}$ respectively. Relatively high concentrations of Cu and Zn were observed in the sediment (Cu, 37 $\mu g\ g^{-1}$; Zn, 68.8 $\mu g\ g^{-1}$) and tissue of bivalves (Cu, 128-201 $\mu g\ g^{-1}$; Zn, 70.5-127.3 $\mu g\ g^{-1}$) collected from

Thannirbavi, Mangalore from the vicinity of effluent discharge points of a chemicals and fertiliser factory and an iron ore processing plant. Predominance and persistence of certain species of phytoplankton and a slight decline of zooplankton biomass and density were reported from Thannirbave. Metal concentration in sediment and bivalves from all other sites of coastal waters of Karnataka such as Majali, Argae, Hejmadi, Chithrapur and Someshwar were found to be within the normal range.

According to Blackmore (1998), oysters are a popular food in Hong Kong. Consequently there has been much interest in metal levels in oysters purchased from markets around the territory, particularly the Pacific Oyster (*Crassostrea gigas*), the main commercial species. Chan (1995b) estimated that only 30-40 % of oysters consumed in Hong Kong were produced locally, the remainder being imported from China. This poses a risk since Cd and Hg levels are often higher in the latter (Chan, 1995b).

Philips *et al.*, (1986) reported accumulated body burdens of Cd, Cr, Cu, Hg and Pb concentrations ($\mu g\ g^{-1}$ wet weight) in *C. gigas* purchased from LauFau Shan Market between 1981 and 1983 as follows, 0.23-5.88, 0.02-0.43,12-495, 0.02-0.07 and 0.01-1.0 respectively. Some oysters (18.8 %) were above the upper Cd limit for seafood. Cheung and Wong (1992b) reported accumulated body burdens ($\mu g\ g^{-1}$ dry wt) of As, Cd, Cr, and Cu in *C. gigas* collected from Lau Fau Ahan, North Point, Central and Wan Chai markets as follows 0.12-2.95, 1.44-10.98, 1.25-2.28 and 589-1071 respectively. Chu *et al.*, (1990) measured levels of Cd, Cu, Fe and Zn in *S. cucullata* sampled from Inner and Outer Tolo Harbour in 1986. Cadmium body concentrations varied little with site (5-12 $\mu g\ g^{-1}$). Body concentrations of Cu and Zn were greatest at Sha Tin (Cu 500 $\mu g\ g^{-1}$ and Zn 3000 $\mu g\ g^{-1}$) as compared with Tai Po (Cu 175 $\mu g\ g^{-1}$ and Zn 2000 $\mu g\ g^{-1}$) and Outer Tolo Harbour (Cu

150-200 μg g^{-1} and Zn 2000-2850 μg g^{-1}). Body Fe concentrations were greatest in individuals collected from Tai Po (350 μg g^{-1}) as compared with Sha Tin (300 μg g^{-1}) and Outer Tolo harbour (150-225 μg g^{-1}). Blackmore (1998), described Hong Kong's metal pollution problems as serious. This was due to the reflected elevated metal levels measured in seawater, marine sediments and biomonitors. Metal pollution was considered particularly serious within Harbours, especially, Victoria Harbour, enclosed bays, such as Tolo Harbour and in Typhoon shelters.

Denton and Burdon-Jones (1986) observed that in the muscle tissue of fish from the Great Barrier reef, Zn concentration ranged from 4.3-41.8 μg g^{-1} dry wt with 76 % between 10.0 and 20.0 μg g^{-1}. Copper ranged from 0.47-2.4 μg g^{-1} with 70% between 0.5 and 1.0 μg g^{-1}. Cadmium, Ni and Pb were not detected. Mercury ranged from < 0.002 to 1.9 μg g^{-1} wet weight of which 90% did not exceed 0.200 μg g^{-1}. Zinc, Cu, Cd and Hg in liver samples were often greatly in excess of those present in respective muscle samples while Ni and Pb were rarely detected. Only Hg in fish showed evidence of size and trophic level dependence. Levels of all metals in muscle tissue generally ranked among the lowest reported in the literature, and (with the exception of Hg in 5 % of the total) were well below the Australian National Health and Medical Research Council's standards for human consumption.

Chan (1995a) reported accumulated body burdens of Cd, Cu, Pb and Zn in the Rabbit fish (*Siganus oramin*) collected from four sites within Victoria Harbour (Hong Kong) in 1983. Concentrations of metals were shown to be highest in the viscera and lowest in muscle tissue, although levels were still high overall (Cd 3.3 μg g^{-1}; Cu 5.7 μg g^{-1}; Pb 19.1 μg g^{-1} and Zn 66.6 μg g^{-1}).

Bloxham *et al.*, (1998) concluded that total Hg and other trace metal concentrations in commercial fish catches landed at Irish ports and in shellfish from shellfish growing areas were low, which conformed with previous studies (O'Sullivan *et al.*, 1991; Smyth *et al.*,1997; Rowe *et al.*, 1998). All shellfish tested for mercury in fish was within the European Union human consumption tolerance level of 0.5 $\mu g\ g^{-1}$ wet weight.

Blasco *et al.*, (1998) measured trace metal concentrations (Fe, Cu, Mn, Zn) in samples of liver and muscle from five European Atlantic grey mullet species: *Liza saliens, L aurata, L. ramada, Mugil cephalus and Chelon labrosus*. All fish were collected from the salt-ponds of Cadiz Bay SW Spain. Generally, the values obtained were similar for all species and concentrations of metals were higher in liver than in muscle. The correlation between metal concentration and fish size was variable and depended upon the species and tissue analysed. However, in all cases, concentrations fell as fish size increased. A significant correlation between metals ($p<0.05$) was found only for Cu and Zn in the livers of three species. The results suggested that the concentration of metals in these fish is not of great value as a means of determining levels of contamination.

Chen and Chen (2001) analysed trace elements (Zn, Fe, Cu, Mn and Cd) concentrations in the muscles, livers and gonads of nine species of the most commonly found fishes in the Ann-Ping coastal waters, Taiwan. These workers observed that, the Zn and Fe concentrations were highest; followed by Cu and Mn, Cd being the lowest in the three kinds of fish tissues. The liver metal concentrations of Zn, Fe, Cu, Mn and Cd ranged 4.0-7.28, 2.35-7.72,0.2-0.45,0.2-0.83 and <0.0005 $\mu g\ g^{-1}$ wet wt respectively. The

liver concentrations of the five elements were in the range of 23.0-66.6, 131-646, 3.34-48.2, 0.75-1.94, and 0.08-0.77 μg g^{-1} wet wt respectively. A significant species-specific difference was found. The *Sardinella lemuru* contained higher muscle concentrations of Zn, Mn and Cd than the other species of fishes. However, the *Liza macrolepis* contained the highest liver concentrations of Fe and Cu. The metal concentrations found in that study were similar to the metal levels of the fish collected from slightly polluted waters all over the world and Taiwan. Therefore, no public health problem was raised from the consumption of the fish.

The acceptable heavy metal concentrations (μg g^{-1} wet wt) in seafood in various countries are as shown in Table 2 for copper, zinc and cadmium.

Table 2. Acceptable heavy metal concentrations (μg g^{-1} wet wt) in seafood in various countries

Country	Standard[a]	Zinc	Copper	Cadmium	Reference
America	FDA	-	-	2[b]	Arnac and Lassus (1985)
America	NAS	-	-	0.5[b]	Nabawi *et al* (1987)
Australia	NHMRC	1000	30	2	Bebbington *et al* (1977)
Australia	TPHR	40	30	5.5	Eustace (1974)
Canada	-	-	100	-	Tsen (1996)
Japan	-	-	-	1	Tsen (1996)
United Kingdom	MAFF	50	20	-	Sally *et al* (1996)
United Kingdom	FSC	50	-	-	Eromosele *et al* (1995)

[a] FDA = Food and Drug Administration, NAS = National Academy of Science, NHMRC = National Health Medical Research Council, TPHR = Tasmania Public Health Regulation, MAFF = Ministry of Agriculture Fisheries and Food, FSC = Food Standards Committee,

[b] ug g^{-1} dry wt

Table 3 shows the synopsis of the strictest standard and guidance values applied by various Oslo and Paris Commission (OSPAR) countries for contaminants (in this case copper, lead and cadmium) in shellfish for the assessment of the possible hazards to human health according to Anon, 1992.

Table 3. Strictest standard and guidance values applied by various (OSPAR) countries for contaminants (copper, lead and cadmium ($\mu g\ g^{-1}$) in shellfish for the assessment of the possible hazards to human health (Anon, 1992).

Contaminant	Values	Qualifier	Country
Copper	20	Standard	Spain
Lead	0.8	Guidance	Germany
Cadmium	0.5	Guidance	Germany/Norway

Table 4 shows the synopsis of the strictest standard and guidance values applied by various OSPAR countries for contaminants (in this case copper, zinc, lead and cadmium) in finfish for the assessment of the possible hazards to human health according to Anon, 1992.

Table 4. Strictest standard and guidance values applied by various OSPAR countries for contaminants (copper, zinc, lead and cadmium ($\mu g\ g^{-1}$) in finfish for the assessment of the possible hazards to human health (Anon, 1992).

Contaminant	Values	Qualifier	Country
Copper	10	Guidance	Norway
Zinc	50	Guidance	United Kingdom
Lead	0.5	Standard	Netherlands
Cadmium	0.1	Standard	Netherlands

According to Bowen (1979a) the normal, toxic and lethal concentrations (mg day^{-1}) of copper, zinc, lead and cadmium metals in human diet are as shown in Table 3

Table 5. Normal, toxic and lethal elemental concentrations (mg day^{-1}) in human diet according to Bowen (1979a).

Metal	Deficiency	Normal	Toxic	Lethal
Copper	0.3	0.5-6.0	-	175-250
Zinc	5	5-40	150-600	6000
Lead	-	0.06-0.5	1	10
Cadmium	-	0.007-0.3	3-330	1500-9000

2.2.2. Abiotic Compartments

According to Bryceson (1990) available data on marine contaminants in Eastern Africa are scarce. However, localised hot spots of metal pollution are found in the vicinity of cities and industrial centres that may constitute a danger to the public health.

Some studies of dissolved metals in some Kenyan marine environment were conducted by Norconsult (1977) concluding that the concentrations for Tudor creek fell within the normal range of unpolluted natural seawater. Oteko (1987) studied the Mombasa creek and suggested crustal sources to be responsible for copper concentrations and increased anthropogenic sources from automobile exhausts for cadmium and lead concentrations. Nyatebe (1990) observed that heavy metal content in Port Reitz Creek Sea sediments were higher than for Tudor Creek. These workers attributed that observation to increased anthropogenic inputs in Port Reitz Creek. For instance higher copper (62.2 ppm) concentrations observed in Mbaraki Creek were associated with shipping activities such as ship repair in that area. The higher lead concentrations (138 ppm) in that same station were attributed to use of leaded gasoline and spillage during transportation. Nguta (1993) stated that, although the extent of industrialisation along the Kenyan coast was relatively low, discharges of liquid wastes into the sea had been

reported. Solid wastes, both domestic and industrial, including toxic chemicals were dumped in the uncontrolled landfill at Makupa creek. Leakage from the landfill including run-off containing toxic substances enters the adjoining creek waters. Contamination of sediments by heavy metals showed enrichment factors ranging between 1.2-7.8.

Everaarts and Nieuwenhuize (1995) observed that there was a statistically significant increase in the concentrations of copper and cadmium in surface sediments along transects radiating into the Indian Ocean perpendicular to the Kenyan coast. While that of zinc was only significant at the most southern transect at Gazi. Mean copper and cadmium increased from 5 to 30 $\mu g\ g^{-1}$ dry wt and from 0.01 to 0.34 $\mu g\ g^{-1}$ in shallow coastal (±20m depth) to deep-sea stations (±2000m depth) respectively. These gradients were observed during both the SE and NE monsoons.

Williams *et al.*, (1996) observed that concentrations of several potential toxic trace elements (e.g. Cr, As, Ni, and V) were enriched in suspended particulate matter (SPM) in Tudor Creek, relative to SPM in other inshore and reef front waters. A spatial correlation between these metals and Mn was evident. They concluded that such trends were inconsistent with an anthropogenic control, and were almost certainly attributed to the dominance of mangrove-derived particulate matter in the overall Suspended Particulate Matter (SPM) assemblages in Tudor creek. These workers also reported that, several heavy metals attained high concentrations in surface sediments around Mombasa. With the exception of Pb, Zn and Cu, the signatures were almost entirely related to lithology. Localised enrichment of Pb, Zn and Cu was however evident in close proximity to several known point-sources including sewage outfalls to the east of Mombasa Island, Likoni and Kilindini docks. Temporal flux variation, typically

involving increased trace metal deposition towards the sediment-water interface, were apparent from downcore concentration profiles through the sediments of Makupa Creek, Port Kilindini and Tudor Creek. Following normalisation against Al_2O_3 or TiO_2, however, no clear anthropogenic control was identified. Sedimentary partitioning data for sediments from Makupa Creek indicated that labile geochemical fractions (e.g. reduced oxides) were significant as carriers of Mn, Pb, Cu and Co. Detrital silicates and sulphides form the principal carriers of Fe, Al, V, Co, Cr and Ni. The available partitioning data and complementary data for interstitial pore-waters suggested that the post-depositional alteration of labile phases predominantly resulted in the immobilisation of metals as sulphides. Under such circumstances, the sediment reservoir was considered to constitute a relatively long term contaminant sink.

Kulekana (1997) recorded Pb, 36.8 mg kg^{-1}, Cd, 2.0 mg kg^{-1} and Cu, 6.36 mg kg^{-1} from the same area. Anti-fouling paints and weed killers were some of the attributable sources of the trace elements in this area. De Wolf *et al.,* (2001) observed that, with the exception of Mn and Ni, the concentrations of all metals (Ag, Al, As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sr, and Zn) assessed increased in Msimbazi (Tanzania) sediments between 1988 and 1999. That increase was obvious for Al (530-6375 μg g^{-1} dry wt), Fe (630-3539 μg g^{-1}), and Cr (2.7- 10.1 μg g^{-1}). Iron, Mn and Zn concentrations decreased from Msimbazi to Mbweni, that is, from a polluted to a relatively unpolluted area.

Watling and Emmerson (1981) identified areas of metal input to the river Papenkuils which was considered to be a serious source of pollution to the marine environment around Port Elizabeth, South Africa. In contrast, the estuary of river Swartkops was found generally unpolluted on the basis of metal concentration in water,

surface sediments and sediment cores (Watling and Watling, 1982a). Similar studies also showed that the estuary of river Knysna as well as the Bushmans, Kariega, Kowie and Greatfish rivers were unpolluted (Watling and Watling, 1982b, 1983).

Toma (1981) investigated the distribution of adsorbed metals on the fine fraction of the sediments of the western part of the Nile continental shelf (offshore, neat shore and river environments). They concluded that abundance of metals follows the order Fe>Mn>Zn>Cu, and their distribution was identical with the pattern of sediment transport. High metal concentrations, some reaching potentially toxic levels for aquatic organisms, were recorded at certain localities. This was attributed to contaminated drainage waters. Studies on the surface sediments of El-Mex region of the Mediterranean in front of Alexandria (Saad *et al.,* 1981a) revealed two zones, one of which showed high concentrations of Mn, Cu, Cd, Zn and Fe, as a result of discharges of industrial effluents. Their findings also suggested incorporation of similar proportions of Fe and Mn into the sediments and the co-precipitation of Cu and Zn by iron oxides.

The occurrence of some heavy metals in the sediments of Abu-Kir Bay of the Mediterranean Sea was studied by Saad *et al.,* (1981b). The metals (Cu, Cd, Zn, Fe and Mn) showed a pattern of distribution similar to that of the mud and organic matter content of the sediments. The effects of industrial effluents were found to be restricted to sediments in the vicinity of their discharge.

In Nigeria, studies by Kakulu and Osibanjo (1988, 1992) revealed elevated levels of Pb, Cr, Ni, V and Zn in Port Harcourt and Warri sediments which suggest that effluents from petroleum refineries located in these cities have contributed significantly to the heavy metal pollution of the respective aquatic ecosystems. Okoye (1991) reported

anthropogenic heavy metal enrichment of Cd, Co, Cu, Cr, Fe, Mn, Ni, Pb and Zn in the Lagos lagoon and implicated land based urban and industrial wastes sources.

In Ghana, Akoto (1990) carried out a study in which, heavy metal pollution from gold mining activities at the Obuasi gold mining area was assessed by analysing gold ore, tailings, sediments and water for Cr, Mn, Fe, Cu, Zn, AS, Pb, Rb Sr, Y, Zr and Nb. This study revealed the presence of all the elements in sediments within a concentration range of 0.08 to 49 000 $\mu g\ g^{-1}$, whereas only Fe and Zn were detected in water at levels of 0.08-2.4 ug m L^{-1}.

In Cote d' Ivoire, Kouadio and Tefry (1987) have studied sediments of the Ebrie Lagoon and reported metal concentrations in excess of background levels. This was attributed to the disposal of untreated sewage and industrial effluents.

Subramanian *et al.*, (1988) working on heavy metals in the Ganges Estuary, India, observed that, because of their fine size to the bed load and higher organic matter, the particulates are relatively enriched in all the metals. Fractionation studies of the Ganges sediments have indicated that the particulate phases generally have large proportions of the chemically mobile fractions, such as the organic and metallic hydroxide coatings (Subramanian *et al.*, 1987). The higher concentration of Al in the particulates is due to the dominance of illite (Subramanian, 1980).

Hall and Chang-yen (1986), working on metals in sediments off Trinidad, West Indies, reported that, the highest metal levels were obtained from sediment samples in the vicinity of an area with already established industries. The sediments in that area were classified as mud by grain size analysis while the areas further removed from the

industrial site were mainly sandy. Thus, the enhanced levels could have been possibly due to the proximity of the industrial site and/or the nature of the sediment.

Chye-eng seng *et al.*, (1987) working on sediments off Prai Industrial Estate, Penang, Malaysia observed that zinc showed the highest mean concentration values (73.5 to 109.8 μg g^{-1}) followed by nickel (24.8 to 46.7 μg g^{-1}), lead (20.8 to 33.0 μg g^{-1}), copper (9.3 to13.8 μg g^{-1}) and cadmium (not detectable to 6.8 μg g^{-1}). They further pointed out that, the mean concentrations for Pb, Cu and Zn were comparable to those found in unpolluted estuaries in other parts of the world. However, nickel and cadmium concentrations were comparable to those of polluted estuaries, such as Tolo Harbour in Hong Kong (Wong *et al.*, 1980) and the Severn Estuary in the United Kingdom (Chester and Stoner, 1975).

According to Blackmore (1998), in an overview of trace metal pollution in the coastal waters of Hong Kong, maximum Cd concentrations in Hong Kong sediments (8 μg g^{-1}: Cheung and Wong (1992a)) were similar to maximum levels measured in Taiwan (4.64 μg g^{-1}: Chen and Wu (1995)) and River Tees sediments (8.5 μg g^{-1}: Davies *et al.*, (1991)). The results obtained were, however, much greater than maximum concentrations in Darwin Harbour sediments (3.0 μg g^{-1}: Peerzada and Rohoza (1989)), but lower than maximum levels from the North Sea (30 μg g^{-1}: Everaats and Fischer (1992)). Maximum Cu concentrations in Victoria Harbour (3789 μg g^{-1}: Wong (1995) in Blackmore (1998)) and typhoon shelter sediments (6250 μg g^{-1}) were much greater than those measured in River Tees (1100μg g^{-1}), Darwin Harbour (32.3 μg g^{-1}), Taiwan (988 μg g^{-1}) and North Sea sediments (240 μg g^{-1}). Maximum Pb concentrations in Hong Kong sediments (161 μg g^{-1}) were much less than the River Tees (990 μg g^{-1}). Only maximum Pb concentrations

from typhoon shelter sediments (550 μg g^{-1}) were comparable to those from the North Sea (630 μg g^{-1}). Hong Kong maximum Pb concentrations were, however, greater as compared with Darwin Harbour (91 μg g^{-1}). Maximum Zn concentrations in Hong Kong sediments (610 μg g^{-1}) were much less than those of the River Tees (2900 μg g^{-1}) and the North Sea (4000 μg g^{-1}); concentrations were, however greater than those from Darwin Harbour (270 μg g^{-1}) and Taiwan (203 μg g^{-1}). Hong Kong sediments, in particular those from typhoon shelters, are polluted with Cr, Cu and Ni as compared with known polluted sediments (Chen and Wu, 1995; Davies *et al.*, 1991; Everaats and Fischer, 1992 Peerzada and Rohoza, 1989).

3.0. MATERIALS AND METHODS

3.1. Field Work

3.1.1. Sample Collection

Initially, a reconnaissance survey was carried out in the month of December 2000 to identify priority sampling zones. In Mtwapa Creek sampling stations were chosen so as to assess the influence of inputs from River Lwandani among others, and also to assess the influence of tourism (e.g boating activities) and other human settlement activities (e.g effluent inputs such as the sewage discharge from Shimo la Tewa prison). In Port Reitz Creek, stations were chosen so as to address the influence of the port activities such as mooring of ships and boats, maintenance activities such as painting of ships, spillage of oil during loading and offloading, municipal sewage outfalls, among others. In Makupa Creek, stations were chosen so as to address the influence of industrial effluent inputs, garbage dumpsite and motor activities in the riparian zone of that creek. Shirazi Creek was chosen as a control site since it was considered relatively pristine in comparison to the other creeks due to its location further away from major urbanisation activities. However, stations such as the ones near the former Shirazi oyster culture farm, Bodo landing beach and the area adjacent to Funzi Island and the "Lost paradise found" sandbar were identified as key sampling zones.

Sampling stations were accessed using an out board powered engine boat or by wading where applicable. Sediment samples were collected from 8,11,13 and 7 stations in Mtwapa, Port Reitz, Makupa and Shirazi Creeks respectively as shown in Figures 2, 3 and 4 in the regional setting section (1.4). For each station apart from those in Makupa Creek, samples were taken from at least three substations, preferably one substation in

the middle of the creek channel and the other two on either side of the creek shoreline. The sediment samples were obtained using an Ekman grab and stored in polyethylene bags awaiting pretreatment in the lab. In total 106 samples were collected from the four sites. Sediment samples were labelled according to the site, month of collection, station and substation as follows, for creeks, T = Mtwapa Creek, P = Port Reitz Creek, K = Makupa Creek while S = Shirazi Creek. For Months, J = January, M = March, U = July. Stations are labelled in Arabic numbers while substations are labelled in lowercase alphabet letters.

Fish were collected randomly within the Creeks. The fish were obtained using cast net, gill net and hook and line (where applicable) with the help of local fishermen. One hundred and fifty eight fish individuals from 13 fish species were collected from the four sites. Some fish species were collected from more than one site. Seven fish species were collected from Mtwapa Creek. These were, *Leiognathus equulus* (TLe) (n=15 individuals), *Lutjanus fulviflama* (TLf) (n =7), *Rhabdosargus globiceps* (TRg) (n=9), *Sardinella gibbosa* (TSg) (n=18), *Gerres* Sp. (TGe) (n=13), *Siganus canaliculatus* (TSc) (n=10), and *Leptoscarus vaigensis* (TLv) (n=4). Five fish species were collected from Port Reitz Creek. These were *Leiognathus equulus* (PLe) (n=9), *Polysteganus caeruleopunctatus* (PPc) (n=9), *Strializa canaliculatus* (PStc) (n=5), *Epinephelus Postelli* (PEp) (n=1), and *Lethrinus mahsena* (PLm) (n=4). Only one fish species, *Gerres* Sp. (PGe) (n=9) was collected from Makupa Creek. Species and number of fish caught depends on a number of factors such as gear specificity and time of collection among others. Fishing gears used in the present study were not exhaustive of all the species that might have been present. On the other hand, sample collection was done preferably

during slack waters when the tide was not too high or too low due to logistical problems in accessing the sampling sites. Some fish move in and out of creeks with the tidal currents hence this among other behavioural ecology aspects of the fish may determine their catchability. Nine fish species were collected from Shirazi Creek. These were, *Leptoscarus vaigensis* (SLv) (n=5), *Leptoscarus Sordiditus* (SLs) (n=10), *Lethrinus nebulosus* (SLn) (n=3), *Siganus canaliculatus* (SSc) (n=9), *Epinephelus postelli* (SEp) (n=4), *Plectorhyncus gaterina* (SPg) (n=4), *Plectorhyncus flavomaculatus* (SPf) (n=1), *Platycephalus crocodylus* (SPc) (n=1) and *Lutjanus fulviflama* (SLf) (n=8).

Oysters, particularly *Saccostrea cucullata,* were collected from the same stations as sediment samples where they were available. The oyster samples were collected from stations 3, 5, 6 and 8, 1, 2, 3 and 4, 1 and 2, and 2, 3, 4, 5 and 6 in Mtwapa, Port Reitz, Makupa and Shirazi Creeks respectively. They were dislodged from mangrove roots and rocky substrates using a knife and a hammer and chisel respectively. Oysters were labelled according to creek, month of collection and station just like for sediments, plus type of substrate from which they were dislodged (X = Mangrove, Y = Rock while Z = Tiles) and finally according to the groups into which they were classified for analysis.

The biota samples were put into polyethene bags and stored in a cooler box prior to refrigeration in the laboratory. Identification of the biota samples was done at the Kenya Marine and Fisheries Research Institute and at the National Museums of Kenya, Ichthyology Department, using (Smith and Heemstra 1986; Richmond 1997) guidebooks and Fish Base Data Base (Froese and Pauly, 2000) with the help of research scientists.

3.1.2. Physicochemical Parameters

Temperature (Degrees centigrade (°C)), salinity (Parts per thousand (‰), conductivity (Microsiemens (ms), pH, dissolved oxygen (D.O) (Milligrams per litre (mg L^{-1}) and transparency (Metres (m), physicochemical parameters were assessed on site. Transparency was measured using a secchi disk. Temperature was measured using a mercury thermometer. Oxygen was measured using an oxygen metre, WTW Oxi 320/set (Wissenschaftlich-Technische-Werkstätten, GmbH & Co. KG. Dr. Karl-Slevogt-Strabe-1, D-82362, Weilheim, Germany). pH was measured using a pH metre, WTW pH 320/set. Conductivity was measured using a conductivity metre WTW Cond 315i. Salinity was measured using an RL - 10ATC hand refractometer.

3.2. Laboratory Work

3.2.1. Analytical Techniques

Atomic absorption spectroscopy (AAS) was the main technique used in determining concentrations of heavy metals particularly zinc, copper, lead and cadmium. Energy dispersive X-ray fluorescence spectroscopy (EDXRF) was also used for comparison purposes and validation of the methodology used.

3.2.1.1. Atomic Absorption Specrophotometry (AAS) Principle

Figure 5 shows the basic instrumental layout of an atomic absorption spectrophotometer. AAS is an analytical technique used to measure a wide range of elements in inorganic as well as organic materials. In this technique, the elements present in a sample are converted to gas phase atoms in the ground state. These gas phase atoms are then measured by irradiation of light at a highly specific wavelength causing a transition of some of the gas phase atoms to a higher energy level. The extent to which

light is absorbed is related to the original concentration of ground state atoms. This situation is completely analogous to the Beer-Lambert law in conventional liquid spectrophotometry (Welz, 1985).

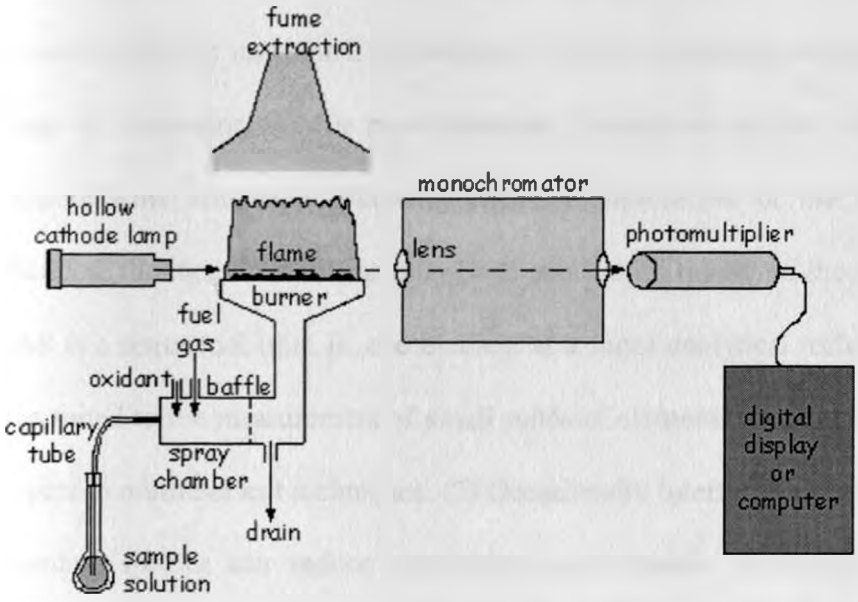


Figure 5. Instrumental layout of a prototype atomic absorption spectrophotometer. (Source: Hughes *et al.*, 1976).

The most common instrument components consist of a hollow cathode lamp source, a pneumatic nebulizer for an atomizer, a conventional grating monochromator photomultiplier tube detector and a digital display. The hollow cathode lamp is made of a glass envelope with a quartz window filled with an inert gas at slightly above atmospheric pressure. The cathode is made of the pure metal of interest. The pneumatic nebulizer aspirates and nebulizes the liquid sample solution when the sample is sucked through a capillary tube. The grating monochromator eliminates much of the background light from the flame and the photomultiplier tube detector detects that light from the

hollow cathode lamp which passes through the flame. Integrated readings of absorbance and concentrations of the elements measured are produced in the microprocessor digital display (Hughes, *et al.*, 1976).

Advantages of AAS include, (1) there are relatively few matrix and other interference effects. (2) Sample throughput is high as each measurement can take only seconds when the instrument is calibrated. (3) The technique is applicable over a wide range of concentrations for most elements. Limitations of the AAS include, (1), all measurements are made following chemical dissolution of the element of interest. Therefore the measurement can only be as good as the quality of the sample digestion. (2) AAS is a sequential (that is, one element at a time) analytical technique. It is therefore best suited to the measurement of small suites of elements as it is not cost-effective with respect to multielement techniques. (3) Occasionally interferences from other elements or chemical species can reduce atomization and depress absorbance, thereby reducing sensitivity. (4) Some elements such as Li, Na, K, Rb and Cs ionise rather easily, again reducing atomization and complicating the measurement technique. (Welz 1985; Chemex labs, 1999). This type of interference may usually be overcome by addition to the sample, and standards, of an ionisation buffer. For instance, for calcium analysis strontium or lanthanum ionisation buffers are used. (Chem Tech Analytical 2000a). Such elements were however not analysed in the present study.

3.2.1.2. Energy Dispersive X-ray Fluorescence Spectrometry (EDXRF) Principle

Figure 6 shows the instrumental layout of a prototype XRF unit while Figure 7 illustrates the principle of the XRF technique. The X-ray fluorescence (XRF) instrument is a downhole probe consisting of an X-ray source and a photon detector. The instrument

probe is placed in a lined borehole. The sample and the detector are then irradiated with the source X-rays for a specified period of time. The detector receives a combination of Compton backscatter photons, as well as fluorescence photons emitted by atoms in the sample. The system also includes an onboard amplifier, an analog-to-digital converter, a multichannel analyser, and a computer processor. Calibration of the instrument for a particular element and observation of the number of counts appearing in a specific fluorescence range of the energy spectrum results in a quantitative determination of the concentration of the element in the sample (Willard *et al*, 1988).

XRF works by beaming X-rays onto the sample, which excites some of the electrons orbiting the atomic nuclei (inside the atoms of the elements present), to jump to higher energy orbitals. The empty space in the respective orbital shell is replaced by another electron dropping down from a higher energy level. This transition process is accompanied by an emission of an X-ray photon as the electron drops to the lower energy level. This process of atoms emitting secondary X-rays in response to excitation by a primary X-ray source is called X-ray fluorescence. The secondary X-ray photons are emitted by the atoms of the elements in the sample in characteristic discrete frequency peaks, their fingerprint line spectra. The elements in the sample can therefore be identified by their spectral wavelengths for qualitative analysis and the intensity of the emitted spectral lines enables quantitative analysis. This is accomplished by directing the secondary (fluorescence) radiation from the sample into a narrow beam by slit collimator and onto a crystal plate. The crystal is commonly lithium fluoride. The various wavelengths in the beam are diffracted by the crystal lattice atoms in the plate at various angles proportional to their frequency (analogous to white light passing through a prism).

A radiation detector is rotated by degrees around an accurate track (goniometer) and the individual frequencies and their intensities thus measured. The on-board computer then reduces this data to elemental or oxide concentration. The analysis is rapid and non-destructive but is generally impractical for determining elements lighter than fluorine (Bertin, 1970) The operational features of this analytical technique have been broadly described by Kinyua (1982).

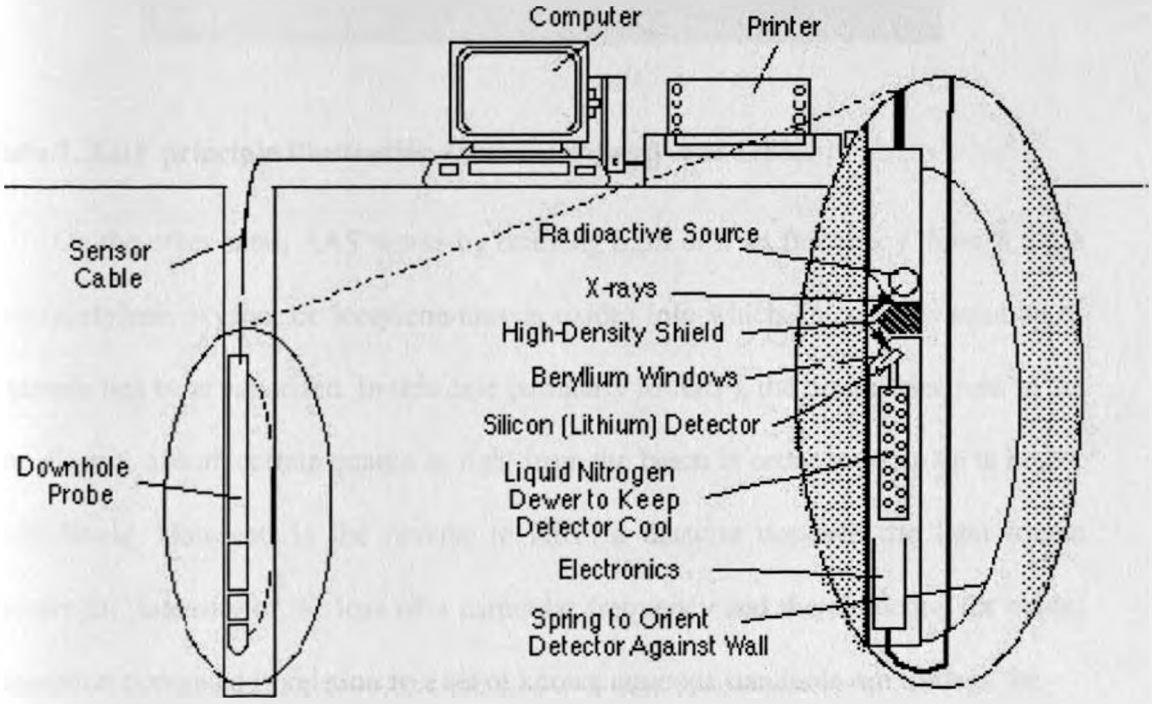


Figure 6. Instrumental layout of a prototype XRF unit (Source: Willard et al 1988).

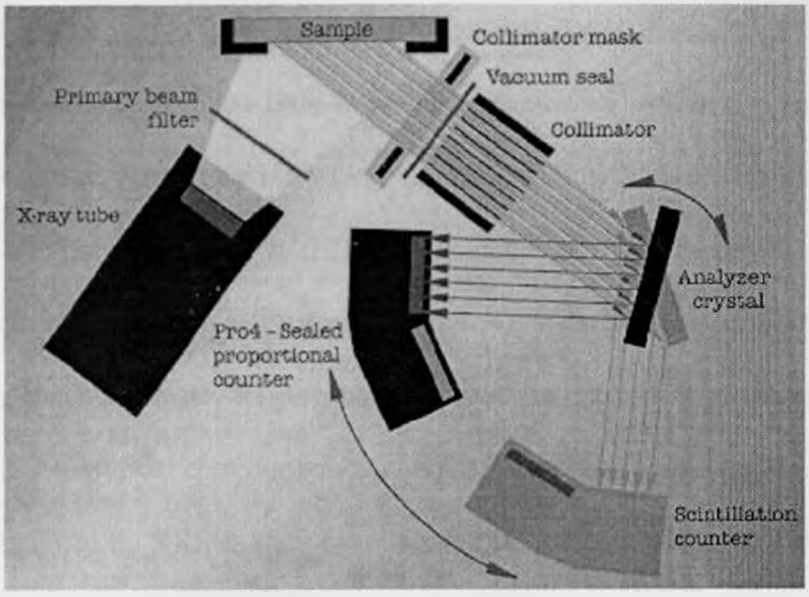


Figure 7. XRF principle illustration (Source:Willard *et al* 1988).

On the other hand, AAS works by beaming light of a set frequency through a gas flame (acetylene-oxygen, or acetylene-nitrous oxide) into which an aqueous solution of the sample has been vaporised. In this case (similarly to XRF), the orbital electrons in the flame plasma, absorb certain quanta of light from the beam in order to jump up to higher energy levels. However, in the reverse to XRF, a detector opposite the light source measures the intensity of the loss of a particular frequency and the elemental (or oxide) composition computed in relation to a set of known aqueous standards run through the AAS alternately with samples (Bertin, 1970; Matlock et al 1998)

Energy dispersive X-ray fluorescence has a number of advantages for environmental analysis when compared to other spectroscopic techniques. One, spectral or chemical matrix interference can be eliminated through calibration and spectral deconvolution. Two, samples can be analysed for metals non-destructively and utilised

for additional measurements of organic or inorganic ions. Three, elements can be analysed over a wide range from low ppm to percent levels, Four, qualitative and/or semiquantitative analysis requires little sample preparation and reduces the cost per test. Five, Rapid on-site analysis of a wide variety of environmental samples can be performed (Driscoll, 1998). The limitations of EDXRF include, one, fluorescent X-rays can be easily absorbed by the sample itself (self-absorption), it is therefore important that the sample matrix match as closely as possible to that of the calibration standards. If this is not possible, then empirical correction factors must be applied. Two, lighter elements are not easily determined by XRF as they have inherently less sensitivity. The lower energy XRF emission from these elements means that they have less penetrating power and hence less sensitivity. Three, sample fusion enhances the XRF measurement technique by minimising particle size effects but sometimes refractory minerals dissolve slowly and do not give satisfactory fusions (Chemex labs, 1999).

3.2.2. Laboratory Apparatus and Chemicals

Laboratory apparatus and equipment used included; 100 ml beakers, digestion tubes, measuring cylinders, 50 ml and 100 ml volumetric flasks, pipettes and sample storage bottles, pestle and mortar, filter funnel and paper (Whatman 12.5cm), clamps and standards, digestion block, electrical hot plate, Oven and an electrical weighing balance. The apparatus were washed thoroughly with detergent, leached with dilute nitric acid (HCl) (10% v/v) for at least 24hrs, followed by rinsing at least twice with distilled water and finally dried in the oven at 80 ^{o}C where applicable. All pipettes used were always left immersed in dilute Nitric acid in a large measuring cylinder (500ml).

Laboratory chemicals and other materials were used included; detergent, concentrated nitric acid (HNO_3), concentrated hydrochloric acid (HCL), concentrated Sulphuric acid (H_2SO_4), 30% (v/v), hydrogen peroxide (H_2O_2), copper, zinc, lead and cadmium metals, silicone anti-foaming agent and distilled water. All chemicals and reagents used were from Merck and Company Incorporated (Merck and Company Incorporated Whitehouse Sation, NJ, USA) and were of analytical reagent grade.

3.2.3. Preparation of Calibration Standards

3.2.3.1. Stock Solutions

One thousand parts per million (1000 ppm) stock solutions were made from salts/metals of the respective elements as recommended in the AAS (Chem Tech Analytical 2000b) operators manual. Zinc metal was dissolved into a minimum volume of 1:1 hydrochloric acid. This was then diluted to one litre using distilled water to make 1000 ug/ml solution. Amounts weighed for each salt/metal were as follows, $CuSO_4.5H_2O$ = 3.9486 g, Zn = 1.0005 g, $Pb(NO_3)_2$ = 1.6064 g and $Cd(NO_3)_2.4H_2O$ = 2.7719 g. The amount used for each salt was calculated using the following formula.

$$W = \frac{Mw}{Aw} \times \frac{100}{P} \times \frac{V}{1000}$$

Where:

W = Amount weighed in order to get 1000 ppm of the metal

Mw = Molecular weight of the metal element

P = Purity of the salt (Assay in %)

V = Volume of the stock solution prepared

Aw = Atomic weight of the metal element

3.2.3.2. Working and Calibration Standards

A working standard of 100 ppm was first made from the 1000 ppm stock solution employing the formula, $C_1V_1 = C_2V_2$. Where C_1 is the concentration of the stock solution, V_1 is the unknown volume of the stock solution that is required to make the desired concentration, C_2 of a certain volume ,V_2 of solution. Equal amounts of reagents as used in the digestion of samples were incorporated into the 100 ppm working standards. Hydrochloric acid (20 ml) and hydrogen peroxide (1 ml) reagents were incorporated into the standards used for sediment analysis. Nitric acid (16 ml), silicon antifoaming agent (1-2 drops), sulphuric acid (4 ml) and hydrogen peroxide (2 ml) reagents were incorporated into the standards used in analysis of biological samples. Five millilitres of the 1000 ppm stock solution was pipetted into a 50 ml volumetric flask. The respective reagent blanks were added next and these were then topped up to the 50 ml mark with distilled water. The contents were mixed by inversion of the stoppered volumetric flasks several times. Other calibration standards were made as follows. More than 2 ppm calibration standards were made from a 100 ppm working standard, between 0.5 and 2 ppm calibration standards were made from a 10 ppm working standard, while less than 0.5 ppm calibration standards were made from 1 ppm working standard.

The calibration standards were made within the optimum working range for each element. These were, 0.02 - 2 ppm, 0.4 - 25 ppm, 0.3 - 30 ppm and 0.02 - 2 ppm for zinc, copper, lead and cadmium respectively, according to Chem Tech Analytical (2000b). The particular standards were thus selected so as to ensure that Beer's (Absorbance is proportional to concentration) law was obeyed. Within the linear working range the

absorbance is directly proportional to the concentration but beyond this range the relationship becomes asymptotic.

3.2.4. Evaluation of Analytical Procedure

3.2.4.1. Accuracy

International Atomic Energy Agency (IAEA) Soil-7, IAEA/MA-M-2 fish flesh homogenate and IAEA/MA-A-2 mussel tissue certified reference materials (CRMs) plus some experimental samples (KU1, KU12, TJ4c, TJ6a, PM10a, PM11c, SU1b, SM6c) were digested and analysed in replicates to evaluate the accuracy of the AAS procedure. Reagent blanks were prepared and analysed in the same manner so as to cater for matrix effect. The CRMs and experimental samples were also analysed using EDXRF.

3.2.4.2. Precision

To evaluate the precision of the method used some samples (TJ5c, PM1a, SJ2a, SPg2 and SEp2) were digested in 6 replicates to assess repeatability while others (TJ6a, PM2c and SJ2b) were digested in at least 6 different weeks to assess reproducibility.

3.2.5. Sample Preparation and Analysis

3.2.5 1. Preparation and Digestion of Sediment Samples

Sediment samples were prepared by drying them in an oven at 105 ^{o}C to constant weight. The coarse particles were removed and the samples were then sieved to obtain a 63 μ grain size sub sample. This grain size has been recommended in previous investigations e.g. Donazzolo *et al* (1984). Some samples formed conglomerates after drying due to the clayey nature of particularly mangrove sediments. These were thus crushed using a pestle and mortar to loosen them up before sieving. The vigorous shaking

by the machine during sieving also ensured that a homogenous subsample was obtained. The subsamples were stored in 10 ml glass bottles with plastic tops prior to chemical analysis. During analysis, 1±0.1 g of replicate sub samples of each sample were weighed into 15 cm long 1" diameter pre-labelled glass boiling tubes using a Fisher Scientific, A - 160, analytical balance, with a precision of up to four decimal places. Sets of 18 samples were analysed at a time as dictated by the capacity of the heating block (described by Onyari 1985). To all the boiling tubes containing the weighed samples, 20 ml of concentrated hydrochloric acid was added and shaken slowly to avoid spillage of the reaction mixture due to frothing. The tubes were then fixed into the digestion block which was placed on a thermostat-controlled hot plate. To minimise frothing, heating was initially done at 70 °C for 30 minutes. Shaking of the tubes was done regularly. The temperature was then increased to 100 °C. The heating was continued for 3 hours with occasional stirring. The digested mixture was then allowed to cool to room temperature and 1 ml hydrogen peroxide carefully added. Tubes were then returned to the block and heating continued for another half hour, after which the samples were left to cool prior to filtration. Reagent blanks were prepared in a similar manner for every batch of samples to cater for matrix effects in the sample analysis.

The digests were filtered into 50 ml volumetric flasks through glass wool (initially soaked in dilute nitric acid) stuck into the stem of glass funnels. Filter papers were used where necessary. Both the digestion tubes and funnels were rinsed several times with distilled water to ensure quantitative transfer. The filtrate was topped up to a final volume of 50 ml with distilled water. The volumetric flasks were stoppered and gently shaken to

mix the contents, which were then transferred into 50 ml polypropylene storage bottles, ready for elemental analysis.

3.2.5.2. Preparation and Digestion of Fish Muscle

The total length of fish was measured and total weight taken. Fish muscle was then dissected from the region below the dorsal fin, and between the opercular bone and the caudal peduncle. 5±1 g of the muscle was weighed (as recommended in previous research e.g Onyari (1985)) into similar boiling tubes as used in sediment digestion. Into each boiling tube, 4ml conc. HNO_3 was then carefully added, plus a drop of silicon antifoaming agent followed by 4 ml conc. H_2SO_4. The tubes were regularly swirled then placed on the heating block and heated at a temperature of about 60 ^oC for 30 minutes. The tubes were then removed from the hotplate and 12 ml conc. HNO_3 carefully added then they were returned to the hotplate and heated at around 80 ^oC, 100 ^oC and 120 ^oC for one hour each respectively. After this the tubes were removed from the heating block and allowed to cool to room temperature. 2 ml H_2O_2 were then added and the samples were heated for a further half hour after which the samples were left to cool prior to filtration. Filtration was carried out as explained in section 3.2.5.1. Reagent blanks were prepared in the same manner for every batch of samples so as to cater for matrix effects in the sample analysis.

3.2.5.3. Preparation and Digestion of Oyster Soft Tissues

Oysters of close sizes were clustered into groups of individuals in the range of 1-12. The grouping was done so as to obtain combined oyster soft tissues weighing upto at least 5 g where possible. The length (from the hinge joint (rostral carina) to the longest part of the cup shell) and width (measured perpendicularly along the central point of the

length line) of each individual oyster was measured. The oyster bivalve shells were opened up using a stainless steel knife. The soft tissues of all the members of a group were put into one boiling tube and weighed. The digestion and filtration procedures were similar to those used in preparation of fish muscle tissue.

3.2.5.4. Elemental Analysis

A Chem Tech Analytical make, model 2000, atomic absorption spectrophotometer was used for elemental analysis. The instrumental operating parameters (See Table 6) were tabulated as recommended by the manufacturer (Chem Tech Analytical, Alpha-line Division, 4 Railton Road, Wolseley Business Park Kempston, Bedford, U.K.).

Table 6. Instrumental operating parameters for particular elements according to Chem Tech Analytical 2000b.

Element	Fuel	Oxidant air	Burner height	HCL-Lamp (mA)	Slit Width (nm)	Wavelength (nm)
Cu	1.8	6.5	7	4	2	324.7
Zn	2	5.9	7	4	2	213.9
Pb	2	7.2	7	4	3	217.0
Cd	2.2	7.2	7	3	3	228.8

(mA = Milliampheres, nm = nanometres)

All analyses were carried out using an air-acetylene flame. Respective calibration standards were first run and the calibration curves drawn as illustrated in section 4.2 of results and discussion. A suitable calibration standard, preferably the median one along the linear working range, was always run at 10 samples interval during analysis of the experimental samples. This was done as a point check to guard against deviation from the instrumental operating conditions and reslope the curve accordingly where necessary. Samples with absorbance falling out of the linear working range for a given metal were

diluted and re-run accordingly. The absorbance and concentration values, along with the standard deviations were read directly from the instruments digital display.

3.3. Statistical Analysis

Actual concentrations of metals were calculated in $\mu g\ g^{-1}$ using the formula A*V/D. Where A is the concentration read minus that of the reagent blank, V is the final volume to which the digests were made and D is the weight of the particular sample. This was done using Excel programme. Analysis of variance of elemental concentrations within and between creeks and compartments, and tests of significance of the variations were done using Statistica programme.

4.0. RESULTS AND DISCUSSION

4.1. Physicochemical Parameters

Values for physicochemical parameters assessed are reported in Table 7 to 10.

Table 7. Mean and standard deviation ($\bar{x}\pm\delta$) values of physicochemical parameters in Mtwapa Creek (The means are the averages for three months hence n = 3).

Station	Temp (^{0}C)	Sal (‰)	Cond (ms)	pH	O_2 (mg/l)	Secchi (m)
T1	29.6±3.0	31.5±2.6	49.5±1.2	8.0±0.1	6.0±1.0	0.7±0.5
T2	29.5±2.1	32.6±2.4	50.2±1.3	8.1±0.3	6.1±0.9	1.0±0.3
T3	29.3±1.9	33.11±1.2	51.3±2.4	8.0±0.1	6.0±1.2	1.2±0.6
T4	29.7±2.8	32.7±3.3	50.7±3.1	8.0±0.2	6.0±1.1	1.1±0.4
T5	29.7±2.9	32.5±3.0	51.2±1.5	8.2±0.1	6.1±1.1	1.4±0.5
T6	29.2±2.6	33.6±1.7	51.4±0.6	8.4±0.1	6.2±1.1	2.1±0.9
T7	29.6±2.5	33.8±2.3	51.6±1.8	8.3±0.2	6.3±1.4	2.9±1.2
T8	29.3±3.0	33.7±1.2	51.6±0.4	8.4±0.1	6.6±1.2	3.2±1.0

Table 8. Mean and standard deviation ($\bar{x}\pm\delta$) values of physicochemical parameters in Port Reitz Creek (n = 3).

Station	Temp (^{0}C)	Sal (‰)	Cond (ms)	pH	O_2 (mg/l)	Secchi (m)
P1	25.8±1.7	33.1±1.1	51.3±1.2	8.2±0.3	5.3±2.1	0.9±1.3
P2	26.2±1.0	33.9±0.9	51.5±2.1	8.0±0.2	5.5±1.9	1.1±0.9
P3	27.1±2.2	34.1±0.8	51.7±1.0	8.0±0.2	6.1±1.5	1.6±1.2
P4	26.4±2.1	34.0±1.1	51.7±2.9	8.4±0.1	6.2±1.1	2.0±2.1
P5	26.1±1.1	34.2±0.6	51.9±1.4	8.1±0.5	6.5±1.7	2.3±1.4
P6	26.4±2.4	33.4±1.1	52.2±1.7	8.2±0.1	6.3±2.0	2.5±2.0
P7	26.5±1.0	34.4±0.3	52.0±2.0	8.1±0.2	6.6±1.4	2.9±1.4
P8	27.3±2.5	34.2±0.5	51.8±1.9	8.4±0.1	6.7±1.2	3.1±1.2
P9	26.5±2.2	34.3±0.8	52.1±0.8	8.5±0.2	6.0±1.2	2.6±2.3
P10	26.2±2.9	34.2±1.2	52.0±0.7	8.1±0.4	6.1±1.4	2.8±1.2
P11	26.9±2.6	34.5±0.6	51.9±1.3	8.4±0.1	6.4±1.8	1.9±1.5

Table 9. Mean and standard deviation ($\bar{x}\pm\delta$) values of physicochemical parameters in Makupa Creek (n = 3).

Station	Temp (^{0}C)	Sal (‰)	Cond (ms)	pH	O_2 (mg/l)	Secchi (m)
K1	26.3±1.5	34.2±0.1	51.4±1.0	8.0±10.7	5.6±1.4	0.9±0.2
K2	27.4±1.3	34.7±0.4	51.2±2.1	8.1±0.5	5.5±1.0	0.9±0.5
K3	26.8±2.4	34.3±0.5	52.1±1.1	8.7±0.1	5.7±2.0	0.9±0.4
K4	27.8±2.0	34.5±0.1	52.1±1.3	9.2±0.5	6.3±0.9	0.9±0.6
K5	26.8±1.2	34.5±0.4	52.2±1.6	8.4±0.6	6.1±1.1	1.1±0.3
K6	27.2±2.5	34.4±0.2	52.2±2.2	8.8±0.3	5.8±1.4	0.9±0.8
K7	27.2±1.5	34.4±0.5	52.0±3.1	8.7±0.2	6.2±1.5	1.3±0.4
K8	27.4±2.8	34.0±1.1	51.5±1.5	8.1±0.8	6.4±1.3	1.0±0.5
K9	27.6±1.9	34.0±0.8	51.6±2.4	8.1±0.5	6.0±2.1	1.2±0.6
K10	27.4±2.3	34.4±0.6	52.0±1.1	8.1±0.7	6.2±1.2	0.9±0.1
K11	28.8±1.1	34.3±0.3	51.8±1.0	8.0±0.6	6.1±1.3	1.4±0.2
K12	26.8±1.9	34.4±0.5	52.1±1.9	8.1±0.1	5.7±1.0	1.5±0.3
K13	27.3±2.4	34.5±0.1	52.2±0.8	8.2±0.3	6.2±1.6	2.3±0.8

Table 10. Mean and standard deviation ($\bar{x}\pm\delta$) values of physicochemical parameters in Shirazi Creek (n = 3).

Station	Temp (^{0}C)	Sal (‰)	Cond (ms)	pH	O_2 (mg/l)	Secchi (m)
S1	29.2±1.6	33.5±2.0	49.0±3.2	7.6±0.5	5.9±1.3	2.0±0.1
S2	29.6±2.0	33.7±1.8	49.0±4.8	7.9±0.2	6.1±1.8	2.3±0.6
S3	29.3±2.2	34.0±1.0	51.5±1.1	8.0±0.2	6.5±1.7	2.6±0.4
S4	29.9±2.0	34.5±2.0	50.0±2.1	8.0±0.3	5.6±0.7	2.0±0.5
S5	28.8±2.1	34.0±0.8	51.0±0.4	8.0±0.1	5.7±2.0	3.0±0.2
S6	29.7±1.4	34.0±0.4	50.4±1.3	8.2±0.2	6.0±1.2	3.5±0.8
S7	28.3±2.5	34.0±0.3	51.0±0.5	8.5±0.1	6.8±1.0	4.8±0.9

Standard deviations of values obtained for physicochemical parameters (Tables 11 to 14) indicate that there were no significant variations during the months sampled. Values depended on many factors such as what time of the day the sampling was done and the location of the station at which the parameters were taken. However, physicochemical parameters also depend on climatic conditions and the sites sampled fall

under the same climatic regime hence the lack of significant variations. In the East African Coast, there are two main seasons characterised by particular monsoon winds. The period between April and September is characterised by the South East Monsoons and is mainly the wet season. The period between October and March is characterised by the North East Monsoons, and is mainly the dry season. However, the precise timing and extent of each season varies annually (Grove *et al.*, 1985). Thus, proper assessment of the prevailing climatic conditions' effects on physicochemical parameters requires collection of data on monthly basis as well as on diurnal cycles.

4.2. Calibration Standards

Figures 8 to 11 show examples of calibration curves for Cu, Zn, Pb and Cd standards with different reagent matrices respectively. HNO_3 matrix refers to standards into which HNO_3, H_2SO_4, H_2O_2 and silicon antifoaming agent reagents were added. HCl matrix refers to standards into which HCl and H_2O_2 reagents were added while H_2O refers to standards into which no reagents were added. Added reagents were equal in amount to those that were used in the digestion processes as indicated in section 3.2.3.2 of materials and methods, for either sediments or the biological tissues. Sample matrix is everything in the unknown sample other than the substance being analysed. Large sample ionic strength, molecules with broad spectra absorbances or other interfering components make up the sample's matrix (Welz 1985). Matching the reagent matrices in the calibration standards with those used in the experimental samples helped counteract this effect. As shown in Figures 8 to 11, different acid matrices had varying effects of depression or enhancement on the sensitivity in various elemental concentration

determinations. This is because the interfering components on each element vary within the particular reagent matrices.

However, as indicated by the correlation coefficient(s) (R^2), which is a quantity that gives the quality of a least squares fitting to the original data, Beer-Lambert's law was obeyed in all cases. Beer's law states that, light absorption is directly proportional to the concentration of the absorbent medium and to the thickness of the sample traversed by the light. Lambert's law states that, the fraction of transmitted light by a transparent medium is independent of the incident light intensity. The combination of these two laws gives the Beer-Lambert's law which thus states that, the measurement of absorbance gives an absolute measurement of the transparency of the medium with respect to the wavelength (Welz, 1985).

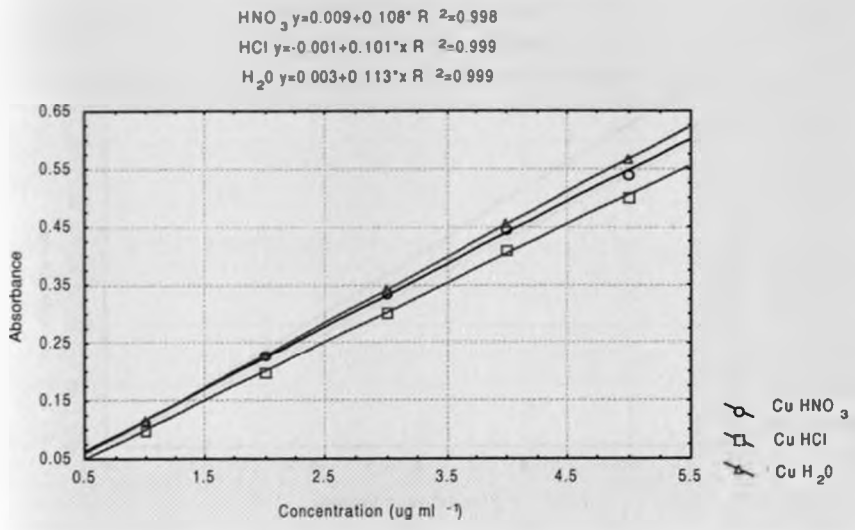


Figure 8. Calibration curves for copper standards containing different reagent matrices

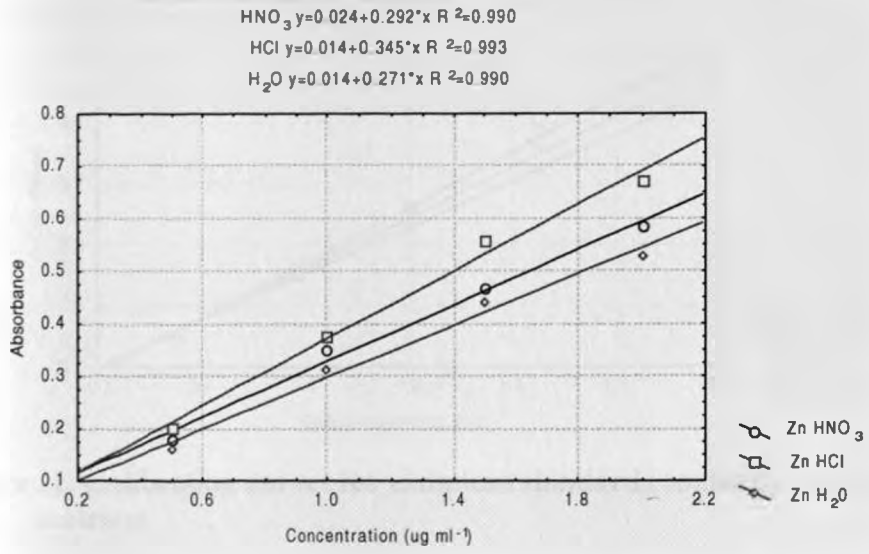


Figure 9. Calibration curves for zinc standards containing different reagent matrices

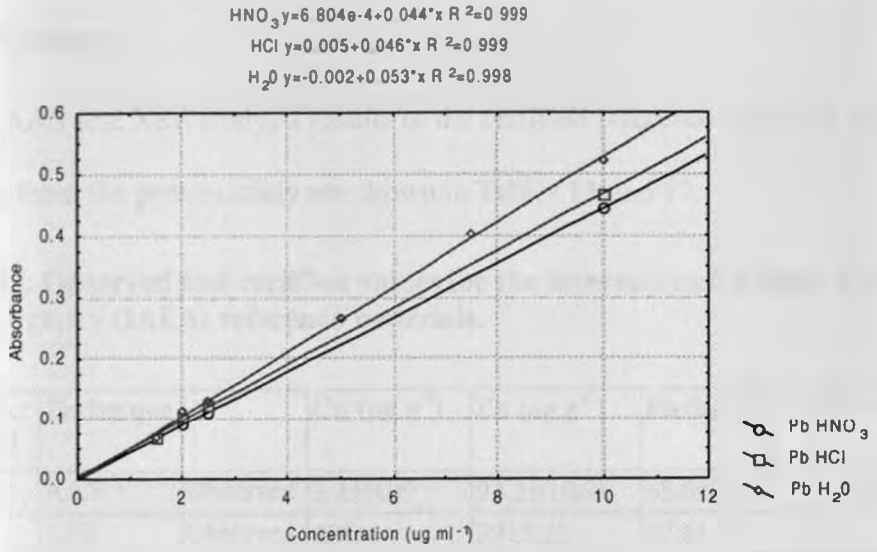


Figure 10. Calibration curves for lead standards containing different reagent matrices

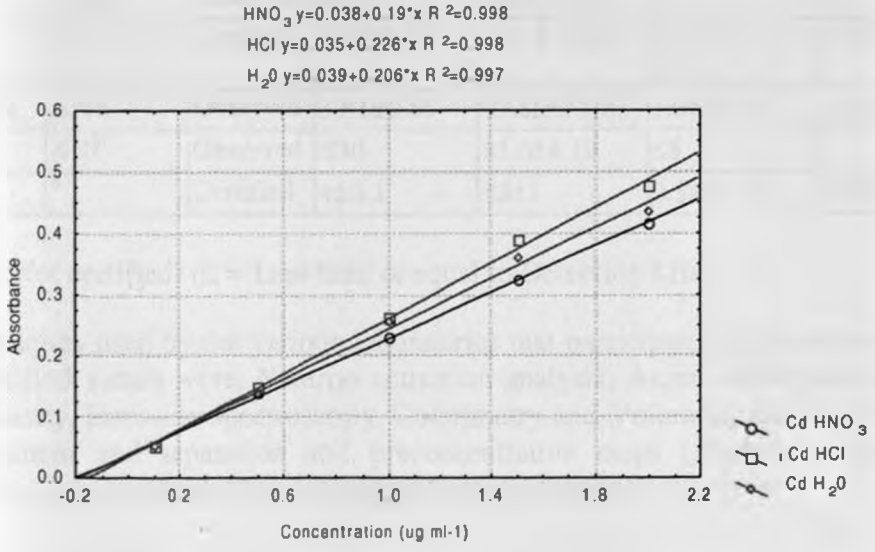


Figure 11. Calibration curves for cadmium standards containing different reagent matrices

4.3. Evaluation of the Analytical Procedure

4.3.1. Accuracy

AAS and XRF analysis results of the certified reference materials and some other samples from the present study are shown in Tables 11 and 12.

Table 11. Observed and certified values for the International Atomic Energy Agency (IAEA) reference materials.

Reference Material	Technique		Cu (μg g^{-1})	Zn (μg g^{-1})	Pb (μg g^{-1})	Cd (μg g^{-1})
Soil-7	AAS	Observed	9.4±0.09	92.2±0.063	65.6±0.04	2.3±0.05
	XRF	Observed	≤30	99±5.28	67.6±1.7	
	*	Certified	9-13	101-113	55-71	1.1-2.7 (N.C)
MA-M-2	AAS	Observed	8.08±1.24	142.33±1.89	1.15±0.10	1.27±0.03
	XRF	Observed	≤30	150.7±3.6	≤5	
	*	Certified	7.53-8.44	152.8-166.7	1.53-2.5 (N.C)	1.16-1.54
MA-A-2	AAS	Observed	3.81±0.56	32.85±1.02	1.04±0.91	0.054±0.08
	XRF	Observed	≤30	31.6±4.19	≤5	
	*	Certified	4±0.1	33±1	0.58±0.07	0.066±0.004

(N.C = Not certified) (≤ = Less than or equal to Detection Limit)

* Techniques used by the various laboratories that participated in the intercomparison of the certified values were, Neutron activation analysis, Atomic absorption spectrometry, Fluorimetry, Emission spectroscopy, Colorimetry and Volumetry with or without sample pretreatment and separation and preconcentration steps (Analytical Quality Control Services - International Atomic Energy Agency, Austria)

Accuracy is the degree of conformity of a measure to a standard or a true value. Table 11 shows that values obtained through the employed methodology were comparable to the certified values.

4.3.2. Precision

4.3.2.1 Comparative analysis of samples using AAS and XRF techniques

Table 12. Comparative analysis of samples using AAS and XRF techniques

Site	Technique	Sample	Cu (μg g^{-1})	Zn (μg g^{-1})	Pb (μg g^{-1})	Cd (μg g^{-1})
Makupa	AAS	KU1	116.4±0.08	3199.5±2.60	111.2±0.18	46.9±0.93
	XRF	KU1	125.2±9.32	3213.9±20.74	108.5±4.41	
	AAS	KU12	49.7±0.82	336.0±1.71	65.5±1.03	64.2±0.44
	XRF	KU12	52.5±5.42	352.3±6.29	65.9±2.13	
Mtwapa	AAS	TJ4c	28.1±0.25	49.5±0.53	34.1±0.70	0.90±0.02
	XRF	TJ4c	30±6.91	53±12.21	46.9±9.16	
	AAS	TJ6a	81.6±1.39	73.2±0.94	68.8±1.90	0.58±0.06
	XRF	TJ6a	72.5±8.70	82.1±9.42	77±3.67	
Port Reitz	AAS	PM10a	31.7±0.59	89.2±1.24	46.8±0.97	2.0±1.27
	XRF	PM10a	40.7±6.96	106.4±11.30	53.8±8.54	
	AAS	PM11c	46.2±0.08	90.1±0.57	67.4±2.32	1.89±0.73
	XRF	PM11c	42.8.1±3.38	121.4±12.01	70.1±8.60	
Shirazi	AAS	SU1b	9.9±1.04	23.01±0.46	13.3±0.17	0.9±0.09
	XRF	SU1b	≤25	27.9±0.85	17±2.28	
	AAS	SM6c	7.1±0.15	17.2±0.92	38.0±1.23	3.5±0.69
	XRF	SM6c	≤25	20.5±0.34	41.3±4.19	

(≤ = Less than or equal to Detection Limit)

Results obtained in Table 11 and 12 further show that the two techniques were in close agreement with each other. Cadmium could not be analysed with the XRF equipment (Canberra, Detector Model SL80175) that was used because the primary X-ray excitation source was radioactive ^{109}Cd.

Figures 12 to 15 shows spectra of sediment samples from Makupa, Shirazi, Mtwapa and Port Reitz Creeks respectively. The Shirazi Creek sample spectra (Figure 13) shows that some elements particularly copper, zinc and lead are orders of magnitude less in that creek as compared to the other creeks. This is in agreement with the hypothesis of the present study that, Shirazi Creek is less influenced by potential pollutants of anthropogenic activity origin.

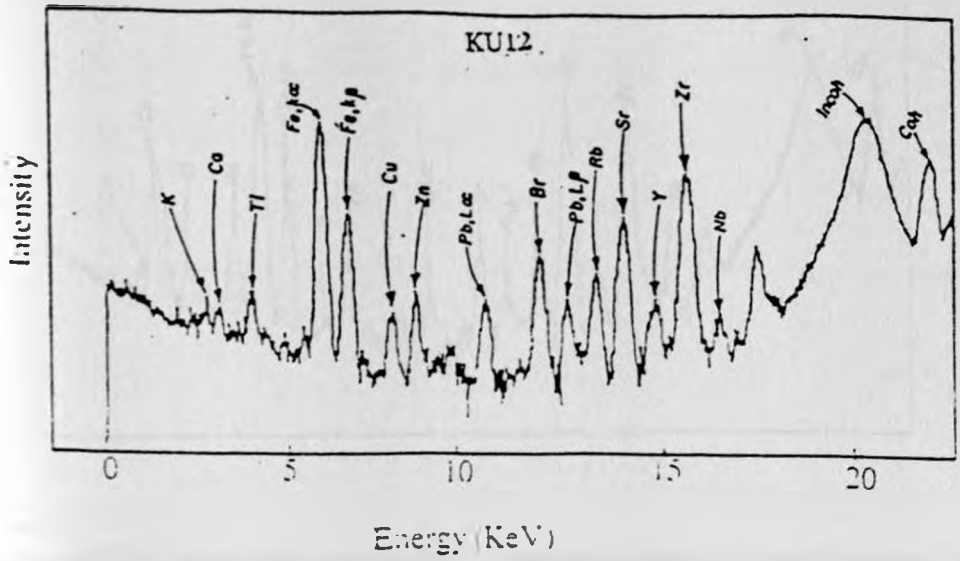


Figure 12 XRF elemental spectrum of a sediment sample from Makupa Creek

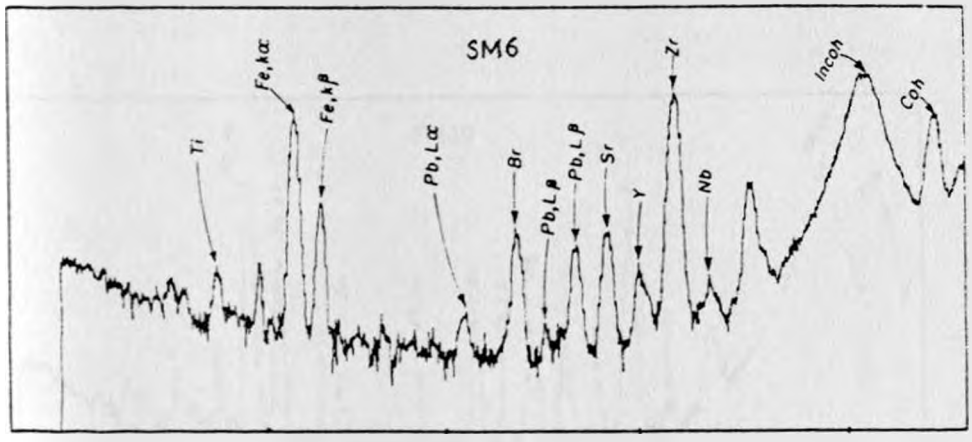


Figure 13 XRF elemental spectrum of a sediment sample from ShiraziCreek

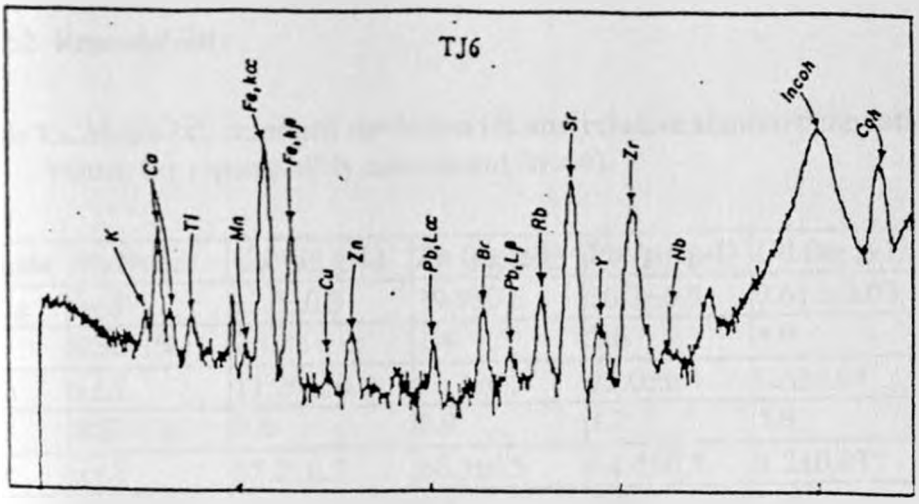


Figure 14 XRF elemental spectrum of a sediment sample from Mtwapa Creek

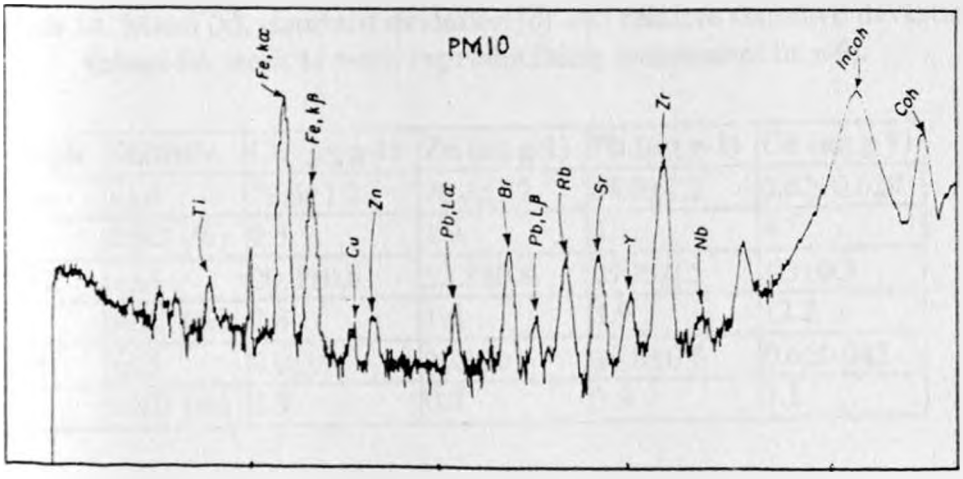


Figure 15 XRF elemental spectrum of a sediment sample from Port Reitz Creek

4.3.2.2. Repeatability

Table 13. Mean ($\bar{x}$), standard deviation (δ) and relative standard deviation (RSD) values for repeatability assessment (n = 6).

Sample	Statistic	Cu (µg g-1)	Zn (µg g-1)	Pb (µg g-1)	Cd (µg g-1)
PM1a	$\bar{x}\pm\delta$	13.3±0.3	39.9±0.6	20.3±0.5	0.613±0.03
	RSD (%)	2.1	1.4	2.6	4.9
SJ2a	$\bar{x}\pm\delta$	11.296±0.4	22.2±0.2	22.0±0.4	0.6±0.04
	RSD (%)	3.6	0.9	1.7	5.9
TJ5c	$\bar{x}\pm\delta$	35.2±0.5	66.3±0.5	64.4±0.5	1.2±0.03
	RSD (%)	1.3	0.8	0.8	2.1
SPg2 (Fish)	$\bar{x}\pm\delta$	0.209±0.014	2.91±0.157	1.02±0.047	0.107±0.008
	RSD (%)	6.5	5.4	4.6	7.683
SEp2 (Fish)	$\bar{x}\pm\delta$	0.199±0.009	2.79±0.2	1.25±0.044	0.244±0.014
	RSD (%)	4.3	5.7	3.5	5.6

4.3.2.3. Week to Week Reproducibility

Table 14. Mean ($\bar{x}$), standard deviation (δ) and relative standard deviation (RSD) values for week to week reproducibility assessment (n = 6).

Sample	Statistic	Cu (µg g-1)	Zn (µg g-1)	Pb (µg g-1)	Cd (µg g-1)
TJ6a	$\bar{x}\pm\delta$	79.3±1.2	70.3±1.3	69.9±1.2	0.67±0.029
	RSD (%)	1.5	1.9	1.7	4.7
PM2c	$\bar{x}\pm\delta$	20.3±0.6	52.8±0.8	27.7±0.5	1.3±0.3
	RSD (%)	2.8	1.6	1.9	12.2
SJ2b	$\bar{x}\pm\delta$	9.9±0.4	20.1±0.1	14.8±0.6	0.6±0.042
	RSD (%)	3.9	0.7	3.9	7.1

The performance of a test may be described in terms of its accuracy and precision. An accurate test correctly reflects the true status of the sample, on average. An accurate test may or may not have good precision. A precise test provides consistent, repeatable

results. Unfortunately, those results may or may not be accurate. Tests can be consistently, repeatedly, and precisely, wrong.

The repeatability of a test may therefore be viewed as its ability to agree with itself. In some situations, we may be interested not only in a test's agreement with itself, but also agreement between test systems. Thus, repeatability is within time test of precision whereas reproducibility is between time test of precision. The results obtained in Tables 13 and 14 show that elemental values obtained within and between time were in close agreement with each other.

4.4. Sediments

4.4.1. Mtwapa Creek Sediments

The spatial distribution of copper, zinc, lead and cadmium in Mtwapa Creek sediments are shown in Figures 16 to 19 respectively.

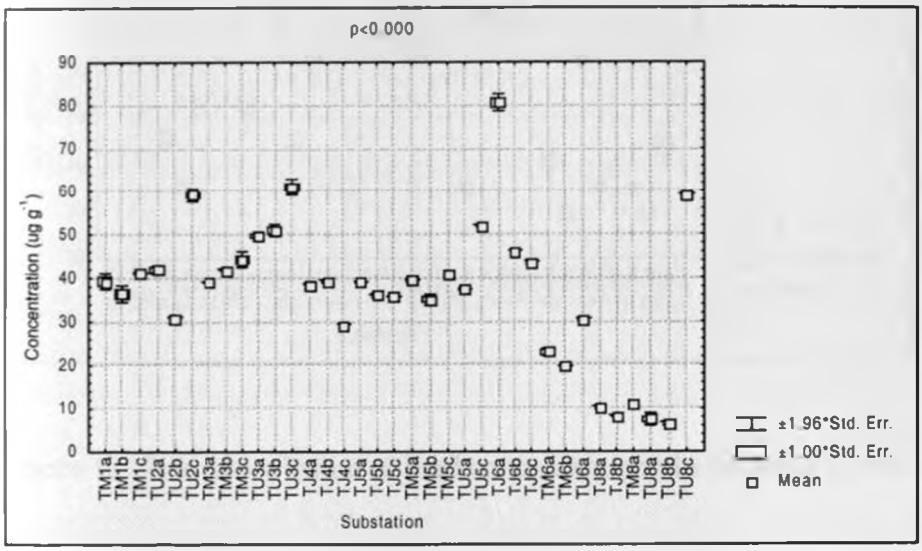


Figure 16. Spatial variation of copper concentrations in Mtwapa Creek sediments

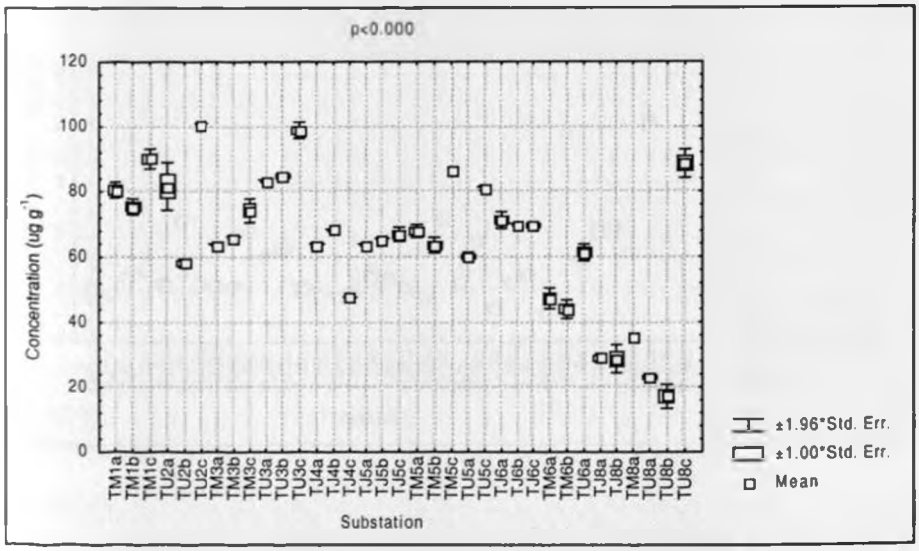


Figure 17. Spatial variation of zinc concentrations in Mtwapa Creek sediments

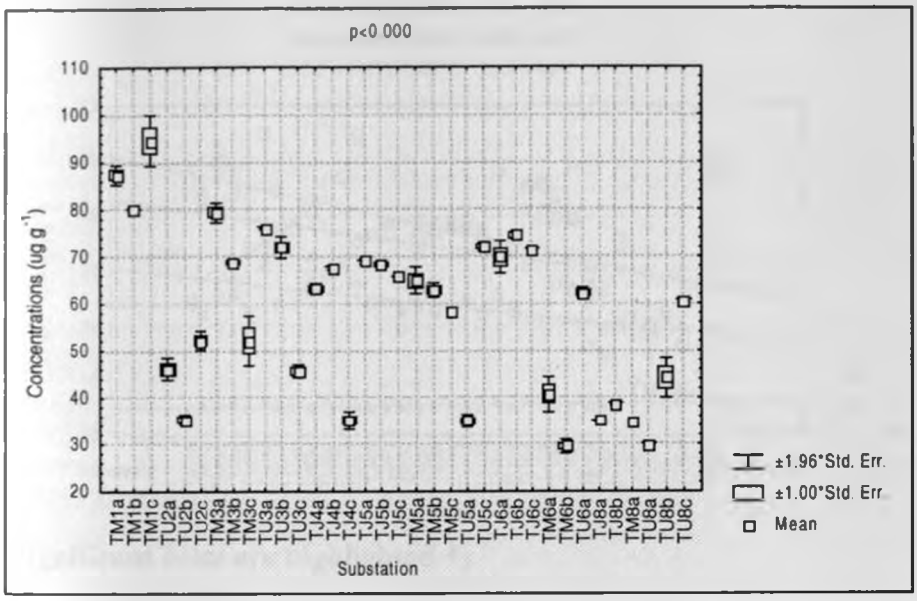


Figure 18. Spatial variation of lead concentrations in Mtwapa Creek sediments

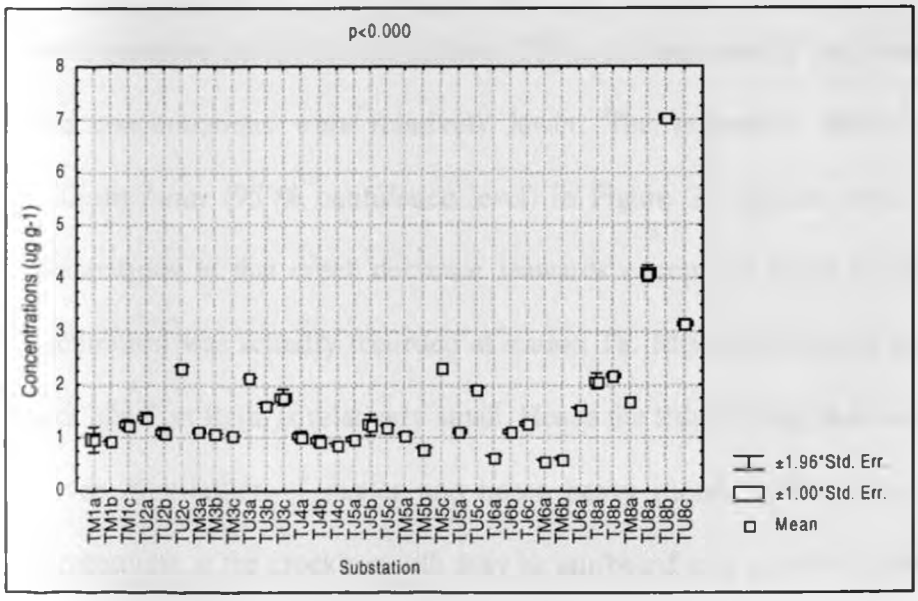
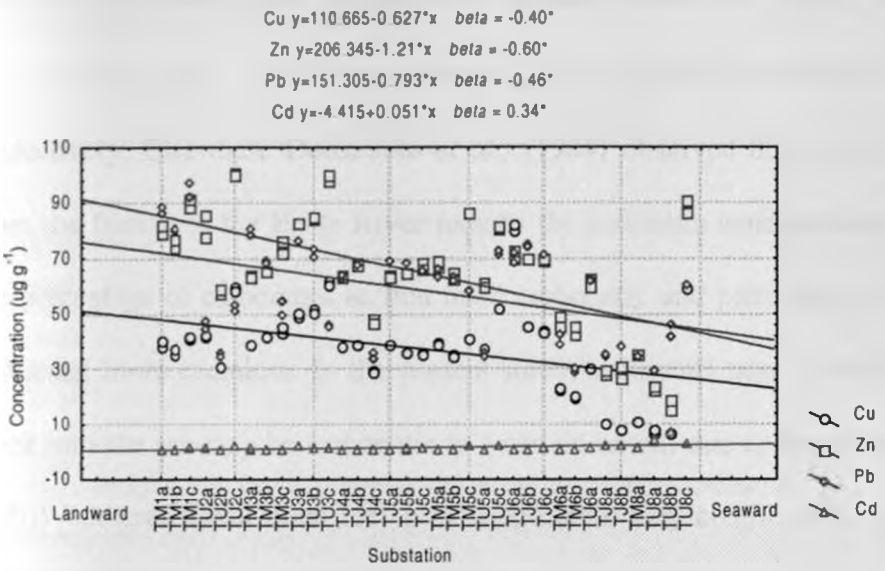


Figure 19. Spatial variation of cadmium concentrations in Mtwapa Creek sediments



(Significant *betas* are highlighted *)

Figure 20. Landward-seaward elemental concentration trends in Mtwapa Creek sediments

The elemental concentrations seemed relatively evenly distributed along the stations sampled except for the station (T8) at the entrance of the creek into the ocean where concentrations were relatively lower. The regression trends as indicated by significant *betas* (95 % confidence level) in Figure 20 indicate that indeed elemental concentrations in that creek decrease seawards except for those of Cd whose highest concentration was actually recorded at station T8. Mtwapa Creek as compared to other creeks like Port Reitz is relatively small. Hence the tidal mixing may be enough to cause the even distribution of matter and hence heavy metals within the creek. The lower concentrations at the creek's mouth may be attributed to a possible dilution effect at that point.

Trends of seaward increase in cadmium concentrations have been observed in previous studies on the Kenyan coast. For instance Everaarts and Nieuwenhuize (1995)

observed that mean copper and cadmium increased from 5 to 30 μg g^{-1} dry wt and from 0.01 to 0.34 μg g^{-1} in shallow coastal (±20 m) to deep-sea stations (±200 m depth) respectively. Elsewhere Donazzolo *et al.*, (1984) observed that, in the area extending from the Isonzo to the Piave River mouths the cadmium concentrations increased with the percentage of carbonates so that more carbonatic and particularly calcitic sediments contained more cadmium. In the present study, sediments near the entrance of Mtwapa creek into the sea may be carbonatic to a certain extent due to the influence of the coral reef. Weathered fossil coral reef plus dead corals may contribute to the formations of carbonatic sediments, since during growth, coral polyps develop an external skeleton of calcium carbonate that surrounds and protects their soft bodies. Also coralline algae which contributes to coral reef formation by growing among the corals and cementing them together, contains large amounts of calcium carbonate. However, sediment characterisation studies in this creek among others on the Kenyan coast are warranted before conclusive remarks can be made on the same.

Another exception in Mtwapa Creek was station T7 (See Table 15) at which relatively higher zinc and cadmium concentrations were recorded in comparison to concentrations observed in other stations. This station was near the Marina hotel, a place where a number of boats and small ships are moored. The contribution of such human activities to elemental influxes may not be ruled out. Lead and copper concentrations from this station were within the ranges observed elsewhere within that Creek.

In this creek, elemental concentrations especially copper and zinc in samples taken from the substations (For instance, TM1c, TUc, TM3c, TU3c TM5c TU5c and TU8c) at the centre of the creek generally showed higher concentrations than those in samples

collected from the shoreline substations (The ones whose labels end with suffix a or b). This may be an indication that there is transport of matter and particularly heavy metals along the creek causing the build up at its centre. The lack of detailed sediment dynamics data for Mtwapa creek is certainly a limitation towards understanding such a phenomenon.

4.4.2. Makupa Creek Sediments

Figures 21 to 24 illustrate the spatial variation of copper, zinc, lead and cadmium in Makupa Creek sediments respectively.

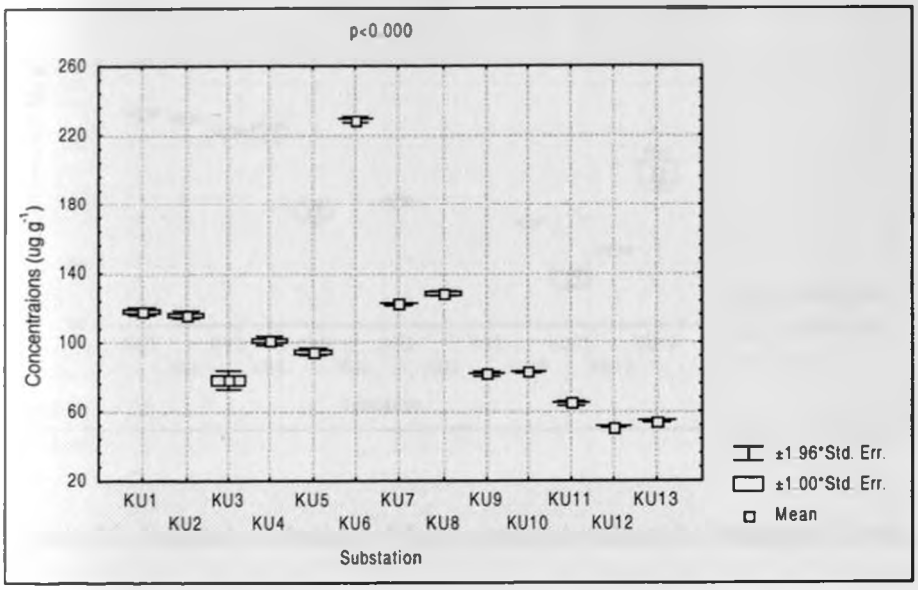


Figure 21. Spatial variation of copper concentrations in Makupa Creek sediments

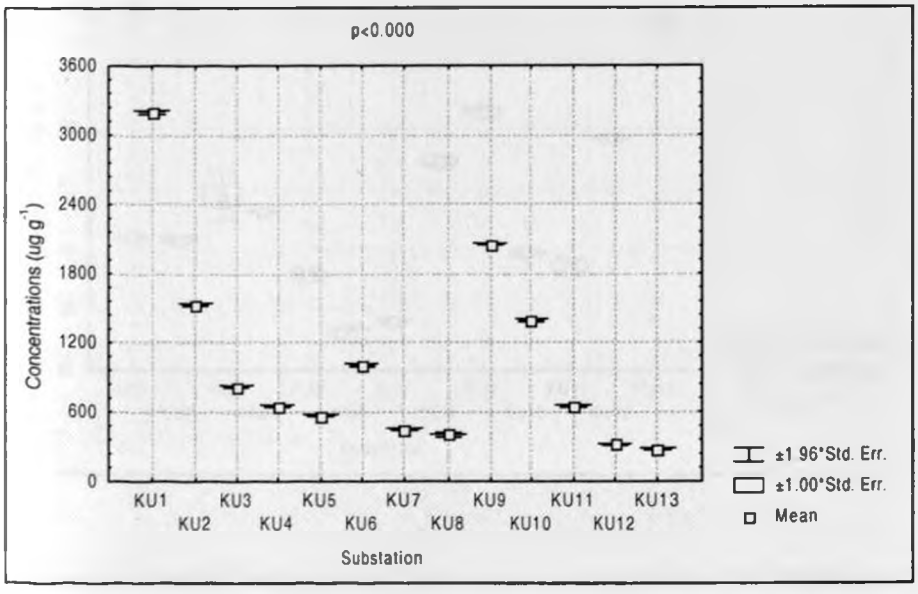


Figure 22. Spatial variation of zinc concentrations in Makupa Creek sediments

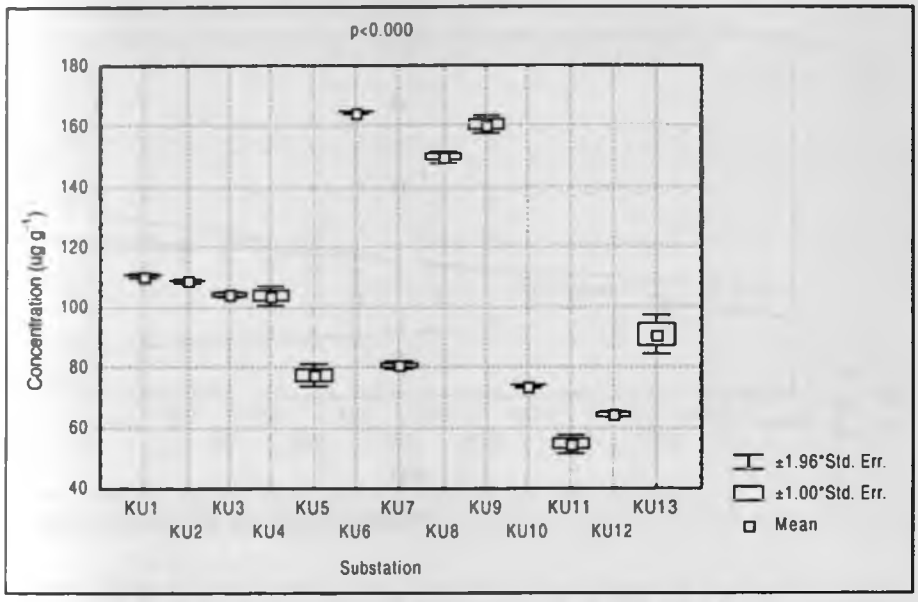


Figure 23. Spatial variation of lead concentrations in Makupa Creek sediments

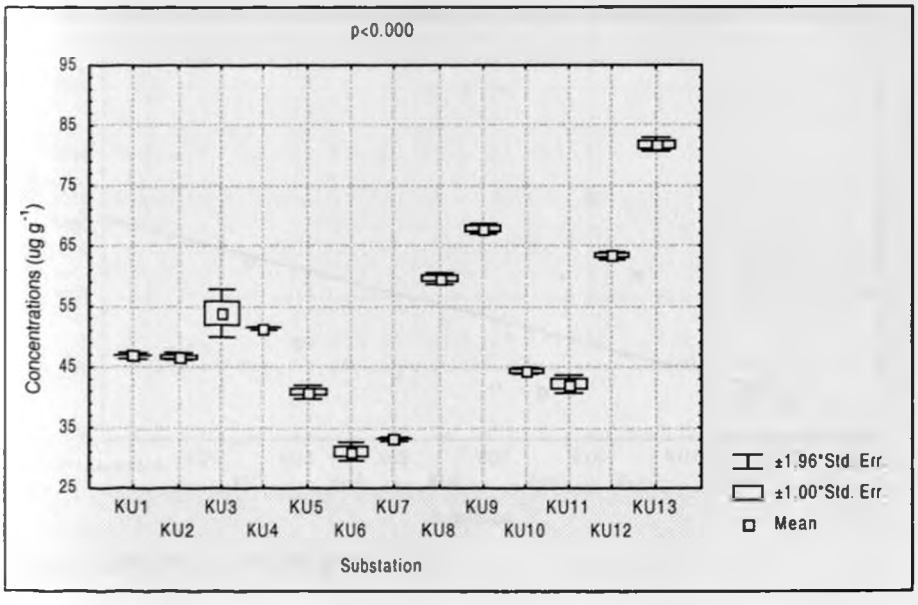
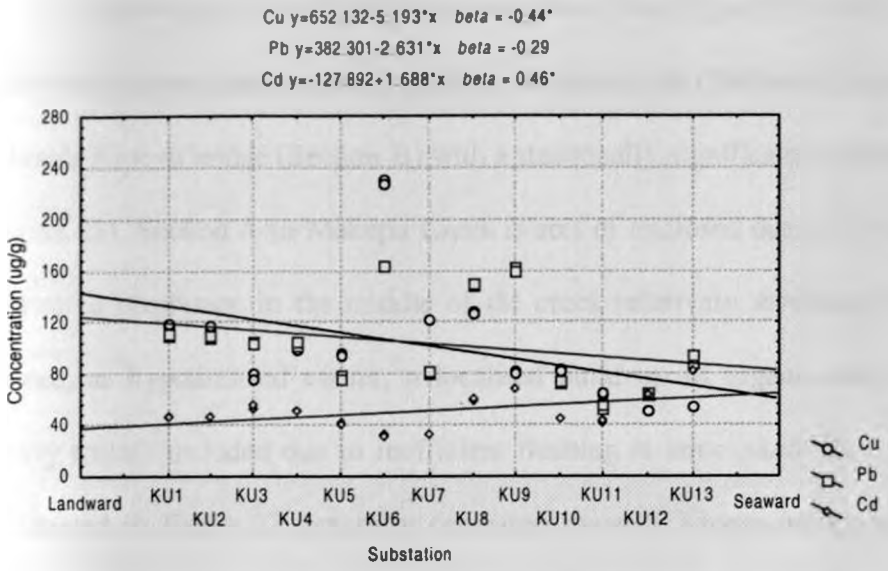
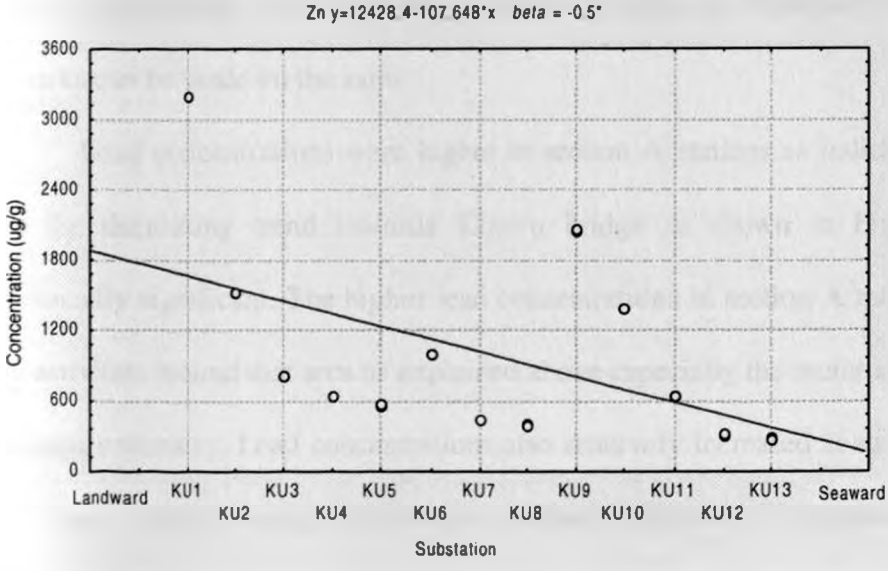


Figure 24. Spatial variation of cadmium concentrations in Makupa Creek sediments



(Significant *betas* are highlighted*)

Figure 25. Landward-seaward elemental (Cu, Pb and Cd) concentration trends in Makupa Creek sediments



(Significant *beta* is highlighted *)

Figure 26. Landward-seaward zinc concentration trend in Makupa Creek sediments

In Makupa Creek, copper concentrations (See Figure 21) were higher in stations near the Makupa causeway and Kibarani dumping site (Section A) as opposed to those towards Kipevu bridge (Section B) with a statistically significant regression gradient (See Figure 25). Section A in Makupa Creek is sort of enclosed due to the presence of some terrestrial protrusion in the middle of the creek relatively separating the two sections. Hence, as hypothesised earlier, a localised build up of organic and inorganic matter, heavy metals included due to inefficient flushing is anticipated. Zinc concentrations as illustrated in Figure 22 generally decreased towards Kipevu bridge with a statistically significant regression gradient (Figure 26). However, the trend was interrupted at stations KU9 and KU10 where zinc concentrations relatively increased. There are effluent outfalls from some of the industries along this creek. These may be composed of substances that may cause the increased zinc concentrations. However, specific investigations into the actual compositions of those, among other effluents is important before conclusive remarks can be made on the same.

Lead concentrations were higher in section A stations as indicated in Figure 23, but the decreasing trend towards Kipevu bridge as shown in Figure 25 was not statistically significant. The higher lead concentrations in section A may be attributed to the activities around that area as explained above especially the motor activities along the Makupa causeway. Lead concentrations also relatively increased at station KU13 which was near Kipevu bridge. Again yet another indication of possible motor activity influence. Previous research, done by Nyatebe (1990) and Onyari *et al.,* (1991) have shown that roadside soils contain higher levels of lead.

Cadmium concentrations increased towards Kipevu bridge as shown in Figure 24, with a statistically significant regression gradient (Figure 25). This trend may be attributed to a number of factors. Around stations KU8 and KU9 there are effluent pipes whose source is attributable to nearby oil storage facilities among other industries. At station KU12 there is yet another effluent outfall emanating from a nearby power station. In general, it should however be noted that further research work is necessary in order to identify the exact source of the effluents. The constituents of the effluents at the fallout point should be assessed and correlated with the constituents of the production process effluents as well as solid wastes from suspect industries. The shoreline along the above mentioned stations is covered by a layer of black substance, indicating probable presence of oil in the effluents deposited into that creek. Though further investigation is needed on the specific sources and actual components of those effluents, their contribution to the elevated levels of cadmium among other elements may not be ruled out. Cadmium concentration in this creek was highest at station KU13 which was near Kipevu bridge.

Inputs of cadmium to the environment are from a variety of often diffuse sources. For example, the wear of automobile tyres contain 20-90 ppm, the impurity in the zinc oxide used as a curing accelerator is yet another source, phosphate rock may contain 100 ppm, cadmium and phosphate fertilizers are also a potential source, coal contains 0.25-5.0 ppm and heating oils average 0.3 ppm cadmium while sewage sludge contains up to 30 ppm cadmium (Clark, 1986). At station KU 13 there is a likely input of cadmium from the automobile tyre wear especially due to the heavy traffic in and out of the Kilindini Port. On the western side of Mombasa Island near Kipevu bridge there is one of the

sewage outfalls from the Island. This is yet another possible source of elevated cadmium at that point.

4.4.3. Port Reitz Creek Sediments

The distribution of copper, zinc, lead and cadmium in Port Reitz Creek sediments is given in Figures 27 to 30 respectively.

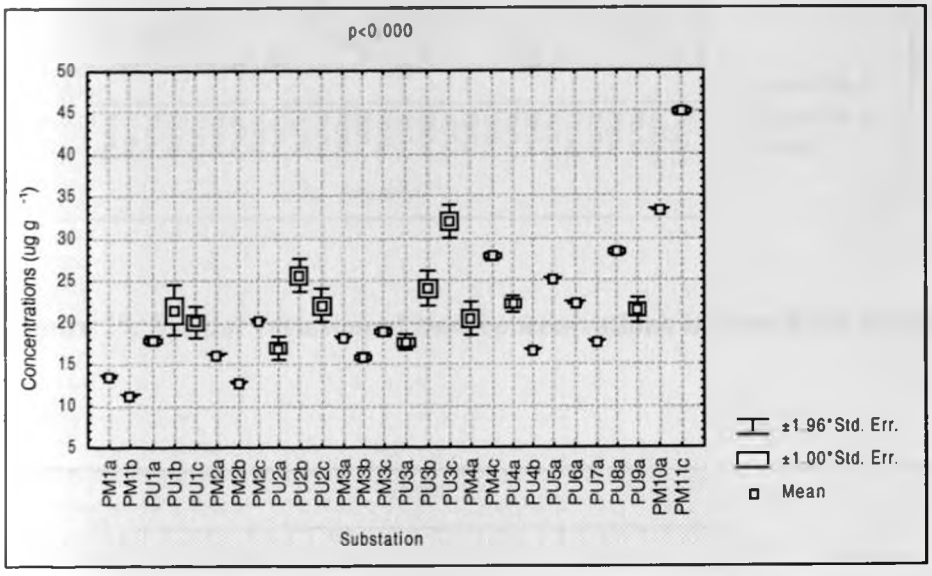


Figure 27. Spatial variation of copper concentrations in Port Reitz Creek sediments

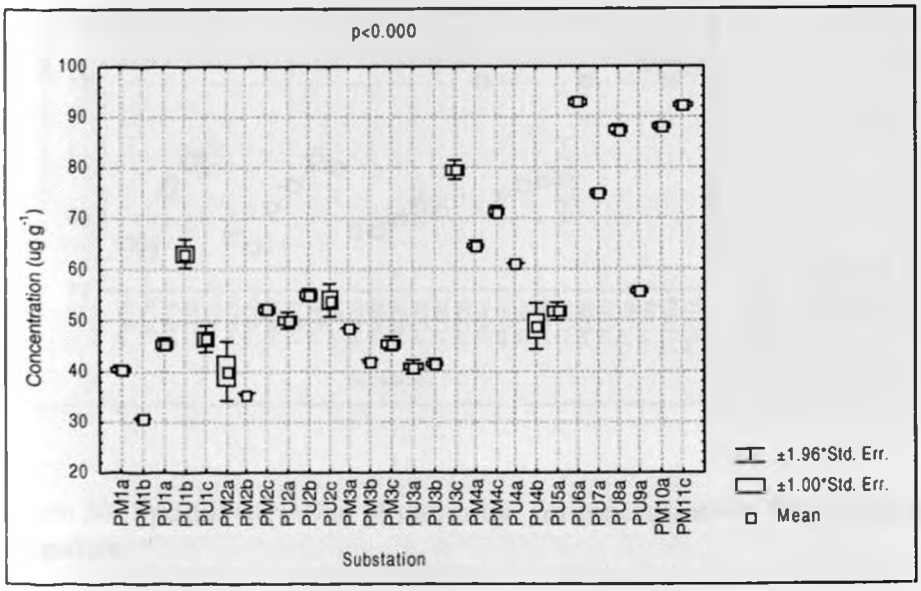


Figure 28. Spatial variation of zinc concentrations in Port Reitz Creek sediments

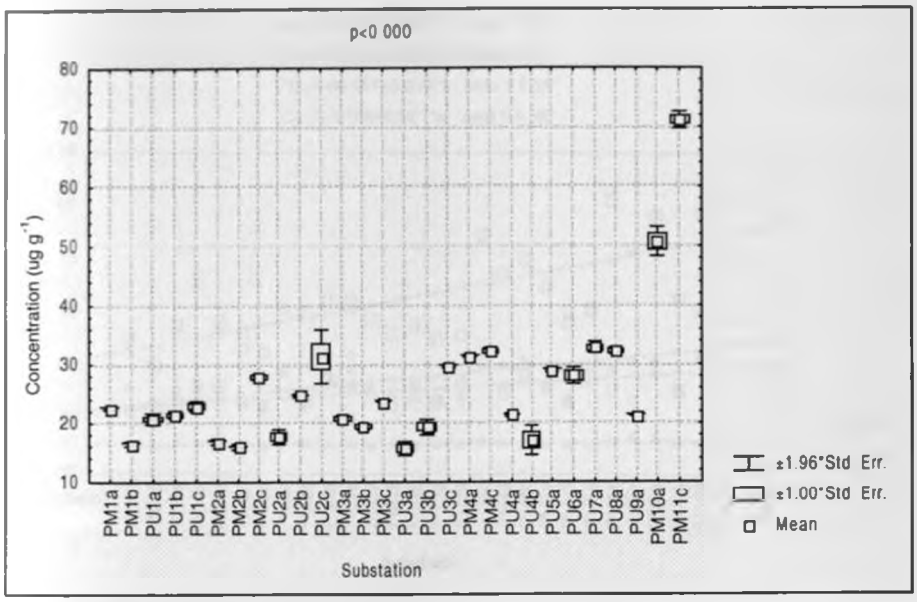


Figure 29. Spatial variation of lead concentrations in Port Reitz Creek sediments

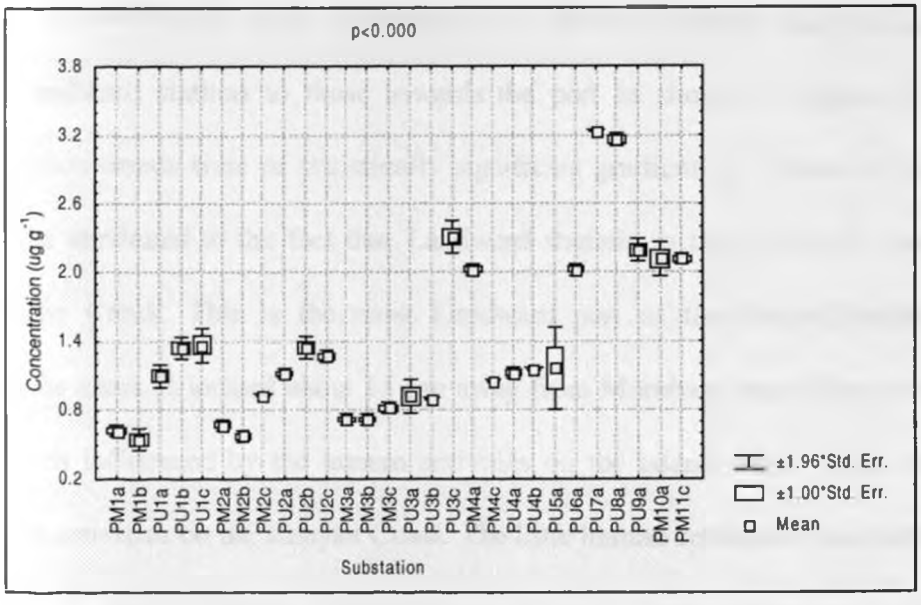
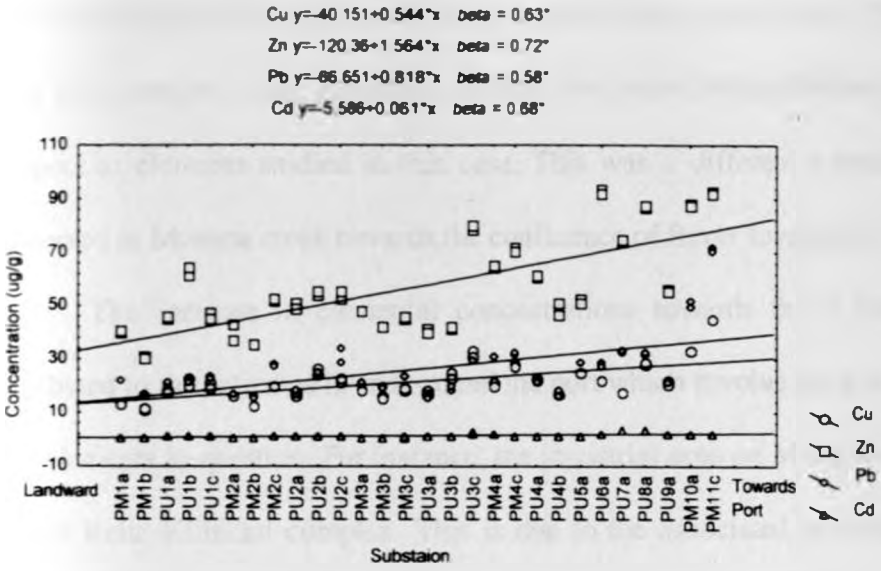


Figure 30. Spatial variation of cadmium concentrations in Port Reitz Creek sediments



(Significant *betas* are highlighted *)

Figure 31. Landward-seaward elemental concentration trends in Port Reitz Creek sediments

In Port Reitz Creek, concentrations of the four elements analysed increased from the Landward stations to those towards the port as shown in Figures 27 to 30. The regression trends were of statistically significant gradients as shown in Figure 31. This may be attributed to the fact that Landward stations in this case were basically within Mwache Creek. This is the most Landward part of the Reitz-Kilindini complexes. Mwache creek is located about 15 km away from Mombasa town. Hence this part is not so much influenced by the human activities on the island which is the centre of most human activities on the Kenyan Coast. The little human settlements and activities around this creek, and its riparian catchment area do not yet have pronounced influence on the creek. For instance by the time this study was carried out there was only one outboard engine powered boat ferrying the Sunza villagers from their village to the Miritini Jetty. In addition there seems to be no obvious inputs of the elements analysed from Mwache

River which enters Mwache creek at the creeks furthest point inland. This is an indication that the activities in the catchment of that river have little influence on the creek with respect to elements studied in this case. This was a different scenario from what was observed in Mtwapa creek towards the confluence of River Lwandani.

The increase in elemental concentrations towards the Kilindini Port may be attributed to the activities in and around the port which involve the use of and emission of the elements in question. For instance, the industrial area on Mombasa Island is adjacent to the Reitz-Kilindini complex. This is due to the associated advantages of having for instance warehouses near the port or having industries where there is easy access of imported raw materials among other goods. The increased elemental concentrations are partly attributable to port activities such as loading and offloading of various goods, cleaning, ballasting, maintenance practices such as painting, antifouling applications and fuelling, among others. For instance, copper is used in electrical equipment, alloys, anti-fouling paint for ships' hull, as an algaecide and as a wood preservative among other uses. According to Clark (1986) the anti-fouling paint releases all its copper into the sea, and some paints contain 500 g L^{-1} of copper. Zinc, despite being ubiquitous in nature is used in form of zinc oxide in paint formulations among other applications. Lead in its metallic form is generally used in the battery casings and plates among other applications. Tetraethyl lead has for a long time been used as a petrol additive thus, use of leaded gasoline in ships and boats as well as spillage during shipment may contribute to the increasing lead concentrations in the port.

Increasing levels of cadmium towards the port may also be attributed to its uses. Cadmium occurs together with zinc in nature, and thus certain zinc ores may contain

about 5 % cadmium (WHO 1987). In addition, Stubbs (1982) observed that 95 % of primary cadmium is obtained from zinc production and hence deduced that it is the level of production of zinc and not the demand for cadmium that governs the supply of cadmium. Besides, cadmium compounds are used in areas such as electroplating of metals, as pigments or stabilisers in plastics, in alkaline batteries and in alloys with other metals such as copper. It follows then that, uses of the other elements (particularly Zn and Cu) as explained earlier would consequently contribute to increased levels of cadmium in the environment in this case Port Reitz creek basin.

However, the sources of these elements are diffuse and their fates not specific. Hence further investigations on these among other aspects would be indispensable in understanding such phenomena as observed in this study.

4.4.4. Shirazi Creek Sediments

The spatial distribution of copper, zinc, lead and cadmium in Shirazi Creek sediments is provided in Figures 32 to 35

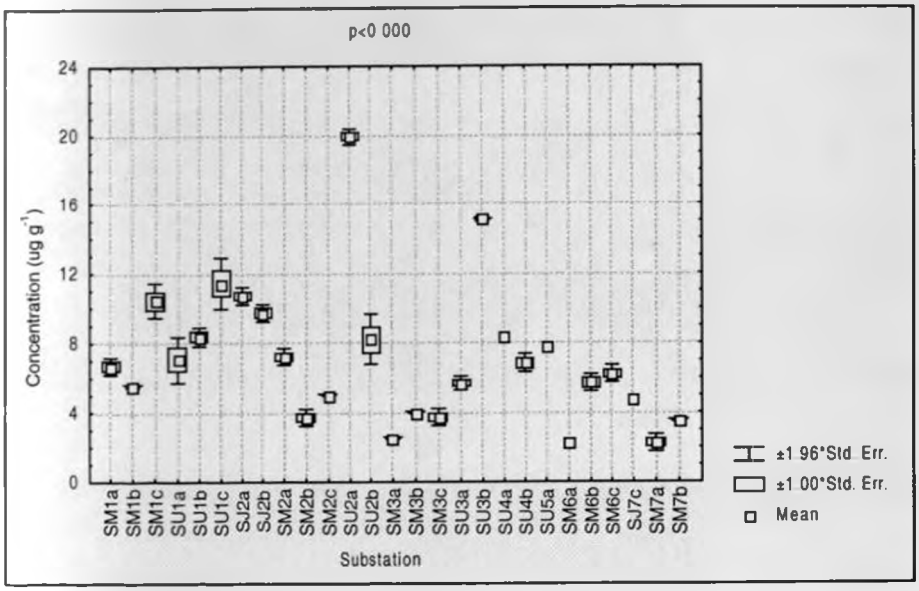


Figure 32. Spatial variation of copper concentrations in Shirazi Creek sediments

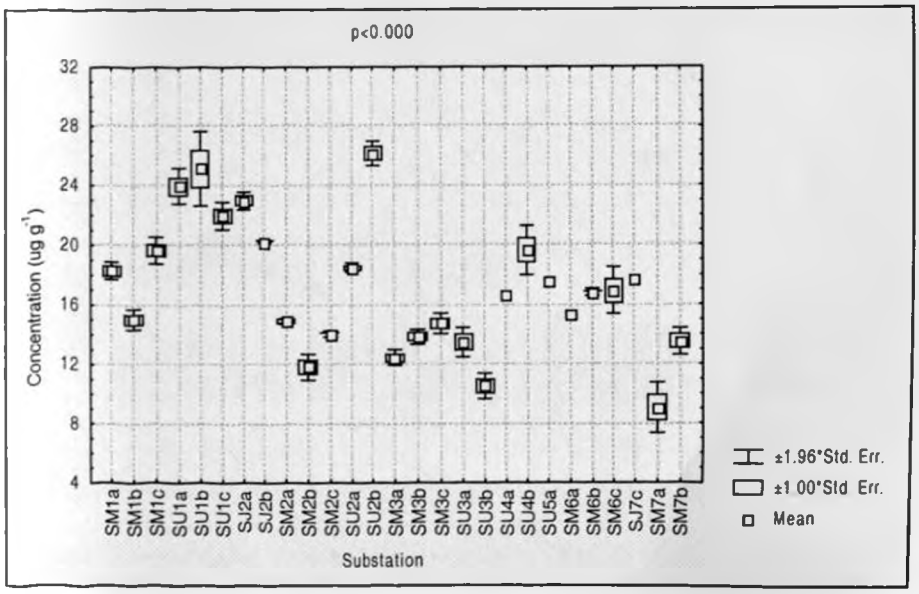


Figure 33. Spatial variation of zinc concentrations in Shirazi Creek sediments

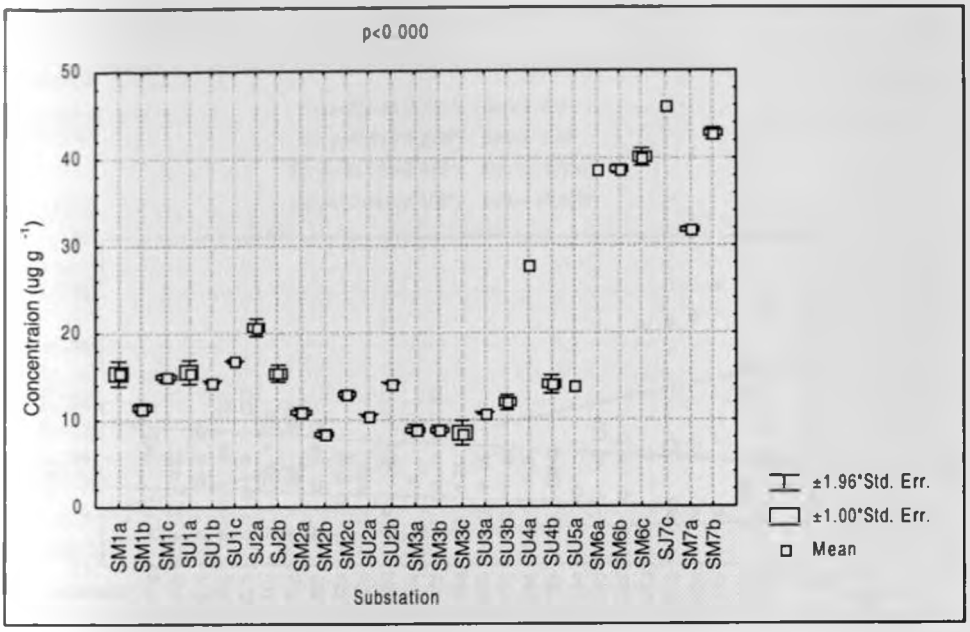


Figure 34. Spatial variation of lead concentrations in Shirazi Creek sediments

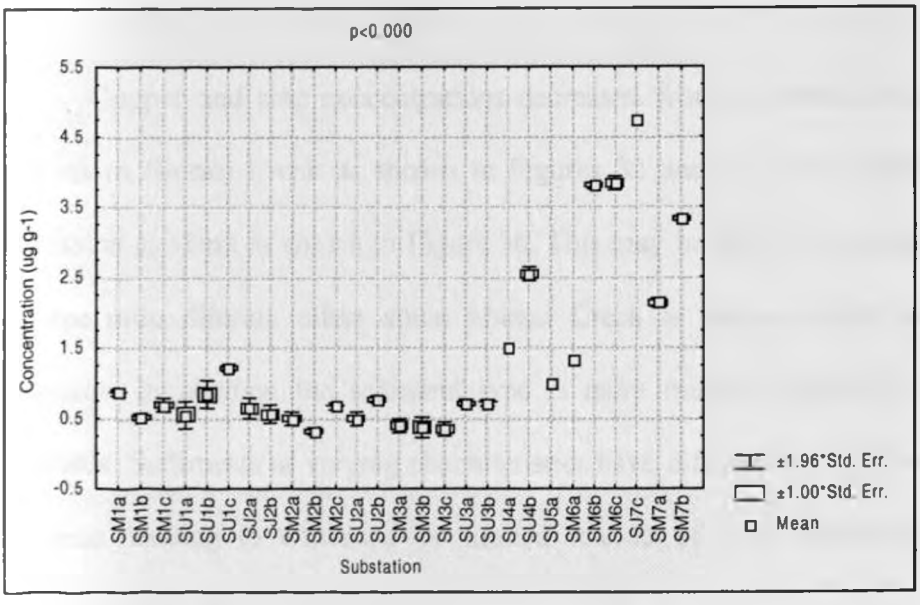
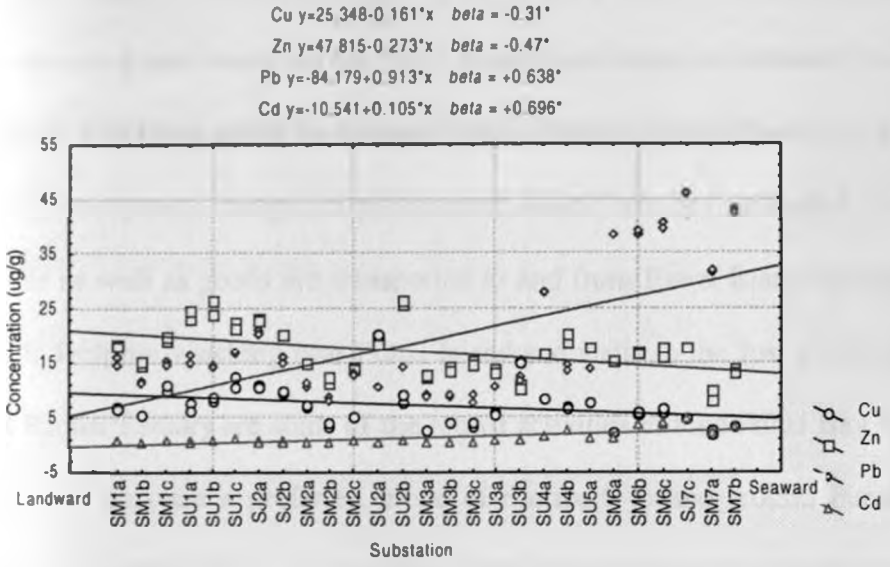


Figure 35. Spatial variation of cadmium concentrations in Shirazi Creek sediments



(Significant *betas* are highlighted *)

Figure 36. Landward-seaward elemental concentration trends in Shirazi Creek sediments

Copper and zinc concentrations decreased from Landward stations to seaward stations in Shirazi Creek as shown in Figures 32 and 33 with statistically significant regression gradient as shown in Figure 36. This may be due to a possible surface area to volume ratio dilution effect since Shirazi Creek is narrow inland and broadens up seawards. In addition the sediment type is more muddy Landward and more sandy seawards. Sediments of varying characteristics have different interactions with particular elements leading to enhanced or limited release of those elements. Shirazi Creek sediments may not be exempted from this, though the lack of sedimentology studies in that creek limits the understanding of the observed phenomenon.

Lead and cadmium concentrations increased seawards as shown in Figures 34 and 35 with significant regression gradients as illustrated in Figure 36. Funzi bay and its

associated creeks have been considered less influenced by human activities due to their location which is relatively further away from major human settlements. Tourism activities in Funzi Island are not yet at an advanced stage as compared to other areas such as Nyali and Diani along the Kenyan Coast. However, the influence of tourism activities on that ecosystem, though not pronounced, should not be overlooked. Tourists and local people as well as goods are transported to and from Funzi Island through Bodo landing beach. Dolphin watching near Funzi Island and visits to the 'lost paradise found' sandbar and Ramisi Estuary are some of the tourist activities around Funzi Bay. Outboard engine powered boats are a preferred mode of transport to and around Funzi Island and its associated creeks. Thus, the increasing lead concentrations seawards may be associated with the use of fuel for transport. The increase of cadmium seawards may probably be attributed to among others, a possible carbonatic sediment characteristic as explained in section 4.4.1. Otherwise, the sources of elevated cadmium levels in this creek were not apparent and warrants further investigation.

4.4.5. Comparison of Elemental Concentrations in Sediments between Creeks and with those Observed in Previous Research

Figure 37 to 40 shows histograms of the observed concentration means and standard deviations per element in Makupa, Mtwapa (station T7 included), Port Reitz and Shirazi Creeks. Elemental concentration ranges, mean values and standard deviations observed per site are shown in Table 15. The results are comparable with heavy metal concentrations in sediments collected from the same (where applicable) and other coastal areas of the world.

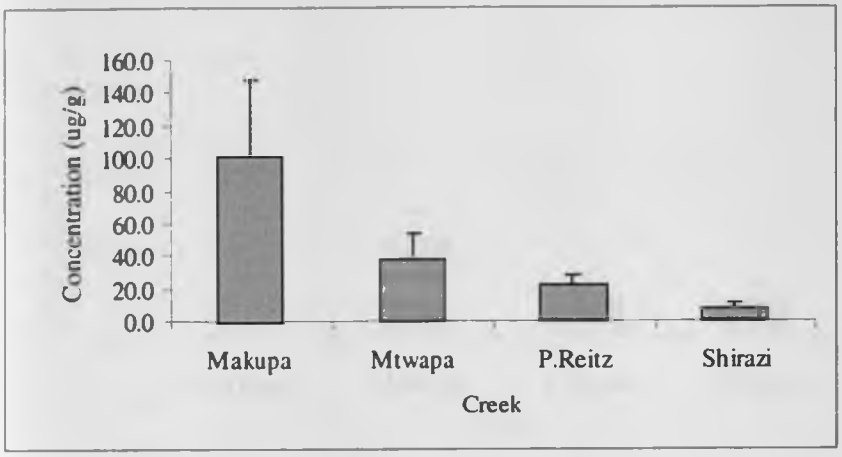


Figure 37. Mean copper concentrations in sediments per creek

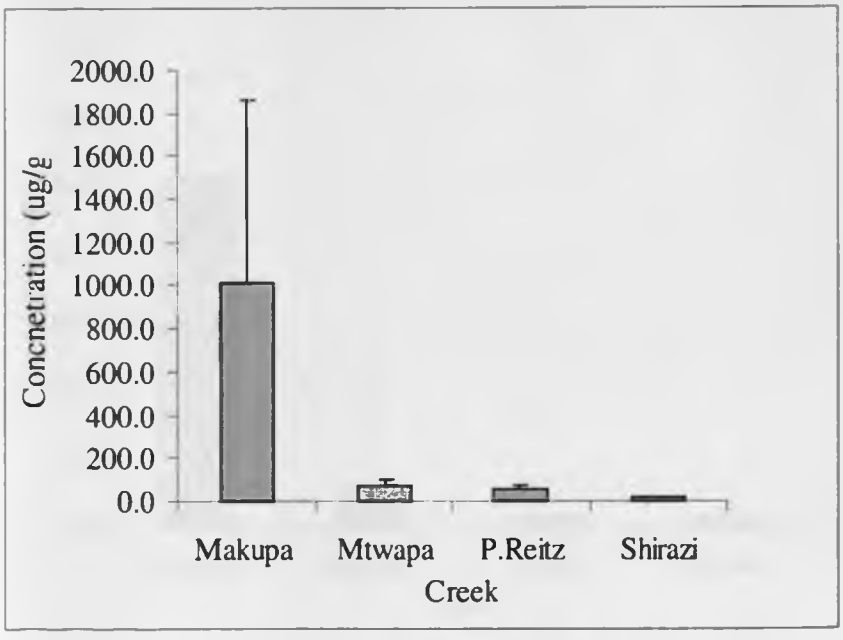


Figure 38. Mean zinc concentrations in sediments per creek

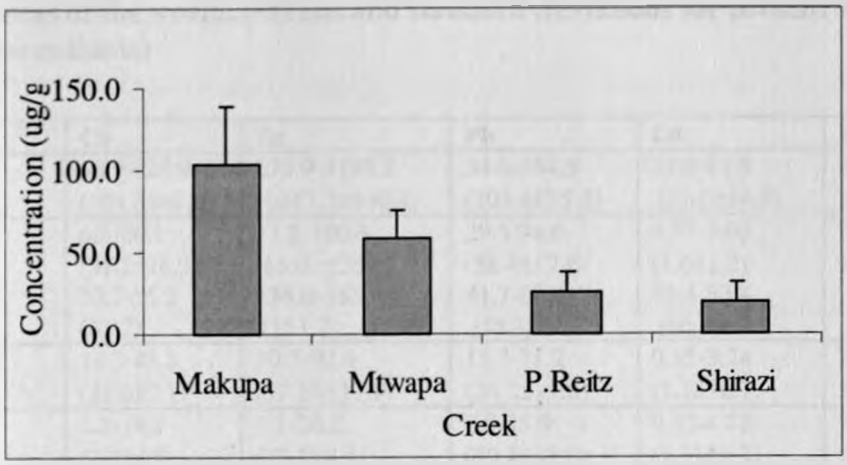


Figure 39. Mean lead concentrations in sediments per creek

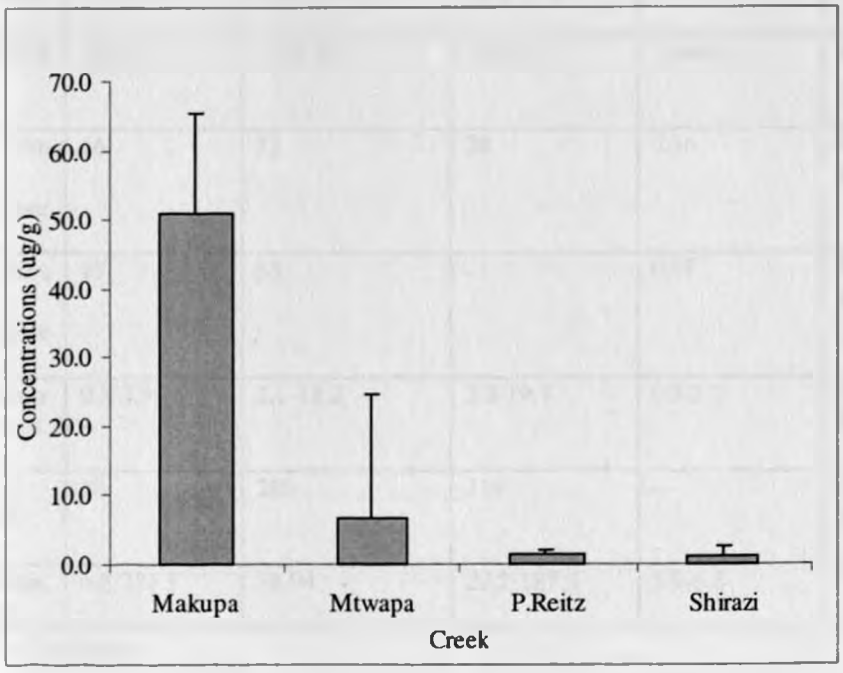


Figure 40. Mean cadmium concentrations in sediments per creek

Table 15. Heavy metal concentrations (μg g^{-1} dry wt) in sediments collected from the coastal region of Kenya compared with those observed in other marine areas of the world. (Means and standard deviations for present study in parenthesis)

Area	Cu	Zn	Pb	Cd	References
Makupa	50.9-228.9 (101.7±46.0)	275.9-3193.2 (1017.2±840.4)	54.6-164.5 (103.4±35.8)	31.0-81.9 (51.0±14.3)	Present study
Mtwapa Station T7	6.5-80.7 (37.2±16.3) 33.7-55.2 (41.2)	17.2-100.3 (65.0. ±20.6) 134.0-185.4 (151.2)	29.5-94.6 (58.4±17.6) 41.7-69.4 (55.7)	0.57-7.02 (1.6±1.2) 55.4-83.4 (66.1)	Present study
Port Reitz	11.3-45.1 (21.6±7.1)	30.7-92.9 (57.14±17.9)	15.7-71.2 (26.2±11.6)	0.55-3.24 (1.38±0.7)	Present study
Shirazi	2.2-19.9 (7.1±4.0)	9.1-26.2 (17.1±4.4)	8.5-45.9 (19.4±11.9)	0.32-4.73 (1.31±1.2)	Present study
Port Kilindini & Port Tudor	32±20	110±76	55±47	2.5±1.8	Nyatebe (1990)
Port Tudor, Kilindini and Port Reitz systems, Kenya			34-427	1.5-3.0	Williams *et al.*, (1996)
Juru Estuary, Malaysia	9.3-13.8	73.5-109.8	20.8-33.0	N.D.-6.8	Hamilton, (Ed), (1987)
Chao Phrya Estuary, Thailand	26±10	71±6.9	140±28	1.20±0.5	Menasveta *et al.*,. (1981)
St. John Harbour, Canada. Inner Harbour	16	53	24	0.16	Ray and Macknight (1984)
St. John Harbour, Canada. Outer Harbour	15	63	-	0.07	Ray and Macknight (1984)
Mediterranean Coastal Area, Israel	0.3-2.9	2.1-18.2	3.9-19.7	0.3-2.2	Roth and Hornung (1977)
Severn Estuary. UK	38	280	119	-	Chester and Stroner (1975)
Tolo Harbour, Hong Kong	6.8-231.3	38.94	20.2-187.3	5.9-6.8	Wong *et al.*,. (1980)

N. D = Not detected

Notably high elemental concentrations were observed in Makupa Creek. This Creek is closely influenced by a number of human activities such as the Kibarani dumping site, Kipevu oil terminus and the domestic sewage outfalls on the eastern side of Mombasa Island among others. Williams *et al.*, (1996) reported that, heavy metal profiles in sediment cores from most of their Mombasa sampling sites (including potentially perturbed localities such as Makupa Creek) showed little clear evidence of increased contaminant deposition in recent decades providing a matrix within which any subtle variations of anthropogenic input were indiscernible. These workers did, however, point out the possibility that, increasing metal fluxes occurring during recent decades have been disguised by a simultaneous increase in mass sedimentation. Elemental concentrations observed in Makupa Creek during the present study might thus be a testimony to some increased metal fluxes into that Creek.

Dead mangrove trunks observed in Makupa Creek especially near Makupa causeway were evidence of mangrove ecosystem destruction. Most of mangrove sediments metabolism is through sulphate reduction which releases high quantities of hydrogen sulphide and bicarbonate to pore waters and even to waters overlying the sediments. Under this physicochemical conditions the formation of sulphide minerals is favoured, precipitating dissolved trace metals, in particular the "soft" B type metals which includes most heavy metal pollutants such as Zn, Hg, Ni, Cu and Cd (Berner, 1984; Harris *et al.*, 1993). However, after many years of research on the fate of trace metals in mangrove ecosystems in Australia, Harbinson (1981, 1984, 1986) concluded that although mangroves act as a sink of many trace metals, changing physical-chemical conditions can turn the ecosystem into a net source of these pollutants, conveying them to

local food chains. This is consistent with Lacerda's (1998) observation that the immobilisation of pollutants in mangroves is tightly linked to the ecosystem health and once the typical conditions of mangroves are changed (e.g. through deforestation, erosion, fish farming), they shift from long term sinks into sources of the accumulated pollutants. It is possible then that such a situation in Makupa Creek may exist though this phenomenon requires further investigation.

Elemental concentrations observed in other creeks did not raise as much concern as those observed in Makupa creek. Nevertheless, a Turkey honest significant difference test showed that on average, there was significant variation ($p<0.05$) in elemental concentrations between Mtwapa (station T7 included), Port Reitz and Shirazi Creeks as shown in Table 16. However, the lead concentration variation between Port Reitz and Shirazi Creeks was not significant. This is because as explained before, most of the samples obtained from Port Reitz Creek were from Mwache Creek. which in terms of anthropogenic activity influence is relatively comparable to Shirazi Creek. Cadmium concentrations in Mtwapa, Port Reitz and Shirazi creek did not show significant variation. This may be an indication that cadmium is relatively evenly distributed along the Kenyan Coast.

Table 16. P-values for a Turkey honest significant difference (HSD) test at 95 % confidence level for comparison of mean elemental concentrations in Mtwapa, Port Reitz and Shirazi Creeks' sediment.

Copper				**Zinc**			
	{1}	{2}	{3}		{1}	{2}	{3}
Means	37.5	21.6	7.1		71.8	57.1	17.1
Mtwapa {1}		0.00011	0.00011	{1}		0.02915	0.00011
P.Reitz {2}	0.00011		0.00012	{2}	0.02915		0.00011
Shirazi {3}	0.00011	0.00012		{3}	0.00011	0.00011	
Lead				**Cadmium**			
	{1}	{2}	{3}		{1}	{2}	{3}
	58.1	26.2	19.4		6.7	1.4	1.3
{1}		0.00011	0.00011	{1}		0.16150	0.16034
{2}	0.00011		0.18691	{2}	0.16150		0.99978
{3}	0.00011	0.18691		{3}	0.16034	0.99978	

4.4.6. Elemental Concentrations Classification in Sediments According to Donazzolo et al., (1984).

Sediment elemental concentrations ($\mu g\ g^{-1}$) observed in this study have also been classified into low (L), medium (M) and high (H) level ranges according to the classification by Donazzolo *et al.*, (1984). For copper, L = <15, M = 15 to 50 while H = >50. For zinc L = <40, M = 40 to 200 while H = >200. For lead, L = <40, M = 40 to 60 while H = >60. For cadmium, L = <1.5, M = 1.5 to 6 while H = >6.

Figure 41 to 44 shows the sample percentages observed for each class per site for copper, zinc, lead and cadmium respectively.

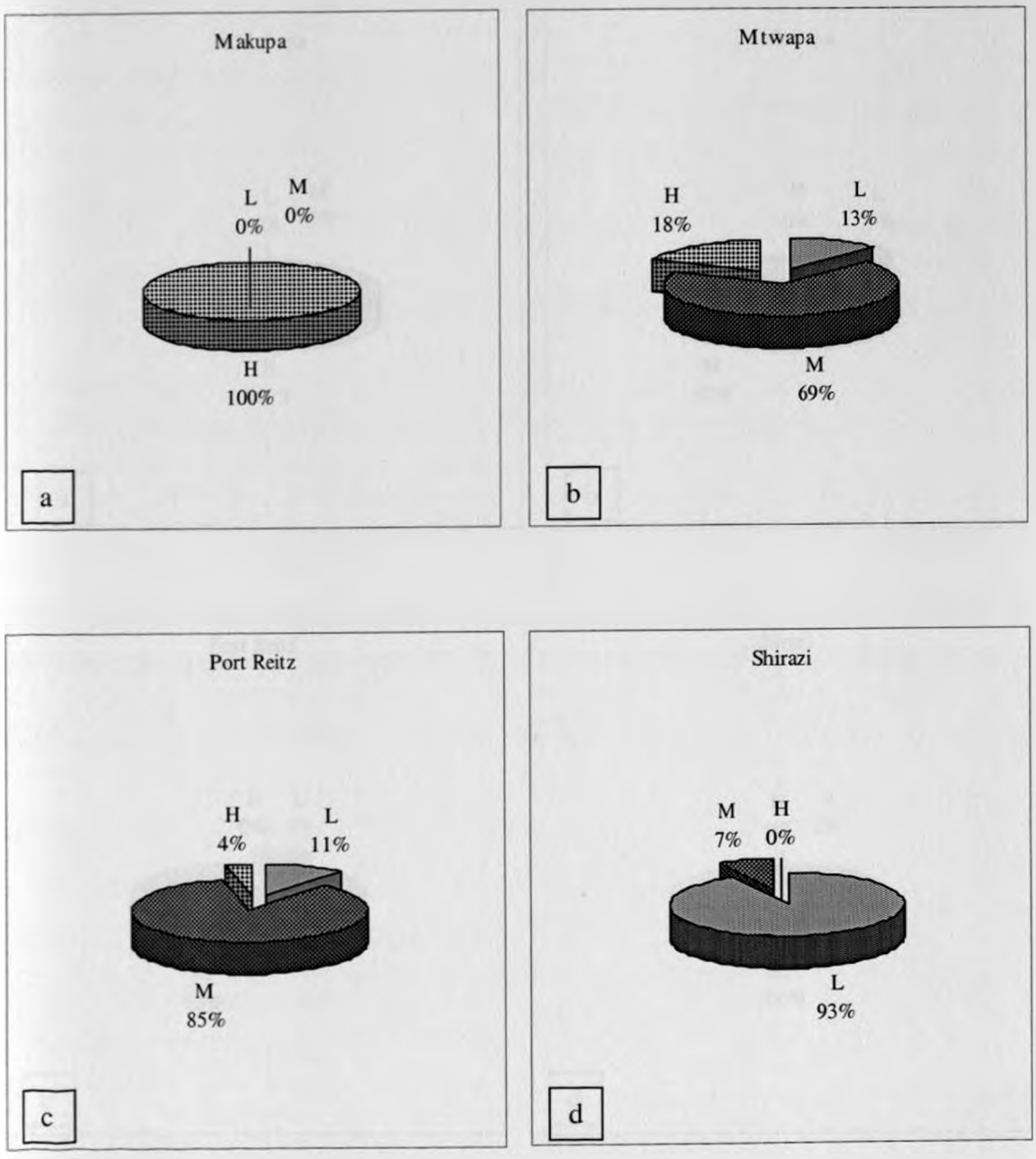


Figure 41. Classification of copper concentrations in sediments per creek

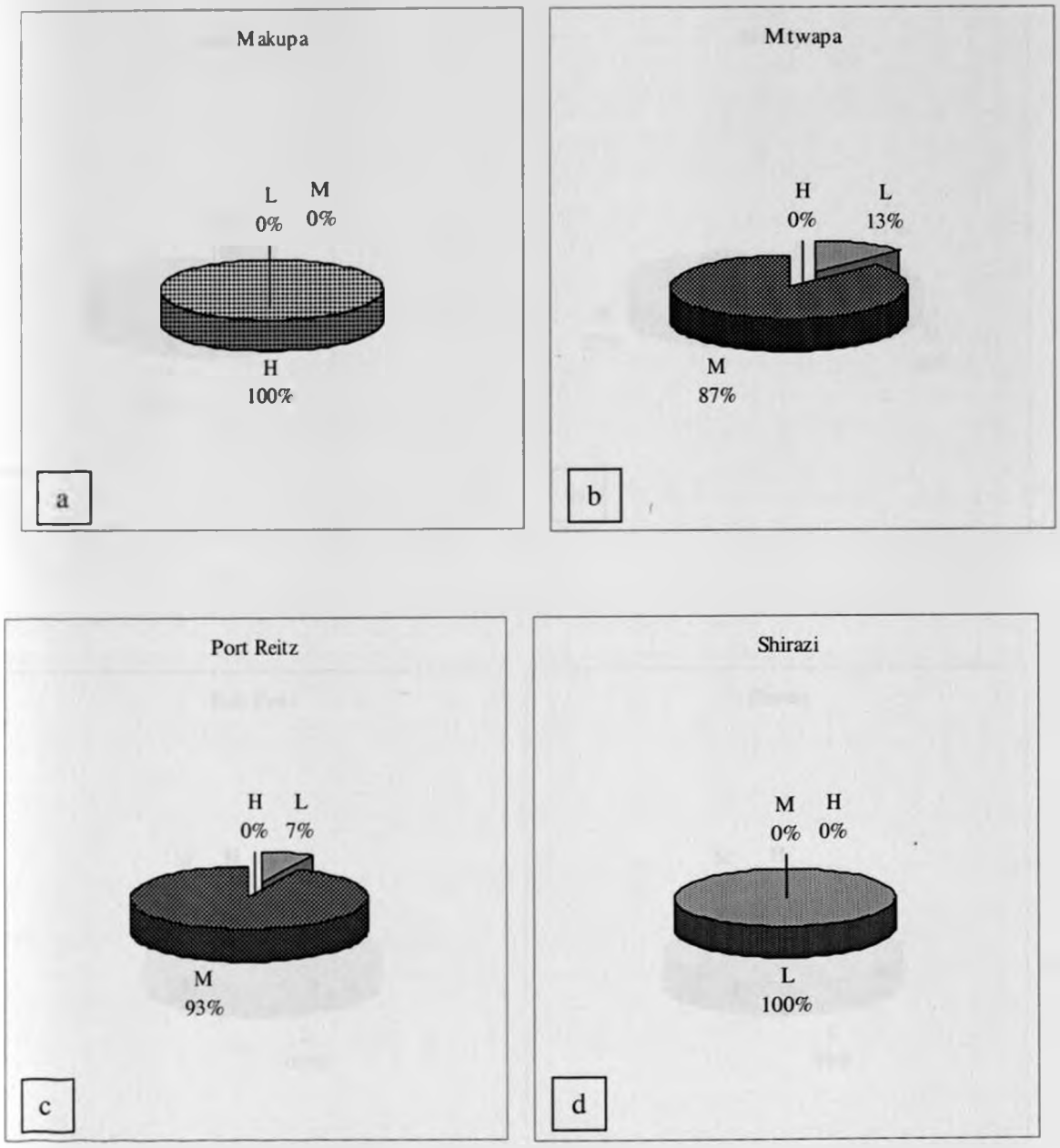


Figure 42. Classification of zinc concentrations in sediments per creek

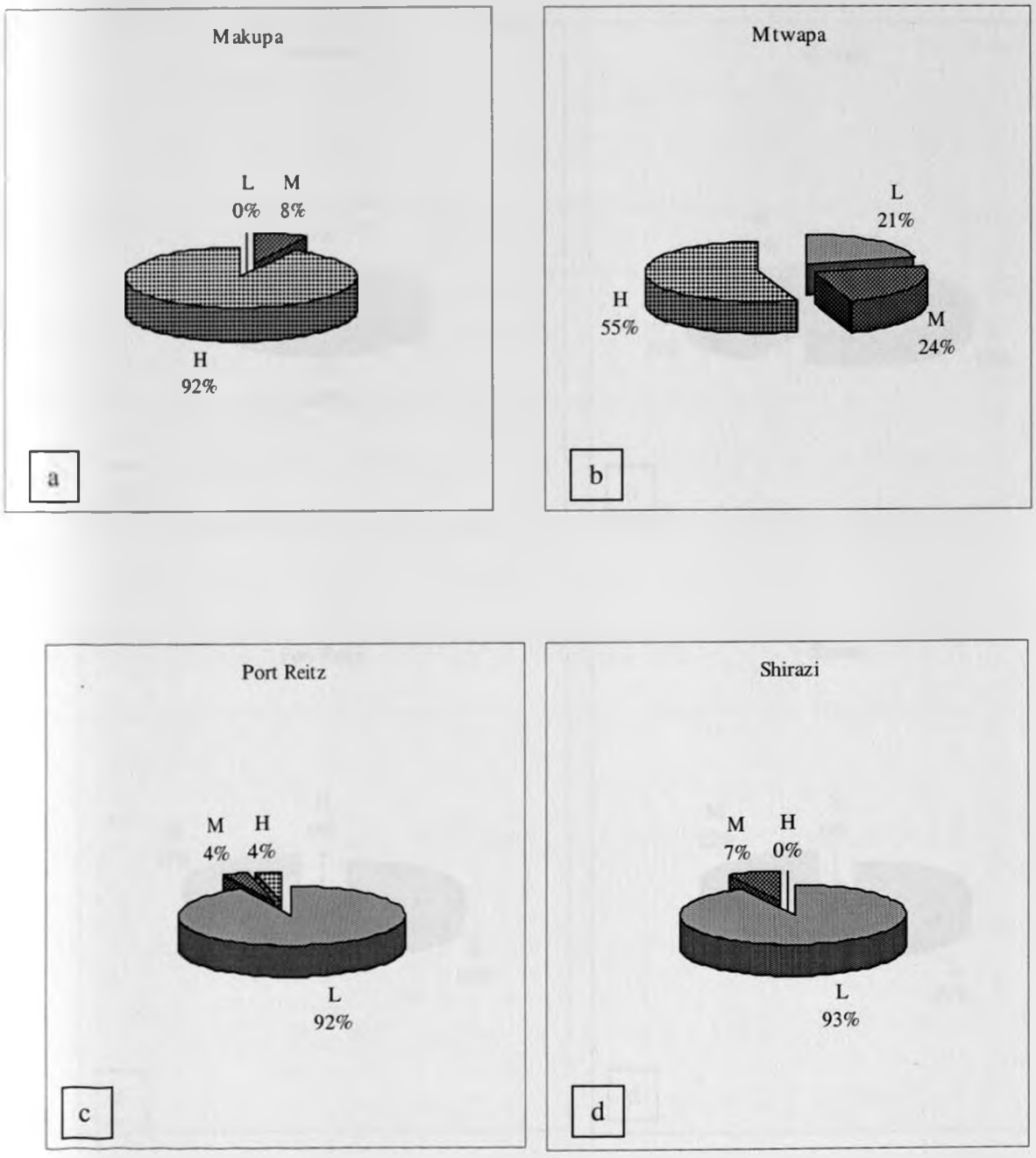


Figure 43. Classification of lead concentrations in sediments per creek

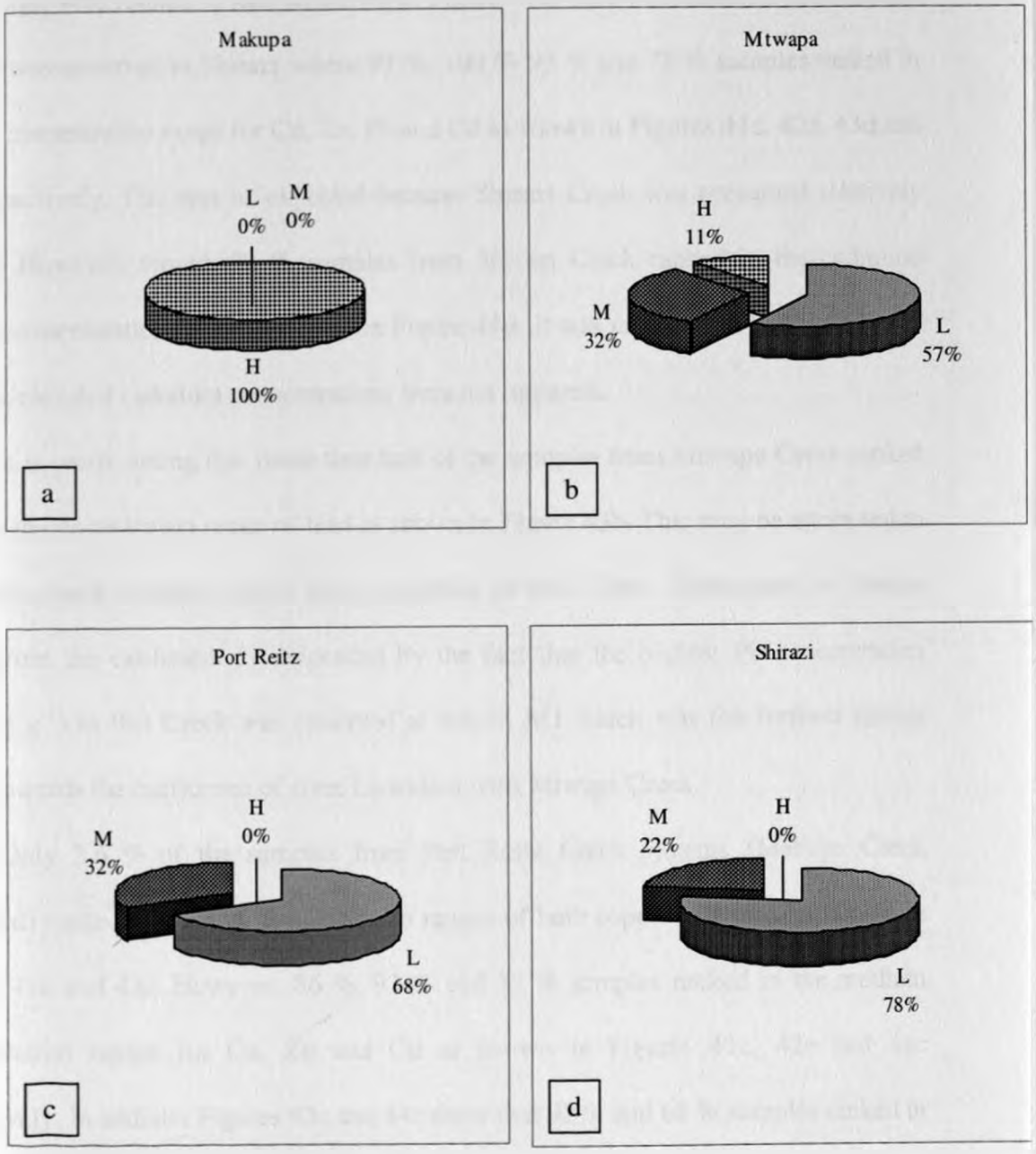


Figure 44. Classification of cadmium concentrations in sediments per creek

In Makupa Creek, 100 % samples ranked in the high concentration range for copper, zinc and cadmium as shown in Figures 41a, 42a and 44a respectively, while 92 % ranked high with respect to lead as shown in Figure 43a. This was almost a total inverse of what was observed in Shirazi where 93 %, 100 % 93 % and 78 % samples ranked in the low concentration range for Cu, Zn, Pb and Cd as shown in Figures 41d, 42d, 43d and 44d respectively. This was as expected because Shirazi Creek was presumed relatively pristine. However, though 22 % samples from Shirazi Creek ranked in the cadmium medium concentration range as shown in Figure 44d, it was unexpected and the sources for these elevated cadmium concentrations were not apparent.

It is worth noting that more than half of the samples from Mtwapa Creek ranked in the high concentration range of lead as shown in Figure 43b. This may be attributed to the boating and shipping (small ships) activities in that Creek. There may be further inputs from the catchment as evidenced by the fact that the highest Pb concentration (94.6 $\mu g\ g^{-1}$) in that Creek was observed at station M1 which was the furthest station inland towards the confluence of river Lwandani with Mtwapa Creek.

Only 3.6 % of the samples from Port Reitz Creek systems (Makupa Creek exempted) ranked in the high concentration ranges of both copper and lead. as shown in Figures 41c and 43c. However, 86 %, 93 % and 32 % samples ranked in the medium concentration ranges for Cu, Zn and Cd as shown in Figures 41c, 42c and 44c respectively. In addition Figures 43c and 44c show that 92 % and 68 % samples ranked in the low concentration ranges for Pb and Cd respectively. This observation may be attributed to the fact that a number of samples were collected from Mwache Creek, which has relatively lower anthropogenic influence compared to the other Port Reitz creek

systems. Besides, there was a sampling limitation because the Kilindini port channel is about 30 metres deep as a result of the dredging activities in this port. It was thus impractical to sample at this depth using the Ekman grab. In addition, the substrate in some areas of the port is rocky rendering it impossible to sample using the above tool.

The grain size of the sub-samples analysed was 63 μ. A finer grain sample provides more surface area for interaction with the digestion medium. It thus gives results that are more representative of the elemental concentrations in that sample than a course grain sample would. Previous research has nevertheless shown that finer grains accumulate more trace elements than the coarse ones. For instance, Donazzolo *et al.*, 1984, working on heavy metal content and lithological properties of sediments in the Northern Adriatic reported that, all the metals investigated accumulated in the fine fraction (<63 μ) with the following percentages, Hg, 95 %; Zn, 86 %; Pb, 82 %; Cu, 79 %; Cd, 74 %; Ni, 70 %; Cr, 65 %; Co, 65 % and Fe, 64 %. This phenomenon may be attributed to the greater surface area for adsorption of matter, heavy metals included, on the finer grains. However, in the present study the sediments in the Kilindini Port were mainly sandy and the 63 μ grain-size was rarely obtained through sieving.

In addition, due to the vast nature of the creek plus the relatively efficient mixing of the water in the main basin, there may be a greater dilution effect on potential pollutants that may get into the creek systems unlike in Makupa Creek where inefficient mixing of the water is apparent in some parts leading to localised retention of potential pollutant inputs.

According to guidelines proposed in a Draft Criteria Document at an International Sediment Quality Forum in 1992 (Van Veen and Strotelder, 1998) the limit values

proposed were Cu, 400 μg g^{-1}, Zn, 2500 μg g^{-1} and Cd, 30 μg g^{-1}. In the present study, none of the stations sampled exceeded the proposed copper limit guideline, only one station in Makupa (KU6) Creek exceeded the zinc limit guideline. While all the stations in Makupa Creek plus one station in Mtwapa Creek (T7) exceeded the cadmium limit guideline. Lead limit guideline was not proposed at that forum.

From this study, the creeks under investigation are influenced by possible inputs from anthropogenic activities at varying degrees and can be classified in order of most to least influenced as follows, Makupa Creek>Mtwapa Creek> Other Port Reitz Creeks (including the Mwache Creek and the main port basin) >Shirazi Creek. However, there is need for further investigations into establishing the sources and fates of these potential pollutants in the ecosystem.

4.4.7. Elemental Correlations in Sediments

Table 17. Sediment elemental correlations per creek

Creek	Significant correlations
Mtwapa	Cu-Zn, Pb Zn-Cu, Pb, Cd
Port Reitz	All (Cu, Zn, Pb and Cd) correlated positively
Makupa	Cu-Pb, Cd*
Shirazi	Cu-Zn Pb-Cd

(* Marked correlations are negative)

Elements may be correlated as shown in Table 17 if for instance their sources into a particular site are similar or associated. The sources may be natural or anthropogenic induced. For instance, zinc, despite being ubiquitous in nature provides the most cost-effective and environmentally efficient method of protecting steel from corrosion. It is

also used in making brass and other alloys, automotive equipment and household appliances, tyres and all rubber goods among other uses. In the creeks under investigation, zinc uses may be applicable in components such as engines and mooring equipment of ships and boats and in making landing jetties near some hotels. In addition, Munga *et al.*, (1993) stated that in their assessment of heavy metal pollution loads in inshore waters around Mombasa Island, there was an indication of chromium, zinc and iron emissions from iron and steel industries with relatively lower levels from electricity generation and petroleum refining. It follows then that, copper being used in for instance electroplating, in petroleum refining, as a chemical catalyst in antifouling paints and in production of wood preservatives, may be associated with some uses of zinc as those mentioned above. Lead inputs may result from use of leaded fuel in the ships and boats as stated in section 2.1.3 of literature review. Since cadmium occurs together with zinc in nature, it is the level of production of zinc but not necessarily the demand for cadmium that governs the supply of cadmium. However, cadmium compounds are used in electroplating of metals, as pigment stabilisers in plastics, in alkaline batteries and in alloys with other metals such as copper. Consequently, it is the production and uses of the elements assessed among others, that leads to similar or associated sources of their inputs into the aquatic environment particularly the sites under investigation in this study. However, detailed studies on the sediment chemistry of each creek would give a better understanding of elemental correlations such as those observed in this research. Such studies were beyond the scope of the present investigation.

4.5. Fish

4.5.1 Inter-Creek Comparison of Elemental Concentrations in Fish Species

Figure 45a to 45d shows the mean elemental concentrations in fish species per site.

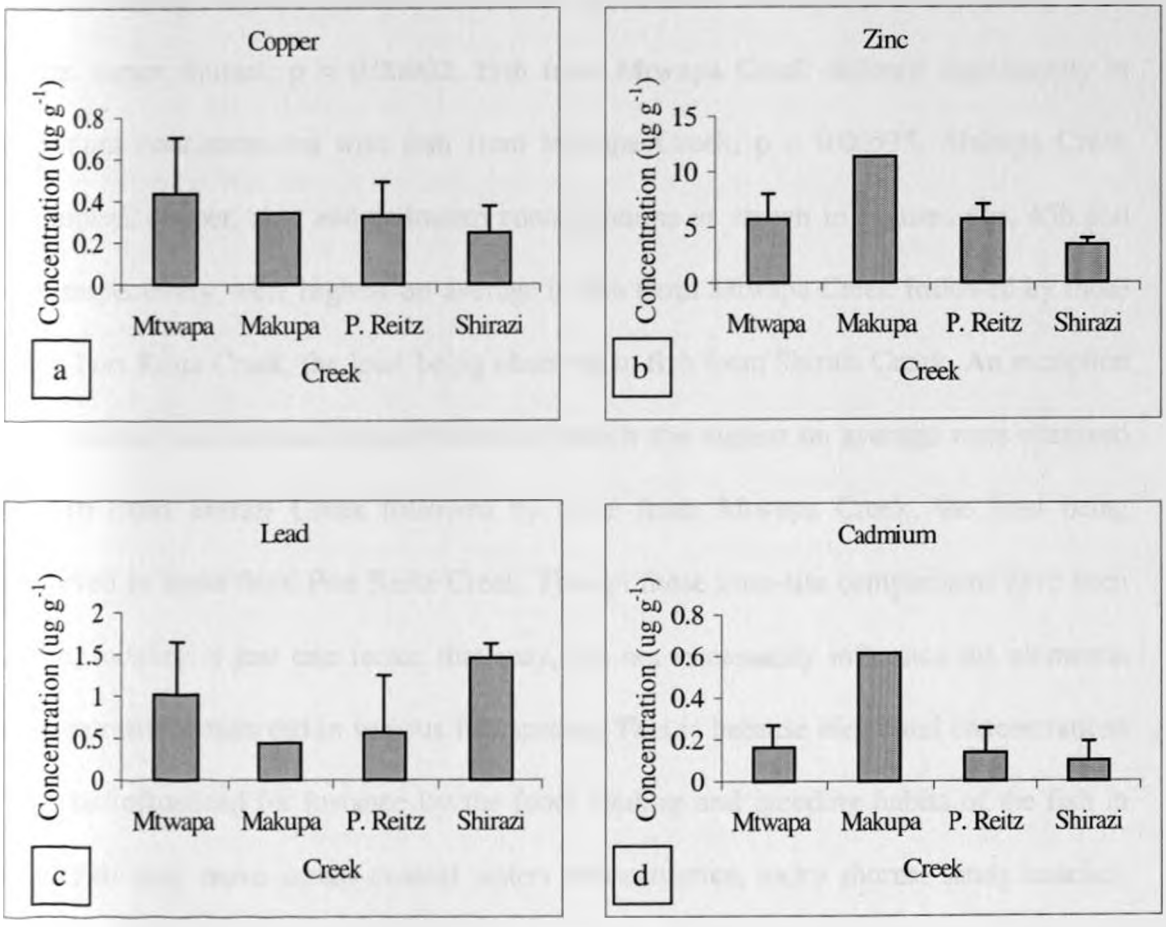


Figure 45. Mean elemental concentrations in fish per site.

The results in Figure 45 show that for each creek a certain fish species would have elemental concentrations within the indicated standard error limits. Makupa Creek is exempted from this since only one species was obtained (hence there is no degree of

freedom) for probable reasons as explained in section 3.1.1 under materials and methods. On average, Shirazi Creek fish differed significantly at 95 % confidence level, in copper concentration with Mtwapa Creek fish, P = 0.00032. Again, fish from Shirazi Creek differed from Mtwapa and Port Reitz Creek fish in zinc concentrations, p = 0.00002 in both cases. Lead concentrations significantly differed between fish from all the three creeks. Mtwapa verses Port Reitz and Shirazi, p = 0.0201 and 0.000026 respectively. Port Reitz verses Shirazi, p = 0.00002. Fish from Mtwapa Creek differed significantly in cadmium concentrations with fish from Mtwapa Creek, p = 0.00535. Makupa Creek exempted, copper, zinc and cadmium concentrations as shown in Figures 45a, 45b and 45d respectively, were highest on average in fish from Mtwapa Creek followed by those from Port Reitz Creek, the least being observed in fish from Shirazi Creek. An exception to this trend was the lead concentrations of which the highest on average were observed in fish from Shirazi Creek followed by those from Mtwapa Creek, the least being observed in those from Port Reitz Creek. Though these inter-site comparisons have been made, locality is just one factor that may, but not necessarily influence the elemental concentrations observed in various fish species. This is because elemental concentrations may be influenced for instance by the food, feeding and breeding habits of the fish in that, fish may move across coastal waters into estuaries, rocky shores, sandy beaches, coral reefs, seagrass areas and mangrove zones in search of food or spawning grounds. For example, estuaries and mangrove areas are preferred spawning grounds and juvenile nursery areas. To give an insight into the ecological interspecific diversity, the following is a general brief description of the natural histories of some of the fish species collected in various sites in the present study. A natural history description of their relatives from

other marine areas of the world particularly the South African Coast (George et al 1994) has been provided where information of the particular species was not available.

Leiognathus equula (Forsskal, 1775) Common or greater ponyfish

This common shoaling fish of coastal waters and estuaries is tolerant of very turbid environments, as well as almost fresh water. It is generally not very active, and large shoals can often be observed suspended in midwater. Feeding occurs at two different levels, depending on size. Young fish feed on midwater, planktonic crustaceans such as copepods. Crab larvae and shrimps, while larger specimens eat small crabs, prawns and marine worms that live on the bottom. Sexual maturity is attained at a length of 15 cm and spawning has been recorded from October to March along Natal coast, in the vicinity of river mouths. Juveniles make extensive use of estuaries and mangrove-lined waters as nursery areas, and large shoals of 3-8 cm long fish can be netted in these regions during late summer. In addition to exuding great amounts of mucus, the slimy often procures a croaking sound when captured. This is very evident when large numbers are caught.

Lutjanus fulviflamma (Forsskal, 1775) Spotsnapper, greedy guts, black spot snapper

The spotsnapper is certainly one of the most widespread of the Lutjanidae. It is especially common off rocky shores, but is equally at home in estuaries, over muddy bottoms of in stands of eelgrass. Most of those frequenting estuaries, however, are juveniles ranging from 2-12 cm in length. The diet includes a variety of small crustaceans, particularly crabs, isopods, prawns, mantis shrimps, mysids and marine worms. Small fish especially anchovies and gobies, are also eagerly consumed when

available. Although not a shoaling species, the spotsnapper does congregate in groups, and the young often associate with juvenile stumpnose in estuaries. The spoiling of many estuarine nursery areas. and the removal of eelgrass beds have resulted in a lowered abundance of this species in some regions. Sexual maturity is attained at a length of 16-17 cm and spawning takes place over deeper reefs from August to December.

Rhabdosargus globiceps (Cuvier, 1830) White stumpnose

The white stumpnose is a coastal species, often occurring in large shoals which range to depths of 60 m. Juveniles up to 15 cm in length are common in estuaries along the cape coast. And in the sheltered areas of False Bay, especially at night. Adult white stumpnose are usually found over sandy sea-beds, but frequently near small reefs or rocky outcrops. The composition of the diet changes with size and age from omnivorous to exclusively carnivorous. Juveniles feed on filamentous algae, eelgrass, polychaete worms and small crustaceans such as mud-prawns and cracker-shrimps, while larger fish feed on crabs bivalve molluscs, worms and other crustaceans. Isopod parasites often clog the mouth about 25 per cent of landed specimens have intestinal worm infestations. Shoals migrate to warmer regions during winter and spawning occurs close to inshore areas during spring and summer. The fertilised eggs are known to float near the surface. Sexual maturity is attained in the third year, at a length of approximately 30 cm. As juveniles depend on estuaries as nursery areas, it is important that the degradation of these environments be prevented to ensure the long-term viability of this fish. As with other Sparidae, growth patterns on the otoliths may be used to determine age.

Sardinops ocellatus (Pappe, 1853) (Clupeidae) Pilchard, Sardine

This offshore species forms vast shoals and has for many years formed the backbone of the South African pelagic fishing industry. It is also the species responsible for the famous annual 'sardine run' along the East Coast when ocean currents and frenzied game fish often drive the shoals, which normally occur several kilometres out to sea, right into the surf zone. The diet consists of planktonic animals such as krill, larval crabs and other small crustaceans. The pilchard is, in turn, an important 'fodder' fish for numerous larger gamefish, birds, dolphins, seals and man. Though the traditional breeding grounds are located off the western Cape and Namibian coasts, recent research has revealed that spawning also occurs off the East Coast during the winter months. Sexual maturity is attained after the third year when fish exceed 20 cm in total length. Age and growth rates have been determined from the annual rings marking the otoliths, or ear-stones. Closely related species occur in California and Ausralia.

Gerres acinaces Bleeler, 1854 Smallscale pursemouth, pouter, majora, silver-belly. Silver biddy

The small fish is commonly in the brackish and shallow waters of tropical and subtropical regions, where it usually occurs in small, loosely packed shoals. It is known to be tolerant of considerable salinity fluctuations and is therefore, frequently encountered in estuaries. It is a clear-water species. However, and though it is found all along the Natal Coast, it is understandably most prolific in relatively slit-free systems such as Kosi Bay. The smallscale pursemouth is primarily a bottom feeder, and it preys to a large extent on the syphons of burrowing bivalve molluscs, when these are projected above the sea-bed. The diet also includes amphipods, small crabs and polychaete worms.

The fish's highly protractile mouth being particularly well suited to selecting these foods items from the mud. The fine gill rakers assist in filtering out smaller food organisms. This species is continuously abundant and appears to breed all year round. Individuals exceeding 8-9 cm in length are sexually mature. Spawning occurs at sea, and it would appear that once mature fish leave their estuarine nursery grounds hey do not return.

Gerres filamentosus Cuvier, 1830 Threadfin pursemouth, pouter, whipfin majora, threadfin silverbelly, silver biddy.

The threadfin pursemouth prefers shallow water, especially in tropical estuaries, and is fairly tolerant of low salinities. It usually occurs in small shoals, which are common in the lagoons of Mozambique and Zululand, particularly Kosi Bay. However, many have been recorded periodically in estuaries to the south. Feeding takes place during the day only, and prey includes, in order of importance: amphipods, polychaete worms, bivalve molluscs, dead organic matter, small crabs and shrimps and. occasionally, plant material. These food organisms all occur on the sea-bed, and are scooped up from the mud or sand in the protractile mouth, which is fully extended during feeding to form a dredger-like bucket. Spawning has been recorded as far south as Delagoa Bay, and the juveniles enter estuaries soon after hatching.

Siganus sutor (Valenciennes, 1835) Whitespotted rabbitfish, whitespotted spinefoot, shoemaker spinefoot

A shoaling fish of shallow, tropical waters, the whitespotted rabbitfish is equally at home in estuaries, and is fairly common off the Natal Coast during summer. As with all rabbit fishes, the members of this species are browsers, and their vegetarian diet

consists primarily of filamentous seaweeds and eelgrasses. During feeding, however, numerous small invertebrates clinging to these plants are also accidentally ingested. Juvenile whitespotted rabbitfish feed on diatoms. Although plant matter is digested completely, the low calorie content of seaweed necessitates continual feeding. Spawning occurs in tropical regions, but shoals of juveniles are known to migrate into southern African waters during summer. As the spines of rabbit fihes are very sharp and coated with toxic mucus, these fishes should be handled with extreme care. Accidental jabs are painful, but respond rapidly to immersion in very hot water which breaks down the protein poison.

Leptoscarus sp.

The diet is omnivorous and consists primarily of red and green seaweeds, sponges, and tunicates such as redbait. The strong beak is an effective adaptation for nibbling and tearing at foods attached to the reed. Juveniles occur in tidal pools or beneath floating objects at sea.

Polysteganus caeruleopunctatus Kunzinger, 1870 Blue skin

During winter, the blue skin is quite common around reefs as deep as 100 m. It is mainly a solitary species, and feeds primarily on crustaceans such as crabs. Details of its life cycle and general behaviour are not known, but its seasonal fluctuations would seem to indicate that migrations take place. The blueskin's large eyes appear to be a successful adaptation to the lower reaches of its habitat, where little light penetrates. The blueskin was first 'discovered' in the Red Sea. It is known to be widespread throughout the

Western Indian Ocean, but despite this extensive distribution, information pertaining to its biology is remarkably sparse.

Liza richardsonii (Smith, 1846) Southern mullet, harder

Dense shoals of this abundant, cool-water species may often be seen off the rocky points and sandy beaches of the southern and western cape coast. Many also frequent estuaries where tolerance to low salinities enables the young to use these regions as nursery areas. In place of a stomach, the harder has a long muscular crop, rather like a gizzard of a bird. The diet consists primarily of easily digestible, microscopic plant organisms known as diatoms. Fine sand particles are also taken in through the mouth, possibly as a mechanical aid to digestion. The totally non-aggressive harder is freely preyed upon by many large gamefish. Sexual maturity is attained at a length of about 20 cm and spawning takes place during spring in shallow areas such as False Bay.

Epinephelus andersoni Boulenger, 1903 Catface or spotted rockcod

The catface rockcod is one of the most common and widely distributed members of the Serranidae in Southern African waters. It frequents the shallow surf zone, but also ranges to depths of at least 50 m. Occasionally, it ventures into estuaries, but it is not tolerant of low salinity conditions. It is always associated with rocky reefs, often lying motionless on the floor of a gully. Here, well camouflaged against the rocky backdrop, the catface rockcod lies in wait, ready to pounce on blennies, crayfish and crabs that venture too closely. A number of other fish species also supplement the diet. Despite its rather sluggish habits, it is one of the most important inshore reef predators along the East Coast. This resident species is present throughout the year and breeding has been

recorded off the Natal Coast during the late winter and spring. Sexual maturity is attained at 50-60 cm, and spawning takes place after courtship displays which involve two or more fish. Juveniles migrate to the shallow, intertidal zone after their egg and larval phases.

Lethrinus nebulosus (Forsskal, 1775) Blue emperor, scavenger, mata-hari

This common tropical fish inhabits coral and rocky reefs. Though it often frequents shallow water, it is also found to depths of 50 m. Small, loosely packed shoals often remain suspended several meters above the reef's surface, and sometimes the only sign of life from individual members is the occasional movement of the pectoral fins to maintain stability and direction. This behaviour is typical of members of this genus. And enables the fish to take maximum advantage of rich midwater nutrients. The diet consists mainly of small crabs, marine worms and molluscs, but suspended or planktonic organisms such as mantis shrimps, small shrimps, crab larvae and juvenile fish are also taken. Sexual maturity is attained during the fourth year at a length of 50-60 cm. Spawning occurs in warmer water, primarily during March to July and the fry are widely distributed by ocean currents. Some have been recorded off the Natal Coast, presumably borne down from regions further to the north by the powerful Agulhas Current.

Plectorhinchus flavomaculatus (Ehrenberg, 1830) Lemon fish

The lemon fish is fairly common in coastal waters, where it is generally confined to coral and rocky reefs as deep as 80 m. It is a sluggish species and is most active during the half-light of dawn and dusk when it preys mainly on bottom living invertebrates including small crabs, marine worms and shrimps. Small fish are also sometimes eaten.

Young lemonfish have a curious, fluttering swimming style not unlike the motion of a drifting leaf; this behaviour could be a form of protective mimicry, but it is not clearly understood and disappears with age. Whereas adults ate mainly solitary, juveniles may congregate in shallow tidal pools with good stands of seaweed. Very little is known of the species' life history. Observations by divers however, confirm the lemonfish's bottom-dwelling habits, as it is frequently encountered skulking near reefs. Though essentially rather timid, it is nevertheless inquisitive, and initially will swim right up to a diver before retreating behind some rocky outcrop or into a cave.

Platycephalus indicus (Linnaeus, 1758) Bartail flathead, sand or river Gurnard.

The non-shoaling bartail flathead is common in estuaries and in open water where silt has been deposited. Its own muddy coloration blends well with these surroundings, and the fish is often very inconspicuous, especially when it buries itself below mud with only its eyes exposed. Here it lies, ready to snatch prey. Shrimps and gobbies are particularly favoured, but polychaete worms, small crabs, mysids and other bottom-living invertebrates are also included in the diet. The sharp spines on the head are to be avoided, and, while undoubtedly a successful defence against many predators, they tend to snag trawl nets, thereby making the fish vulnerable to capture. Sexual maturity is attained at a length of 50 cm and spawning occurs in the vicinity of Natal's estuaries from July to November. The juveniles make extensive use of estuarine mangrove areas for shelter and feeding, showing remarkable tolerance to turbid water and fluctuating salinities.

Basically, factors that influence elemental concentrations in various fish species are the factors that influence the growth of the fish. Food and feeding habits of fish are important in the growth of the fish. The food and feeding habits are influenced by for

example food quality and quantity. For instance in Lake Sibaya (Republic of South Africa). *Oreochromis mossambicus*, although fast-growing as juveniles, grow slowly as adults (Bowen, 1979b). The fish eat detritus, which is abundant, but at the depths at which adults feed it provides insufficient protein to prevent them from experiencing malnutrition. With an increase in depth, the energy content of the organic component of the detritus does not change, but the ratio of digestible protein to digestible energy decreases. In terms of size spectrum of food, the size spectrum of prey influences the pattern of growth of the predator. There is thus a limited range of prey sizes that a fish can take and as the fish grows the mean size of prey depends on the prey's total energy content in relation to the time and energy needed for the fish to detect, pursue and handle a prey of that size. Thus if a fish is unable to select prey which yield an energy return sufficient to support a further increase in size this may result in stunted growth as observed in some populations of perch (Craig, 1987). Perch can become piscivorous if they grow to a size at which they can capture and handle fish prey (Wootton 1998).

The growth performance subsequently affects the organism's ability to take up essential elements and discriminate against or eliminate non-essential elements. In addition change from one food type to another may affect elemental concentration levels in the prey since ingestion in one of the element uptake routes in organisms. Some fish species obtained in the present study also change their food types with age. For instance, for *Leiognathus* sp. feeding occurs at two different levels depending on size. Young fish feed on mid-water planktonic crustaceans such as copepods, crab larvae and shrimps, while larger specimens eat small crabs, prawns and benthic marine worms. For *Rhabdosargus* sp. the composition of the diet changes with size and age from omnivorous

to exclusively carnivorous. The diet of *Lutjanus* sp. includes a variety of small crustaceans but small fish especially anchovies and gobies are also eagerly consumed when available. Thus availability of food types also affects the food and feeding habits of some fish especially the opportunistic feeders. Due to bioconcentration and biomagnification effects along the food chain, piscivorous fish for instance may be at a higher risk of exposure to elements already bioaccumulated in the prey organism. Carnivorous fish are also at a higher risk of exposure to elements accumulated in benthic organisms such as marine worms living in the sediments, since the sediments may act as a source or sink of the trace elements.

One of the protective mechanisms which animals have evolved to deal with toxicants is sequestration. Storage of toxicants, especially storage in inert tissues such as fat, teeth, hair, horns and scales, means that these substances are removed from the general circulation and their toxicity is reduced (Lam *et al.*, 1999). In some fish, a cycle of storage and mobilisation of lipids is associated with the reproductive cycle (Shul'man, 1974). This cycle may lead to changes in the energy content that are only weakly correlated with changes in body weight and not correlated at all with changes in length. For instance, in the North Sea herring, *Clupea harengus*, fat reserves are accumulated during a period of intensive feeding during spring and early summer, then mobilised as the fish cease feeding with the onset of sexual maturation (Iles, 1984). This cycle of storage and mobilisation links a feeding cycle with the reproductive cycle and so allows sexual maturation and spawning to take place at a time that is favourable to the progeny but bioenergetically unfavourable to the adults (Wootton, 1979). According to Grove *et al.*, 1985). In the East African Coast, there are two main seasons characterised by

particular monsoon winds. The period between April and September is characterised by the South East Monsoons and is mainly the wet season, The period between October and March is characterised by the North East Monsoons, and is mainly the dry season. The precise timing and extent of each season however, varies annually. Such climatic cycles in the Kenyan Coast also influence the reproductive and in essence the feeding cycles of the fish in favour of the progeny.

According to fish base reports (Froese and Pauly 2000), among the fishes collected in the present study, *Lutjanus* sp. has been reported to spawn during the months of August to March in the East African Coast. *Rhabdosargus* sp. spawns between the months of August to February in South Africa. *Siganus* sp. spawns from March to June in Hong Kong and January to April in Singapore. Lethrinus sp. spawns from October to November in the Southern Hemisphere distribution range. The spawning season thus corresponds with the North East Moonsonal period, which is mainly the drier season and is characterised by warmer waters. The cycle of storage and mobilisation of fats in correspondence with the reproductive cycle would subsequently involve the storage and mobilisation of trace elements since fat is one of the inert storage tissues.

4.5.2. Comparison of Elemental Concentrations in Fish Species Collected from More than one Creek

Leptoscarus species.

Leptoscarus species was collected from both Mtwapa and Shirazi Creeks. There was significant difference in lead concentrations between *Leptoscarus vaigensis* from Mtwapa Creek and Leptoscarus species (*L.vaigensis* and *L sordiditus*) from Shirazi Creek. In both cases p = 0.00017. However, there was no significant difference (p = 0.308) between the two species of the same genus from Shirazi Creek.

Lethrinus species.

Lethrinus nebulosus was collected from Shirazi Creek while *L. mahsena* was collected from Port Reitz Creek. Elemental concentrations observed in this species were compared with each other and with those observed in *L. miniata* bought from Likoni Market Mombasa by Onyari (1985). There was a significant difference in length, copper and zinc concentrations between *L. miniata* and the other two species (*L. nebulosus* (p = 0.002, 0.001 and 0.013 respectively) and *L. mahsena* (p = 0.001, 0.01 and 0.017 respectively)) A significant difference was also observed in lead concentrations between *L. mahsena* and the other two species *L. miniata* and *L. nebulosus.* P = 0.0005 and 0.011 respectively. The cadmium concentrations in *L. nebulosus* were significantly different from those in *L. miniata* and *L. mahsena.* P = 0.0002 in both cases.

Lutjanus species

Lutjanus fulviflama species was collected from both Mtwapa and Shirazi Creeks. Though there was significant differences in length (p = 0.0002) between the individuals from the two sites, only zinc concentrations showed a significant difference (p = 0.005) between the same.

Siganus species

Siganus canaliculatus species was collected from both Mtwapa and Shirazi Creeks. This species showed almost a total inverse of what was observed in *Lutjanus* species, though the two species were collected from the same Creeks. As observed in *Lutjanus* sp., there was a significant difference in length (P = 0.0002) between individuals of *S. canaliculatus* from the two creeks. In both cases, fish from Mtwapa Creek were smaller than those from Shirazi Creek. However, only zinc concentrations showed no significant differences between individuals of *S. canaliculatus* from the two sites contrary to what was the case in individuals of *L. fulviflama*. Copper lead and cadmium concentrations showed significant differences between *S. canaliculatus* individuals from the two creeks. P = 0.005, 0.002 and 0.0002 respectively.

Gerres species

Gerres species were collected from Mtwapa and Port Reitz Creeks. In this case there was no significant difference in length between individuals from the two creeks. However, zinc and cadmium did show significant difference between the same. P = 0.0002 in both cases.

Leiognathus species

Leiognathus equulus species was collected from both Mtwapa and Port Reitz Creeks. Only zinc and cadmium concentrations showed significant differences (p = 0.001 and 0.006 respectively) between individuals from the two creeks.

Epinephelus species

Epinephelus postelli was collected from both Port Reitz and Shirazi Creeks. Only zinc concentrations showed a significant difference ($p = 0.009$) in individuals from the two sites. However, this comparison was based on only one individual from Port Reitz Creek.

Results of varying elemental concentrations in similar fish species collected from different creeks in this study are not anomalous because, for example, one of the major characteristics of fish growth is the growth flexibility. Such that the same species of fish may show very different patterns of growth in different environments, with even sexual maturity being reached at different sizes or at different ages. For instance, Donald et al., (1980) observed that the weights of five-year-old brook trout from lakes in the Canadian rocky Mountains ranged from 65 g in Temple Lake to 1751 g in Lake Patricia. These differences were correlated with the density of amphipods, a major food item for that fish. Even within a population fish recruited in different years can show different growth patterns. For instance, in Windermere, U. K., perch recruited in 1959 grew more slowly and had a smaller asymptotic size than perch recruited in 1968 (Craig, 1987). This is because the flexible growth patterns provide a mechanism for adaptive phenotypic responses to a changing environment (Wootton 1998). The flexibility in growth will consequently influence the uptake and elimination of elements into and out of the fish.

Nevertheless, there are both passive and active mechanisms involved in the absorption and transport of metals and these mechanisms are dependent on for instance, water quality, choice of food, metabolic activity, developmental stage, previous exposure and occurrence of other metals in multiple exposure situations (Goyer, 1992). Thus, the

inter-site and inter-specific relationships cited in this section may be due to biological inter an intra-specific specificity, but not necessarily inter-site ecosystem variability.

4.5.3. Elemental Correlations in Fish Species

Table 18 shows the elemental correlations in fish species per site. Only significant correlations were presented. In most cases, irrespective of species, copper concentrations correlated positively with zinc concentrations, while lead concentrations correlated with cadmium concentrations. This may be attributed to the fact that copper and zinc are essential elements in fish metabolism, while lead and cadmium are not. Thus the fish acquires copper and zinc at the same rate, hence their positive correlation. On the other hand, the organism may be eliminating lead and cadmium at the same rate leading to a positive correlation, for instance in *S. gibbosa* from Mtwapa Creek. However, in some cases for instance in *L. equulus* from Mtwapa Creek and *Gerres Sp.* from Makupa Creek, other factors may influence the simultaneous elimination of the two elements leading to a negative correlation.

In some cases, where an essential element correlated with one that is not needed in the body, the relationship was negative. For instance, lead correlated negatively with copper in *E. postelli* and *L. fulviflama* from Shirazi Creek and also with zinc in the latter. This may be an indication that the organism endeavours as much to acquire essential elements as it does to eliminate those that are not needed in the body hence the negative correlation.

4.5.4. Comparison of Elemental Concentrations Per Fish Species with Those Observed in Previous Research

The elemental concentration ranges means and standard deviations in all fish species per creek are shown in Table 19. A comparison between the present study results with those of other workers in other marine areas of the world plus WHO (Kakulu *et al.*, 1987) guidelines has been made. The elemental concentration ranges and means per species per creek are shown in Tables 20, 21 and 22 for Mtwapa, Port Reitz and Makupa, and Shirazi Creeks respectively.

Table 18. Elemental correlations in fish species per creek

Site	Species	Significant elemental correlations
Mtwapa Creek	*Leiognathus equulus*	Cu-Zn, Pb Pb-Cd*
	Lutjanus fulviflama	Zn-Cu, Cd
	Rhabdosargus globiceps	None
	Sardinella gibbosa	Cu-Zn Pb-Cd
	Gerres Sp.	Cu-Zn
	Siganus canaliculatus	None
	Leptoscarus vaigensis	None
Port Reitz	*Leiognathus equulus*	None
	Polysteganus caeruleopunctatus	None
	Strializa canaliculatus	None
	Lethrinus mahsena	None
Makupa	*Gerres* Sp.	Pb-Cd*
Shirazi	*Leptoscarus vaigensis*	None
	Leptoscarus Sordiditus	Cu-Zn
	Lethrinus nebulosus	Cu-Zn
	Siganus canaliculatus	None
	Epinephelus postelli	Cu-Pb*
	Plectorhyncus gaterina	None
	Lutjanus fulviflama	Cu-Zn Pb-Cu*, Zn*

(* Marked correlations are negative)

Table 19. Heavy metal concentration ($\mu g\ g^{-1}$ wet wt) ranges, means and standard deviations of averages in fish species collected from the coastal region of Kenya compared with those observed in other marine areas of the world.

Location and Spp n	Cu	Zn	Pb	Cd	Reference
Mtwapa 7 Spp	0.141-0.954 (0.437±0.270)	2.691-8.510 (5.696±2.290)	0.025-1.880 (1.031±0.634)	0.054-0.333 (0.164±0.104)	Present study
Port Reitz 5 Spp	0.136-0.598 (0.334±0.168)	4.124-6.869 (5.666±1.316)	0.005-1.648 (0.561±0.671)	0.039-0.304 (0.147±0.107)	Present study
Makupa 1 Spp	0.341	11.373	0.443	0.614	Present study
Shirazi 9 Spp	0.116-0.450 (0.246±0.129)	2.711-4.568 (3.423±0.573)	1.196-1.670 (1.450±0.171)	0.003-0.291 (0.097±0.093)	Present study
Mombasa markets	0.36-2.04	4.67-40. 8	1.22-6.48	0.04-0.38	Wandiga and Onyari (1987)
Egypt	1.65	4.23	0.07	0.004	El Nabawi *et al.*, 1987
Nigeria	11.3	27.5	2.28	<0.1	Okoye, 1991
Ghana	0.46	4.63	0.36	<0.1	Institute of aquatic biology, 1990
U K	0.2-1.7	6.0-19.5	0.1-0.72	0.05-0.15	Wharfe *et al.*, (1977)
U.S.A	0.5-1.1	5.2-6	<0.8-1.4	<0.1	Greig and Wenzloff (1977)
Finland	0.54±0.16	3.4±1	<0.6-5±0.02 and<0.2-4.3	0±0.003	Perttila *et al.*, (1982)
WHO limits (finfish and shellfish)	30	1000	2	2	Kakulu *et al.*, (1987)

Table 20. Heavy metal concentrations (μg g^{-1} wet wt) in fish species collected from Mtwapa Creek.

Species	Length (mm)	Cu	Zn	Pb	Cd
Leiognathus equulus (N-15)	73.5-159.0 (113.6±34.9)	0.169-1.898 (0.397±0.042)	6.273-11.746 (8.510±1.76)	0.005-4.807 (1.269±1.45)	0.002-0.561 (0.211±0.22)
Lutjanus fulviflama (N-7) *Tembo	69.5-85.0 (76.0±5.3)	0.245-1.165 (0.499±0.36)	4.017-6.512 (5.506±0.84)	0.005-3.002 (1.880±1.09)	0.002-0.889 (0.333±0.37)
Rhabdosargus globiceps (N-9)	126.0-184.0 (146.7±19.5)	0.307-0.451 (0.357±0.05)	3.173-3.656 (3.398±0.15)	0.005-2.342 (0.921±0.73)	0.180-0.320 (0.247±0.04)
Sardinella gibbosa (N-18) *Simu	97.5-125.0 (110.0±7.3)	0.001-1.218 (0.954±0.29)	0.006-10.055 (8.258±2.24)	0.316-2.635 (1.630±0.55)	0.024-0.125 (0.078±0.03
Gerres Sp. (N-13)	87.0-183.0 (101.8±25.3)	0.185-1.928 (0.523±0.47)	5.856-9.693 (6.903±1.13)	0.005-2.398 (0.960±0.85)	0.002-0.418 (0.054±0.11)
Siganus canaliculatus (N-10) *Tafi	280.0-329.0 (298.6±16.1)	0.108-0.183 (0.141±0.02)	3.615-5.623 (4.605±0.72)	0.301-1.016 (0.535±0.25)	0.006-0.146 (0.077±0.04)
Leptoscarus vaigensis (N-4) *Pono	202.0-292.0 (232.0±40.7)	0.060-0.267 (0.188±0.10)	1.564-3.432 (2.691±0.080)	0.005-0.085 (0.025±0.04)	0.002-0.577 (0.146±0.29)

* Local name

Table 21. Heavy metal concentrations (μg g^{-1} wet wt) in fish species collected from Port Reitz and Makupa Creeks.

Creek	Species	Length (mm)	Cu	Zn	Pb	Cd
Port Reitz	Leiognathus equulus (N-9)	109.0-126.0 (114.8±5.7)	0.130-0.396 (0.291±0.08)	4.130-7.666 (6.869±1.10)	0.005-0.801 (0.243±0.28)	0.002-0.275 (0.111±0.11)
	Polysteganus caeruleopunctatus (N-9)	136.0-159.0 (144.8±8.6)	0.160-0.604 (0.357±0.17)	3.746-5.632 (4.354±0.64)	0.354-1.103 (0.761±0.31)	0.158-0.258 (0.204±0.03)
	Strializa canaliculatus (N-5)	93.0-115.5 (104.4±10.4)	0.419-0.873 (0.598±0.17)	5.598-7.472 (6.395±0.77)	1.132-2.302 (1.648±0.46)	0.002-0.076 (0.021±0.03)
	Epinephelus Postelli (N-1) *Tewa	370	0.136	6.586	0.005	0.304
	Lethrinus mahsena (N-4)	115-132 (124.0±8.3)	0.253-0.324 (0.290±0.03)	3.557-4.690 (4.124±0.55	0.005-0.297 (0.150±0.13)	0.027-0.066 (0.039±0.02)
Makupa	Gerres Sp. (N-9)	100.0-127.0 112.7±9.1	0.455-0.595 (0.515±0.04)	6.977-14.738 (11.37±2.78)	0.476-1.437 (0.444±0.49)	0.351-0.810 (0.614±0.15)

* Local name

Table 22. Heavy metal concentrations (μg g^{-1} wet wt) in fish species collected from Shirazi Creek.

Species	Length (mm)	Cu	Zn	Pb	Cd
Leptoscarus vaigensis (N-5) *Pono	155.0-230.0 (191.6±33.3)	0.044-0.206 (0.120±0.06)	2.255-3.750 (2.823±0.55)	1.220-1.725 (1.497±±0.18)	0.002-0.226 (0.130±0.11)
Leptoscarus Sordiditus (N-10) *Pono	150.0-265.0 (184.6±36.5)	0.001-0.624 (0.163±0.20)	1.826-6.667 (3.032±1.52)	1.220-2.060 (1.670±0.25)	0.002-0.028 (0.007±0.01)
Lethrinus nebulosus (N-3)	120.0-120.0 (120.0)	0.064-0.209 (0.130±0.07)	3.299-3.857 (3.559±0.28)	0.981-1.394 (1.254±0.24)	0.251-0.370 (0.291±0.07)
Siganus canaliculatus (N-9) *Tafi	121-155 (136.0±11.7)	0.138-0.638 (0.304±0.16)	3.632-5.760 (4.568±0.72)	0.597-1.959 (1.196±0.51)	0.002-0.014 (0.003±0.004)
Epinephelus postelli (N-4) *Tewa	193.0-510.0 (353.8±174.9)	0.107-1.353 (0.450±0.60)	2.634-3.722 (3.320±0.48)	0.206-2.062 (1.345±0.81)	0.028-0.252 (0.092±0.11)
Plectorhyncus gaterina (N-4) *Fute	100.0-450.0 (342.5±163.6)	0.207-0.654 (0.431±0.19)	2.998-3.973 (3.474±0.40)	1.184-2.711 (1.589±0.66)	0.072-0.122 (0.092±0.02)
Plectorhyncus flavomaculatus (N-1) *Fute	152.0	0.262	2.711	1.344	0.051
Platycephalus crocodylus (N-1)	350.0	0.116	3.391	1.629	0.029
Lutjanus fulviflama (N-8) *Tembo	107-125.0 (115.4±6.1)	0.070-0.624 (0.240±0.18)	2.896-5.864 (3.932±0.93)	1.135-1.816 (1.524±0.22)	0.002-0.305 (0.176±0.14)

* Local name

Irrespective of site or species, Zn concentrations were generally highest of the four elements analysed while Cd concentrations were generally the least. Highest mean Cu (0.954 μg g^{-1}) and Pb (1.880 μg g^{-1}) concentrations were observed in *Sardinella gibbosa* and *Lutjanus fulviflama* respectively both from Mtwapa Creek. Highest mean Zn (11.373 μg g^{-1}) and Cd (0.614 μg g^{-1}) concentrations were observed from *Gerres* Sp.

from Makupa Creek. There was significant inter and intra-specific variation in elemental concentrations. This was as expected due to species specificity in for instance food and feeding habits. Inter-specific variation may not be necessarily attributed to site specificity since many fish are migratory and not confined to one locality. The intra-specific variation may be attributed to intra-specific differences in metabolism in relation to aspects such as size, age, sex, and maturity stage of the fish among others.

Previous researchers have observed comparable results. For instance, Wandiga and Onyari (1987) working on fish bought from Mombasa markets observed, elemental concentrations of 0.36-2.04, 4.67-40.8, 1.22-6.48 and 0.04-0.38 $\mu g\ g^{-1}$ wet wt, for Cu, Zn, Pb and Cd respectively in fish muscle. Though these workers observed slightly higher metal concentrations in the marine fishes as compared to fish from Lake Victoria, the reported concentrations did not pose an immediate danger to the fish industry. Elemental concentrations observed in the present study were generally lower than those observed by these workers (Wandiga and Onyari, 1987).

Chen and Chen (2001) observed that, whether in tissues or by gender, the concentrations of Zn, Fe, Cu, Mn and Cd in the nine common fishes from Ann-Ping coastal waters of Taiwan, all showed the trend, Zn=Fe>Cu=Mn>Cd. The ranges of essential elements Zn, and Cu in fish muscle were 4.0-7.28 and 0.2-0.45 $\mu g\ g^{-1}$ wet wt respectively, while the muscle concentration of non-essential Cd was below the detection limit of 0.005 $\mu g\ g^{-1}$. These workers further observed, distinctive species differences of metal concentrations in the 9 species ($p<0.05$) of their study and that generally speaking, among those species, higher concentrations of Zn, Fe, Cu, Mn and Cd in all tissues were found in *Sardinella Lemuru* and *Liza macrolepis*. These workers concluded that the

heavy metal concentrations of the nine species in Ann-Ping coastal waters were similar to those of slightly polluted waters, and were far below the daily intake allowance set for safety metal concentrations in fisheries products by various countries. Concentrations reported in the present study are below the WHO limits (Kakulu *et al.*, 1987).

Cross *et al.*, (1973) stated that, it was generally believed that fish actively regulate Zn concentrations in their muscle tissue and as a result do not reflect changes in ambient available levels of this element in their environment (Philips, 1980). Denton and Burdon-Jones (1986) however argued that generally higher ranges of Zn concentrations had been reported from relatively polluted areas of the world (Halcrow *et al.*, 1973; Eustace, 1974: Sims and Presley, 1976; Roth and Hornung, 1977; Plaskett and Potter, 1979) which inferred that regulation of this element may not be complete.

Though, (Phillips, 1980) stated that Cu like Zn is an essential element in fish and is thought to be strictly regulated in muscle tissue, Denton and Burdon-Jones (1986), further argued that generally higher mean Cu levels in fish axial muscle (i.e. 1.0 $\mu g\ g^{-1}$) had been reported for species taken from waters suspected of being relatively enriched in this element (by virtue of their proximity to the coast, major rivers, urban and industrial growth centres etc.) in Australia (Burdon-Jones *et al.*, 1975: Plaskett and Potter, 1979) and elsewhere (e.g. Portman, 1972; Halcrow *et al.*, 1973; Windom *et al.*, 1973; Powell *et al.*, 1981; Philips *et al.*, 1982). However, Denton and Burdon-Jones (1986) did point out that such differences may simply reflect species-specific requirements for this and other essential elements rather than locational differences in their ambient availability. In the present study, highest average lead concentrations in fish, though not beyond the WHO limit guidelines, were observed in fish species from Shirazi Creek. Ironically, in section

4.4.6, it was noted that lead concentrations in Shirazi Creek sediments ranked in the low concentration range according to Donazzolo's (1984) classification. It may be possible that, the little lead present in that creek is in a form that is released to the water column and hence available to the biotic community. Nevertheless, inter-specific differences in elemental concentrations in fish in the present study could not be attributed to locality due to other possible explanations as stated earlier in this section. However, more specific research focusing on this aspect is warranted.

4.6. Oysters

4.6.1. Inter-Creek Comparisons of Average Lengths, Widths and Elemental Concentrations in Oysters

Figures 46 and 47 show the variations in average lengths and widths between oysters from various creeks respectively. Figures 48a to 48d show the variation in respective average elemental concentrations in oysters from various creeks.

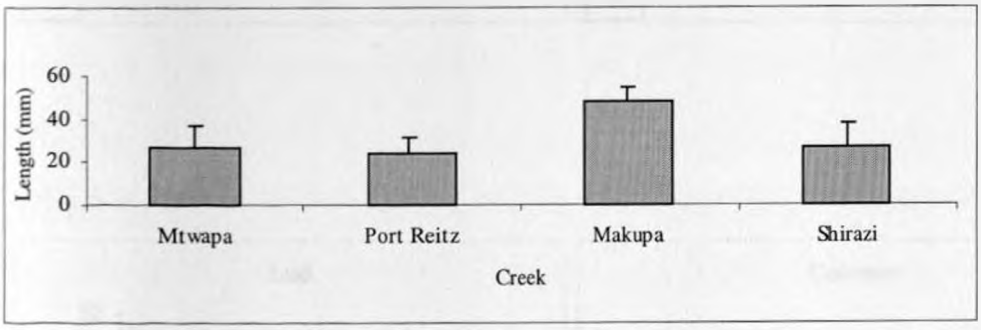


Figure 46. Oyster length variation between creeks

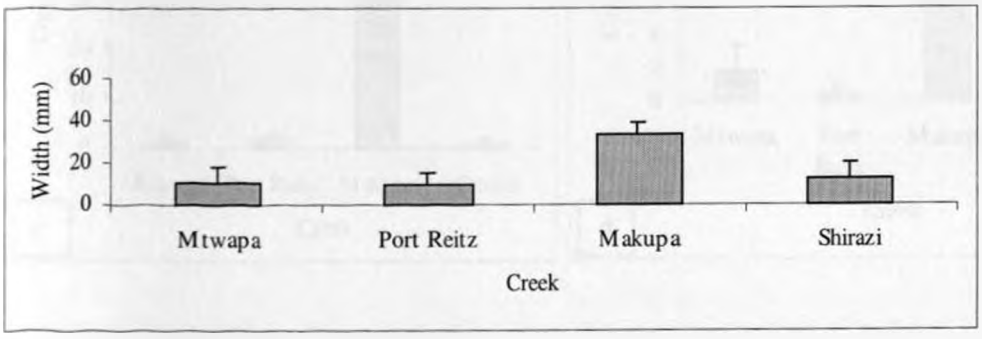


Figure 47. Oyster width variation between creeks

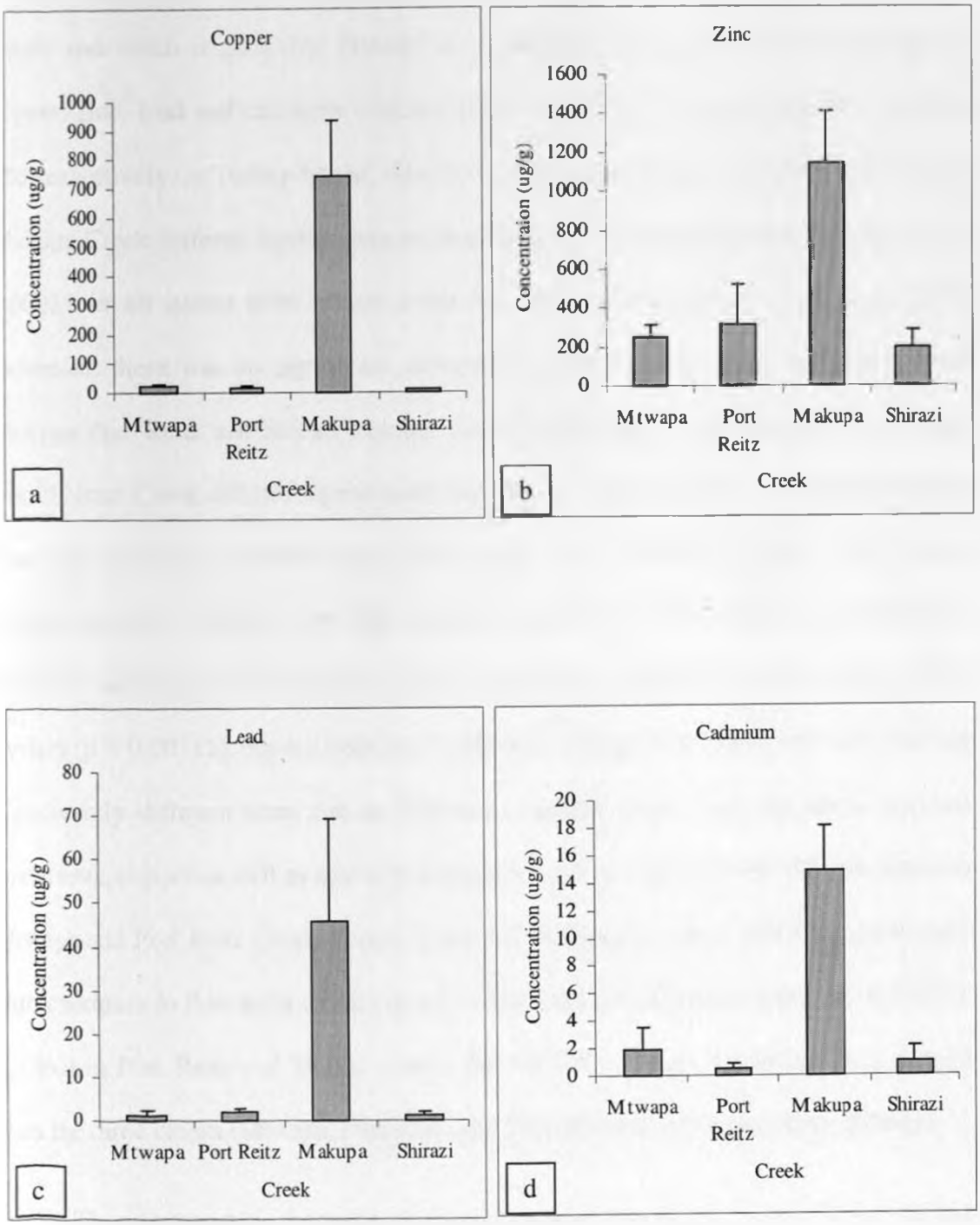


Figure 48. Mean elemental concentrations in oysters per creek.

Oysters from Makupa Creek were longer and wider as compared to oysters from the three creeks Mtwapa, Port Reitz and Shirazi Creeks as shown in Figures 46 and 47 for length and width respectively. Oysters from Makupa Creek also recorded the highest copper, zinc, lead and cadmium concentrations as shown in Figures 48a, 48b, 48c and 48d respectively. A Turkey honest significant difference test revealed that oysters from Makupa Creek differed significantly in length, width and elemental concentrations ($p = 0.00015$ in all cases) with oysters from the other creeks. However, Makupa Creek exempted, there was no significant difference in lengths and widths of oysters from Mtwapa Port Reitz and Shirazi Creeks. Nevertheless, copper concentrations in oysters from Shirazi Creek differed significantly from copper concentrations in oysters collected from Mtwapa ($p = 0.00011$) and Port Reitz ($P = 0.00017$) Creeks. The copper concentrations in oysters from Mtwapa and Port Reitz Creek were not significantly different. Similarly, zinc in Shirazi oysters significantly differed from zinc in Port Reitz oysters ($p = 0.00711$), but not with that in Mtwapa oysters. Yet zinc in the latter was not significantly different from that in Port Reitz oysters. Thus, from the above last two statements, copper as well as zinc concentrations were not significantly different between Mtwapa and Port Reitz Creek oysters. Cadmium in Mtwapa oysters differed significantly with cadmium in Port Reitz oysters ($p = 0.01074$) and with Shirazi oysters ($p = 0.04074$), but that in Port Reitz and Shirazi oysters did not differ. Lead concentrations in oysters from the three creeks (Mtwapa, Port Reitz and Shirazi) were not significantly different.

The relationships between elemental concentrations in oysters from various creeks as observed above may be as a result of many interactive factors such as source and availability of particular elements in respective creeks. For instance, the source of an

element in the various creeks may be similar but the determinant in the level of availability of that element to the biota may differ between the creeks. Consequently, patterns of elemental relationships in environmental and biological compartments may be confounded. For example in section 4.4.5 it was observed that lead concentrations in Mtwapa Creek sediments differed significantly from those of Shirazi and Port Reitz creeks, yet those of the latter two creeks did not differ. However, there was no significant difference in lead concentrations in oysters from the three creeks. Another confounding example was that, Mtwapa Creek oysters significantly differed in their cadmium concentrations from Shirazi Creek and Port Reitz Creek oysters, yet the latter showed no significant difference. However, cadmium concentrations in sediments from the three creeks showed no significant difference.

4.6.2. Elemental Correlations in Oysters

Elemental regression analyses were performed in the data obtained for oysters collected from various creeks. Significant elemental correlations in oysters per creek are reported in Table 23.

Table 23. Significant elemental correlations in oysters per creek.

Creek	Significant correlations
Mtwapa	None
Port Reitz	Zn-Cu, Cd*
Makupa	Cd-Cu, Pb
Shirazi	Cu-Zn Cd-Cu*, Zn*

(* Marked correlations are negative)

In Mtwapa Creek, there were no significant correlations between the elements assessed. Zinc and copper concentrations were positively correlated with each other but negatively with cadmium in both Port Reitz and Shirazi Creeks. Just like it was observed in fish in section 4.5.3, elements of biological value to the biota seem to have the propensity to positively correlate with each other but negatively correlate with elements of no biological value to the organisms. However, for Makupa Creek oysters, cadmium correlated positively with copper and lead. May be in such a situation the supply of these elements surpasses the ability of the organism to discriminate nonessential elements against the essential one.

4.6.3. Elemental Content in Oysters and Sediments

Organisms acquire trace elements through water, sediment and food among other pathways. However, distribution processes of a chemical in the environment influence the exposure to the biota of the trace elements among other chemicals. These distribution processes include physical movement as well as chemical transformations. Thus, filter feeders will be exposed to a chemical on suspended matter as well as that dissolved in the water mass. Also biota in the sediment will be exposed to a chemical which has been distributed from the water into the sedimentary mass. In addition the bioavailabily of a specific chemical will also influence its entry into the biota. In the present study exceptionally high elemental concentrations in sediments and oysters were observed in samples collected from Makupa Creek. Elemental concentrations in these two compartments did not however equate. This is because the two compartments are not directly linked due to the ecosystem dynamics as explained above.

4.6.4. Comparison of Elemental Concentrations in Oysters with Literature Data

The observed elemental concentration ranges and means in Oysters per site are summarised in Table 24. Values of elemental concentrations observed in the same genus in other marine areas of the world have also been provided for comparison purpose.

Table 24. Heavy metal concentrations (µg g^{-1} wet wt) in *Saccostrea cucullata* collected from the coastal region of Kenya compared with concentrations observed in *Saccostrea* sp. in other marine areas of the world.

Location	Cu	Zn	Pb	Cd	Reference
Mtwapa	9.3-44.7 (21.0±9.2)	166.1-393.2 (247.5±63.7)	0.005-3.9 (1.4±1.1)	0.002-5.6 (1.9±1.6)	Present study
Port Reitz	15.2-35.4 (20.3±6.1)	171.5-736.5 (315.2±207.1)	0.54-3.10 (1.81±0.90)	0.002-0.90 (0.54±0.28)	Present study
Makupa	310.6-1090.6 (744.3±192.5)	635.7-1538.7 (1146.5±262.5)	12.2-97.6 (45.9±23.3)	6.2-19.6 (14.8±3.3)	Present study
Shirazi	3.3-17.7 (9.5±4.3)	46.8-404.8 (196.8±90.8)	0.005-3.8 (1.01±1.07)	0.01-4.2 (1.07±1.04)	Present study
South Africa	2.35	213.0	0.08	1.62	Walting and Walting, 1982a
Nigeria	5.8	628.0	2.09	0.17	Okoye, 1991
Cameroon	8.45	407.0		0.25	Mbome, 1988
India; Near caustic soda plant	21.55±1.00 to 48.78±1.16	103±11.6 to 156.9±17.4	0.2±0.04 to 2.02±0.73	0.16±0.02 to 3.19±0.16	Krishnakumar (1990)
India; Away from caustic soda plant	38.6±13.6	91.1±51.2	0.308±0.007	1.82±0.4	Krishnakumar (1990)
India	128.0-201.0	31.0-70.3	0.3-7.5	1.47-10.9	Krishnakumar *et al.*, (1998)
Hongkong	735.0-1742.0	3492.0-8629.0	<0.1-0.4	1.53-14.7	Phillips and Yim (1981)
Hongkong	150.0-500.0	2000.0-3000.0	-	5.0-12.0	Chu *et al.*, (1990)
WHO limits (finfish and shellfish)	30	1000	2	2	Kakulu *et al.*, 1987

Exceptionally high concentrations were observed in oysters from Makupa Creek. As stated earlier this Creek is influenced by a number of anthropogenic activities. Due to the improper flushing of the water, there is localised accumulation of inputs from both point source and diffuse sources. Hence biota in that creek may be at a higher risk of exposure to heavy metals among other inputs.

Of the elements analysed, Zn concentrations were highest in oyster soft tissues followed by those of Cu, Pb and Cd. Elemental concentrations were generally higher in oysters as compared to fish but were less than those observed in sediments. On average, the WHO limit guidelines (Kakulu *et al.*, 1987) of elemental concentrations in finfish and shellfish were exceeded in only oysters from Makupa creek for all the four elements analysed.

Results of this study are comparable to those reported by other workers. For instance, Krishnakumar *et al.*, (1990) reported that concentration of trace metals in the pelagic species like sardine, mackerel and squid were lower than those of benthic animals like crab and prawn. These workers also observed that Cu is the next preferred metal after Zn for accumulation in tissues of bivalves. This is consistent with reports by Goldberg *et al.*, (1978) and Martincic *et al.*, (1984) who described the oyster as an organism with a very high ability to accumulate Zn and Cu. Oysters have been demonstrated to be more effective bioaccumulators of Zn, Cu and Cd when compared to mussels and seaweeds (Ikuta, 1988). Oysters have also been known to accumulate high levels of Zn with concentrations as high as 11,000 mg g^{-1} wet weight being found in the digestive gland of oysters (Clark *et al.*, 1997). Concentrations of Zn in oysters, *Crassostrea gigas* and *Ostrea edulis*, from Irish waters in1996 ranged from 192.7-532.7 mg kg^{-1} wet weight,

while the range in mussels, *Mytilus Edulis*, was from 11.5-27.7 mg kg^{-1} wet weight (Bloxham *et al.*, 1998). These workers also stated that, at the time, the UK was the only country to set down a guideline value of 50 mg kg^{-1} for Zn in food, however, this excluded shellfish. The level in Shellfish is expected to be well in excess of 100 mg kg^{-1} wet weight (Anon., 1992).

Krishnakumar *et al.*, (1998) later observed that, there were relatively high concentrations of Cu and Zn in sediment (Cu, 37 μg g^{-1} Zn 68.8 μg g^{-1}) and tissue of bivalves (Cu, 128-201 μg g^{-1}; Zn 70.5-127.3 μg g^{-1}) collected from Thannirbavi, Mangalore from the vicinity of effluent discharge points of a Chemical and Fertiliser Factory and a Iron Ore processing plant while metal concentration in sediment and bivalves from all other sites of coastal waters of Karnataka had concentrations more or less within the normal range.

Frew *et al.*, (1997) reported that the commercially fished oyster (*Tiostrea chilensis*) in Foveaux strait, New Zealand contained unusually high levels of Cd, contrary to their expectation since that was a relatively remote region lacking obvious industrial or domestic sources of Cd. Average dry wt concentrations in that report exceeded 20 μg g^{-1}. Highest Cd concentrations and uptake rates were found nearest Stewart Island and this corresponded to the region of greatest Cd concentration in the sediments. In general the highest sediment concentrations were found in the deepest regions of the sea floor, suggesting that the high levels of Cd levels in the oysters might have been supported by high transport rates of Cd-rich particulate matter into the region, rather than high local concentrations in the sediment.

The high concentration factors frequently found in filter feeding organisms are due to a multiple exposure of for instance the oyster to many environmental compartments containing trace metals. As filter feeding organisms, they incorporate their trace metal load through direct absorption of dissolved metals from the water and from the ingestion of contaminated suspended particles and re-suspended bottom sediments. Although dissolved trace metals are more bioavailable than other forms. Sediments can also be a significant source of contaminants in the changing tidal estuarine environment (Bryan, 1986; King and Davies, 1987).

5.0 GENERAL DISCUSSION

Results of the present study show that elemental concentrations varied within and between creeks and compartments. Basically, irrespective of the creek, assessed elemental concentrations were highest in sediments, followed by those observed in oyster soft tissues (NB: Bivalves have the ability to concentrate and integrate chemicals in their tissues yet with limited ability to metabolise most chemicals than other species such as fish (Bayne *et al.*, 1985; Widdows and Donkin 1992)) while fish muscle recorded the least concentrations.

For metals, bioconcentration (the net result of uptake and elimination processes) depends more on physiological processes. For instance, the presence of active uptake and elimination processes, as well as the capacity of an organism to induce the synthesis of a metal storage protein, metallothionein, are manifestations of physiological processes, which may differ greatly between organisms (Van Leeuwen and Hermens, 1995). Consequently, differences in elemental concentrations between species are not aberrant. An important physicochemical property of some heavy metals which influences bioconcentration, is the similarity of these metals to essential ions, like that of cadmium to calcium (Van Leeuwen and Hermens, 1995).

The direct monitoring of trace metals in the marine environment is often made difficult by short-term variations in the concentrations of trace metals in water. To avoid the analysis of an extensive number of water samples both marine organisms (such as molluscs) (Darracott and Watling, 1975; Goldberg *et al.*, 1978; Stephenson *et al.*, 1979; Popham *et al.*, 1980) and sediments (Cauwet, 1987) have been used as indicators of trace metals contamination. Both have the advantages that they are believed to integrate

temporal and spatial variations and to concentrate most trace elements to an extent which greatly simplifies subsequent analysis (Martin, 1979). Trace element concentrations in sediment can be at least three orders of magnitude greater than the same elements in aqueous phases because trace elements often sorb to particle surfaces (Horowitz, 1991). Nevertheless, compared to sediments, molluscs exhibit greater spatial sensitivity and these are a most reliable tool for identifying sources of biologically available trace metal contamination (Thomson et al., 1984; Goldberg et al., 1978; Koide et al., 1982). Biomonitors have been defined as species which accumulate trace contaminants in their tissues, responding to that fraction in the environment which is of direct ecotoxicological relevance, i.e. the bioavailable form (Rainbow and Philips, 1993). A good biomonitor, according to Moragwa (2000), should be sessile, easy to identify, a dominant member of the communities in the particular ecosystem, has a wide geographical distribution, accumulates contaminants in its body tissues and is available for sampling through out the year. Thus, from the present study results, and in conformity with the above statements, oysters are indeed, a potential biomonitor for trace element contaminants in the investigated creeks among others along the Kenyan Coast.

Fish are often used as indicators of marine pollution in confined coastal ecosystems since they are relatively large and easily identified. Baseline surveys of concentrations of heavy metals in selected fish species have been conducted in several coastal waters around the world (Turgeon and O'Connor, 1991; Essink, 1989; Sharif et al., 1991;). There are surveys, such as The National Status and Trends Program of The National Oceanic and Atmospheric Administration, which monitor heavy metal pollution in coastal and estuarine waters by recording metal concentrations in fish muscle and liver.

However, accurate monitoring is rendered difficult by seasonal changes in fish (Mance, 1987), their different ages, sizes and weights (ICES, 1989; Cossa et al., 1992; Law and Singh, 1991) and their mobility. Environmental factors such as temperature and salinity also affect metal uptake (Philips, 1980). Though it is recognised that using a suite of biomonitors to cover all uptake routes would provide a complete picture of bioavailable metals (Rainbow and Philips, 1993), constraints of time however, often make this impossible. In the creeks investigated during the present study, fish would be a less preferable biomonitor in comparison to oysters since those ecosystems are not confined and hence the fish in them may not be resident.

For all the compartments assessed the highest elemental concentrations were generally observed in samples from Makupa Creek and the least from Shirazi Creek samples. Stormwater contamination from domestic, agricultural and industrial waste is an urban environmental problem. Urban run off contains contaminants such as heavy metals and various organic compounds that eventually accumulate in wetlands, mangroves and inner creek flats. Mangrove swamps in particular act as a type of "buffer zone" receiving inputs from both land and sea. In this low energy environment, the build up of contaminants in the sediment tends to be high thus causing a continual fluctuation of contaminants that is in the long run detrimental to the biota living in these areas (Moragwa 2000). Shirazi Creek is located in a less industrialised zone as compared to the other creeks, Makupa, Port Reitz and Mtwapa. Thus, the spatial variation observed in elemental concentrations between the creeks assessed, may be attributed to the variation in urbanisation activities around the creeks.

5.0. CONCLUSION

It can be inferred from this study that:

The anthropogenic influence on the marine tidal creeks along the Kenyan Coast varies according to the magnitude of human activities in a particular creek and along its riparian zone. The creeks under investigation can be classified from the present study findings, in order of most to least influenced as follows, Makupa>Mtwapa>Port Reitz>Shirazi.

The trace element loads in the muscle tissues of the fish species assessed in this study are not yet at levels that pose danger to human health since they were below the World Health Organisation (WHO) limit guidelines.

The trace element loads in oyster (*Saccostrea cucullata*) soft tissues collected from the various creeks are not yet at levels dangerous to human health except those from Makupa Creek which indeed exceeded the WHO limit guidelines.

There is inadequate comprehensive data and information on trace element input sources and fates in the creeks along the Kenyan Coast. Particularly those under investigation in the present study. Information on sediment characteristic and sediment dynamics in those creeks is also limited especially for Mtwapa and Shirazi Creeks.

6.0. RECOMMENDATIONS

There is need for the evaluation of the actual components of discharges from industries, municipal sewage outfalls and waste disposal areas around the creeks under investigation, particularly Makupa Creek. The influence of the activities in the catchment areas of the creeks also need to be evaluated. This can be achieved through the assessment of the contents of rivers flowing into the creeks where applicable especially in Mtwapa Creek

Clean-up and remediation measures in and around contaminated sites should be initiated and implemented. The recent Kenyan government proposal to relocate Kibarani dumpsite, should it be effected, is one way forward. This will not only ease the nuisance of the foul smell but also reduce the burden of potential pollutants into the adjacent ecosystems such as Makupa Creek. There is need however, for proper modelling and predictive ecological risk assessment before such projects are undertaken. This would minimise the risk of relocating the problem to another area.

The economic, political and social advantages associated with the construction of the Makupa causeway may not be underestimated. Nevertheless, this barrier impeded the confluence of Makupa Creek with Tudor Creek. Consequently, this enhanced the confinement and hence localisation of inputs in Makupa Creek due to obstruction of tidal mixing and flushing of that creek. Inclusion of culverts in the construction of this causeway would have to a certain extent precluded that somewhat overlooked problem. This may be worth consideration in a remedial action plan for Makupa Creek.

Shirazi Creek ranked least influenced by anthropogenic activities among the creeks under investigation. Human activities particularly the tourism industry in and

around this creek may not be as lucrative as that in other areas along the Kenyan Coast but has however, high potential for proliferation. Thus, developers in that sector should take appropriate measures to cater for such expansion in future. For instance, with respect to heavy metals, use of unleaded fuel in transport vessels would be a favourable measure.

Further research on sources and fates of trace element inputs in the Kenyan Coast Creek ecosystems is also required. Emphasis should be laid particularly on bioavailability and transformations of the trace elements within and between environmental and biological compartments. Sediment dynamics and sediment characterisation research will be indispensable in the understanding of the ecosystem dynamics with regard to trace elements.

Future research should also focus on molecular, biochemical, physiological and behavioural responses of different organisms to the influence of various trace elements. This is imperative in understanding the effects of heavy metals on population, community and ecosystem structure and function.

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9.0. APPENDIX

Table 25. Means ($\bar{x}$) and standard deviations (δ) of elemental concentrations ($\mu g\ g^{-1}$ dry wt) per substation in Mtwapa Creek sediments

Sub-stn	Cu($\bar{x}$)	*Cu(δ)*	Zn($\bar{x}$)	*Zn(δ)*	Pb($\bar{x}$)	*Pb(δ)*	Cd($\bar{x}$)	*Cd(δ)*
TM1a	39.311	*1.289*	80.465	*1.727*	87.333	*1.495*	0.970	*0.173*
TM1b	36.399	*1.382*	75.392	*1.775*	80.030	*0.291*	0.922	*0.036*
TM1c	41.188	*0.336*	90.039	*2.186*	94.607	*3.843*	1.248	*0.070*
TU2a	41.896	*0.675*	81.584	*5.277*	46.159	*1.689*	1.388	*0.069*
TU2b	30.635	*0.002*	58.057	*0.920*	35.318	*0.808*	1.096	*0.071*
TU2c	59.128	*1.096*	100.318	*0.176*	52.122	*1.477*	2.335	*0.002*
TM3a	38.916	*0.047*	63.613	*0.135*	79.330	*1.506*	1.123	*0.037*
TM3b	41.791	*0.076*	65.522	*0.091*	68.656	*0.578*	1.070	*0.037*
TM3c	44.221	*1.301*	74.138	*2.631*	52.089	*3.819*	1.035	*0.036*
TU3a	49.562	*0.711*	82.785	*0.024*	76.036	*0.187*	2.117	*0.035*
TU3b	50.890	*1.012*	84.643	*0.713*	71.994	*1.663*	1.621	*0.034*
TU3c	61.042	*1.358*	98.840	*1.775*	45.694	*0.983*	1.769	*0.107*
TJ4a	38.452	*0.046*	63.570	*0.418*	63.172	*0.782*	1.024	*0.072*
TJ4b	38.945	*0.006*	68.155	*0.292*	67.655	*0.363*	0.949	*0.070*
TJ4c	29.128	*0.348*	47.500	*0.627*	35.102	*1.403*	0.846	*0.000*
TJ5a	38.936	*0.047*	63.545	*0.206*	69.036	*0.436*	0.973	*0.036*
TJ5b	36.050	*0.364*	64.964	*0.153*	68.370	*0.328*	1.243	*0.141*
TJ5c	35.569	*0.377*	66.934	*1.560*	65.665	*0.046*	1.194	*0.001*
TM5a	39.444	*0.331*	67.850	*1.402*	64.996	*2.073*	1.042	*0.001*
TM5b	34.940	*0.913*	63.541	*1.718*	62.890	*1.079*	0.799	*0.005*
TM5c	40.793	*0.000*	86.247	*0.000*	58.275	*0.000*	2.331	*0.000*
TU5a	37.392	*0.358*	60.175	*0.908*	34.998	*0.982*	1.122	*0.035*
TU5c	51.636	*0.015*	80.947	*0.517*	72.067	*0.726*	1.921	*0.035*
TJ6a	80.649	*1.436*	71.216	*1.820*	69.847	*2.489*	0.647	*0.000*
TJ6b	45.694	*0.000*	69.683	*0.281*	74.501	*0.702*	1.118	*0.035*
TJ6c	43.444	*0.360*	69.411	*0.758*	71.496	*0.015*	1.266	*0.035*
TM6a	22.941	*0.645*	47.301	*2.310*	40.643	*2.715*	0.574	*0.001*
TM6b	19.634	*0.351*	43.941	*2.039*	29.476	*1.054*	0.596	*0.000*
TU6a	30.178	*0.009*	61.278	*1.852*	62.250	*0.829*	1.546	*0.000*
TU7a	33.663	*0.688*	133.978	*1.759*	55.868	*0.074*	83.441	*0.729*
TU7b	34.586	*0.538*	134.183	*0.430*	41.741	*0.450*	55.404	*0.371*
TU7c	55.227	*1.622*	185.405	*0.196*	69.356	*0.190*	59.381	*1.312*
TJ8a	10.231	*0.346*	28.973	*1.044*	34.937	*0.025*	2.071	*0.104*
TJ8b	7.969	*0.003*	28.715	*3.145*	38.352	*0.014*	2.167	*0.034*
TM8a	10.955	*0.000*	35.305	*0.000*	34.608	*0.000*	1.668	*0.000*
TU8a	7.441	*1.059*	23.140	*0.616*	29.861	*0.025*	4.092	*0.109*
TU8b	6.476	*0.363*	17.162	*2.706*	44.210	*3.033*	7.023	*0.059*
TU8c	58.945	*0.176*	88.546	*3.148*	60.492	*0.047*	3.155	*0.050*

Table 26. Means ($\bar{x}$) and standard deviations (δ) of elemental concentrations (µg g^{-1} dry wt) per substation in Port Reitz Creek sediments

Sub-stn	Cu($\bar{x}$)	*Cu(δ)*	Zn($\bar{x}$)	*Zn(δ)*	Pb($\bar{x}$)	*Pb(δ)*	Cd($\bar{x}$)	*Cd(δ)*
PM1a	13.44	*0.010*	40.50	*0.559*	22.30	*0.017*	0.62	*0.035*
PM1b	11.25	*0.052*	30.69	*0.283*	16.50	*0.278*	0.55	*0.068*
PU1a	17.93	*0.370*	45.41	*0.871*	20.79	*0.649*	1.10	*0.072*
PU1b	21.56	*2.157*	63.14	*2.041*	21.49	*0.480*	1.34	*0.070*
PU1c	20.08	*1.372*	46.41	*1.892*	22.88	*0.631*	1.36	*0.107*
PM2a	16.11	*0.001*	40.11	*4.204*	16.86	*0.352*	0.67	*0.035*
PM2b	12.73	*0.001*	35.41	*0.108*	15.97	*0.352*	0.57	*0.035*
PM2c	20.12	*0.003*	52.15	*0.730*	27.82	*0.355*	0.93	*0.004*
PU2a	16.93	*1.004*	50.06	*1.159*	17.68	*0.931*	1.12	*0.032*
PU2b	25.64	*1.408*	54.99	*0.880*	24.65	*0.211*	1.34	*0.070*
PU2c	22.08	*1.432*	53.99	*2.311*	31.35	*3.294*	1.27	*0.037*
PM3a	18.12	*0.000*	48.29	*0.316*	20.85	*0.351*	0.72	*0.035*
PM3b	15.88	*0.354*	42.03	*0.219*	19.35	*0.355*	0.72	*0.035*
PM3c	18.87	*0.350*	45.49	*0.980*	23.59	*0.002*	0.82	*0.035*
PU3a	17.68	*0.687*	40.91	*0.973*	15.68	*0.830*	0.92	*0.105*
PU3b	24.08	*1.497*	41.63	*0.647*	19.29	*0.944*	0.89	*0.003*
PU3c	32.02	*1.417*	79.56	*1.348*	29.64	*0.184*	2.31	*0.103*
PM4a	20.48	*1.421*	64.69	*0.660*	31.20	*0.000*	2.02	*0.035*
PM4c	27.81	*0.343*	71.35	*0.783*	32.29	*0.369*	1.04	*0.000*
PU4a	22.20	*0.704*	61.05	*0.281*	21.32	*0.245*	1.12	*0.035*
PU4b	16.69	*0.008*	48.88	*3.230*	17.07	*1.805*	1.15	*0.001*
PU5a	25.16	*0.002*	51.77	*1.229*	28.95	*0.213*	1.16	*0.258*
PU6a	22.19	*0.016*	92.91	*0.594*	28.03	*1.007*	2.02	*0.037*
PU7a	17.68	*0.024*	74.89	*0.548*	32.85	*0.713*	3.24	*0.004*
PU8a	28.38	*0.308*	87.41	*0.710*	32.29	*0.405*	3.16	*0.040*
PU9a	21.44	*1.067*	55.80	*0.548*	21.19	*0.009*	2.19	*0.071*
PM10a	33.33	*0.016*	88.06	*0.501*	50.73	*1.784*	2.11	*0.107*
PM11c	45.05	*0.330*	92.21	*0.623*	71.19	*1.018*	2.12	*0.034*

Table27. Means ($\bar{x}$) and standard deviations (δ) of elemental concentrations (µg g^{-1} dry wt) per substation in Makupa Creek sediments

Sub-stn	Cu($\bar{x}$)	*Cu(δ)*	Zn($\bar{x}$)	*Zn(δ)*	Pb($\bar{x}$)	*Pb(δ)*	Cd($\bar{x}$)	*Cd(δ)*
KU1	117.98	*1.584*	3196.23	*9.704*	110.64	*0.563*	46.89	*0.391*
KU2	116.16	*1.626*	1517.64	*1.081*	108.78	*0.492*	46.82	*0.444*
KU3	78.18	*3.940*	810.99	*1.853*	104.37	*0.631*	53.91	*2.837*
KU4	101.05	*1.948*	641.05	*1.255*	103.88	*2.368*	51.40	*0.181*
KU5	94.70	*1.442*	565.11	*4.681*	77.47	*2.705*	40.89	*0.805*
KU6	228.94	*1.221*	997.83	*8.249*	164.53	*0.305*	31.04	*1.101*
KU7	122.06	*0.533*	437.66	*0.523*	80.82	*0.952*	33.11	*0.245*
KU8	128.24	*1.036*	400.19	*13.752*	149.80	*1.402*	59.58	*0.673*
KU9	81.69	*1.032*	2052.06	*2.799*	160.55	*2.076*	67.82	*0.600*
KU10	82.68	*0.435*	1381.36	*2.449*	73.47	*0.255*	44.43	*0.388*
KU11	64.64	*0.970*	641.94	*3.425*	54.55	*2.216*	42.19	*1.081*
KU12	50.88	*0.175*	315.67	*4.406*	64.45	*0.694*	63.33	*0.464*
KU13	54.19	*0.437*	275.91	*4.839*	90.94	*4.703*	81.90	*0.835*

Table 28. Means ($\bar{x}$) and standard deviations (δ) of elemental concentrations (µg g^{-1} dry wt) per substation in Shirazi Creek sediments

Sub-stn	Cu($\bar{x}$)	*Cu(δ)*	Zn($\bar{x}$)	*Zn(δ)*	Pb($\bar{x}$)	*Pb(δ)*	Cd($\bar{x}$)	*Cd(δ)*
SM1a	6.690	*0.358*	18.296	*0.423*	15.367	*1.044*	0.868	*0.035*
SM1b	5.487	*0.000*	15.013	*0.493*	11.472	*0.353*	0.524	*0.035*
SM1c	10.463	*0.712*	19.639	*0.637*	14.921	*0.341*	0.696	*0.070*
SU1a	7.053	*0.946*	23.965	*0.860*	15.556	*0.994*	0.546	*0.140*
SU1b	8.359	*0.389*	25.130	*1.807*	14.364	*0.075*	0.844	*0.142*
SU1c	11.427	*1.056*	21.964	*0.667*	16.790	*0.177*	1.219	*0.035*
SJ2a	10.712	*0.360*	22.960	*0.428*	20.676	*0.719*	0.648	*0.106*
SJ2b	9.734	*0.358*	20.164	*0.014*	15.375	*0.699*	0.565	*0.093*
SM2a	7.228	*0.349*	14.904	*0.135*	10.966	*0.348*	0.498	*0.070*
SM2b	3.723	*0.355*	11.824	*0.630*	8.446	*0.353*	0.323	*0.035*
SM2c	4.976	*0.000*	14.032	*0.142*	12.937	*0.353*	0.672	*0.035*
SU2a	19.910	*0.327*	18.492	*0.223*	10.503	*0.084*	0.498	*0.070*
SU2b	8.218	*1.038*	26.149	*0.596*	14.192	*0.030*	0.770	*0.035*
SM3a	2.488	*0.001*	12.464	*0.382*	8.956	*0.356*	0.398	*0.070*
SM3b	3.966	*0.002*	13.829	*0.352*	8.925	*0.346*	0.372	*0.105*
SM3c	3.743	*0.353*	14.723	*0.494*	8.485	*1.059*	0.349	*0.071*
SU3a	5.687	*0.284*	13.459	*0.716*	10.652	*0.019*	0.720	*0.036*
SU3b	15.085	*0.089*	10.514	*0.620*	12.002	*0.601*	0.722	*0.033*
SU4a	8.297	*0.000*	16.615	*0.000*	27.827	*0.000*	1.492	*0.000*
SU4b	6.846	*0.377*	19.634	*1.184*	14.056	*0.749*	2.547	*0.070*
SU5a	7.829	*0.000*	17.600	*0.000*	13.937	*0.000*	0.987	*0.000*
SM6a	2.202	*0.000*	15.316	*0.000*	38.529	*0.000*	1.321	*0.000*
SM6b	5.713	*0.351*	16.817	*0.178*	38.752	*0.346*	3.801	*0.036*
SM6c	6.228	*0.351*	16.941	*1.124*	40.112	*0.713*	3.837	*0.070*
SJ7c	4.727	*0.000*	17.608	*0.000*	45.942	*0.000*	4.727	*0.000*
SM7a	2.239	*0.362*	9.053	*1.235*	31.828	*0.208*	2.138	*0.046*
SM7b	3.482	*0.011*	13.498	*0.651*	42.772	*0.481*	3.332	*0.024*

Table 29. Lengths (mm), means ($\bar{x}$) and standard deviations (δ) of elemental concentrations ($\mu g\ g^{-1}$ wet wt) per individual in fish collected from Mtwapa Creek.

Indiv	L (mm)	Cu($\bar{x}$)	*Cu(δ)*	Zn($\bar{x}$)	*Zn(δ)*	Pb($\bar{x}$)	*Pb(δ)*	Cd($\bar{x}$)	*Cd(δ)*
TRg1	126.0	0.338	*0.140*	3.409	*0.811*	0.652	*0.259*	0.251	*0.016*
TRg2	127.0	0.323	*0.001*	3.173	*0.132*	0.358	*0.437*	0.240	*0.021*
TRg3	130.0	0.307	*0.033*	3.564	*0.096*	1.392	*0.119*	0.180	*0.008*
TRg4	135.0	0.384	*0.090*	3.284	*0.037*	1.623	*0.953*	0.256	*0.037*
TRg5	147.0	0.341	*0.000*	3.379	*0.000*	2.342	*0.000*	0.215	*0.000*
TRg6	152.0	0.328	*0.035*	3.656	*0.122*	0.851	*0.359*	0.235	*0.097*
TRg7	154.0	0.422	*0.046*	3.234	*0.071*	0.635	*0.590*	0.215	*0.095*
TRg8	165.0	0.451	*0.018*	3.461	*0.392*	0.427	*0.596*	0.320	*0.035*
TRg9	184.0	0.320	*0.014*	3.426	*0.155*	0.005	*0.000*	0.310	*0.000*
TLf1	69.5	0.245	*0.000*	4.017	*0.000*	0.005	*0.000*	0.757	*0.000*
TLf2	70.0	0.252	*0.000*	5.306	*0.000*	2.659	*0.000*	0.002	*0.000*
TLf3	75.7	0.846	*0.000*	6.512	*0.000*	2.894	*0.000*	0.002	*0.000*
TLf4	76.4	1.165	*0.000*	6.428	*0.000*	3.002	*0.000*	0.889	*0.000*
TLf5	76.5	0.267	*0.000*	5.625	*0.000*	1.997	*0.000*	0.002	*0.000*
TLf6	79.0	0.268	*0.000*	5.450	*0.000*	1.306	*0.000*	0.402	*0.000*
TLf7	85.0	0.447	*0.000*	5.206	*0.000*	1.300	*0.000*	0.280	*0.000*
TLe1	73.5	1.898	*0.000*	11.746	*0.000*	4.807	*0.000*	0.002	*0.000*
TLe2	73.8	0.200	*0.000*	6.555	*0.000*	2.359	*0.000*	0.002	*0.000*
TLe3	74.5	0.259	*0.000*	7.047	*0.000*	1.236	*0.000*	0.002	*0.000*
TLe4	76.0	0.322	*0.000*	7.520	*0.000*	2.660	*0.000*	0.002	*0.000*
TLe5	81.0	0.353	*0.000*	6.965	*0.000*	3.319	*0.000*	0.002	*0.000*
TLe6	84.9	0.275	*0.000*	7.050	*0.000*	0.898	*0.000*	0.002	*0.000*
TLe7	86.4	0.325	*0.000*	6.273	*0.000*	1.889	*0.000*	0.002	*0.000*
TLe8	121.5	0.261	*0.020*	9.775	*1.118*	0.005	*0.000*	0.169	*0.236*
TLe9	139.0	0.380	*0.028*	11.733	*0.631*	0.137	*0.133*	0.358	*0.051*
TLe10	145.0	0.285	*0.011*	9.385	*1.078*	0.543	*0.062*	0.417	*0.003*
TLe11	145.0	0.257	*0.015*	9.560	*0.066*	0.005	*0.000*	0.355	*0.025*
TLe12	147.0	0.281	*0.018*	7.658	*0.671*	0.426	*0.001*	0.519	*0.011*
TLe13	148.0	0.337	*0.020*	9.119	*0.046*	0.107	*0.104*	0.385	*0.100*
TLe14	149.0	0.359	*0.122*	9.437	*0.119*	0.005	*0.000*	0.390	*0.038*
TLe15	159.0	0.169	*0.020*	7.832	*1.390*	0.637	*0.051*	0.561	*0.058*
TSg1	97.5	0.755	*0.000*	9.686	*0.000*	0.802	*0.000*	0.024	*0.000*
TSg2	102.0	0.888	*0.000*	9.991	*0.000*	1.833	*0.000*	0.112	*0.000*
TSg3	102.0	0.727	*0.000*	8.699	*0.000*	0.316	*0.000*	0.029	*0.000*
TSg4	103.0	0.001	*0.000*	0.006	*0.000*	2.098	*0.000*	0.090	*0.000*
TSg5	106.6	1.034	*0.000*	7.982	*0.000*	1.943	*0.000*	0.125	*0.000*
TSg6	107.0	0.985	*0.000*	8.969	*0.000*	2.434	*0.000*	0.095	*0.000*
TSg7	109.0	1.093	*0.000*	9.365	*0.000*	1.319	*0.000*	0.079	*0.000*

Table 25. Lengths (mm), means ($\bar{x}$) and standard deviations (δ) of elemental concentrations (µg g-1 wet wt) per individual in fish collected from Mtwapa Creek. Cont.

Indiv	L (mm)	Cu($\bar{x}$)	*Cu(δ)*	Zn($\bar{x}$)	*Zn(δ)*	Pb($\bar{x}$)	*Pb(δ)*	Cd($\bar{x}$)	*Cd(δ)*
TSg8	109.4	0.629	*0.000*	7.267	*0.000*	1.352	*0.000*	0.052	*0.000*
TSg9	110.0	1.140	*0.000*	9.107	*0.000*	2.635	*0.000*	0.086	*0.000*
TSg10	110.0	1.150	*0.000*	9.020	*0.000*	1.878	*0.000*	0.085	*0.000*
TSg11	111.0	1.052	*0.000*	8.913	*0.000*	1.736	*0.000*	0.123	*0.000*
TSg12	112.7	1.078	*0.000*	9.002	*0.000*	1.282	*0.000*	0.068	*0.000*
TSg13	113.0	1.096	*0.000*	8.026	*0.000*	1.215	*0.000*	0.064	*0.000*
TSg14	114.4	0.992	*0.000*	10.055	*0.000*	1.799	*0.000*	0.121	*0.000*
TSg15	119.0	1.052	*0.000*	8.065	*0.000*	1.586	*0.000*	0.077	*0.000*
TSg16	119.9	1.218	*0.000*	6.757	*0.000*	1.873	*0.000*	0.060	*0.000*
TSg17	120.9	1.143	*0.000*	8.374	*0.000*	1.780	*0.000*	0.080	*0.000*
TSg18	125.0	1.142	*0.000*	9.355	*0.000*	1.467	*0.000*	0.028	*0.000*
TGe1	87.9	1.928	*0.000*	9.693	*0.000*	0.982	*0.000*	0.002	*0.000*
TGe2	89.0	0.267	*0.000*	5.856	*0.000*	2.137	*0.000*	0.042	*0.000*
TGe3	89.5	0.269	*0.000*	5.982	*0.000*	2.398	*0.000*	0.026	*0.000*
TGe4	90.0	0.735	*0.000*	8.093	*0.000*	2.334	*0.000*	0.047	*0.000*
TGe5	92.0	0.320	*0.000*	6.360	*0.000*	0.759	*0.000*	0.010	*0.000*
TGe6	92.5	0.185	*0.000*	6.091	*0.000*	1.445	*0.000*	0.053	*0.000*
TGe7	93.0	0.318	*0.000*	6.143	*0.000*	0.236	*0.000*	0.002	*0.000*
TGe8	93.0	0.282	*0.000*	5.974	*0.000*	0.005	*0.000*	0.032	*0.000*
TGe9	96.6	0.489	*0.000*	6.638	*0.000*	0.433	*0.000*	0.002	*0.000*
TGe10	100.5	0.295	*0.000*	6.372	*0.000*	0.658	*0.000*	0.019	*0.000*
TGe11	106.0	0.889	*0.000*	7.159	*0.000*	0.575	*0.000*	0.022	*0.000*
TGe12	110.0	0.624	*0.000*	7.732	*0.000*	0.512	*0.000*	0.021	*0.000*
TGe13	183.0	0.200	*0.001*	7.647	*2.729*	0.005	*0.000*	0.418	*0.000*
TSc1	280.0	0.119	*0.011*	3.615	*0.744*	0.625	*0.032*	0.039	*0.041*
TSc2	281.0	0.130	*0.027*	4.942	*0.201*	0.301	*0.418*	0.006	*0.005*
TSc3	285.0	0.140	*0.029*	3.944	*0.138*	0.310	*0.122*	0.091	*0.012*
TSc4	292.0	0.146	*0.075*	5.623	*0.791*	0.382	*0.188*	0.142	*0.019*
TSc5	293.0	0.157	*0.005*	4.054	*0.644*	0.470	*0.345*	0.047	*0.000*
TSc6	299.0	0.174	*0.055*	5.600	*0.820*	1.016	*0.212*	0.077	*0.041*
TSc7	299.0	0.183	*0.006*	5.279	*1.225*	0.614	*0.071*	0.081	*0.009*
TSc8	311.0	0.108	*0.025*	4.206	*0.953*	0.905	*0.311*	0.080	*0.047*
TSc9	317.0	0.120	*0.002*	4.561	*0.542*	0.341	*0.474*	0.146	*0.028*
TSc10	329.0	0.133	*0.025*	4.228	*0.272*	0.388	*0.164*	0.064	*0.023*
TLv1	202.0	0.262	*0.017*	2.993	*0.564*	0.005	*0.000*	0.577	*0.039*
TLv2	214.0	0.163	*0.006*	3.432	*0.683*	0.005	*0.000*	0.002	*0.000*
TLv3	220.0	0.267	*0.198*	2.774	*0.230*	0.085	*0.113*	0.002	*0.000*
TLv4	292.0	0.060	*0.013*	1.564	*0.064*	0.005	*0.000*	0.002	*0.000*

Table 30. Lengths (mm), means ($\bar{x}$) and standard deviations (δ) of elemental concentrations (µg g-1 wet wt) per individual in fish collected from Port Reitz Creek.

Indiv	L (mm)	Cu($\bar{x}$)	*Cu(δ)*	Zn($\bar{x}$)	*Zn(δ)*	Pb($\bar{x}$)	*Pb(δ)*	Cd($\bar{x}$)	*Cd(δ)*
PLe1	109.0	0.130	*0.182*	7.510	*1.356*	0.153	*0.210*	0.016	*0.019*
PLe2	110.0	0.244	*0.344*	4.130	*4.744*	0.005	*0.000*	0.150	*0.185*
PLe3	110.0	0.396	*0.069*	7.666	*0.217*	0.005	*0.000*	0.041	*0.027*
PLe4	110.0	0.317	*0.022*	7.592	*0.136*	0.540	*0.446*	0.002	*0.000*
PLe5	115.0	0.335	*0.003*	6.412	*0.038*	0.112	*0.151*	0.038	*0.014*
PLe6	116.0	0.280	*0.006*	7.132	*0.101*	0.801	*0.156*	0.275	*0.001*
PLe7	117.0	0.387	*0.037*	7.302	*0.206*	0.005	*0.000*	0.002	*0.000*
PLe8	120.0	0.293	*0.005*	6.760	*0.212*	0.221	*0.204*	0.259	*0.025*
PLe9	126.0	0.240	*0.056*	7.316	*0.154*	0.340	*0.473*	0.214	*0.119*
PPc1	136.0	0.259	*0.365*	4.754	*0.947*	0.354	*0.418*	0.183	*0.066*
PPc2	136.0	0.177	*0.009*	3.843	*0.177*	0.439	*0.005*	0.210	*0.002*
PPc3	138.0	0.187	*0.057*	4.091	*0.153*	1.008	*0.387*	0.202	*0.009*
PPc4	141.0	0.316	*0.024*	5.632	*0.044*	0.981	*0.087*	0.258	*0.004*
PPc5	143.0	0.604	*0.178*	4.877	*0.470*	0.356	*0.124*	0.209	*0.002*
PPc6	144.0	0.160	*0.007*	3.746	*0.017*	1.048	*0.248*	0.194	*0.028*
PPc7	149.0	0.464	*0.010*	4.487	*0.203*	0.649	*0.158*	0.199	*0.028*
PPc8	157.0	0.460	*0.048*	3.852	*0.192*	0.906	*0.134*	0.158	*0.039*
PPc9	159.0	0.552	*0.158*	3.907	*0.379*	1.103	*0.000*	0.227	*0.004*
PStc1	93.0	0.419	*0.000*	5.598	*0.000*	2.302	*0.000*	0.002	*0.000*
PStc2	94.0	0.873	*0.000*	6.657	*0.000*	1.670	*0.000*	0.002	*0.000*
PStc3	107.4	0.618	*0.000*	6.557	*0.000*	1.291	*0.000*	0.076	*0.000*
PStc4	112.0	0.592	*0.000*	5.690	*0.000*	1.132	*0.000*	0.009	*0.000*
PStc5	115.5	0.487	*0.121*	7.472	*1.546*	1.846	*0.086*	0.015	*0.009*
PEp1	370.0	0.136	*0.105*	6.586	*0.149*	0.005	*0.000*	0.304	*0.427*
PLm1	115.0	0.324	*0.000*	4.481	*0.000*	0.071	*0.000*	0.027	*0.000*
PLm2	119.0	0.253	*0.000*	3.766	*0.000*	0.005	*0.000*	0.032	*0.000*
PLm3	130.0	0.269	*0.000*	3.557	*0.000*	0.297	*0.000*	0.031	*0.000*
PLm4	132.0	0.315	*0.000*	4.690	*0.000*	0.225	*0.000*	0.066	*0.000*

Table 31. Lengths (mm), means ($\bar{x}$) and standard deviations (δ) of elemental concentrations (µg g^{-1} wet wt) per individual in fish collected from Makupa Creek.

Indiv	L (mm)	Cu($\bar{x}$)	*Cu(δ)*	Zn($\bar{x}$)	*Zn(δ)*	Pb($\bar{x}$)	*Pb(δ)*	Cd($\bar{x}$)	*Cd(δ)*
KGe1	100.0	0.455	*0.000*	10.213	*0.000*	1.437	*0.000*	0.351	*0.000*
KGe2	103.0	0.489	*0.000*	10.915	*0.000*	0.977	*0.000*	0.557	*0.000*
KGe3	109.0	0.481	*0.000*	11.370	*0.000*	0.555	*0.000*	0.540	*0.000*
KGe4	109.0	0.563	*0.000*	14.108	*0.000*	0.476	*0.000*	0.552	*0.000*
KGe5	110.0	0.595	*0.000*	12.171	*0.000*	0.231	*0.000*	0.650	*0.000*
KGe6	115.0	0.547	*0.000*	14.738	*0.000*	0.193	*0.000*	0.810	*0.000*
KGe7	116.0	0.514	*0.000*	14.178	*0.000*	0.005	*0.000*	0.778	*0.000*
KGe8	125.0	0.496	*0.000*	7.684	*0.000*	0.114	*0.000*	0.763	*0.000*
KGe9	127.0	0.496	*0.000*	6.977	*0.000*	0.005	*0.000*	0.523	*0.000*

Table 32. Lengths (mm), means ($\bar{x}$) and standard deviations (δ) of elemental concentrations (µg g^{-1} wet wt) per individual in fish collected from Shirazi Creek.

Indiv	L (mm)	Cu($\bar{x}$)	*Cu(δ)*	Zn($\bar{x}$)	*Zn(δ)*	Pb($\bar{x}$)	*Pb(δ)*	Cd($\bar{x}$)	*Cd(δ)*
SLv1	155.0	0.131	*0.000*	2.666	*0.000*	1.220	*0.000*	0.183	*0.000*
SLv2	160.0	0.206	*0.105*	3.750	*1.678*	1.725	*0.087*	0.029	*0.014*
SLv3	197.0	0.044	*0.061*	2.726	*0.422*	1.499	*0.382*	0.210	*0.038*
SLv4	216.0	0.131	*0.019*	2.255	*0.145*	1.549	*0.582*	0.002	*0.000*
SLv5	230.0	0.089	*0.001*	2.720	*0.104*	1.491	*0.293*	0.226	*0.002*
SLn1	120.0	0.064	*0.043*	3.299	*0.258*	1.394	*0.216*	0.370	*0.142*
SLn2	120.0	0.116	*0.003*	3.520	*0.184*	1.388	*0.664*	0.252	*0.126*
SLn3	120.0	0.209	*0.033*	3.857	*0.201*	0.981	*0.379*	0.251	*0.003*
SSc1	121.0	0.438	*0.016*	4.465	*0.154*	0.597	*0.441*	0.002	*0.000*
SSc2	125.0	0.369	*0.039*	4.476	*0.377*	0.640	*0.270*	0.002	*0.000*
SSc3	130.0	0.209	*0.079*	5.760	*3.137*	1.959	*0.449*	0.002	*0.000*
SSc4	130.0	0.195	*0.129*	3.957	*0.168*	1.802	*0.393*	0.014	*0.007*
SSc5	130.0	0.266	*0.072*	4.745	*0.534*	1.284	*0.022*	0.002	*0.000*
SSc6	138.0	0.638	*0.528*	4.705	*0.935*	0.829	*0.161*	0.002	*0.000*
SSc7	145.0	0.200	*0.281*	3.847	*0.086*	1.209	*0.020*	0.002	*0.000*
SSc8	150.0	0.288	*0.025*	3.632	*0.038*	1.620	*0.385*	0.002	*0.000*
SSc9	155.0	0.138	*0.193*	5.524	*0.201*	0.821	*0.270*	0.002	*0.000*
SEp1	193.0	0.121	*0.033*	3.365	*0.878*	2.062	*0.224*	0.029	*0.014*
SEp2	212.0	0.107	*0.014*	3.559	*0.066*	1.738	*0.088*	0.058	*0.000*
SEp3	500.0	1.353	*0.627*	2.634	*0.757*	0.206	*0.285*	0.028	*0.000*
SEp4	510.0	0.218	*0.045*	3.722	*1.616*	1.372	*0.169*	0.252	*0.011*
SPg1	100.0	0.359	*0.046*	3.973	*0.026*	2.577	*0.189*	0.076	*0.004*
SPg2	390.0	0.505	*0.130*	3.439	*0.251*	1.301	*0.429*	0.098	*0.042*
SPg3	430.0	0.207	*0.002*	2.998	*0.090*	1.184	*0.014*	0.122	*0.015*
SPg4	450.0	0.654	*0.596*	3.486	*0.994*	1.296	*0.244*	0.072	*0.020*
SPf1	152.0	0.262	*0.001*	2.711	*0.163*	1.344	*0.121*	0.051	*0.046*
SPc1	350.0	0.116	*0.014*	3.391	*1.405*	1.629	*0.436*	0.029	*0.014*
SLs1	150.0	0.001	*0.000*	2.621	*0.000*	1.596	*0.000*	0.002	*0.000*
SLs2	155.0	0.088	*0.000*	4.786	*0.000*	1.486	*0.000*	0.002	*0.000*
SLs3	163.0	0.086	*0.013*	2.187	*0.015*	1.784	*0.088*	0.006	*0.005*
SLs4	165.0	0.366	*0.335*	2.623	*0.678*	2.060	*0.564*	0.002	*0.000*
SLs5	170.0	0.170	*0.053*	2.317	*0.151*	1.675	*0.689*	0.002	*0.000*
SLs6	175.0	0.624	*0.881*	6.667	*5.314*	1.496	*0.297*	0.002	*0.000*
SLs7	176.0	0.189	*0.266*	2.944	*0.563*	2.001	*0.635*	0.006	*0.005*
SLs8	197.0	0.058	*0.014*	1.826	*0.084*	1.220	*0.494*	0.002	*0.000*
SLs9	230.0	0.001	*0.000*	1.913	*0.146*	1.616	*0.214*	0.028	*0.013*
SLs10	265.0	0.049	*0.068*	2.440	*0.480*	1.771	*0.432*	0.016	*0.019*
SLf1	107.0	0.306	*0.159*	4.126	*0.018*	1.324	*0.297*	0.269	*0.113*
SLf2	110.0	0.624	*0.491*	5.864	*3.483*	1.135	*0.324*	0.290	*0.019*
SLf3	110.0	0.285	*0.297*	4.590	*0.480*	1.426	*0.589*	0.305	*0.004*
SLf4	115.0	0.119	*0.031*	3.558	*0.050*	1.620	*0.837*	0.002	*0.000*
SLf5	116.0	0.197	*0.085*	3.477	*0.377*	1.633	*0.610*	0.002	*0.000*
SLf6	120.0	0.070	*0.005*	2.896	*0.082*	1.816	*0.215*	0.002	*0.000*
SLf7	120.0	0.243	*0.155*	3.512	*0.418*	1.676	*0.235*	0.280	*0.022*
SLf8	125.0	0.077	*0.011*	3.436	*0.642*	1.559	*0.844*	0.256	*0.002*

Table 33. Ranges ® means ($\bar{x}$) and standard deviations (δ) of lengths (L) and widths (W) (mm) of oysters per group and elemental concentrations (μg g^{-1} wet wt) per group in oysters collected from Mtwapa Creek.

Group	L®	L($\bar{x}$)	L(δ)	W®)	W($\bar{x}$)	W(δ)	Cu	Zn	Pb	Cd
TM3X1	26.5-41.5	33.1	5.8	8.5-13.5	11.0	2.4	17.767	215.088	1.331	1.155
TM3X2	15.5-31.5	26.3	4.8	6.5-11.5	8.8	1.8	15.774	194.299	1.716	1.251
TM3X3	11.5-20.5	15.4	2.9	2-9.5	5.1	2.7	15.177	172.187	1.332	1.127
TU3X1	25.5-30.5	27.8	2.2	6.5-13.5	10.6	2.3	15.426	176.641	0.967	1.330
TU3X2	39.5-44.5	42.0	3.5	16.5-25.5	21.0	6.4	28.909	376.353	1.491	0.911
TU3X3	14.5-20.5	17.6	2.8	3.5-10.5	6.2	2.7	12.926	166.121	1.890	1.596
TM5X1	14.5-30.5	23.7	7.0	3.5-12.5	8.2	3.6	21.792	268.237	2.911	2.151
TM5X2	8.5-26.5	18.3	6.1	2-9.5	4.8	2.8	18.779	214.327	2.044	1.820
TM5X3	13.5-21.5	17.2	2.9	2-14.5	5.6	4.3	23.334	217.587	3.875	1.584
TM5Y1	43.5	43.5	0.0	22.5	22.5	0.0	21.618	213.356	1.940	0.592
TM5Y2	29.5-33.5	32.1	2.3	7.5-21.5	15.2	7.1	41.931	295.200	1.412	0.763
TM5Y3	22.5-24.5	23.8	1.2	16.5-20.5	17.8	2.3	44.699	249.696	2.116	0.932
TU5X1	52.5	52.5	0.0	31.5	31.5	0.0	9.746	285.722	0.005	1.980
TU5X2	48.5-49.5	49.0	0.7	23.5-27.5	25.5	2.8	15.678	180.657	0.005	1.281
TU5X3	25.5-33.5	29.5	3.4	8.5-13.5	11.5	2.2	16.238	221.856	0.005	0.924
TM6X1	15.5-30.5	21.0	5.7	2.5-9.5	6.5	2.6	19.033	300.888	1.732	5.167
TM6X2	15.5-24.5	19.0	3.0	2-7.5	4.0	2.2	21.332	251.653	1.607	4.943
TM6X3	9.5-20.5	16.1	3.6	2-4.5	2.6	0.8	15.738	286.863	3.038	5.632
TU6X1	31.5-38.5	34.1	3.8	10.5-14.5	12.2	2.1	15.121	218.373	0.005	5.101
TU6X2	28.5-36.5	31.5	3.7	3.5-14.5	8.8	5.1	12.192	188.055	0.005	3.256
TU6X3	12.9-25.5	18.8	4.5	3.5-9.5	6.5	2.0	20.007	202.211	0.005	3.264
TM8Y1	22.5-38.5	29.7	6.3	9.5-24.5	12.9	6.5	38.229	231.807	0.537	0.932
TM8Y2	14.5-24.5	20.7	3.7	7.5-10.5	8.7	1.3	34.283	229.924	0.763	0.854
TM8Y3	17.5-21.5	19.7	1.5	2.5-9.5	6.1	2.5	23.332	246.626	1.256	0.862
TU8X1	16.5-26.5	22.3	3.9	2.5-6.5	5.1	1.7	9.261	295.745	1.121	0.447
TU8X2	16.5-23.5	20.6	2.9	2-3.5	2.3	0.6	21.633	393.229	0.806	0.288
TU8X3	13.5-17.5	15.9	1.8	2-4.5	2.4	0.9	17.286	389.453	3.694	0.002

Table 34. Ranges ® means ($\bar{x}$) and standard deviations (δ) of lengths (L) and widths (W) (mm) of oysters per group and elemental concentrations (µg g^{-1} wet wt) per group in oysters collected from Port Reitz Creek.

Group	L®	L($\bar{x}$)	L(δ)	W®)	W($\bar{x}$)	W(δ)	Cu	Zn	Pb	Cd
PM1X1	33.5-46.5	37.5	6.2	12.5-21.5	17.0	3.7	15.469	258.005	1.652	0.724
PM1X2	24.5-32.5	30.1	3.2	11.5-20.5	14.5	3.5	19.164	227.709	1.354	0.580
PM1X3	20.5-25.5	23.1	2.2	2.5-15.5	7.6	4.9	22.874	261.038	1.710	0.639
PU2X1	21.5-34.5	25.1	4.9	7.5-13.5	10.1	2.1	16.229	225.281	0.718	0.878
PU2X2	19.5-29.5	24.3	3.8	3.5-6.5	5.3	1.2	15.163	221.031	2.852	0.727
PU2X3	11.5-19.5	14.5	3.3	2-7.5	5.1	2.3	16.908	185.249	3.089	0.524
PM3X1	28.5-37.5	32.0	4.0	15.5-24.5	19.0	4.0	16.189	248.535	0.539	0.265
PM3X2	25.5-28.5	26.8	1.5	7.5-11.5	9.5	1.4	17.324	208.577	1.557	0.482
PM3X3	10.5-23.5	17.5	4.4	2.5-6.5	4.4	1.4	25.382	171.497	3.010	0.900
PM4Y1	16.5-22.5	19.5	2.5	4.5-13.5	9.0	3.7	23.658	724.319	1.066	0.243
PM4Y2	9.5-17.5	13.3	3.5	2-5.5	3.9	1.5	35.360	736.538	2.363	0.002

Table 35. Ranges ® means ($\bar{x}$) and standard deviations (δ) of lengths (L) and widths (W) (mm) of oysters per group and elemental concentrations (µg g^{-1} wet wt) per group in oysters collected from Makupa Creek.

Group	L®	L($\bar{x}$)	L(δ)	W®)	W($\bar{x}$)	W(δ)	Cu	Zn	Pb	Cd
KU1Y1	47-65	55.3	9.1	41-51	45.3	5.1	310.63	927.76	17.37	6.15
KU1Y2	49-53	50.7	2.1	38-40	38.7	1.2	593.26	1092.63	12.19	13.10
KU1Y3	56-61	58.5	3.5	32-40	36.0	5.7	701.52	1422.83	38.96	12.93
KU1Y4	48-51	49.5	2.1	34-39	36.5	3.5	1090.68	1538.74	36.29	15.91
KU1Y5	45-51	47.7	3.1	32-35	33.7	1.5	799.69	1504.03	34.80	14.24
KU1Y6	43-52	48.7	4.9	21-36	30.3	8.1	805.30	1031.66	22.25	15.21
KU1Y7	52-54	53.0	1.4	29-33	31.0	2.8	590.82	1150.11	42.90	15.54
KU2Y8	44-54	50.0	5.3	29-38	33.3	4.5	663.03	895.82	53.97	16.56
KU2Y9	47-49	48.0	1.4	32-41	36.5	6.4	682.35	1077.54	54.43	18.61
KU2Y10	41-49	45.0	4.0	27-37	33.0	5.3	889.08	1032.96	51.65	16.48
KU2Y11	35-42	38.0	3.6	21-30	25.7	4.5	948.83	1202.50	63.91	14.02
KU2Y12	30-42	34.0	6.9	20-25	21.7	2.9	834.31	635.71	97.60	19.57
KU2Y13	36-48	41.0	6.2	25-32	29.0	3.6	766.73	1392.09	69.65	13.89

Table 36. Ranges ® means ($\bar{x}$) and standard deviations (δ) of lengths (L) and widths (W) (mm) of oysters per group and elemental concentrations (µg g^{-1} wet wt) per group in oysters collected from Shirazi Creek.

Group	L®	L($\bar{x}$)	L(δ)	W®)	W($\bar{x}$)	W(δ)	Cu	Zn	Pb	Cd
SM2Z1	42.5-56.5	47.9	5.6	25.5-31.5	28.3	2.3	3.656	112.523	0.640	1.618
SM2Z2	27.5-45.5	36.5	8.6	12.5-25.5	20.5	5.2	5.249	141.622	1.328	1.328
SM2Z3	20.5-31.5	27.5	3.9	10.5-21.5	15.0	3.8	4.225	112.806	1.762	1.442
SM2X1	9.5-25.5	18.7	6.5	5.5-11.5	8.1	2.3	11.098	171.139	3.738	0.695
SM2X2	12.5-24.5	16.5	4.7	4.5-12.5	8.7	3.4	8.129	152.208	3.780	0.930
SM2X3	9.5-15.5	11.8	2.0	2.5-13.2	6.3	3.6	9.411	137.603	1.730	0.692
SU2X1	20.5-29.5	25.3	3.7	7.5-11.5	8.9	1.7	6.693	278.071	0.272	0.412
SU2X2	13.5-20.5	17.1	2.7	6.5-8.5	7.3	0.8	10.589	223.318	0.005	0.414
SU2X3	11.5-20.5	15.3	3.9	2-5.5	3.9	1.5	6.757	132.649	0.795	0.552
SU2Z1	36.5-52.5	44.5	8.0	14.5-25.5	20.1	5.5	9.192	247.749	0.989	0.119
SU2Z2	33.538.5	36.0	2.1	11.5-15.5	13.0	1.7	12.013	198.607	0.005	0.012
SU2Z3	21.5-37.5	27.9	6.2	6.5-12.5	10.5	2.5	12.447	270.531	0.712	0.010
SM3X1	24.5-31.5	28.0	3.1	11.5-19.5	16.2	3.6	9.840	302.956	1.012	0.564
SM3X2	24.5-25.5	25.0	0.6	6.5-13.5	10.3	3.3	8.203	164.859	2.104	0.576
SM3X3	11.5-23.5	18.5	4.7	3.5-12.5	8.8	4.2	6.628	142.592	1.211	0.611
SU3X1	20.5-30.5	26.3	3.7	3.5-16.5	9.3	5.5	7.773	219.587	1.585	0.630
SU3X2	14.5-28.5	20.0	4.9	3.5-9.5	6.0	2.6	3.795	101.002	0.425	0.971
SU3X3	9.5-15.5	12.8	1.8	2-5.5	2.8	1.1	3.274	84.269	0.526	0.468
SM4X1	37.5-51.5	43.3	5.5	16.5-28.1	21.8	4.8	16.856	324.351	1.330	0.784
SM4X2	32.5-48.5	41.5	6.4	17.5-26.5	22.1	3.7	14.806	328.364	0.939	0.778
SM4X3	37.5-44.5	40.9	3.5	12.7-27.5	18.6	6.1	17.709	404.793	0.005	0.665
SU4X1	40.5-43.5	42.0	2.1	18.5-22.5	20.5	2.8	17.085	327.658	0.709	1.032
SU4X2	27.5-37.5	33.1	5.1	11.5-26.5	19.5	7.6	14.185	256.061	1.021	0.729
SU4X3	19.5-30.5	23.6	3.9	6.5-10.5	8.8	1.9	15.642	329.597	0.993	0.826
SM5X1	37.5-45.5	41.0	3.3	16.5-31.5	25.5	6.4	9.149	220.308	0.005	1.049
SM5X2	26.5-31.5	28.2	2.4	15.5-22.5	18.8	3.3	5.782	117.034	0.005	0.856
SM5X3	20.5-26.5	24.5	2.8	8.5-14.5	11.7	3.2	9.784	138.712	0.005	1.177
SU5X1	17.5-30.5	22.8	4.7	2-8.5	4.8	2.7	3.583	46.826	1.580	4.178
SU5X2	15.5-20.5	18.1	2.1	2-4.5	2.6	1.0	4.655	52.676	0.138	4.017
SU5X3	4.5-11.5	7.7	2.4	2-2.5	2.0	0.1	6.024	91.806	3.707	4.058
SM6Y1	14.5-25.5	19.4	2.9	7.5-14.5	12.1	2.4	13.694	249.897	0.017	0.808
SM6Y2	16.5-26.5	21.6	3.9	2.5-13.5	18.1	4.3	13.420	226.378	0.259	1.252
SM6Y3	9.5-29.5	16.6	6.0	3.5-8.5	6.0	1.8	11.455	187.457	0.005	0.915