CORAL REEF ECOSYSTEM OF LAKSHADWEEP ARCHIPELAGO - A BIOGEOCHEMICAL FACSIMILE

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CERTIFICATE

This is to certify that the thesis titled "Coral Reef Ecosystem of Lakshadweep Archipelago - A Biogeochemical Facsimile" is an authentic record of the research work carried out by Anu Gopinath under my supervision and guidance in the Department of Chemical Oceanography, School of Marine Sciences, Cochin University of Science and Technology, in partial fulfilment of the requirements for PhD degree of Cochin University of Science and Technology and no part of this has been presented before for any degree in any University.

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Preface

Coral reefs are one among nature's greatest spectacles, producing some of the finest examples of natural architecture in the world. The coral communities of startling complexity are essential to the health of the world's oceans and to many human communities as well. They are one of the most sensitive ecosystems easily susceptible to destruction.

A large number of coral ecosystems located all over the world is on the brink of extinction. Global warming, pollution effect and increased sea surface temperature are projected as major factors responsible for this phenomenon. Besides these, destructive fishing practices, oil spills, tourism activities, sedimentation process, collection of rare species etc. also play an important role in coral bleaching.

The present study is entitled as "*Coral Reef Ecosystem of Lakshadweep Archipelago - A Biogeochemical Facsimile*" – which focuses an the biogeochemical aspects of six islands belonging to Lakshadweep Archipelago - namely Kavaratti, Kadamath, Kiltan, Androth, Agathy and Minicoy. Lakshadweep, which is an area of biologically significant due to isolation from the major coastline, remains as one of the least studied areas in the Indian Ocean. The proposed work process out the distributional pattern of trace metals among the biotic (corals, sea weeds and seagrass) and abiotic component (sediments) of the ecosystem. An effort is made to picturise the spatial distribution pattern of different forms of nitrogen and phosphorus in the various sedimentary environments of the study area. Studies on the biogeochemical and nutrient aspects of the concerned study area are scanty. In Lakshadweep, the local life is very much dependent on reefs and its resources, so a well defined understanding of the concerned ecosystem is necessary from the ecological point of view.

The thesis is divided into seven Chapters. The first Chapter gives a general introduction on coral reef ecosystem and Lakshadweep Archipelago. In addition to this, citations of previous work and aim and scope of this work are addressed here. The second Chapter discusses about the study area, sampling protocols and various analytical options adopted for the study.

Chapter 3 picturises the distributional characteristics of trace metals among the corals, seaweeeds and seagrass. In addition to this, a study related to sclerothermometry (preliminary attempt) is also included here. Fourth Chapter summarizes the nutrient characteristics of the different sedimentary environments in the study area.

Chapter 5 deals with the chemo-variability (trace metals) among the abiotic components (sediments) of the six islands. Chapter 6 is a predictive mathematical modeling which gives an idea about metal- nutrient interactions of the ecosystem. Chapter 7 illustrates the perspectives and safe guards of coral ecosystem.

List of references are given at the end of each chapters.

CONTENTS

Chapter 1

INTRODUCTION

Ecosystems, of which man and social system are an integral part, are governed by the following principle, "everything affects everything, all living things exist as parts of system, in each system there are factors that limit the growth; each system has a definite capacity to carry the organisms of that system, in these systems all natural cycle are used, but the energy of the system flows in one direction – downward to uselessness; stability of system increases with specialization" (Srivastava, 1992).

Most of this planet we call Earth is covered by water – a vast network of oceans and seas. We have give each body of water a separate name. But in reality, they are all connected an immense, watery habitat for a spectacular variety of plants and animals we rarely see, and therefore know little about.

Located in some of the ocean's clear, blue, warm waters are complex communities teeming with life known as "coral reefs'. Coral reefs are spectacular to behold, lush gardens in the sea, supporting a staggering diversity of marine life in a densely packed, thriving marine metropolis. In fact, coral reefs harbour the greatest diversity of life in the oceans, and are second only to tropical rainforests in the number of species found in one and area of Earth. Reefs are built by tiny animals, each smaller than pencil eraser. Nowhere else on earth we can find living organisms with such spectacular colours or fantastic shape as coral reefs. In them, the most wonders and mysterious of all natural phenomena, life has found its fullest expression. Complementing and enhancing this extraordinary intensity of life is its exquisite beauty of form, colour and motion. This is truly nature's richest realm, a fairytale world beyond imagining were if not real. They are not of the most diverse and vulnerable ecosystems characterized by an intricate network of plants and animals. Coral reefs, which are known as 'rainforests" of the ocean's are noted for their productivity, rich biodiversity and are regarded as centres of scientific research.

Corals are small animals, belonging to class Anthozoa, living in vast colonies in a symbiotic association with microscopic algae (zooxanthellae). These algae together with various pigments render their host a colourful appearance. The major advantage of this symbiotic relationship is that corals get nourished from the photosynthetic products of algae and the symbionts in turn are provided with shelter and various nutrients from the excretory products of corals.

Coral reefs, of course, function by the same basic laws as other ecosystems, but there is cause to view them as an end member of a continuum because of their structural resources including a variety of species of echinoderms, sponges, molluscs, gorgonids, crustaceans and marine algae. The annual production of the reefs ranges from 2000 - 5000 g C m^{-2} yr^{-1}, which is due to efficient recycling of nutrients.

Reefs may be found in both tropical and temperate areas of the world. Temperate reefs occur in colder waters where the temperature averages below 18^{0}C and are usually formed on existing rocky outcrops. Some seaweeds such as coralline algae produce encrusting calcium carbonate that helps build up these rocky reefs. While they may not be as famous as their tropical cousins, temperate reefs are still home to a diverse range of species and are extremely important to the food chains of nutrient rich temperate waters. Tropical reefs occur in warmer waters that average around 18^0 C and can reach into the high 20's. These reefs are built by the animals who live there, especially algae and corals. These are often called coral reefs, as a large part of the framework for the reef in encrusted by the coral polyps themselves.

Coral reefs are life's most awesome creations. They confront one with a potent mixture of exquisite beauty, fascinating history and functioning, profound insights into life and something even beyond that. Coral reefs are unique among biological environments in that their inhabitants create and maintain major geological features of the earth itself. Scientifically, reefs afford unique opportunities to investigate and understand the phenomenon of life from manifold aspects. Reef creatures are also providing to be a cornucopia of biologically active compounds of potential pharmacological value.

Over a long geological time scale, reefs have undergone periods of growth and decline, brought about b events such as the movement of the earth's continents (plate tectonics), the rise and fall of the sea and interruptive events, such as meteor impacts and global ice ages. The structures which we recognize as reefs today, basely resemble what the reefs of the past would have looked like. A whole different group of animals, plants, bacteria and environmental conditions helped to set the stage for a dynamic transition from the reefs of 2000 million years ago, to the modern reefs of today.

Reefs can be generally classified into three main types

- ***Fringing Reefs***
- ***Barrier Reefs***
- ***Atolls***

Fringing Reefs

These are well developed reefs (with platform reefs) next to the mainland or continental islands. The reef framework develops along the shoreline and then grows or develops towards the sea for sometimes hundreds of meters. This type of reef has no lagoon between it and the main landmass. (e.g. coral reefs adjoining the shores of Red Sea).

Barrier Reefs

They are separated from the shore by a lagoon, the width of which may vary considerably along the coasts and with the progressive narrowing of the lagoon, a barrier reef may become fringing (e.g., Great Barrier Reef)

Atolls

They are the classically recognized type of coral reef. They are circular reefs that do not have a near landmass exposed above the surface of the ocean.(e.g., many Indo-Pacific reefs).

Based on their role in reef-building processes, Scleractinian corals can be divided into two groups – hermatypic (reef building) and ahermatypic (non reef building). Though, they are structurally similar, there are differences which lie in the presence of endosymbiotic zooxanthellae in ahermatypic corals, and the extent of their distributions in seas. While ahermatypic corals are distributed at all latitudes, hermatypic corals are stenotypic which are limited to warm saline waters, essentially between the tropics of Cancer and Capricorn, where the minimum water temperature do not fall below 20^0C.

Coral reefs of the world

The total area covered by the reefs of the world comes around $6x10^5km^2$ (equivalent to 0.2 % of the world ocean area). Out of these 54% lies in the Asiatic, Mediterranean and Indian Ocean. Among the others, Pacific reefs account for 25%, Atlantic reefs 6%, Caribbean reefs 9%, Red sea reefs 4% and Persian Gulf reefs 2% (Smith, 1978).

Coral reefs of Indian mainland

Despite the vastness of the Indian subcontinent and the warm temperature of its coastal waters, coral reefs are present on only a few widely scatted parts of the mainland coast which can be attributed to the occurrence of major river systems and the sedimentary region on the continental shelf (Mulaey et al, 2000). Gulf of Kutch in the northwest and Palk Bay and Gulf of Mannar in the southwest, which are widely separated, are the important reef areas in the Indian subcontinent.

Lakshadweep Archipelago – the study area

Scattered some 200-400 km west off the Kerala coast, lie the islands of the Union Territory of Lakshadweep, an archipelago of coral islands and open reefs. Out of these, only 10 islands are inhabited. They are Androth, Amini, Agathy, Bitra, Chetat, Kadamath, Kalpeni, Kavaratti, Kiltan and

Minicoy. The main islands are Kavaratti, Minicoy and Amini. Kavaratti is the headquarters of these islands, while Bitra is the smallest of all, with a nominal population.

In the early history of Lakshadweep, it is generally believed that Cheraman Perumal, the last king of Kerala, as a result of shipwreck on the strong Arabian seas, made the first settlement on these islands. But the historical record show that, around the 7th century, a Muslim saint was shipwrecked on the island of Amini. Despite initial opposition, he covered the inhabitants here to Islam. Although the sovereignty remained in the hands of the Hindu Raja of Chirakkal, it eventually passed to the Ali Raja of Cannanore in the 16th century, the only Muslim royal family of Kerala and later in 1873 to Tipu Sultan, following the defeat of Tipu Sultan by the British, at Srirangapattanam in 1799, the islands were annexed by East India Company. Until independence, it remained with British and it was make a Union Territory of the Indian Union in 1956.

India has a coastline of 7516, of which the mainland accounts for 5422 km. The coastline of the Lakshadweep islands is 132 km and that of Andaman and Nicobar islands is 1,962 km. The Exclusive Economic Zone generated by taking into consideration of the offshore islands is about 2 million km^2, which is about two-thirds of the land area (2.9 million km^2). The charm of Lakshadweep islands (known as Laccadives islands till 1973) lies in their remoteness. The Lakshadweep islands are India's only coral islands. Far from the chaos of civilization, as we know it, they represent a rather magical realm of existence. Each island is densely covered with coconut palms, and serenely set in a sea, the waters of which range from palest aquamarine and turquoise, to deepest sapphire and lapis lazuli.

Geology and Geomorphology

These islands form an integral part of the N-S and NE-SW tending Chagos – Laccadive Ridge. The geological histories of Lakshadweep remain unravelled due to the lack of reliable information on the sinking history of Chagos-Laccadive Ridge itself. From foraminiforal fossils it can be inferred that the ridge got fractured at intervals and sank rather rapidly to the present depth of our 1500 m from Paleocene time and that the corals grew at suitable level around some peaks of the subsiding ridge. The foraminiforal fauna present in the calcareous sediments of the islands indicate that these islands are not older than Holocene (Ramachandran, 1981).

The islands are ruddily characterized by three physiographic regions, namely, the strong beach, the central depression and the low dune adjoining the lagoon (CESS, 1997). According to ICAR (1990), the soil is structureless, formed by the disintegration of corals. Over 95% of soil consist of $CaCO_3$ without any sand, silt or clay. Soil is alkaline and is poor in organic content.

Rainfall and climate.

The islands experience a tropical monsoon climate, with an average rainfall of about 1600 mm, from May to October. Since these are no streams in any of the islands, the only 'natural' water source is groundwater.

Since the islands are within the tropics and on tending to the equatorial belt, they experience tropical humid climate. No distinct and well marked seasons are experienced here. The temperatures are almost uniform, increasing but to slightly from south to north.

Agriculture and Industry.

The main stay is agriculture and economy of Lakshadweep is coconuts which constitute 99.4% of net won area. In addition to this there is cultivation of vegetables, banana, rice and other. Lakshadweep is considered as a 'no industry zone'. Coconut is the major crop grown here and the main industry in the islands is coconut fiber extraction and conversion of its fiber products. The other major activity here, is fishing. Immense potential for development in fisheries has resulted in the setting up of boat-building yards, canning and processing factories and adoption of mechanical fishing boats.

Islands selected for study.

1. Kavaratti

The administrative capital, Kavaratti is the most developed of the islands with the highest percentage of non-islanders as residents. Fifty-two mosques are spread out over the island, the most beautiful being the Ujra mosque. A well, within its precincts, is believed to contain water of curative powers. The lagoon is on the western side, which is about 6km in length and measures about 1.5m across.

2. Minicoy

Furthest from Kavaratti island, 200 km away to the south and also nearest to the Maldives, Minicoy has a culture very different from any other island. This is the southern most island in Lakshadweep Archipelago. Minicoy has a very large lagoon on the western side measuring about 6 km across with two entrances, one in the west and the other in the northern most point.

3. Kadamath

The even depth and an endless shoreline make Kadamath a haven of solitude. This is the only island with lagoons on both eastern and western sides. This is a long and narrow island and is about 570m wide at the broadest point. The eastern reefs are exposed at low tide and form a level platform stretching from the sea beach for about 100 meters.

4. Kiltan

Kiltan possess 1.63 km^2 area and it has a large shallow lagoon on the northern and southern ends of the island. The reef fringes the west side of the island enclosing a shallow lagoon. This island is in a strategic position as it is close to the international shipping route.

5. Androth

This is the largest island in the Lakshadweep Archipelago and is nearer to the Malabar Coast. This island possess and east-west orientation and has no lagoon. The island possesses the whole interior of the atoll.

6.Agathy

Agathy has one of the most beautiful lagoons in Lakshadweep archipelago. Agathy is the most westerly of this group of islands.

Literature survey

Exploration of corals was started in the Red Sea by a Danish expedition in 1762-1973 (Scheer, 1984). The first expedition to the Indian Ocean (1839) was of "HMS Beagle' in which Charles Darwin was onboard and it has been considered as the first classic research work on the corals.

Mayer (1914 In Wafar, 1986), studied the effect of water temperature on corals. Murray postulated a theory on the origin of coral reefs in 1880 (Campbell, 1980). Landmark and Milne Edwards in 19th century initiated the work on taxonomy of corals and in 1903, Meigen (in Chave, 1954) conducted studies on Heliopora. Alexander Agassiz carried out work on the growth rates and ecology of corals towards the end of 19th century.

Members of the British Great Barrier Reef Expedition carried out physiological studies between 1928-1929, to understand the nutrition and growth of corals. Japanese marine biologist working in the Palan before World War II made significant contributions towards reef coral physiology and biochemistry.

Experimental studies on coral reefs began as early as in 1910 (Goreau, 1961). Ma in 1937 (Dodge and Vaisnys, 1975) reported for the first time incremental banding in coral skeleton and also later on by Wells (1963). Chemical composition of corals was first studied by Silliman (1953).. Chave (1954) studied the biochemistry of Mg in Medreporarian and Alcypharian corals and other calcareous marine organisms. Carr and Turekian (1961) analysed two corals from Bahamas and determined cobalt concentrations. Co, Ag and U concentrations were analyzed in corals of Pacific Ocean by Veeh and Turekian (1968). Uranium contents were analyzed in individual coral skeletons (Schroeder et al., 1970) and from Red Sea corals (Friedman, 1968). Minute differences of U concentrations between modern and Pleistocene corals were reported by Kaufman et al., (1971).

Thompson and Livingston (1970) collected modern hermatypic and ahermatypic corals from shallow to deep oceans and the concentrations of

Ca, U, Sr is then compared with same temperature and found to be independent . Thompson and Livingston (1970) also reported various trace elements (Ca, Sr, U, Ba, Cu, B, Li, Zn, Si. Ti, Cr, Co, Fe, Mn, Ni, Pb, and Sc) for the same corals. Amiel et al., (1973) tried to study the distributional and nature of incorporation of Sr, Mg, Na and K in three modern aragonite corals. Amiel (1973) found out the sites of U in modern corals.

Weber (1973) did an extensive study on 2020 well characterized corals belonging to seventy three genera and subgenera from 17 localities to understand the incorporation of Sr in corals. He compared Sr concentrations with water temperature, growths of corals, water depths and genetic effects. Weber (1974) studied different varieties of corals to find out the relationship between Mg content and water temperature, water depth, genetic factors and the rate of Mg content removal from seawater by corals in reef enrichment. St. John (1974) have reported the concentrations of Cu, Fe, Zn, Co, Cd, Pb and Ni on 265 different varieties of corals from the reef of Capricorn group and established a relationship between trace elements in corals of the Coral Sea and oceanographic factors.

Goreau (1977a and b) investigated the seasonal variations of trace metals (Ca, Mg, Sr, Fe and Al) and stable isotopes (C^{13} and O^{18}) in *Montastrea annularis* of Jamaica and discussed in detail the physiological and environmental regulation of trace metals and stable isotopes. Flor an Moore (1977) studied Ra: Ca and V:Ca ratios from Grand Cayman and West Indies (Western Atlantic) corals.

All these studies has been triggered to attempt the new concept, sclerothermomety i.e., thermometry based on the use of coral, by Smith

(1979). Schneider and Smith (1982) carried out a study on calcium, strontium and magnesium and their significance I predicting seawater temperature based on Sr/Ca ratio form differing environments (Pacific, Atlantic and Indo-Pacific). Cross and Cross (1983) measured U from Holocene and Pleistocene corals. Dodge and Gilbert (1984) studied banded corals species, *Montastrea annularis* and indicated that coral skeletons as historical records of concentration and levels of Pb pollution in seawater. Shen et al. (1987), Shen and Boyle, (1988) and Lea et al. (1989) carried out work to find out the lattice bound trace elements from annually formed scleractinian corals. Shen et al. (1988) also reported lattice bound cadmium from the annually formed corals, selecting cadmium as an indicator of upwelling and industrial fallout.

In 1991, Naqvi carried out a study on the geochemistry of recent corals from Lakshadweep group of islands and its implications to the past climate. The partitioning of metals between tissue and skeletal parts of corals was studied by Mc Conchie and Harriott (1992). A detailed study was conducted by Esslemont (1999.2000, 2002 (personnel communication)) on the partitioning behaviour of trace metals in the skeleton and tissue phases of various coral species. Anandaraj (2002) studied the petrography, geochemistry and diagenesis of coral deposits of Kavaratti and Minicoy islands, Lakshadweep, India. In 2002, Elizalde et al., measured lead contamination in the coral Montastrea annularis.

More details of the recent literatures have been consulted in explaining the results of the present work in the respective chapters.

Objectives and scope of the present study

Coral reefs are one of the most sensitive ecosystems easily susceptible to destruction. A large number of reefs located all over the world is on the brink of extinction. Global warming, El Nino effect and increased sea surface temperature are projected as the major factors responsible for this phenomenon. Besides these, destructive fishing practices, oil spills, tourism activities, sedimentation process, collection of rare species etc., also play an important role in coral beaching. Quarrying corals for various purposes, destruction of wetlands, pollution of marine environment due to modern agricultural practices including pesticides, organic and inorganic fertilizers, untreated effluent from industries and urban sewage have made their contribution in the mass mortality of corals. Coastal communities for their livelihood as well as for commercial purposes also exploit these biological resources. Such an over dependence on reefs as means of human sustenance has put an additional pressure on them which makes them easily susceptible to destruction.

Studies on the geochemistry of coral sediment and their distribution along the Indian coast are scanty. Analysis of the chemical nature of the reef sediments play an important role in cycling, regeneration and concentration of trace elements and other chemical species in the oceans. The geochemical aspects of trace elements within the reef (including the flora and fauna) and also of the surrounding environment (sediment) requires an attention as it can give an insight into the structure and organization of ecological communities and the response of the biotic and abiotic components of the reefs to their immediate environment.

The present study entitled "***Coral Reef Ecosystem of Lakshadweep Archipelago – A Biogeochemical Facsimile***" focuses on the geochemical and nutrient aspects of the sedimental environment of six islands belonging to Lakshadweep Archipelago, *viz.* Kavaratti, Kadamath, Androth, Agathy, Kiltan and Minicoy on a spatial basis.

The objectives of this study include:

- Intervariability of trace metals (Fe, Mn, Cu, Co, Ni, Zn, Pb, Cd and Cr) in the sedimentary environment of selected islands (inter compartmental and inter segmental variability) focusing on transport, fate and diagenesis of trace metals.
- Inter colony variation of trace metals within the tissue and skeletons of five selected coral species - selection of proxy viable indicator organism for environmental monitoring.
- Assessment of extent of partitioning of trace metals between the skeleton and tissue phases – inter element and inter species variation.
- Experiments related to metal releasing agent from coral skeleton – the effect of lanthanum chloride.
- Variation of trace metals between seaweeds (Rhodophyceae and Phaeophyceae family) and seagrass
- Studies related to nutrient budget and nutrient dynamics – N and P budgets an effort has been given to picturize the spatial distribution pattern of nutrient elements, nitrogen and phosphorous, as they play a vital role in determining the fertility potential of the concerned area. The study has been extended to monitor the variation of different forms of

nitrogen (nitrite, nitrate and total nitrogen) as well as phosphorous (exchangeable, inorganic, calcium bound, organic + residual form as well as total phosphorous).

- General sedimentlogical characteristics like pH, texture and sedimentary organic carbon have been tried to correlate with the distributional behaviour of trace elements and nutrients.
- Sclerothermometry- A preliminary attempt has been made to use Sr/Ca ratios of coral skeletons in determining temperature because Sr/Ca ratios in skeletons have the potential to be used as a recording thermometer when combined with chronological record preserved in coral density band.
- Ecosystem modelling – A predictive mathematical model based on multiple regression analysis has been applied to assess the relationship between trace metals(Fe and Mn) and nutrient forms(different forms of both N and P).
- Statistical methods involving 3-way ANOVA, Student t-test, Multivariate factor analyses by Q-mode and R-mode have been applied to determine the extent of interdependence between the parameters selected for this study.

The interdependence of these parameters on reef development and any variation from the normal distributional pattern can furnish idea about the proper management of the reefs and the quality of their environment. In Lakshadweep, the total life is very much dependent on reef and its resources and therefore a well defined understanding of the concerned ecosystem is necessary and can be beneficial. A competent monitoring programme is an essential adjust to any attempt to manage a coral reef in an ecologically sound and sustainable manner.

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Chapter 2

MATERIALS AND METHODS

This chapter describes the study area, sampling locations and the analytical methods employed in the estimation of various analytical parameters.

Study Area:

Lakshadweep is an archipelago consisting of 12 atolls (Fig.2.1), three reefs and five submerged banks. It is located between 8^0 – 12^0 13" N latitude and 71-74 E longitude, and 220 - 440 kms away from the coastal city of Kochi in Kerala. Lakshadweep is a uni-district Union Territory with an area 32 km^2 and it has 10 inhabited islands. Kavaratti, Agathy, Amini, Androth, Kiltan, Kalpeni, Kadamath, Chetlat, Bitra and Minicoy are the inhabited islands. Among these Androth possess largest land area and Bitra the smallest.

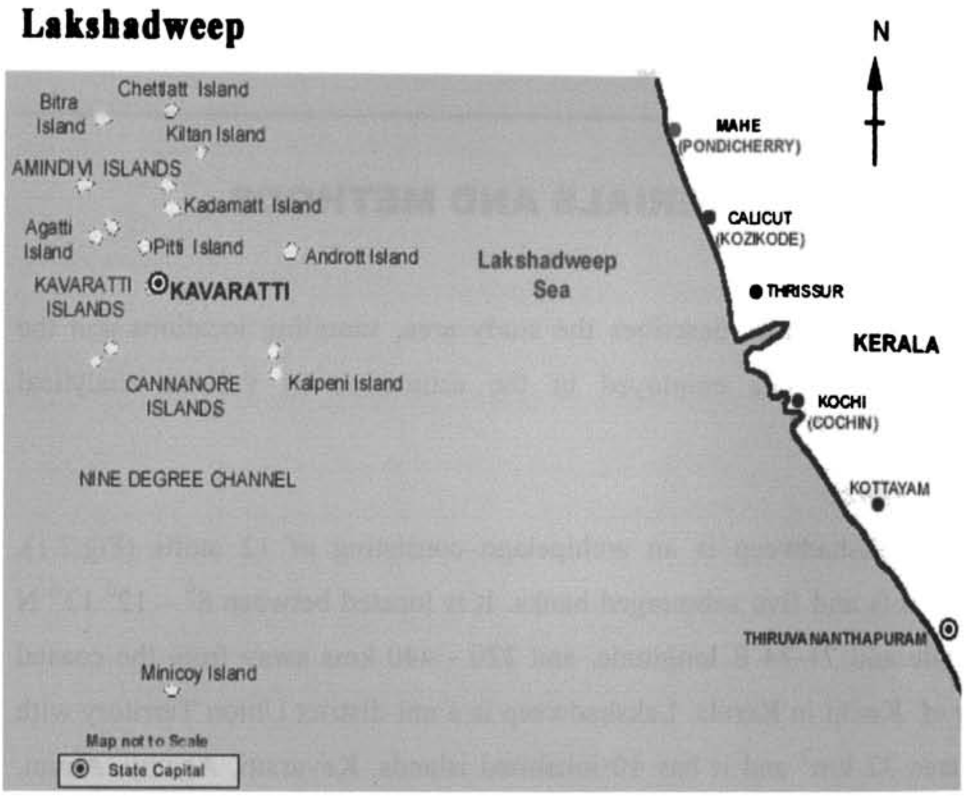


Fig. 1. Location map of Lakshadweep Archipelago

The islands are ring-shaped atolls lying along a north-south axis (except Androth) with lagoon on the west and open sea on the east. The islands posses a lagoon area of 4,200 km^2, territorial water 20,000 km^2 and 4 lakhs km^2 of economic zone.

Profile of islands selected for study:

Agathy

Agathy is the most westerly of this group of islands. The southern portion of the island is sparsely planted, but the rest of the land is planted up. Agathy has no storm beach. The eastern shore is composed of only sand rising from the level of the reef flat which gets exposed to low tide.

Androth

Androth is an island, which has an east -west orientation and has no lagoon. The island occupies the whole interior of the atoll. Except at the northeast extremity, the reef flat is exposed at low tide. The western side of Androth witnesses a unique phenomenon every year during and after monsoon. This area called 'Moola' has block of shifting white sand that keeps moving from the north to south.

Kavaratti

Kavaratti is the capital island with a land area of 3.63 km^2. The reef is situated on the northern side of the island, which encloses a lagoon in between. At the northern side, the lagoon is shallow and coral growth is maximum. The southern part of the island has a narrow area popularly called 'chicken neck' area. Kavaratti is the most centrally located island in the Lakshadweep archipelago. Fifty-two mosques are spread out over the island, the most beautiful being the Ujra mosque(situated north). A well, within its precincts, is believed to contain water of curative powers.

Kadamath

This is the longest island with an area of 3.12 km^2, which possess very white and striking beaches. The eastern side of the reef is composed at low tide and form a level platform stretching from the beach. A high ridge of sand runs down the western side of the island.

Kiltan

Kiltan possess 1.63 km^2 area and it has a large shallow lagoon on the northern and southern ends of the island. The reef fringes the west side of the island enclosing a shallow lagoon.

Minicoy

Minicoy has a strategic position in the Arabian Sea and is separated from the rest of the Lakshadweep by the Nine Degree Channel. This island possesses a land area of 4.37 km^2. Marco Polo described this island in the 13th century as 'a female island in the Indian Ocean'. Lagoon is on the north-western part of the island covering a large area.

Sampling Sites:

Sampling was done from the biotic (corals, seaweeds and seagrass) as well as abiotic (sediment) components of Lakshadweep Archipelago in September 2000. Sediment samples were collected from six islands, *viz.* Agathy, Androth, Kadamath, Kavaratti, Kiltan and Minicoy. Samples were collected from different environments of each island (Fig.2.2). From Kavaratti, two core samples were collected upto 120 cm depth at an interval of 30 cm. from the northern as well as southern part of the island. In addition to this sampling was done from the lagoon and also near the famous mosque, Ujrapally. In Kadamath, sampling was done near high tides and low tide stations and also from the lagoon. In Minicoy, sampling was from the lagoon area and also from the mangrove. In Agathy, samples were collected near the lagoon side as well as sea side. From Androth, two core samples were collected, one near the sea (1 m) and the other from land (1.3 m). In addition to this, trough soil and crest soil was also collected from

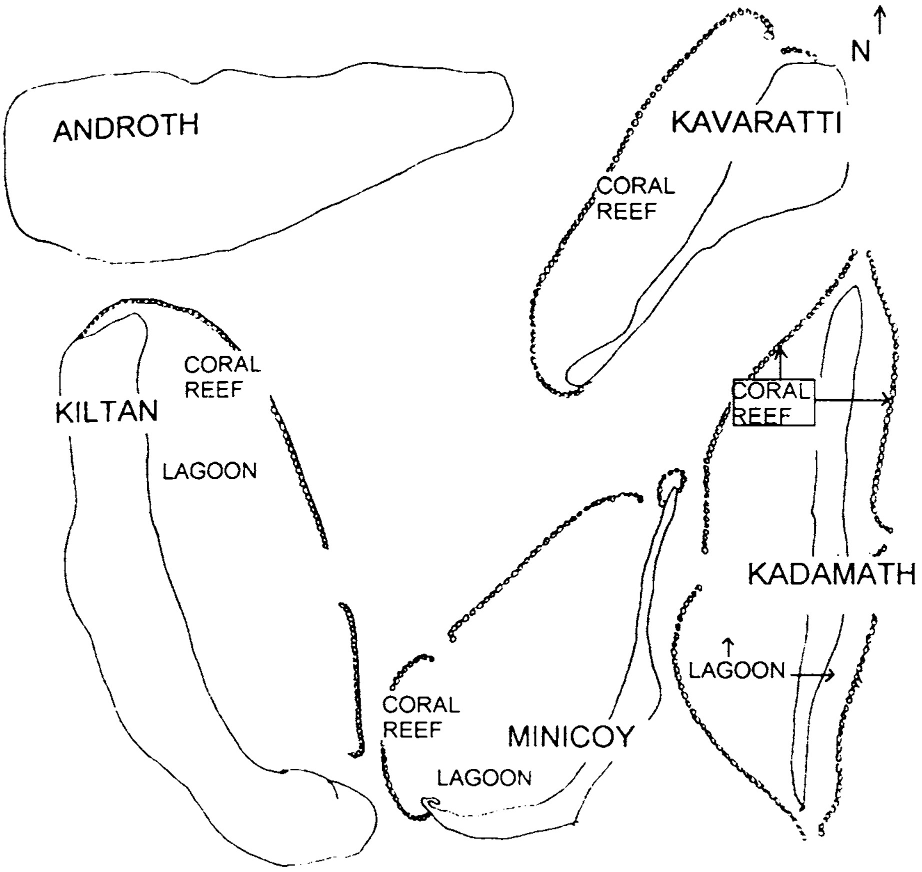


Fig. 2.2 Location Map.

Androth. In Kiltan, samples were taken from the lagoon side as well as sea side (both northern and southern side). In addition to this a core sample was also collected from the land (0, 0.5 m and 1.3 m depths).

Analytical Options:

A. CORALS

Trace metal analysis in coral tissues and skeletons:

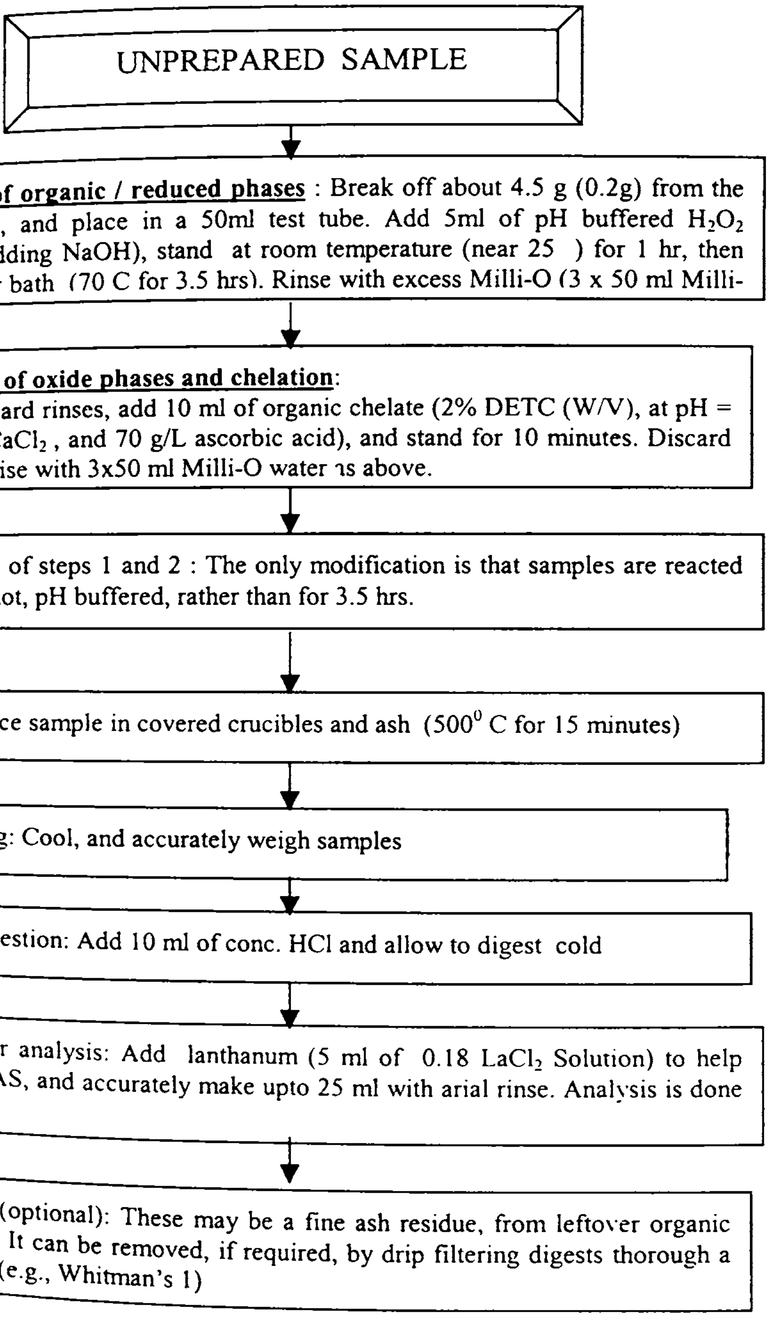
Five coral species were collected from Lakshadweep Archipelago and their names taxonomic classification are given in Table 2.1.

Table 2.1. Names of coral species and their taxonomic classification.

No.	Species Name	Genus	Family
1	*Lobophyllia corymbosa*	*Lobophyllia*	*Mussidae*
2	*Porites andrewsi*	*Porites*	*Poritidae*
3	*Montipora digitata*	*Montipora*	*Fungiidae*
4	*Acropora formosa*	*Acropora*	*Acroporidae*
5	*Psammocora contigua*	*Psammocora*	*Siderastreidae*

The collected samples were carefully washed with water to remove sediment and associated fauna. It was then washed with deionized water and finally in Milli-Q water. The trace metal analyses were carried out on coral skeleton as well as on tissue by accepting the modified procedure of Esslemont (1999; 2000 a & b; 2002) and it is schematically represented in Figs.2.3 and 2.4 respectively.

Fig. 2.3 . Flow chart for the analysis of trace metals in coral skeletons.



UNPREPARED SAMPLE

1 Oxidation of organic / reduced phases : Break off about 4.5 g (0.2g) from the coral skeleton, and place in a 50ml test tube. Add 5ml of pH buffered H_2O_2 (pH=8.2 by adding NaOH), stand at room temperature (near 25) for 1 hr, then heat in a water bath (70 C for 3.5 hrs). Rinse with excess Milli-O (3 x 50 ml Milli-

2 Reduction of oxide phases and chelation:

Discard rinses, add 10 ml of organic chelate (2% DETC (W/V), at pH = 5, 1.30 g/L $CaCl_2$, and 70 g/L ascorbic acid), and stand for 10 minutes. Discard chelate. and rise with 3x50 ml Milli-O water as above.

3.Two repeats of steps 1 and 2 : The only modification is that samples are reacted for 1.5 hrs in hot, pH buffered, rather than for 3.5 hrs.

4. Ashing: Place sample in covered crucibles and ash (500^0 C for 15 minutes)

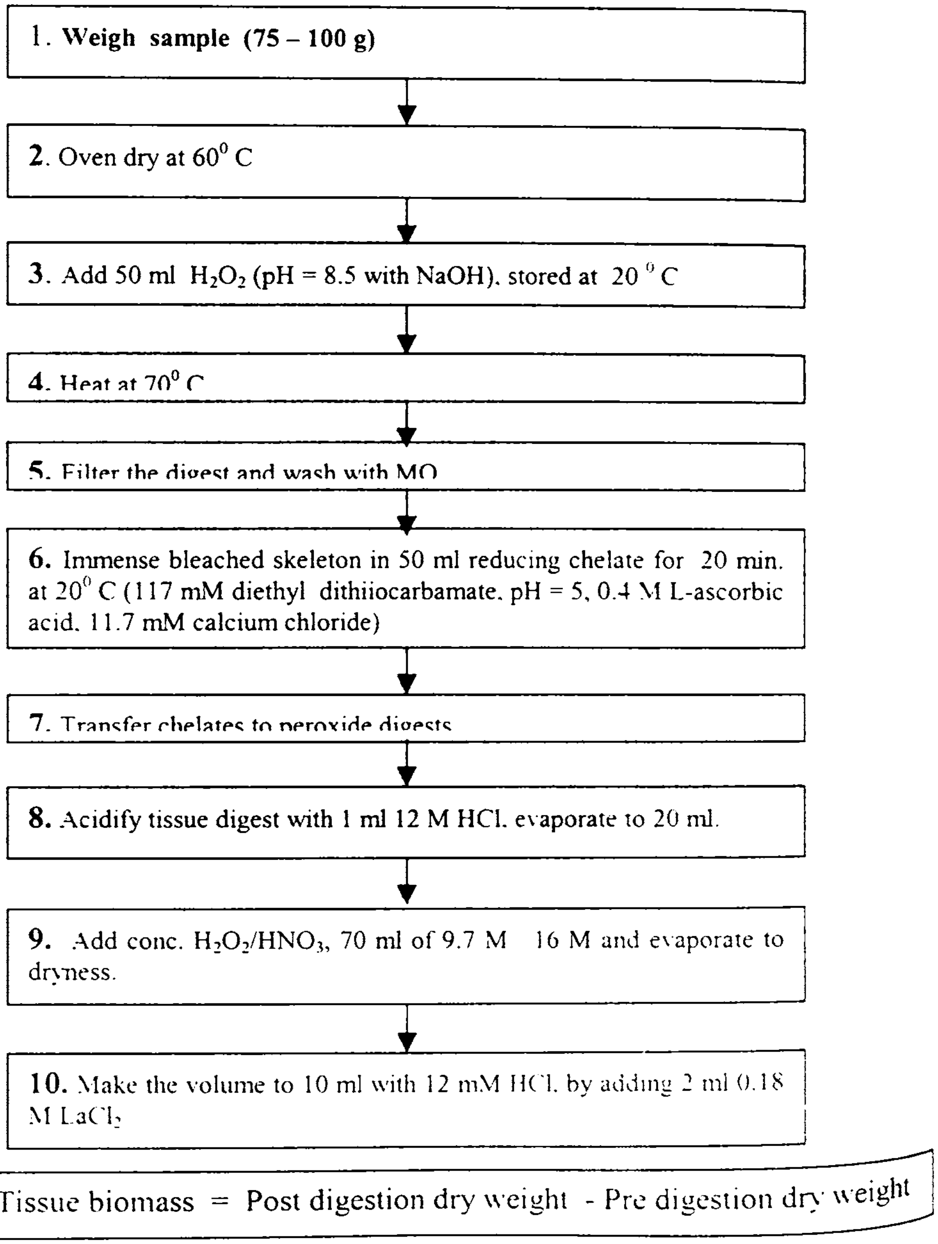
5.Weighing: Cool, and accurately weigh samples

6.Sample digestion: Add 10 ml of conc. HCl and allow to digest cold

7. Dilution for analysis: Add lanthanum (5 ml of 0.18 $LaCl_2$ Solution) to help analysis by AAS, and accurately make upto 25 ml with arial rinse. Analysis is done by AAS.

8. Filtration (optional): These may be a fine ash residue, from leftover organic chelate rinse. It can be removed, if required, by drip filtering digests thorough a coarse grade (e.g., Whitman's 1)

Fig. 2.4.Flow chart for the analysis of trace metals in coral tissues.



1. **Weigh sample (75 – 100 g)**

2. Oven dry at 60^0 C

3. Add 50 ml H_2O_2 (pH = 8.5 with NaOH), stored at 20 ^{0} C

4. Heat at 70^0 C

5. Filter the digest and wash with MQ

6. Immense bleached skeleton in 50 ml reducing chelate for 20 min. at 20^0 C (117 mM diethyl dithiiocarbamate, pH = 5, 0.4 M L-ascorbic acid, 11.7 mM calcium chloride)

7. Transfer chelates to peroxide digests

8. Acidify tissue digest with 1 ml 12 M HCl, evaporate to 20 ml.

9. Add conc. H_2O_2/HNO_3, 70 ml of 9.7 M 16 M and evaporate to dryness.

10. Make the volume to 10 ml with 12 mM HCl, by adding 2 ml 0.18 M $LaCl_2$

Tissue biomass = Post digestion dry weight - Pre digestion dry weight

Trace metal analysis in seaweeds and seagrasses;

Trace metal analysis were also carried out in seaweeds and seagrass collected from the Lakshadweep Archipelago (Table 2.3), by adopting the procedure of Say et al. (1986). For this samples were collected (5-10 g) and washed thoroughly with water to remove sediment, debris and associated fauna. Final washings were done by using deionized and Milli-Q waters and then dried at 105^0 C for 24 hrs. Dried material was ground to fine powder and again redried for 3 hrs. All samples were analyzed in duplicate by digesting 0.5 g sample in 10 ml 2M HNO_3 by heating to near dryness. Residue was dissolved in 10 ml 2M HNO_3, filtered and make upto 25 ml with Milli-Q. Reagent blanks were also prepared. This was then analyzed for trace metals (Cu, Co, Cd, Cr, Pb, Ni, Zn, Mn and Fe) using a graphite furnace atomic absorption spectrophotometer (Perkin-Elmer 3110). Estimation of the accuracy and precision of the analysis was performed using standard spiking techniques as detailed in sedimental trace metal analyses.

Table 2.2. Seaweeds and sea grass collected for study.

No.	Species Name	Family
	Seaweeds	
1	*Laurencia pupillosa* (Forssk)	Rhodophyceae
2	*Jania adhaerens* (Lamour)	Rhodophyceae
3	*Gracilaria cylindrica*	Rhodophyceae
4	*Gracilaria crassa* (Harv)	Rhodophyceae
5	*Hypnea musciformis*	Rhodophyceae
6	*Sargassum tenerimum*	Phaeophyceae
	Seagrasses	
1	*Thalassia hemprichii* (Ehrenberg)	Hydrocharitaceae

B. Sediments

Textural characteristics

Two techniques were applied for the determination of textural characteristics of sediments. Sediments having particle size less than 63 µm a particle analyser (Sympatec, Germany) was employed for the determination of textural characteristics. For sandy sediments, dry sieving was made using a Ro-Tap sieve shaker. For this, bulk sediment were washed, dried and subjected to coning and quartering. A representative portion, about 15-20 g was sieved for 15 minutes using standard set of ASTM sieves at half phi (1/2 Φ) intervals. The fractions left over in each sieve were weighed and cumulative weight percentages were calculated. Standard classification for particles into Wentworth size classes was accepted to classify the textural characterizes of sandy sediments as a) very coarse sand b) coarse sand c) medium sand d) fine sand e) very fine sand and f) silt + clay (Folk, 1963).

Sedimentary pH

Measurement of pH of the sediment samples were carried out by following the procedure of Jackson (1963). For this, a known weight of sediment was shaken with water (1:1 ratio) for 15 minutes using a mechanical shaker and the resulting pH was measured using a digital pH meter (Systronics - Digital No. 333)

Sedimentary organic carbon

Sediment samples were dried in an oven at 80-90^{0}C and finely powdered in an agate mortar. Sedimentary organic carbon was determined using the procedure of Gaudette et al. (1974) with some modifications as per

APHA (1992) procedure for those sediment samples, which have chloride interference.

Nutrients

The method of Keency and Nelson (1982) was applied to sediment samples for the extraction of exchangeable forms of nitrite, nitrate and phosphate. All apparatus were thoroughly cleaned using HCl, washed in deionized water and finally rinsed with Milli-Q water. The different species of nitrogen and phosphorus were estimated by the following analytical procedures.

Nitrogen

Nitrite: Nitrite was estimated by using the standard procedure suggested by Grasshoff et al., (1999), in which the nitrite formed an azo dye with sulphanilamide and N-(1-naphthyl ethylene diamine dihydrochloride. The spectrophotometeric determination was done by using a Hitachi (150-20) UV-Vis spectrophotometer

Nitrate: Nitrate was reduced using copper coated cadmium column and determined as nitrite as outlined above (Grasshoff et al., 1999).

Total Nitrogen: Total N was estimated using a procedure of persulphate oxidation (Libby and Wheeler, 1994; Bronk et al., 2000) and the resulting nitrate -N was subjected to reduction using a cadmium column, which was then analyzed spectroscopic ally by the method referred above (Grasshoff et al., 1999).

Phosphorus

The methodologies referred for the extraction of different forms of sedimental phosphorus are given in Table 2.3. In all extraction procedures, the resulting concentration was measured in terms of phosphate-phosphorus, by the formation of phospho-molybdate complex as described by Grasshoff et al .,1999. The spectrophotometeric determination was done by using a Hitachi (150-20) UV-Vis spectrophotometer.

Table 2.3. Methods adopted for the extraction of different phosphates.

No	Forms of phosphorus	References
1	Exchangeable P	Keeney and Nelson (1982); Hieltjes and Lijklema (1980); Nair (1990)
2	Inorganic P	Aspilla et al. (1976); Golterman (1996)
3	Ca-bound P	Golterman (1982; 1996); Nair (1990);
4	Organic+ Residual P	Graca and Bolalek (1998)
5	Total P	Aspilla et al (1976); Golterman (1996)

Trace metals

All glass wares used for the analyses were thoroughly cleaned in solution and then soaked in 6M HNO_3 for 48 hrs. It is then washed well with de-ionised water and then with Milli-Q water. Unless otherwise specified, all reagents used were MERCK / BDH-GR /Analar grade.

For the determination of total trace metals in sediments, sediment was dried and powdered in an agate mortar. Approximately 1 g of the homogenized sediment was digested with a mixture of conc. HNO_3 and conc. HCl in the ratio 1:3 (aqua regia) at 95^0 C for 24 hrs (Johansson, 1975; Young et al., 1992). The digest is dissolved in a minimum quantity of water and centrifuged at 4000 rpm. The supernatant liquid was filtered using a membrane filter of 0.45 μm pore size and the filtrate was made upto a definite volume. It was then analyzed for trace metals namely Fe, Zn, Cu, Co, Cr, Cd, Mn, Pb and Ni using a graphite furnace atomic absorption spectrophotometer (Perkin Elmer - 3110). The precision of the analysis was performed by standard spiking technique of quadruplicates and expressed as coefficient of variation for each element: Cu 2.8%, Co 3.1%, Cr 2.9%, Cd 2.9%, Pb 4.1%, Zn 3.1%, Ni 2.%, Mn 2.1% and Fe 2.6%.

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Chapter 3

CHEMO-VARIABILITY AMONG THE BIOTIC COMPONENTS

INTRODUCTION

Coral reef is a gathering place in the ocean – a surrealistic landscape which is shredded in blue and surrounded by life. …life in a thousand forms. Within world's oceans, the greatest variety of life is found in an amusing living structure called coral reefs. These fragile reefs play a critical role in sustaining a thriving ocean habitat, especially in tropical oceans. Reefs provide a variety of food and shelter in the tropical oceans or in other words the entire tropical ocean depends upon the coral reefs for sustenance. Thus, conferring the term "the rainforests of the sea". Coral reefs are among nature's greatest spectacles, offering the finest examples of natural architecture in the world. They form communities of startling complexity and are essential to the health of the world's oceans and to many human communities as well.

Coral reef ecosystems are now widely recognized as among the most biologically diverse and complex of ecosystem; they have been called the marine equivalent of tropical rain forests. Like rain forests, their significance and impact extend beyond the tropical environments in which they occur.

Coral reefs are biologically significant. As "oases" of high productivity in typically sterile tropical seas, coral reefs are a source of much needed protein for adjacent human populations. And, the diverse life forms of coral reefs are potential sources of medical and commercial products.

Coral reefs are geologically significant. The mineral skeletons of reef dwellers have contributed significantly to island and shoreline building. Where reefs exist, they function as breakwaters, protecting shorelines and property from damaging ocean waves. And, reef growth over time provides clues to earth's climate record and possibly plays a role in global carbon dioxide balance. Like rain forests, coral reefs are coming under increasing human impact: over harvesting and destructive fishing methods; shoreline dredging and development; sewage, fertilizer, industrial, and other forms of pollution; logging and agriculture that damage shoreline and inland watersheds; poorly managed boating, diving and other recreational activities.

Reef building (or hermatypic) corals are of the order *Scleractinia* in the class *Anthozoa* of phylum *Cnidaria*. Reefs are formed by calcium carbonate produced by tiny coral polyps. While corals are the chief architects of reef structure, they are not the only builders. Coralline algae cement various corals together with compounds of calcium, and other organisms such as tube worms and molluscs donate their hard skeletons .Together these organisms construct many different types of reefs. Reefs are important land builders in tropical areas. forming islands and altering continental shorelines.

The phylum Cnidaria(formerly known as coelenterates) were the first multicellular animals with true tissues. The body is sac-shaped and radially symmetrical, with an opening at the top forming the mouth. Surrounding the mouth are a circlet of tentacles. The cavity of the sac-shaped coelenteron is where digestion takes place. Food enters the sac, and wastes leave via the mouth. The tentacles often possess stinging cells, nematocysts, to stun or kill prey. The inside body wall is folded into mesenteries which increase the surface area to aid in food digestion and absorption. No heart, circulatory, excretory, or respiratory systems are present, and the nervous system is rudimentary.

Two basic feeding orientations exist. Medusa (e.g. jellyfish) are free floating with the mouth and tentacles pointing downward. Polyps (e.g. corals, sea anemones, & hydra) are attached to the bottom with the mouth and tentacles pointing upward. In many cnidarians, the sexual medusa and asexual polyp stages alternate with each other in the life cycle. In other cases, only the medusa or polyp stage is present. Polyps may grow in large colonies.

Class Anthozoans are composed of cylindrical-shaped individuals, whose skeletons are called corallites. These individuals are either solitary or bound together in a group, forming a colony. The base of the corallite is usually attached to a firm substrate, where it remains fixed for its entire adult life (sometimes several centuries). Within each corallite are several partitions called septa, which radiate out from the central axis of the cylinder. Horizontal structures or platforms which extend across each corallite are called dissepiments (if irregular or blister like) or tabulae (if flat plates). The living animal or polyp occupies only the uppermost portio (calyx) of each corallite. During growth, the polyp secretes skeletal materia near its base and slowly moves upward toward the surface.

Most Cnidarians are marine, and many prefer warm tropical shallow water. Many coelenterates (jellyfish, many hydrozoans, and sea anemones do not secrete a skeleton and have a negligible fossil record. Others especially many anthozoan corals, secrete an extensive skeleton and are wel preserved. Because many coral reef organisms can tolerate only a narrow range of environmental conditions, reefs are sensitive to damage from environmental changes (Reichelt and Harrison, 2000). Slight changes in the reef environment may have detrimental effects on the health of entire cora colonies. These changes may be due to a variety of factors; but they generally fall within two categories:-natural disturbances and anthropogenic disturbances. Although natural disturbances may cause severe damages to coral communities, anthropogenic disturbances have been linked to the vas majority of diseases in coral cover and general colony health when cora reefs and humans occur together.

One of the greatest threats to coral reefs is human expansion and development. As development continues to alter the landscape, the amount of freshwater runoff increases. This terriginous runoff may carry large amounts of sediment from land – clearing areas, high levels of nutrients from agricultural areas or septic systems, as well as many pollutants such as heavy metals.

Since most corals spawn and produce floating gametes, pollutants and toxins on the surface can effect coral reproduction and development for a large area. Therefore, much care must be taken to prevent or reduce the spillage and leakage of contaminants to the surrounding reef environment. Most of the industrial and domestic effluents are 'point source' discharges that affect localized reef areas, rather than causing broad scale reef mortality. Industrial effluents also impart coral reefs and their associated fauna and habitats.

High concentration of heavy metals such as lead, mercury, zinc, cadmium, tin, copper, cobalt, iron, manganese, nickel, aluminium, vanadium and silver can kill corals and other coral reef organisms. Lower concentrations can inhibit coral growth and reproduction, and may even contribute to bleaching. Corals absorb chemicals across their outer tissue layer, so whatever contaminants are suspended(floating) in the surrounding water will soon be absorbed into the coral itself (Negri and Heyward, 2000).

The major mechanism of transportation of heavy metals to the nearshore environments from inland is the rivers which includes runoff from agricultural lands, urban areas, storm drains, and sewage pipes which all flow into rivers and ultimately into the sea. Some of these trace metals will get settled on the sediment on river and estuarine bottoms, or will get trapped in mangrove forest sediments. As soon as a channel is dredged for larger ships, or a mangrove forest is cut down to make way for a shrimp farm, those metals are resuspended (stirred up) and once again become a threat to the health of coral reefs (Batley, 1995).

Monitoring both natural and anthropogenic changes in the concentration of heavy metals in marine environment is important for protecting the ecosystems involved and for safe guarding human health where man consumes biota from the ecosystem (McConchie and Harriott, 1992). Although most coral reefs are widely regarded as pristine habitats which are not exposed to high heavy metal inputs, pollution associated with contaminated river water, effluent discharges into the ocean, offshore and near-shore mining, shipping accidents and developments on the reefs themselves is known to have affected coral reefs in several parts of the world (Brown and Holley, 1982; Bell et al., 1989; Scott, 1990).

Metal pollution assessments in marine environments have traditionally involved analysis of the metal load in various species of marine fauna (primarily molluscs), substrate sediments, and the water itself (Forstner and Wittmann, 1981; McConchie 1989; Esslemont, 2000 a and b). The most abundant and readily sampled organisms in coral reef environments are the corals themselves and many species would be suitable as sentinel organism if it can be established that their metal loads adequately reflect environmental conditions and can be measured accurately and efficiently. Metal loads in corals can provide an indication of environmental metal loads and of changes in these loads overtime (Dodge and Gilbert, 1984; Shen et al., 1987; Bell et al., 1989; Glynn et al., 1989; Scott, 1990; Hanna and Muir, 1990). Corals satisfy all the accepted criteria for selection of organisms for biomonitoring (Hanna and Muir, 1990). At polluted sites metal concentrations in skeleton material can be used to monitor changes in environmental metal loads (Scott, 1990).

The term "trace metal" or "trace element" is used in current literature to designate those elements which occur in small concentrations in natural systems. For all practical purposes, the terms such as "trace metals", 'trace in organics", "heavy metals", "micro nutrients" are treated as synonymous with the term "trace elements" (Wittmann, 1983). From a biological perspective , metals may be divided into those that are essential to living organisms, those that are potentially toxic and relatively available, and those that are potentially toxic but which , due to their general rarity in the environment, are relatively unavailable. Examples of essential metals are Cu , Zn and Fe. These elements are vital compounds of enzymes, respiratory proteins and certain structural elements of organisms (Depledge and Rainbow, 1990).

Thus, carbonic anhydrase, carboxy peptidase A and B and several hydrogenases contain Zn; pyruvate carboxylase contain Mn; the metalloid Se is a component of glutathione peroxidase; vitamin B_{12} contains Co; Cu is present in cytochrome oxidase, phaetocyanin and haemocyanin; and hemoglobin and ferrodoxin contain Fe (Bryan, 1976; DeBoer, 1981). A range of trace metals must be delivered to the tissues of an organism in order to meet the diverse metabolic and respiratory requirements whilst at the same time excessive accumulation of potentially toxic metal species must somehow be prevented. Other trace metals, such as Cd, Hg and Pb are considered as non-essential because they have no known biological role; these become highly toxic when found at metabolically active sites, even at relatively low concentrations (Rainbow, 1985).

Pollution pressures associated with urban, industrial and rural development threaten many coastal environment, and as a result the effect of trace metals and other pollutants on aquatic and marine organisms has received widespread attention . Coral reefs are a common feature of many shallow coastal environments in tropical regions, and are at increasing risk from pollution pressures (Reichelt and Jones, 1994). Since scleractinian corals are dominant organisms and key components of coral reef ecosystems, they are useful organisms for determining toxicity thresholds of potential pollutants. It is important to quantify the effects of pollutants on reef corals because it is likely that any adverse effect on corals will ultimately affect many other coral reef organisms, which rely on healthy communities, either directly or indirectly (Bastidas and Garcia, 1997; Esslemont, 1999).

Environmental pollutants can effect all life stages of organisms, however the earlier life stages of marine organisms are often found to be more sensitive to pollutant stress than the adults (Phillips, 1994;1995). Monitoring both natural and anthropogenic changes in the concentration of heavy metals in marine environments is important for protecting the ecosystems involved and for safe guarding human health where man consumes biota from the ecosystem. Living corals have potential advantages, over the conventional use of molluscs and fish, as sentinel organisms for monitoring metal pollution, including ease of sampling, low impact on the target population, wide distribution of target organisms and lack of target organism mobility (McConchie and Harriott, 1992).

Scleractinian corals meet several of the pre-requisites for biological monitors suggested by Philips (1990). They are long lived, sessile organisms that are common in many tropical and subtropical marine ecosystems, compared with other potential indicator species and they yield adequate tissue and skeleton material for analyses of trace metals (Esslemont et al., 2000). Coral skeletons show promise as long term proxy monitors of the indicated environmental factors (Esslemont et al., 2000). Exploratory works conducted on corals from the Caribbean –Indo-Pacific and south Pacific regions indicate that coral skeletons record ambient trace metal concentrations that reflect environmental factors, such as El Nino events (Shen et al., 1987), anthropogenic inputs (Dodge and Gilbert, 1984; Shen et al., 1987), and river discharges (Shen and Sanford, 1990).

MATERIALS AND METHODS

The general methods adopted are detailed in chapter II. The standardization of methodology for the extraction of trace metals from corals using lanthanum chloride is specifically discussed here.

Methods:

A. Measuring the effectiveness of lanthanide chlorides at releasing heavy metals from a t typical skeleton digest, in a working range between 0.1 ppm to 2 ppm.

B. Measuring the capacity of lanthanide chloride at releasing heavy metals over a range of dissolved calcium concentrations.

Method A:

Four heavy metals concentrations of 0.1,0.5,1 and 2 ppm of mixe Cu, Zn, Ni and Cr standards were added to 1.5 g coral skeleton sampl before digestion. The samples were digested in 10 ml aqua regia. accuratel made upto 10 ml with lanthanide chloride : HCl (1 part of lanthanid chloride solution to 9 parts 0.0012 M HCl)

Result: Measured concentrations are represented graphically (Fig.3.1 against actual concentrations. Measured concentrations of heavy metal were consistently lower than their actual concentrations. due to suppressio of signals by sample matrices. Below 0.5ppm, linearity of the plots i excellent. Ni and Cr, above 1 ppm, precision slightly decreased. Lanthanu is found to be an adequate releasing agent for heavy metals from a calciu rich matrix. The matrix interference is found to be varying with differen amount of sample weights.

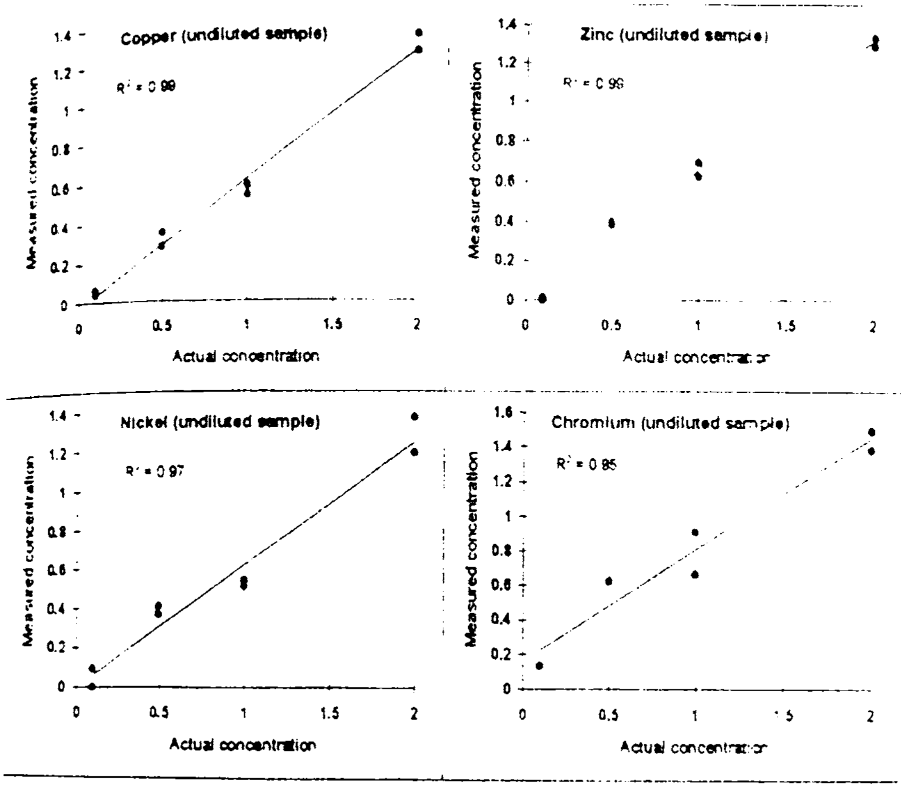

Fig. 3.1. Heavy metal standards (0.1 to 2 ppm) measured in 1.5 gram digested coral skeletons.

Method B:

0.5 2 g of skeleton was weighed, target concentrations of 0.1 ppm and 0.5 ppm are provided, samples were digested I n10 ml aqua regia made upto 10 ml with lanthanide chloride : HCl solution (0.015M lanthanum chloride : 0.0012 M HCl).

Result. As more sample (Fig. 3.2) is dissolved, absorbance decreases, instead of getting a constant metal concentration, absorbance was found to

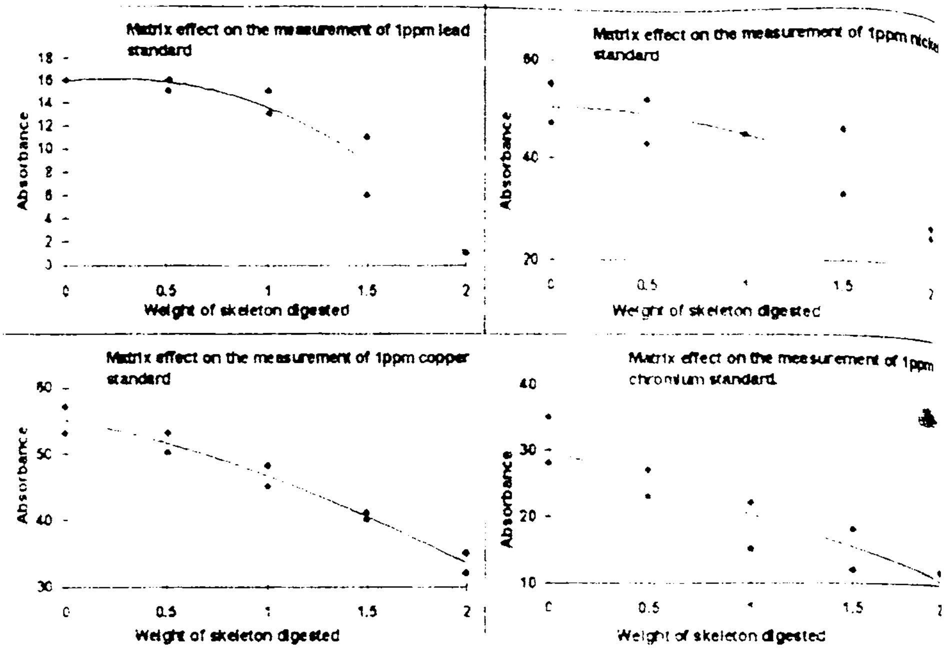

FIGURE 13: Matrix effects upon absorbance readings of 1 ppm standards, caused by progressivel increased amounts of digested coral skeleton.

be decreasing when more sample was dissolved. When more skeleton digested the spike becomes underestimated which indicates pea suppression due to matrix interference.

Conclusion: In the analysis of trace metals using aqua regia, metals can measured only upto 2 g skeleton dissolved in 10 ml digest. When the weig of skeletal samples exceed one gram, peak suppression is quite substantia But for the analysis of heavy metals in corals, since the met concentrations are very low in coral skeleton, we need to for more than weight of sample for metal analysis. In order to overcome the interferen due to matrix effect, an organic separation step was essential. This accordance with this, we ruled out the procedure of aqua regia digestion and adopt a detailed procedure as suggested by Esslemont (1999; 2000 a and b; 2002) which are detailed in materials and methods.

RESULTS AND DISCUSSIONS

Concentrations of trace metals in the skeleton and tissue parts of corals are represented in Figs. 3.3 and 3.4 respectively. Fig.3.5 represents the concentrations of trace metals in the whole body of corals. The variation of partition coefficients (K_D) of trace metals among the coral species are given in Fig. 3.6. Figs. 3.7 to 3.11 shows the percentage wise partition of trace metals receptively for different species namely, *Montipora digitata, Lobophyllia corymbosa, Acropora formosa, Psammocora contigua and Porites andrewsi.*

In focusing the heavy metal concentrations in the skeleton parts of *Montipora digitata*, the highest value of 13.02 mg kg^{-1} was recorded in the case of Lead. The decreasing order of metal concentration within the skeletal part is as follows, Pb>Fe> Ni>Co> Cr>Mn>Cu>Cd>Zn (ranging from 13.02 to 1.24 mg kg^{-1}), whereas in the tissue parts of *Montipora digitata*, Fe recorded the highest value (16.5 mg kg^{-1})and the other metals are found to be concentrated in the order, Cr>Mn>Zn>Ni>Cu>Pb>Co>Cd.

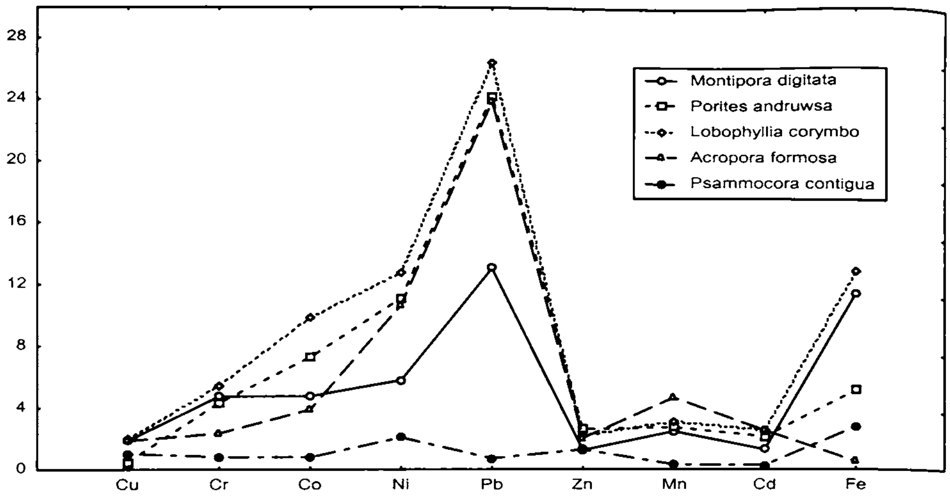

Fig. 3.3. Concentrations of trace metals in the skeleton parts of the corals

Comparing the enrichment of metals in the tissue and skeleton parts of *Montipora digitata*, all the metals except iron exhibited highest concentrations in the skeleton parts. Coming to the percentage wise distribution of trace metals in the skeleton and tissue parts of *Montipora digitata*, the following results are obtained

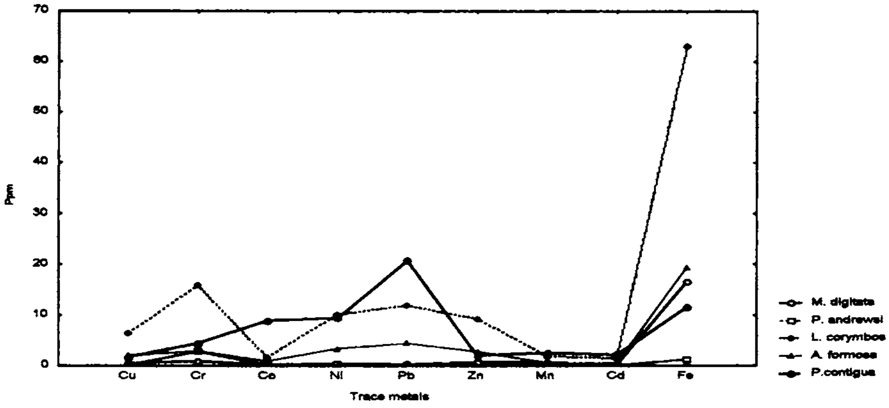

Fig. 3.4. Concentrations of trace metals in the tissue parts of the corals.

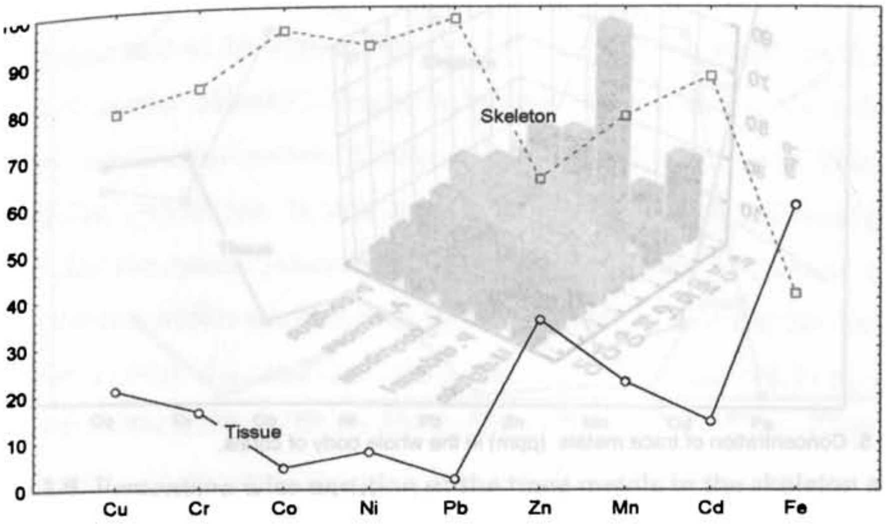

Fig.3.7. Percentage wise partition of the trace metals in the skeleton and tissue parts of *M. digitata.*

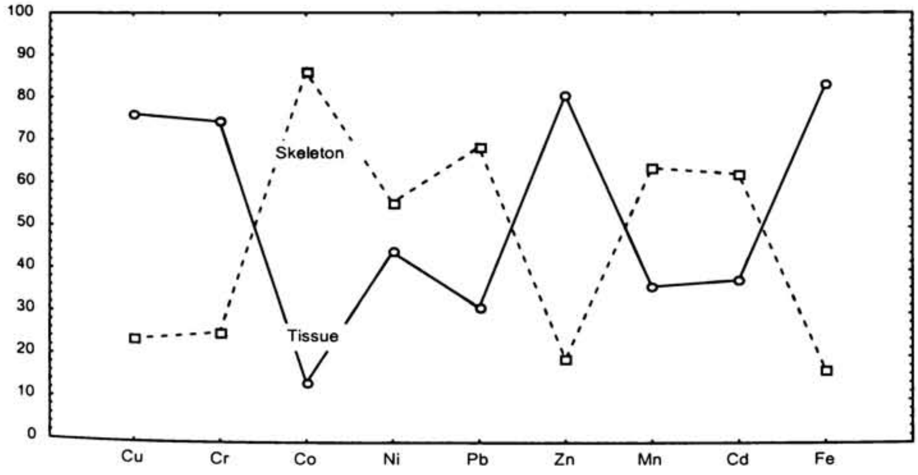

Fig.3.8. Percentage wise partition of the trace metals in the skeleton and tissue parts of *L. corymbosa.*

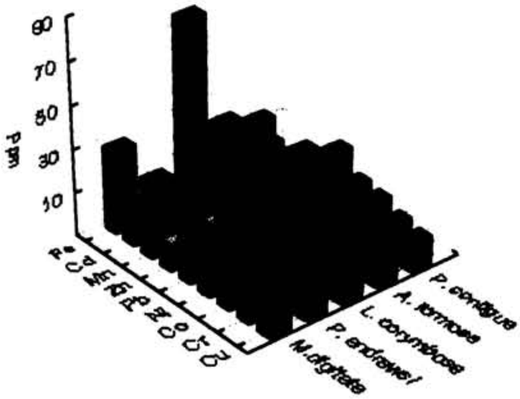

Fig. 3.5. Concentration of trace metals (ppm) in the whole body of corals.

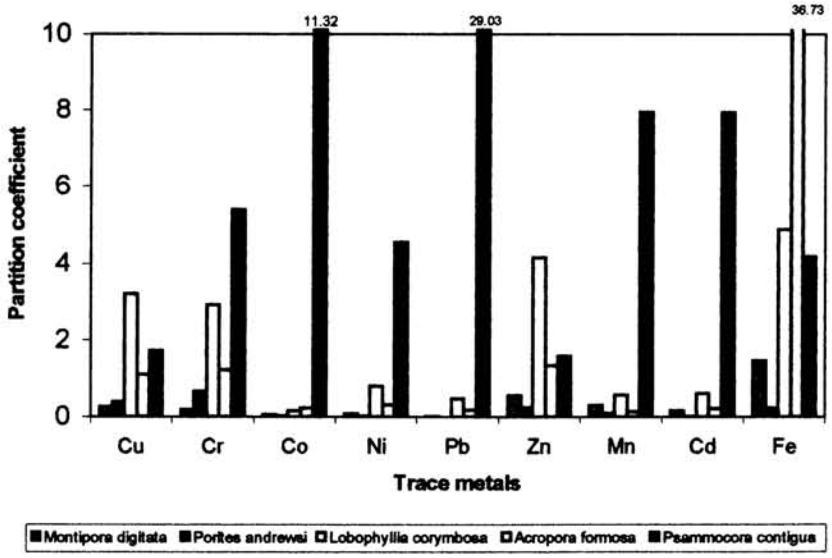

Fig. 3.6. Partition coefficients of various trace metals between the tissue and skeleton parts of corals.

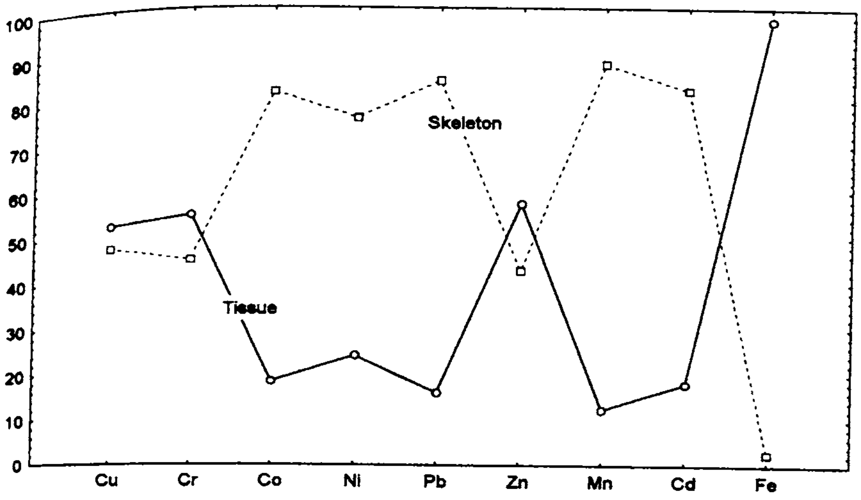

Fig.3.9. Percentage wise partition of the trace metals in the skeleton and tissue parts of *A. formosa.*

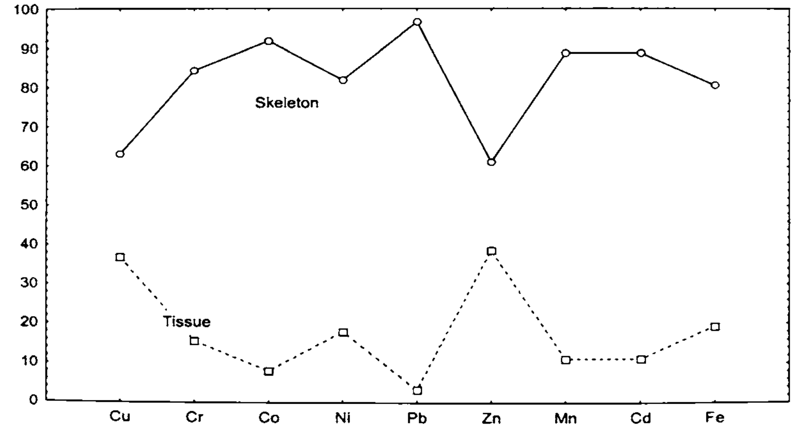

Fig.3.10. Percentage wise partition of the trace metals in the skeleton and tissue parts of *P. contigua.*

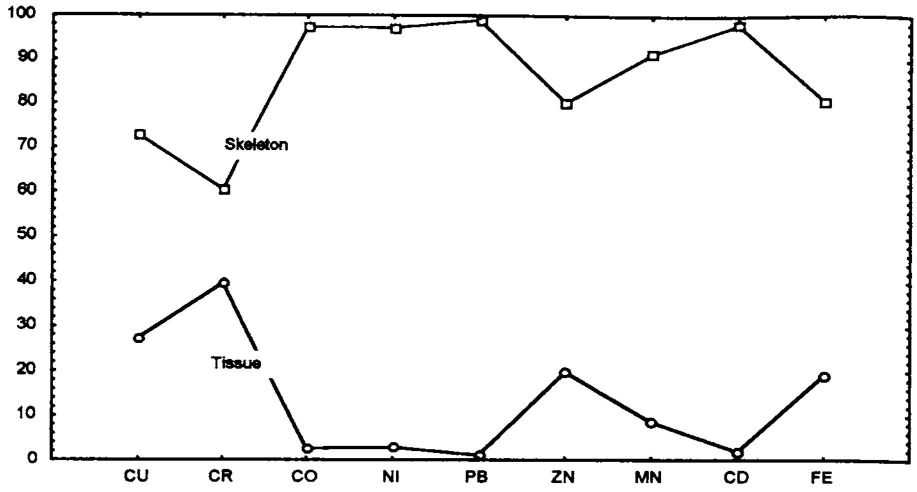

Fig.3.11. Percentage wise partition of the trace metals in the skeleton and tissue parts of *P. andrewsi*

20.9 % of copper is concentrated in the tissue part whereas, 79.1 % in the skeletal part. The partition coefficient, $K_D = [M]_T / [M]_S$, for this metal in *Montipora digitata* is found to be 0.3 . In the case of Co, Ni and Pb < 10 % of the metal is enriched in the tissue compared to skeleton, which gives partition coefficients ≤ 0.1. In the behaviour of Mn and Cd, a greater portion of the metals was accumulated in the skeleton part, 77.5 % and 85.7 % respectively. The concentration of Zn did not vary significantly between the tissue and skeleton of *Montipora digitata* giving a partition coefficient of 0.5.

Tracing the features of *Lobophyllia corymbosa*, the accumulation of trace metals in the skeleton is as follows , Pb> Fe> Ni> Co> Cr> Mn> Cd> Zn> Cu

In the case of tissue, Fe exhibited the highest concentration (62.9 mg kg). The order of enrichment is Fe>Cr>Pb>Ni>Zn>Cu>Mn>Co>Cd. Contrary to the behaviour of *Montipora digitata*, in which all the metals except iron exhibited greater affinity towards the skeleton, various metals exhibited different enrichment pattern between the skeleton and tissue phases of *Lobophyllia corymbosa*. In this species, Cu, Cr, Zn & Fe showed greater affinity for the tissue ,whereas, Pb, Ni, Mn, Co and Cd showed higher concentrations within the skeleton. In the case of Cu and Cr, the partition coefficients were 3.2 and 2.9, indicating 76.8 % and 74.5 % tissue enrichment respectively. For Zn and Fe, more than 80 % of the metal were concentrated in the skeleton giving partition coefficients 4.16 and 4.91 respectively.

In this species, Pb, Ni, Mn, Co and Cd displayed partition coefficients less than 1. For Mn and Cd, partition coefficient is 0.6, exhibiting almost similar pattern of metal partitioning between skeleton and tissue parts. In the behaviour of Co, majority (86 %) is enriched in the skeleton which gives a low K_D value of 0.16.

The trace metal accumulation trend in *Acropora formosa* is exactly similar to that in *Lobophyllia corymbosa*, in which Cu, Cr, Zn & Fe exhibited higher tissue concentrations compared to skeleton values. The trace metal concentrations in the skeleton parts of *Acropora formosa* showed the order Pb>Ni>Mn>Co>Cd>Cr>Zn>Cu>Fe whereas, the tissue concentration showed the order Fe>Pb>Ni>Cr>Zn>Cu>Co>Mn>Cd. In the case of Cu, Cr and Zn, the partition coefficients are slightly greater than 1, i.e. the distribution did not vary significantly between skeleton and tissu parts. Fe showed a very high affinity towards the tissue phase of *Acropor formosa*, which displayed a very high partition coefficient, 36.7, in whic about 97% of the metal concentration was found in the tissue part Considering the behaviour of Pb, Mn and Cd, more than 80 % i concentrated in the skeleton parts which gives K_D values 0.2 for Pb and Cd 0.1 for Mn. Ni exhibited a value of 0.3 as partition coefficient, indicating 7 % metal enrichment within the skeleton.

Contrary to the behaviour of the other three species, in the case *Psammocora contigua* all the metals exhibited higher concentration in tissue compared to the skeleton, indicating K_D >1 for all the metal Regarding the concentrations of metals in the skeleton, the order observe is Fe>Ni>Zn>Cu>Cr>Co>Pb>Mn>Cd, whereas, in the case of tissue th order is Pb>Fe>Ni>Co>Cr>Mn>Cd>Zn>Cu. In the behaviour of Cr, Ni Mn, Cd & Fe more than 80 % of these metals were found within the tiss giving high values of K_D. Pb showed a greater affinity towards the tissue which 96 % of it is found within this phase indicating a very high K_D (2 For cobalt partition coefficient was found to be very high i.e. , 11.32 , which means 91.9% metal concentration in the tissue phase.

Porites andrewsi was also typical in its metal enrichment pattern i which all the metals showed an affinity towards the skeleton. This trac metal accumulation trend traced out is exactly opposite to that o Psammocora contigua, were all the metals are preferably accumulated in th tissue phase. In the skeletal phase of *Porites andrewsi*, highest concentratio was exhibited by lead(24.2mg/kg) as in the order, Pb> Ni> Co> Fe> Cr

Mn>Zn> Cd> Cu ,whereas in the tissue the following pattern was observed, Cr> Fe> Zn> Ni> Pb> Mn> Co> Cu> Cd.In this species, for cobalt. nickel, iron and lead more than 95% of the metal was found within the skeleton giving low values for partition coefficient. The other three metals displayed a similar trend (for Zn and Fe - 80% and for manganese 91%). Clay minerals, hydrated iron and manganese oxide colloids, organic matte and micro organisms are the particulate matte found in sweater. These particulate matter have an ability to collect heavy metal adherents. either through complexing or surface adsorption. Livingston and Thompson's (1977) studies on the stained corals from the deep ocean have shown excess amounts of trace metals on stained corals due to the coating compared to the unstained corals of shallow region which are said to require high amount of concentration from the detritus.

Regarding the variations in the behaviour of Fe among the selected species, in *Montipora digitata*, among the 9 metals studied Fe recorded the highest concentration in the tissue phases. Iron is an essential element required by certain enzymes and proteins that carry electron during photosynthesis and respiration (Govindjee, 1995).

In *Acropora formosa*, Fe recorded the highest concentration within the tissue. in which about 97.3% of the metal was enriched in the tissue phase. In *Lobophyllia corymbosa* and *Psammocora contigua*, Fe showed a greater affinity towards tissue, indicating more than 80 % enrichment within this phase.

Contrary to the behaviour of Fe in the other four species. in *Porites andrewsi* more than 80 % of iron was found in skeleton phase. The tissue enrichment of Fe in all the species except that in *Porites asdruwsa* may due to the biological role of Fe in various enzymatic functions. Hi concentrations of Fe observed in the skeleton of *Porites andre* compared to relatively less concentrations within its tissue points towar the usefulness of this species to monitor anthropogenic loads of iron marine ecosystems. At polluted sites, metal concentrations in skelet material can be used to monitor changes in environmental metal loa (Dodge and Gilbert, 1984; Scott, 1990) but in less polluted settings skele metal is probably too low and too variable to be widely used for th purpose. Higher concentration of some metals in tissue material relative skeletal material have also been reported in other studies (Hanna and Mu 1990) and this difference probably accounts for the observation of Glynn e al. (1989) that higher metal concentrations are measured in sample containing both tissue and skeletal material than in equivalent sample containing skeletal material alone. Metals are probably taken into the cor tissue both from food and directly from solution and it is also likely th the symbiotic algae (zooxanthellae) influence metal transfer reacti (McConchie and Harriott, 1992).

On evaluating the behaviour of Cu in the five species. in *Montip* *digitata*. Cu showed a greater affinity towards the skeletal phase with 79 % enrichment. In *Lobophyllia corymbosa* and *Acropora formosa*. as in the case of iron. Cu concentrations were found to be maximum within the tissu (76 % and 52% respectively). As in the case of *Montipora digitata*. nearl 72 % of Cu enrichment was found in the skeletal phase of *Porites andrews* and 36% for Psammocora contigua. The tissue enrichment is due to the vita role of this essential element as the component of enzymes, respiratory proteins and various structural parts of organism. Cu, Zn and Fe are vital components of enzymes, respiratory proteins and certain structural elements of organisms (Depledge and Rainbow, 1990). Copper is required in relatively low concentrations compared with other essential elements such as zinc. Coral tissues can be used for bioassays of copper because it is accumulated by tissues in relation to availability possibly because they provide useful biochemical function (Esslemont, 2000).

The tissue metal concentrations reflect the amount of metal taken up into the organism, the proportion of that metal which is distributed to each tissue, and the extent to which metal enters and is retained within each tissue. Since copper is an essential trace element, comparative enrichment of Cu in the skeletal phase is not of a series concern, but it may indicate the capacity of skeleton to reflect the changes in environmental metal loads. Copper accumulated in coral skeletons in direct response to environmental availability, but whereas tissue-concentrations of copper varied directly with environmental availability (Esslemont, 2000).

The effect of copper on scleractinian corals is of environmental concern because these are numerous sources of copper to coral reefs and corals are keystone species in tropical coral reef ecosystems (Reichelt and Harrison, 2000). Copper is found in sewage discharges.

Regarding the variations of Pb among the five species, *Montipora digitata*, *Lobophyllia corymbosa* and *Acropora formosa* showed a greater affinity towards skeletal phase than their tissue part, in which *Montipora* *digitata* recorded the highest load of lead (97 %) within the skeleton. I *Psammocora contigua*, 96 % of metal enrichment was found within th tissue. Among all the species, *Porites andrewsi* recorded the highe percentage of total Pb in its skeletal phase (98 %).

Differences in the Pb concentration among the species indicate th differing selectivity of each metal by various species, on the basis o biochemical utility or toxicity. Lead is accumulated in coral skeleton ir direct response to environmental availability, whereas tissue concentrati of lead did not vary over a wide range of environmental availabilities (Esslemont, 2000b). According to Eisler (1981), hard tissues can act as place of lead accumulation. The transfer of lead through tissue int skeletons suggests discrimination by elimination (i.e. tissue regulation of lead concentration) combined with a natural tendency for lead to associat and interface with calcium channels (Babukutty, 1991), because the coral skeleton accumulated lead whereas coral tissue did not. Lead will bind to metallothionenin, but also has an affinity (probably higher) for oth metabolic ligands, often associating with deposited inorganic granules wi high concentration of calcium (Brown and Holley, 1982). Exclusion of lea by the organism would have prevented lead from entering skeletons vi tissue membranes (Esslemont et al., 2000) The enrichment of lead can take place in two ways i.e. either by adsorption on the outer surface or by incorporation into the shell matrix. Ferrell et. al. (1973) and Sturesson (1976) , have explained the pathway of the enrichment of lead due to surface adsorption. Pb^{2+} ions can be expected to substitute some of the Ca^{2+} ions in the 9 co-ordinate aragonite lattice because lead carbonate (cerrusite) and aragonite are isostructural (Chester and Elderfield,1967). Zinc is an essential element for all biological systems (Depledge and Rainbow, 1990).

Considering the behaviour among the selected species, in *Montipora digitata*, slight excess concentration of the metal was found in the skeleton, though it did not show much variation from tissue level. In *Lobophyllia corymbosa*, *Acropora formosa* and *Psammocora contigua*, highest Zn concentrations were observed within the tissue than skeleton. Contrary to this behaviour, nearly 80 % of Zn was found to be accumulated in the skeleton phase of *Porites andrewsi*. Unlike the toxic chemicals that have characteristic man-made signature, trace elements like zinc have both natural and anthropogenic sources (Babukutty, 1991).

Coral tissues accumulate zinc in tissues relative to skeleton because of its role in various biochemical functions. Considering the selectivity of each metal by corals, where metals are conferred into tissue and skeletal parts on the basis of biochemical utility, or tissue-metal concentrations are modified on the basis of toxicity, instead of being passively transferred through tissues into skeleton. The concentration of Zn^{2-} can regulate many metabolic processes through initiation and/or regulation of the activity of the metallo-enzymes. Eisler(1981) observed that accumulation of zinc is mediated by many factors including interaction effects with salts of calcium, cobalt, iron, cadmium and various organic substances.

Regarding the variations in manganese concentrations among the species, higher affinity of the metal towards the skeletal phase was exhibited by *Montipora digitata*, *Lobophyllia corymbosa*, *Acropora formosa* and *Porites andrewsi*, among them *Porites andrewsa* exhibited highest skeletal concentrations of Mn (91 %). In *Psammocora contigua*. about 88% of th metal enrichment is found within the tissue.

After Fe, Mn is the most abundant heavy metal in the lithosphere. is an essential non-toxic element involved in physiological, biochemical an morphological purposes. Mn concentration was found to be higher in th skeletal parts, except that in *Psammocora contigua*. Since Mn^{2+} ion i having ionic radii less than that of Ca^{2+}, it preferentially accumulates in th calcite lattice of coral skeleton. Most metals are probably transferred t skeletal material from the tissue rather than incorporated into the skeleta mass directly fom surrounding water (McConchie and Harriott, 1992). Mn i an essential micronutrient, being involved in many cellular reactions whic involve oxygen (such as photosynthesis) and as an activator of severa enzymes, so that mechanisms of Mn assimilation are widespread amongs microorganisms. The incorporation of manganese into the lattice structur could take place by two routes. One is the usual substitution in the calcit which is quite possible in view of he identical crystal structure of calcite an rhodochrosite(magnesium carbonate). The second pathway of manganes incorporation is by a geologically improbable inclusion of Mn^{2+} into th aragonite lattice by biomineralization occurring during shell formatio (Rosenberg, 1980). Blanchard and Chasteen (1976) reported the occurrenc of manganese in the calcite shell of M.edulis. White et. al.(1977) reporte the presence of Mn^{2+} in the aragonite lattice of M. arenaria.

Mn^{2+} and Fe^{2+} are, of course, abundant in terrigenous detritus an secondary calcite (St. John, 1974; Shen and Boyle 1988). The work by She and Boyle (1988) showed that reports of Mn^{2+} in corals in the ppm range ar the result of natural or artificial contamination of the samples. They found 8 - 20 ppb Mn in coral aragonite that had been prepared for analysis by ultra-cleaning designed to eliminate any trace elements not present within the aragonite itself.

Tracing the variations of Cd observed among the species, as in the case of other metals the skeletal phase of *Montipora digitata* showed much affinity towards the metal. *Lobophyllia corymbosa* and *Acropora formosa* also showed a similar trend. In *Psammocora contigua*, nearly 88 % of the metal enrichment was found within the tissue. As in the case of other metals, cadmium also showed an affinity towards the skeletal phase of *Porites andrewsi* in which 98 % of the metal was distributed in its skeleton part.

The behaviour of the four coral species – *Montipora digitata, Lobophyllia corymbosa*, *Acropora formosa* and *Porites andrewsa* - points towards the fact that skeletons are recommended over tissues for monitoring purposes because they represent environmental metal loads more faithfully. Tissue metal concentrations appear to be regulated possibly by preferential transport of metals into skeletons, or by elimination of metals from tissues. High accumulation of cadmium in the skeleton might have resulted by the substitution of Ca^{2+}byCd^{2+} ions in view of their comparable ionic radii.

Considering the behaviour of chromium, *Montipora digitata* showed highest metal concentrations in its skeleton compared to tissue, whereas in *Lobophyllia corymbosa*, *Acropora formosa* and *Psammocora contigua* Cr showed greater affinity towards the tissue phase. *Porites andrewsi* showed a similar pattern of chromium enrichment as that of *Montipora digitata* i which metal showed a higher proportions in its skeleton (60 %).

Concentration of chromium in tissues and skeleton parts of differe species varied substantially which may be due to growth factors, irregul distribution of particles or metal-bearing phases in coral colonie Biochemical utility and toxicity also modify the distribution strategy concerned metal in a particular species.

Characterizing the variations of cobalt among the species, high skeletal concentration was exhibited by Lobophyllia corymbosa(9.82mg/k whereas Psammocora contigua recorded the highest tissue concentratio (8.89mg/kg). Regarding the partitioning of metals between the skeletal an tissue parts, the highest partition coefficient 11.3 was exhibited b Psammocora contigua in which 92% metal concentration was found in th tissue. Among the others, in Porites andrewsi and in Montipora digitat more than 95% metal enrichment was found in the skeletal phase. I Acropora formosa and in Lobophyllia corymbosa respectively 81.7 an 86.2% metal concentrations were found in the skeleton.

Tracing the features of cobalt, it shows an affinity towards th skeleton except that in Psammocora contigua. The increased enrichmen the skeleton, therefore leads to the conclusion that biologically transport o excess amount of cobalt into the shell structure is an active proces prevailing in the body. Szefer (1986) and Szefer and Szefer (1985) reporte on the values of cobalt in the soft tissues and shells of organisms lik M.edulis,C.glaucum, M.arenaria etc,the levels of cobalt in the shells bein considerably less than that in the soft tissue.

Among the selected species , the highest skeletal as well as tissue concentrations of nickel was found in Lobophyllia corymbosa (12.69mg/kg and 10.06mg/kg respectively). Regarding the partitioning of metals between skeletal and tissue phases, except that in Psammocora contigua, all the species displayed partition coefficients less than one, indicating greater affinity of the metals towards the skeletal phase. Among these, Porites andrewsi exhibited the highest percentage (97%). If the organic phase is removed, metal concentration in the skeleton would have resulted only through physiological or mineralogical processes. During the formation of shells, any trace metal actively incorporated within the shell matrix, is assimilated by the organism (Wilbur and Saleuddin, 1983)

Relating metal concentration to morphology.

According to St. John (1974) , the following classification can be used to describe various forms of corals.

1. Massive corals:- They form more or less thick masses or heads. In this study, Porites andrewsi. belonging to family Poritidae comes under this classification.
2. Ramose corals:- They are branching type corals. Psammocora contigua belonging to family Siderastreidae, Lobophyllia corymbosa belonging to family Mussidae and Acropora Formosa of family Acroporidae comes in this category.
3. Foliaceous corals;- they form thin overlapping sheets with a small basal attachment. Montipora digitata of family Faviidae belong to this classification.

Relating trace metal concentration with morphological featu highest concentration of trace metal was reported for Ramose(branching) type corals – i.e. for Lobophyllia corymbosa wh recorded highest concentrations of Cu, Cr, Co, Ni, Pb, Cd and Fe and als Acropora formosa which recorded highest Mn concentration. The anomaly was in the case of zinc which displayed higher concentration in massive form (Porites andrewsi).

Regarding tissue metal levels, highest concentration for all metals was recorded by ramose type corals (in Lobophyllia corymbosa in Psammocora contigua). Concerning the lowest recorded values , massive form –Porites andrewsi-displayed lowest values for Cu, Ni, Pb, Mn, Cd and Fe. For cobalt , Lobophyllia corymbosa (ramose type) recor lowest value and for chromium this was observed in Montip digitata(foliaceous type). In all the species, except that in Psammoc contigua, highest concentration was displayed by lead.

Increased aquatic activities and number of automobil INEGI,1997; Munoz Chaguin et.al.,1998) along with sewage dischar containing Pb, Cu etc contributes towards lead pollution in environment (Elizalde et. al. 2002).

Qualitative differences in the organic matrix in addition variations in food, feeding characteristics and colonial gr form(St.John.1974) may also be important in determining differe between, as well as within each group.

For many organisms, the key determinants that influence metal accumulation are the relative amounts of metal present in the environment, together with their chemical form. They may give rise to body concentrations in excess of four orders of magnitude above background in non regulating organisms, and clearly, detection of contamination should be easy at grossly polluted sites (Langston and Spence, 1995; Langston and Bebianno, 1998). The uptake and elimination of metals are determined by biological parameters, which include permeability of external surfaces (and modifications caused by secretions), feeding strategies, quantities and types of internal ligands, and the efficiency of excretory systems, while body weight may be affected by nutritional status and condition, growth (size and age), season, and state of reproductive development.

Statistical Approach.

Statistical methods applied are 3 way ANOVA (1) for testing the significance of the difference between skeleton and tissue of coral species with respect to the concentration of trace metals. Having found significant differences, students t test is applied to test – difference between metals and species (algal as well as coral species) at Lakshadweep Archipelago. The significant values of 't' are presented in the form of a Trellis diagram in each case (Fig. 3.12 to Fig.3.15).

		Cu	Cr	Co	Ni	Pb	Zn	Mn	Cd	Fe
Copper	Cu	—	◑	⊕	◑	◑	⊕	⊕	◑	●
Cromium	Cr	2.45	—	⊕	⊕	⊕	⊕	●	●	●
Cobalt	Co	0.18	2.15	—	⊕	◑	⊕	⊕	⊕	●
Nickel	Ni	2.37	0.43	1.98	—	⊕	⊕	●	●	●
Lead	Pb	2.94	1.02	2.74	1.42	—	◑	●	●	◑
Zinc	Zn	1.01	1.66	0.70	1.40	2.37	—	◑	◑	●
Manganese	Mn	1.87	3.45	1.53	3.68	3.61	2.55	—	⊕	●
Cadmium	Cd	2.39	3.89	1.80	3.97	3.77	2.93	1.07	—	●
Iron	Fe	4.22	3.47	4.17	3.64	2.92	4.02	4.48	4.52	—

⊕ $t < 2.31$, ◑ $2.31 \leq t < 3.17$, ● $t \geq 3.17$

Trellis diagram for students t statistic to test the significance of the difference between trace metal concentrations in tissue of coral species.

Fig. 3.12

		Cu	Cr	Co	Ni	Pb	Zn	Mn	Cd	Fe
Copper	Cu	—	●	●	●	●	◑	●	⊕	●
Cromium	Cr	5.14	—	⊕	●	●	●	⊕	●	◑
Cobalt	Co	5.52	2.27	—	◑	●	●	●	●	⊕
Nickel	Ni	7.87	5.14	2.83	—	●	●	●	●	⊕
Lead	Pb	7.40	6.43	5.43	3.83	—	●	●	●	●
Zinc	Zn	2.37	4.13	4.93	7.40	7.29	—	◑	⊕	●
Manganese	Mn	4.57	1.73	4.80	6.20	6.66	2.33	—	◑	●
Cadmium	Cd	1.28	4.15	4.98	7.43	7.33	0.55	2.48	—	●
Iron	Fe	4.59	2.83	0.98	1.39	4.59	4.31	3.46	4.38	—

⊕ $t < 2.31$, ◑ $2.31 \leq t < 3.17$, ● $t \geq 3.17$

Trellis diagram for students t statistic to test the significance of the difference between trace metal concentrations in skeleton of coral species.

Fig. 3.13

		Md	Pa	Lc	Af	Pc
Montipora digitata	Md	–	◑	●	⊕	●
Porites andruwsa	Pa	2·70	–	●	●	●
Lobophyllia corymbosa	Lc	[illegible]	[illegible]	–	●	◑
Acropora formosa	Af	[illegible]	5·21	4·21	–	●
Psammocora contigua	Pc	[illegible]	3·01	[illegible]	[illegible]	–

⊕ $t < 2{\cdot}12$, ◑ $2{\cdot}12 \leqslant t < 2{\cdot}92$, ● $t \geqslant 2{\cdot}92$

Trellis diagram for students t statistic to test the significance of the difference between coral species withrespect to trace metal concentrations in tissue

Fig. 3.14

		Md	Pa	Lc	Af	Pc
Montipora digitata	**Md**	–	⊕	●	⊕	●
Porites andruwsa	**Pa**	1·59	–	⊕	⊕	●
Lobophyllia corymbosa	**Lc**	3·35	1·57	–	◑	●
Acropora formosa	**Af**	0·67	0·74	2·28	–	●
Psammocora contigua	**Pc**	8·30	6·81	8·34	5·72	–

⊕ $t < 2{\cdot}12$, ◑ $2{\cdot}12 < t \leqslant 2{\cdot}92$, ● $t \geqslant 2{\cdot}92$

Trellis diagram for students t statistic to test the significance of the difference between coral species withrespect to trace metal concentration in skeleton.

Fig. 3.15

The concentration of trace metals, in skeleton and tissue of coral spe when subjected to 3 way analysis of variance after row and col standardization showed significant difference between skeleton and ti ($F_{(1,32)}$=382.31, $P<0.01$) and between trace metals ($F_{(8,32)} = 40.31$, P<(which leads to high significance for skeleton tissue and metal nucle ($F_{(8,32)} = 40.31$, $P<0.01$) which leads to high significance for skeleton, ti and metal interaction ($F_{(8,32)} = 29.08$, $P<0.01$) Species wise difference not high ($P>0.05$) indicating that these species accumulate more or same amount of the trace metals in their body parts (Table 3.1). But b on non standardized data between skeleton and tissue the difference found to be not significant ($P>0.05$) where as species wise difference highly significant ($F_{(4,32)} = 4.4295$,$p<0.05$) as indicated by the tr diagram for coral species based on trace metal accumulation in skeleton tissue. The difference was very high between the species *Psammoc* *contigua* and other species ($t>5.72$) and also between *Montipora digit* and *Lobophyllia corymbosa* ($t=3.35$) *Lobophyllia corymbosa* and *Acrop* *formosa* ($t=2.28$) in the case of skeleton. In the case of tissue, h significant difference was observed between all species ($t>2.70$) except between *Montipora digitata* and *Acropora formosa* ($P>0.05$).

Table 3.1 : **Distribution of Coral Species with respect to trace metal accumulation in Lakshadweep**

Species	Mean	Standard Deviation	Coefficient Of Variation
(a) Skeleton			
Montipora digitata	5.18	4.08	78.80
Porites andrewsi	6.67	6.87	103.01
Lobophyllia Corymbosa	8.57	7.54	88.03
Acropora Formula	5.82	6.93	119.18
Psammocora contigua	1.12	0.77	69.27
(b) Tissue			
Montipora digitata	2.29	5.05	220.19
Porites andrewsi	0.66	0.83	125.77
Lobophyllia Corymbosa	13.51	18.10	134.03
Acropora Formula	4.12	5.56	135.13
Psammocora contigua	7.06	5.97	84.53
Trace Metals in Skeleton			
Copper	1.46	0.60	41.11
Chromium	3.53	1.70	48.22
Cobalt	5.31	3.07	57.74
Nickel	8.41	3.94	46.54
Lead	17.62	9.64	54.73
Zinc	1.88	0.54	28.63
Manganese	2.67	1.40	52.38
Cadmium	1.76	0.87	49.40
Iron	6.54	4.80	73.48
Trace Metal in Tissue			
Copper	2.20	2.26	102.88
Chromium	5.39	5.38	99.87
Cobalt	2.36	3.31	140.53
Nickel	4.74	4.24	89.40
Lead	7.57	7.86	103.77
Zinc	3.07	3.20	104.02
Manganese	1.19	0.84	70.93
Cadmium	0.91	0.82	90.77
Iron	22.34	21.21	94.92

Also based on non standardized data the difference between metal was also highly significant ($F_{(8,32)} = 5.8722$, $P<0.05$) (Table 3.2). This i being represented by the trellis diagram for skeleton accumulation of trac metals ($t>2.31$) except that between copper and cadmium; cobalt an chromium; iron and nickel ;iron and lead and between cobalt an manganese which indicate that these metals when compared in pairs hav almost the same average value ($P>0.05$). In tissues, high difference wa observed between iron and all other metals ($t>3.17$) with an average valu of 22.34 for iron where as the average values of the other metals ar between 0.91 (cadmium) and lead (7.57) distribution in tissues was mor variable than the skeleton with respect to species as well as metals (Tabl 3.3).

Table 3.2: 3 way analysis of variance for Coral Species based on non transferred data

Sources	M.S.S.	DOF	F. Ratio
(a) Skeleton & Tissue	**0.07666**	**1**	**0.001915**
(b) Species	**177.303**	**4**	**4.4295**
(c) Metals	**235.052**	**8**	**5.87224**
(AxB)	**132.353**	**9**	
(BxC)	**86.004**	**44**	
(AxC)	166.735	17	
AB interaction	120.473	4	
BC interaction	37.3297	32	3.0097
AC interaction	119.251	8	0.9326
Error	40.0277	32	2.9792

Table 3.3 :3 way ANOVA table for Lakshadweep Archipelago for Skeleton and Tissue accumulation of trace metals.

Source	Mean sum of Squares	d-f	F. Ratio
(a) **Skeleton and Tissue**	34.7064	1	382.31202 **
	0.04988	4	0.5495
(b) Species	3.6595	8	40.3110 **
(c) Trace Metals	3.9273	9	
(AxB)	0.7205	44	
(BxC)	5.0060	17	
AxC)	0.09078	32	
Error	0.1099	4	1.2101
AB interaction	0.06954	32	0.7661
BC interaction	26.400	8	29.0802 **
AC interaction			

** calculated F is significant at 1% level of significance

Allometric considerations

Allometric relationship between log. weight (both tissue and skeleton) vs. log metal concentrations are given in Fig. 3.16 to Fig. 3.19.

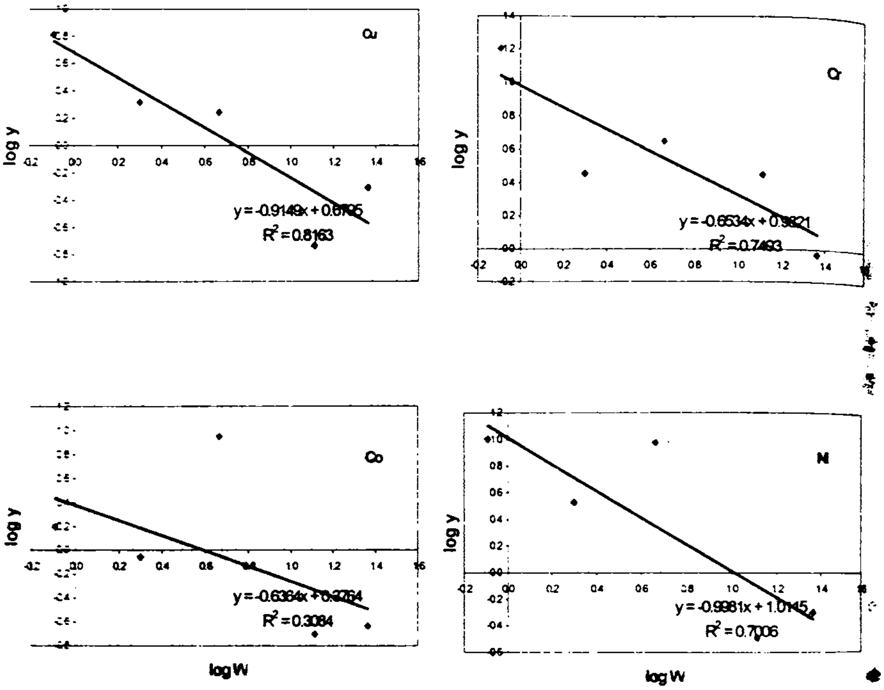

Fig.3.16.Allometric relationship between log tissue weight vs. tissue meta concentration

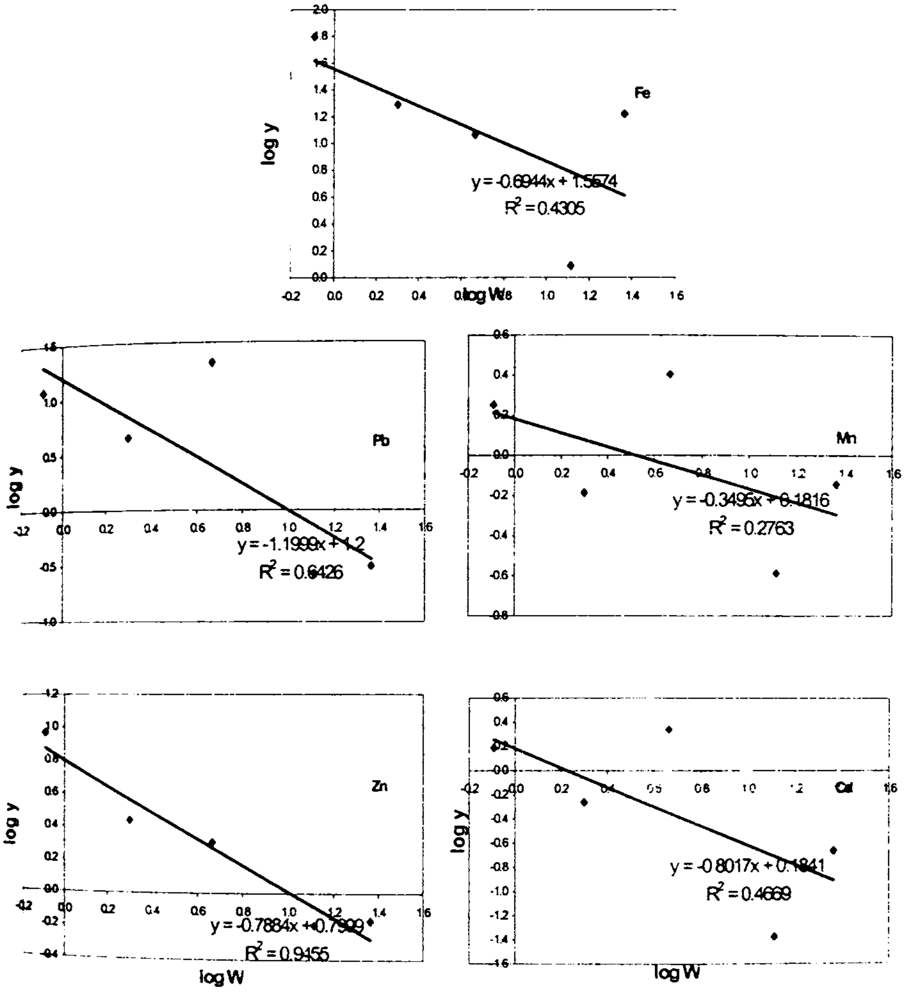

Fig.3.17. Allometric relationship between log tissue weight vs. tissue metal concentration

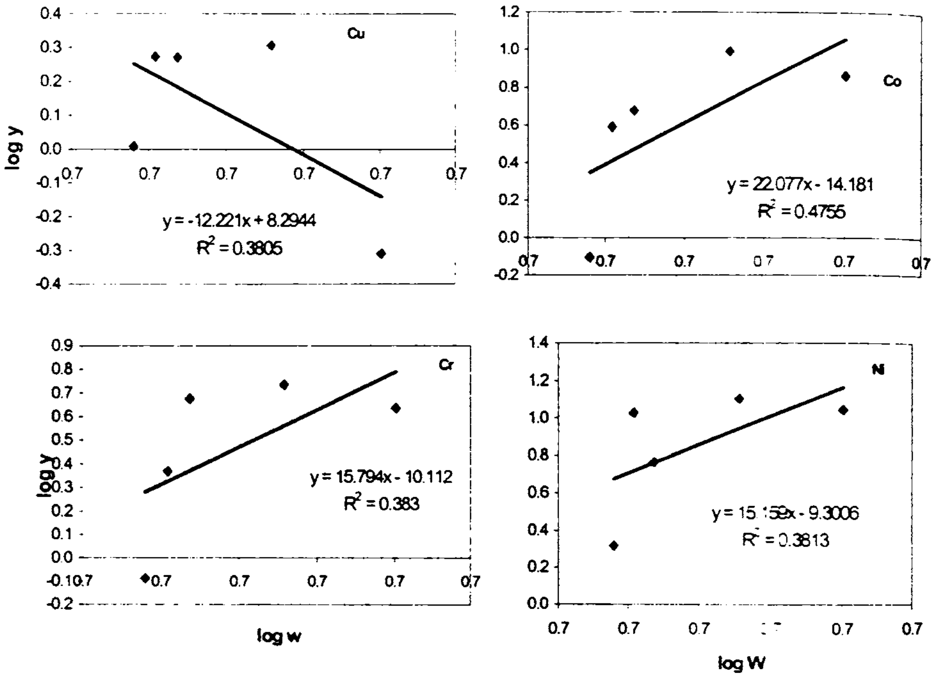

Fig.3.18 Allometric relationship between log skeleton weight vs. tissue metal concentration.

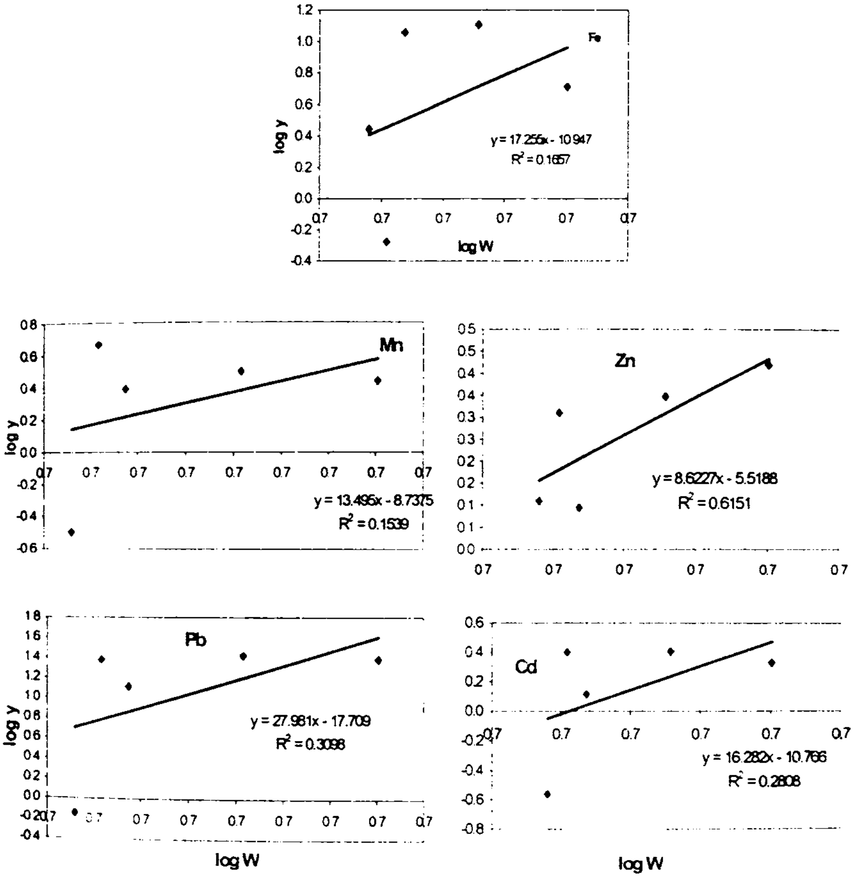

Fig.3.19. Allometric relationship between log skeleton weight vs. skeleton metal concentrations

Metal concentrations are a function of net metal content, expressed on a weight basis; therefore any change in growth or condition, relative t net accumulation, will influence measured body concentrations. Indeed, o all the biological parameters that affect metal concentrations in organisms growth, expressed as length, weight, age or some similar covariable, i probably the most extensively studied – a testimony to its importance Relationships between metals and growth are often described by one o three general scenarios: concentrations either increase, decrease or are independent of size / age (Langston and Spence, 1995).

Relationship can be described using the transformed growth equation as explained Boyden (1977) in illustrating the importance of allometric parameters on metal concentration as follows,

$$Y = \alpha W^{\beta}$$

$$\text{Log } Y = \log \alpha + \beta \log W$$

Where Y = metal content

W = body weight

&

α and $\beta$are fitted parameters

If slope $\beta = 1$, accumulation and turn over of the metal is taking place at a rate that is proportional to growth, implying a connection with metabolism. If the slopes are < 1, accumulation is more rapid on smaller animals, relative to growth, possibly because of the larger ratio of surface area to volume. A slope > 1 suggest net accumulation throughout the life o the organism, which does not reach steady rate: growth may be rapid i young individuals, effectively diluting metal concentrations, but slows down with age and metal is incorporated at a faster rate than new tissue.

On plotting the logarithm of metal concentrations against logarithm of tissue weight, all the 9 metals were found to be exhibiting significant negative correlations. The highest correlation was exhibited by Zn (r = - 0.972) and lowest by Mn (r = - 0.526). The other metals showed the following order of correlation, Cu > Cr > Ni > Pb > Cd > Fe > Co.

On plotting the logarithm of metal concentrations against logarithm of skeleton weight, except copper, all the metals were found to be exhibiting positive correlations. The highest positive correlation was exhibited by Zn (r = 0.784) and lowest by Mn (r = 0.391) .

Metals with slow exchange rate will be more likely to show positive correlations with body size (less likely to achieve steady state) than metals with rapid exchange rates. Metal accumulation occurs more rapidly in smaller, rather than larger individuals leading to negative correlations between size and metal concentrations (Langston and Spence, 1995; Langston and Bebianno, 1998). Similar slopes may be obtained if elimination rates for metals exceed assimilation rates over the organisms' life span.

Very high values of slope ($\beta>>1$) is observed for metals in the skeleton phases, indicating net accumulation of metals throughout the life of the organism, which does not reach steady state. Positive correlation, obtained for metals suggests that metal concentration increases with increase in the weight of skeleton. In such cases, trace metal accumulation is proportional to the amount of metal binding ligands in an animal's entir body (Boyden, 1977; Langston and Spence,1995).

In the behaviour of accumulation pattern of trace metals in th skeleton, except copper, no generalization can be made for th accumulation pattern of essential and non-essential elements. Essentia element, Zn is found be an accumulation pattern similar to that of non-essential elements like Cr, Ni, Pb, Cd etc. as reflected in their correlation coefficient.

This may occur through binding of metals to low molecular weigh cytosolic proteins –metallothioneins- which play an active role in the enhanced enrichment of metals like Cu, Cd, Hg, Zn, Co etc Metallothioneins have a high affinity for these metals and it is generally accepted that the binding of these metals to metallothionein constitutes a metal detoxification (Klerks and Bartholomew, (1991).

Zinc and cadmium are more bioavailable to invertebrates at lower salinities. In the pattern of accumulation of Cu, a negative correlation was obtained, r = -0.617. In the case of metals exhibiting a negative correlation with mass it is expected that these metals are mainly accumulated via adsorption of dissolved ions, with uptake proportional to the number o surface ligands (Phillips, 1994;1995). Non-essential, particle-reactive trac metals like lead have an accumulation pattern directly from dissolved phase while essential elements like copper and zinc are more likely to b accumulated from food. Sediment/detritus feeders are exposed to metal both in solution and through ingestion of metal-enriched particulate materia (Louma,1983).

In tissue phase, highest negative correlation was exhibited by Cu and Zn(r = -0.904 and –0.972 respectively)almost near to 1, which indicates the fact that accumulation and turnover of the metal is taking place at a rate that is proportional to growth, implying a connection with metabolism. Interpretation of concentration ranges for the essential metals (eg:- Cu and Zn) can be complicated by regulation, coupled in some cases with the presence of inherently high tissue burdens. Lattice incorporation of metals like Cu, Zn etc is totally unexpected in view of the incompatibility of their effective ionic radii identical to that of Ca^{2-} If metal assimilation is most rapid in small individuals, negatively sloped correlations would, atypically, be observed when otherwise stabilized populations are exposed to short-term pollution events (Langston and Spence, 1995). Non –essential elements like Cr, Ni, Pb etc.,showed a similar trend as that of essential elements like Zn and Cu, by exhibiting comparatively significant negative correlations (r = - 0.866, -0.837 and –0.802 respectively). Though the correlation coefficients for other metals were not so as high as in the case of above mentioned metals, Fe and Cd exhibited a similar tend of accumulation, so also Co and Mn, as depicted in their correlation coefficients.

There is a chance of submarine precipitation of carbonate in the porous inner corallum of living corals presumably by inorganic means (Hubbard, 1971). Therefore, these mechanisms tend to increase the trace metal abundances in skeletons of corals after its deposition by living coral. There is every possibility that, these mechanisms would operate more effectively in massive corals.

Correlations between flesh density and partition coefficients.

Correlation between flesh density and partition coefficient are given in Fig.3.20 to Fig. 22.

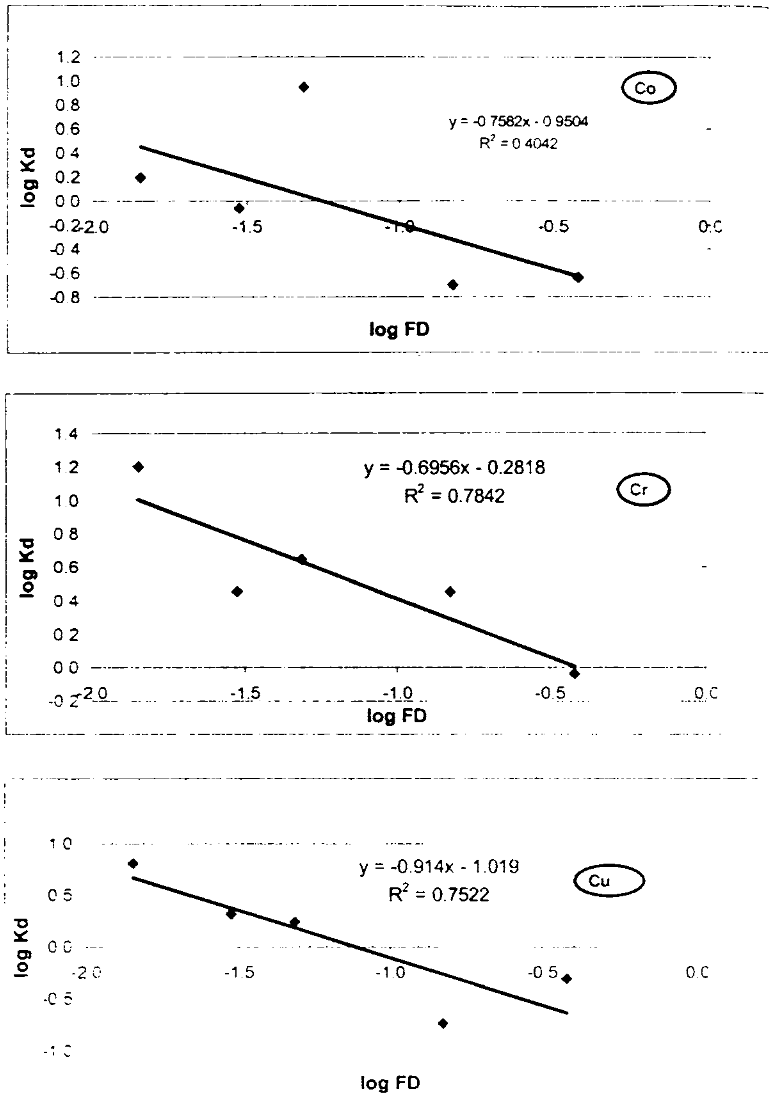

Fig.3.20. Correlations between the Partition coefficient (K_D) and Flesh Density (FD)

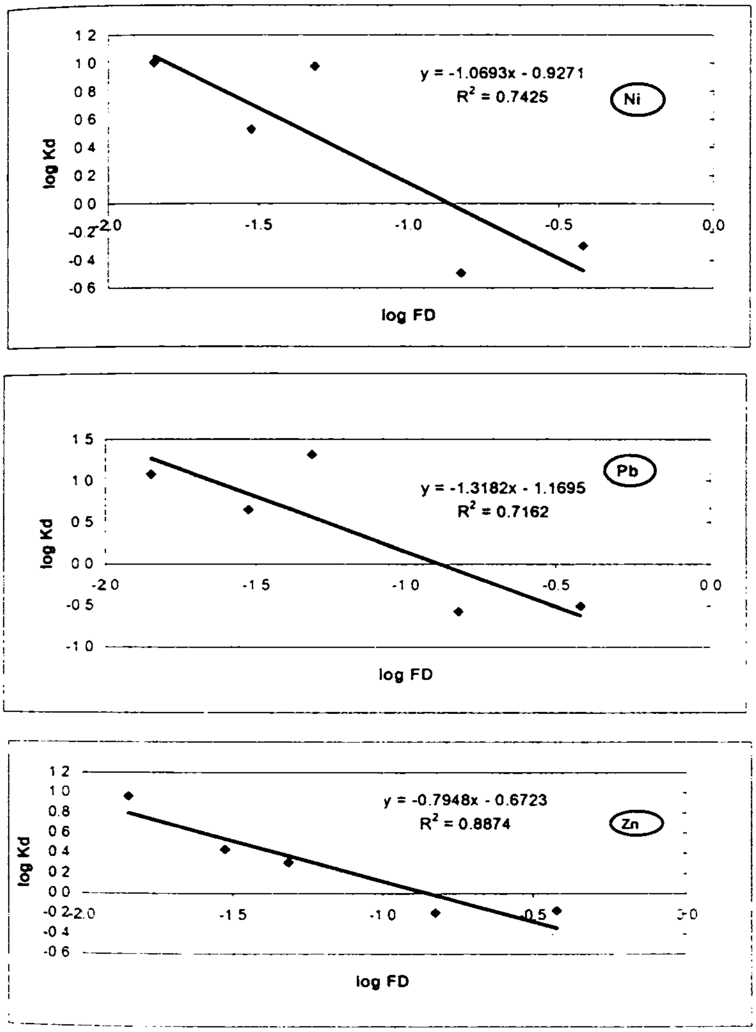

Fig. 3.21. Correlations between the Partition coefficient (K_D) and Flesh Density (FD)

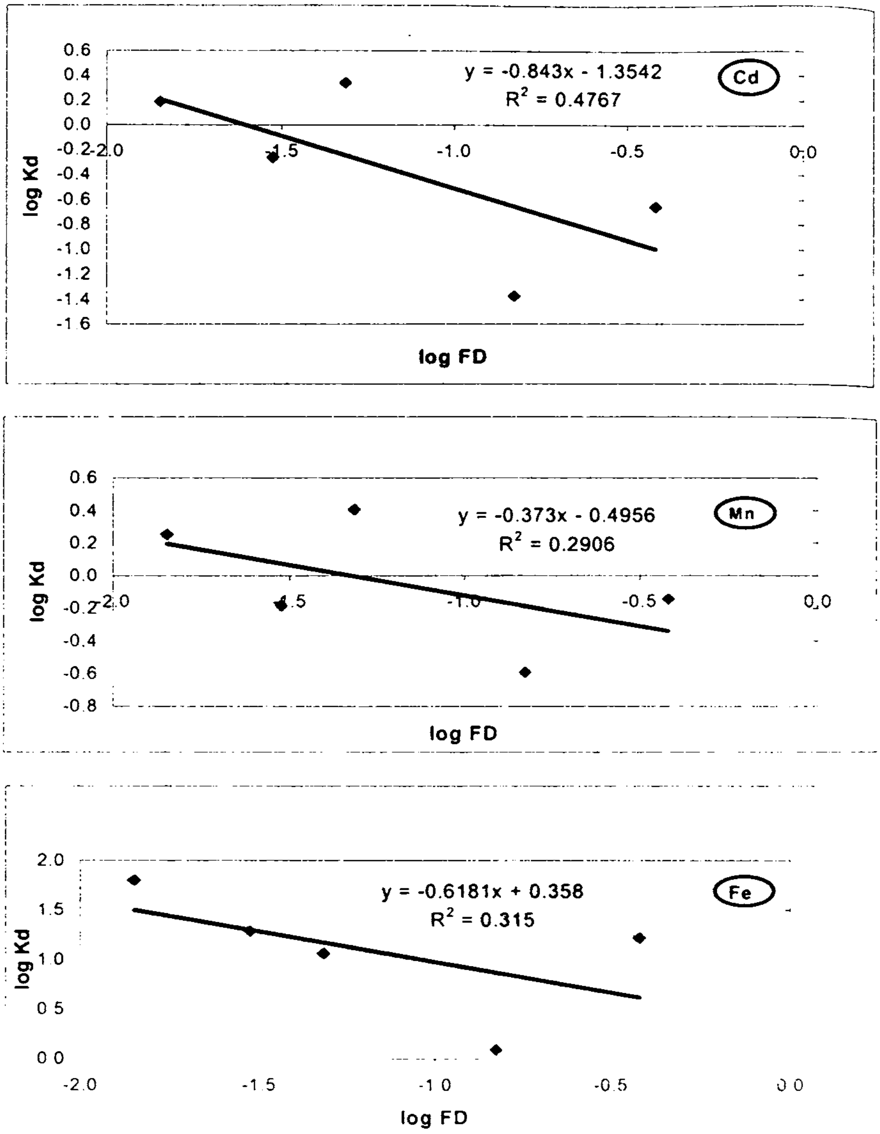

Fig.3.22. Correlations between the Partition coefficients (K_D) and Flesh Density (FD)

In an attempt to correlate flux density with partition coefficient, the following results were obtained. Flux density (F_D) is defined as the ratio of tissue weight to skeleton weight of a particular species.

$$\text{Flesh Density } (F_D) = \frac{\text{Weight of tissue}}{\text{Weight of skeleton}}$$

Partition coefficient K_D, is defined as the ratio of concentration of metal in the tissue to that in the skeleton.

$$\text{Partition coefficient } (K_D) = \frac{\text{Metal concentration in tissue}}{\text{Metal concentration in skeleton}}$$

The F_D, showed a wide variations among the skeleton species, and no correlation was found in the partitioning of tissue and skeleton phase in all the species.

On plotting log F_D against log K_D, all the nine metals exhibited negative correlations and the significance of their correlation coefficients are in the order, Zn>Cr>Cu>Ni>Pb>Cd>Cu>Fe>Mn

Here also, a clear distinction cannot be seen in the behaviour of biologically essential and non-essential elements. The correlation coefficients of Cr, Ni and Pb were comparable to that of Cu and Zn (i.e., biologically essential ones). Whether it is an essential or non-essential element, with increase in tissue weight, the preference of metals towards the tissue phase is found to be decreasing, indicating a regulation in tissue metal burden beyond a certain limit. If the renewal of new tissue is taking place at a faster rate than metal incorporation, it can effectively dilute metal concentration to a considerable extent. The rate of growth of an invertebrate may be so high that growth "dilutes' the metal content ,itself increasing with time, preventing any increase in metal concentration (Rainbow, 199 Langston and Bebianno, 1998; Mohapatra and Rengarajan, 2000).The depositional behaviour of tissue bound metals is related to metabolism and growth effect of the animals, whereas the skeletal accumulation is more less governed by deposition of metals on the skeletal part due to anthropogenic input or it can also be due to competitive interactions between metal ions having radii similar to Ca^{2+} to get substituted for it in the calcite or aragonite lattice of the coral skeleton.

Correlation between partition coefficients of different metals

Correlations between partition coefficients of different metals are given in Table 3.4. Considering the correlation between partition coefficients for different metals, Cu was found to be exhibiting a significant positive correlation with Zn (r = 0.979) which is in agreement with the fact that these two metals are active ingredients of many of the enzymes involved in metabolic functions and both are considered as essential elements. Copper also exhibits, a positive correlation, though not high (r = 0.629) with Cr, this indicates a similar pattern of enrichment for a biologically essentially element (Cu) and a non-essential element (Cr). Except with iron, chromium exhibited significant positive correlations with all the metals, the decreasing order of correlations with different metals is as follows,

Ni>Cd>Mn>Pb>Co>Zn>Cu.

Cr exhibited a pattern of accumulation similar to that of other non-essential elements like Ni, Cd, Pb and also with that of essential elements like Zn, Mn, Co, Cu etc. Co also displayed very significant positive correlations with Ni, Pb, Mn and Cd in which r-value is close to 0.99 in all the cases. Concerning the behaviour of Ni, it is also exhibited coefficients of correlation close to 0.99 with Pb, Mn and Cd.

Considering the correlation of Pb with other metals, it displayed coefficient of correlation close to 0.99 with Mn and also with Cd. In general,zinc,cadmium,copper and iron are concentrated in the soft organs of teleosts such as liver,kidney,spleen,heart,gonads whereas lead and manganese are concentrated in body organs such as gill, backbone and tail. The turnover of lead in the mucus covered tissues such as gills and intestine is a result of lead complexation with mucus. Mn exhibited a significant positive correlation with Cd (0.999).

Among the 9 metals, the accumulation pattern of iron was entirely different from that of other metals in the fact that it displayed almost insignificant correlations with other metals. This means that in all the species, mechanisms of iron incorporation is quite independent of the behaviour of other trace metals.

TRACE METALS IN SEAWEEDS AND SEAGRASS.

Fig. 3.23 shows trace metal distribution in seaweeds and sea grass.

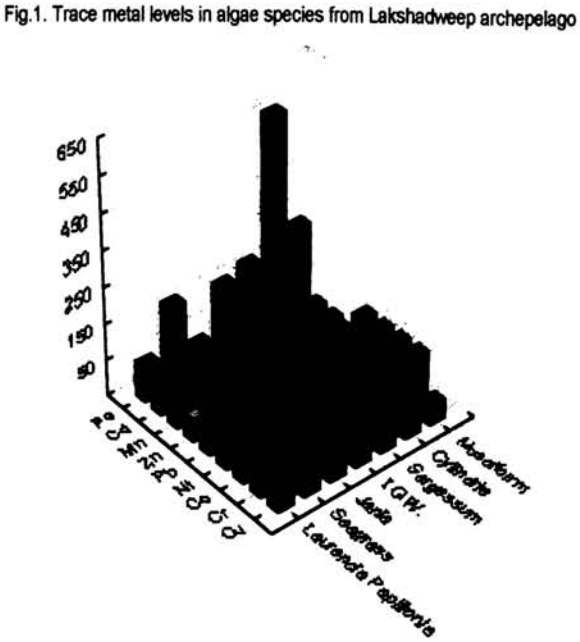

Fig. 3.23.Trace metals levels in seaweeds and seagrass

The plant life in the sea is extremely rich and some exploitation of these resources has taken place over hundreds of years. Seaweeds belong to a rather ill defined assemblage of plants known as the algae. The term "seaweed" itself does not have any taxonomic value, but is rather a popular term used to describe the common large attached (benthic) marine algae found in the groups chlorophyceae, rhodophyceae and phaeophyceae or green, red and brown algae respectively. The algae differ from the higher plants in that they do not possess true roots, stems or leaves.

In the primary classification, the algae are defined into 15 classes, excluding the Cyanophyceae (blue-green algae) which are true prokaryotes.

Of these 15 classes, three are represented by macroscopic forms, present in sufficient quantities in nature to have direct commercial importance. These are the chlorophyceae, rhodophyceae and phaeophyceae. The other classes are principally planktonic (unicellular or colonial), and with the exception of the 'food chain groups', the diatoms (Bacillariophyceae) haptophytes (thaptophyceae) dinflagellates (dinophyceae) and planktonic chlorophyceae have no commercial importance.

Whilst the impacts resulting from the discharge of anthropogenic wastes into marine habitats are often assessed by the changes that occur on the receiving environment, i.e., biomonitoring studies, such studies provide no information on casual associations between biota and the pollutant(s) induced stress (Burridge and Bidwell, 2002).

In attempting to elucidate or model the mechanisms of impacts identified in biomonitoring studies, investigators must inevitably select to identify species specific responses which may base led to population and community impacts (Rainbow, 1993; Phillips, 1995).

Phillips (1990) has associated the use of macro algae as indicator organism for depicting the metal levels in a given milieu. Several investigators subsequently has shown that use of marine algae as in indicator of heavy metal levels gives at least a qualitative picture of heavy metal contamination in the area of study (Bryan, 1969; Preston et al., 1972; Fuge and James, 1974; Morris and Bale, 1974; Foster, 1976; Melhuus et al., 1978; Shiber and Washburn, 1978; Munda, 1978; Sivalingam, 198 Phillips, 1995).

Trace element concentrations in seaweeds vary according to the species (Black and Mitchell, 1952) and may be considerably higher than concentrations in the surrounding sea water (Black and Mitchell, 1952; Bryan, 1969). The sea weed's response to environmental trace element concentration led Preston et al. (1972) to exploit them as indicators of pollution in coastal waters around Britain. Butterworth et al. (1972) and Nickless et al. (1972) used fucoid sea weeds to demonstrate industrial heavy metal pollution of Bristol Channel waters. Published information indicates that brown sea weeds are unable to regulate trace element uptake. Concentrations in the algae depend upon absolute and relative concentrations in the surrounding sea water (Young and Langille, 1958; Fuge and James, 1973). Species belonging to class Rhodophyta (red algae) and Phaeophyta(brown algae) have been selected for study.

From rhodophyceae the following species were selected.

1. Laurencia papillosa (Forssk) Gravel.
2. Jania adhaerens Lamour – a coralline alga.
3. Gracilaria cylindrical.
4. Gracilaria crassa Harv.
5. Hypnea musciformis.

Sargassum tenerimum has been selected fromPhaeophyceae.

The seagrass species selected was Thalassia hemprichii(Ehrenberg)Aschers belonging to family Hydrocharitaceae.

Tracing the variations in trace metal concentrations , all the species showed a greater affinity towards the essential elements , i.e. Fe, Mn, Zn and Cu.Discussing the enrichment pattern of this metals among the species, Gracilaria cylindrica, Gracilaria crassa, Hypnea musciformis and Jania sp.(all belonging to Rhodophyceae) showed a similar pattern .Among the members of Rhodophyceae , the behaviour of Laurencia papillosa was different in the sense that it displayed higher affinity for zinc than for manganese. Discussing about Sargassum sp. cadmium and nickel displayed much higher concentration than the essential elements copper and cobalt. The highest concentration of cadmium displayed by Sargassum sp. indicates the usefulness of this species as an indicator towards metal pollution. One of the salient features observed was that the concentration of lead was below the detection limit in all the species irrespective of their classification. Chromium was also detected in a single species namely, Gracilaria cylindrica. In Hypnea musciformis and in Gracilaria crassa nickel and lead was below the limit of detection. In the case of cobalt. concentrations were displayed by the two Gracilaria species- G. crassa and G. cylindrica- and Sargassum sp. Brown seaweeds are being used in the coastal environment as metal pollution indicators (Phillips,1990).

Generalizing the behaviour of trace metal accumulation by different algal species, it can be seen that a clear distinction between the biologically active or the so called 'essential elements' and the biologically inactive elements or non essential elements. The distribution pattern of Fe. Mn and Zn is exactly the same in all the selected species. which showed first preference for Fe, followed by Mn and then Zn. The next preference was for

Cu in all the species except in Sargassum. Seaweeds from other tropica areas exhibit a similar trend (Sivalingam, 1978; Rao Kesava and Indusekhar 1986; Ganesan et al., 1991). After Fe, seaweeds concentrated Mn confirming the view of Zingde et al. (1976) who reported that seaweeds are better representatives of manganese in seawater than other organisms. Algae accumulate sediment borne metals by scavenging the available resources from surface sediments (Luoma et al., 1982). The high Fe concentration encountered in all the sea weeds as compared to the other trace metals e.g Mn, Zn and Cu, is probably due to cumulative effects of several factors: the established need of iron for normal growth of marine plants (Goldberg 1952) ability of most algal species to biomagnifying iron from the surrounding environment and contamination from industrial and other operations (Eisler, 1981). Seaweeds accumulate certain metals more than their body requirement (Eisler, 1981; Rao Kesava and Indusekhar, 1989) the reason for such accumulation is unknown. It is possible that major part of the trace metal enter complexation with algal polysaccharides in cell walls and small amount is (actual requirement for biochemical budget) stored in vacuoles, granules and inter and intra cellular fluids (Weissner, 1962: Okelly, 1974: Manely and North ,1981). Liberation of free ions which are toxic, from such complexed form may not be possible during the life time of the seaweed (Rao Kesava and Indusekhar, 1989).

Algae in general, accumulates Cu and Zn readily from seawater (Ho. 1988). Mn. Fe. Zn and Cu are essential micronutrients which may limit algal growth (Lobban et al., 1985). It seems that tropical seaweeds tend to accumulate more Fe than Mn, Zn and Cu. In temperate regions, uptake of

Zn and other metals is less because of reduction of photosynthesis due to short day length and low light intensity (Bryan, 1969). Cu and Zn concentrations of the seaweeds analyzed in the present study are less than maximum permissible limits prescribed for seafood for human consumption (10 ppm, 50 ppm respectively) in India (FAO, 1983).

Anyone who spends time in and around tropical marine waters cannot help but notice the vast meadows of underwater plants that typically occupy much of the shoal area. Viewed from above the water, the vegetated patterns of green reflect the plant community's sweeping systematic structure. While perhaps initially drawn by the beauty of these vegetated environments, it does not take an expert's eye to see that these are also important habitats, which nourish, protect, and congregate their abundant tropical animal resources (Kemp, 2000). Seagrasses are becoming widely used as in situ indicators of the relative health and condition of subtropical and tropical estuarine ecosystems.

Seagrasses are a vital component of marine ecosystems and are present in most shallow coastal waters throughout the world (Kurz et al., 2000). Monitoring seagrasses (including all forms of submerged aquatic vegetation (SAV) is rapidly becoming one of the foremost methods to determine the overall health and condition of the aquatic environment (Dennison et al., 1993; Stevenson et al., 1993). Seagrasses have shown particular promise on detecting specific factors that may influence both short and long term changes to near shore aquatic ecosystem (Bortone and Turpin, 2000). Concerning the behaviour of 9 metals studied in the selected seagrass species, three metals, namely chromium, cobalt and lead were below the limit of detection. Among the other metals, iron exhibited height concentration (173 mg kg $^{-1}$), followed by manganese (26 mg kg $^{-1}$).

Various metals exhibited the following decreasing order concentrations, Fe>Mn>Cu>Zn>Cd>Ni

The levels of biologically active or essential elements like Fe, Mn Cu and Zn etc. were higher than level of biologically inactive or non essential elements like Cd, Ni, Cr, Co and Pb in which the last three metals were below the detection limit. Heavy metals are incorporated into seagrass leaves and vascular tissue from either the water column or the sediment (Lyngby et al., 1982; Ward, 1987). Mechanisms of accumulation and the contribution of seagrasses to heavy metal cycling have been documented by many studies (Lyngby et al., 1982; Ward et al., 1986; Schlacher-Hoenlinger and Schlacher, 1998), but less is known about the physiological effects of heavy metal accumulation (Macinnis Ng and Peter, 2002). As the major anthropogenic contaminants of estuaries, heavy metals are of considerable concern to coastal resources managers (Kirkman and Kirkman, 2000). Heavy metal contamination comes from urban run-off, industrial effluents, mining operations, atmospheric and agricultural activity (Batley, 1996; Haynes and Johnson, 2000). Heavy metal uptake in seagrasses is mostly controlled by exposure concentration (Fabris et al., 1982; Malea et al., 1995), and follows a passive surface area dependant process (Ward, 1989).

Metals will be concentrated by seagrasses when the contaminant is released steadily, but when a pulse event occurs, there is a period of rapid uptake through the leaves, after which heavy metals are largely removed by washing from surrounding waters (Schroeder and Thorhaug, 1980). Metals like Zn, Cd, Hg, Pb and Cu interfere with pigment biosynthesis of seagrasses thereby reducing the chlorophyll content (Clijsters and van Assche, 1985; Prasad and Strzalka, 1999). Lower concentrations of copper and zinc are capable of imparting on the photosynthetic activity of seagrass even if the seagrasses are only exposed to the metal for a short period (Macinnis Ng and Peter, 2002).

Statistical approach

In the case of algal species significant difference was observed between species *Laurencia papillosa* and other species,i.e. sea grass ($t = 2.31$), Sargassum ($t = 2.27$) Gracilaria ($t = 2.94$) and Hypnea musciformis ($t = 2.62$). Non-significant differences were more than that of significant differences indicating that most of the species accumulate almost the same level of trace metals except the few cases mentioned above. On comparing between trace metals the accumulation quantity was highly significant in all cases ($t>3.05$) except that between nickel and cadmium ($t<2.18$, $p>0.05$) as indicated in the trellis diagram for algal species and for trace metals (Fig. 3.24 and Fig. 3.25).

		Cu	Cr	Co	Ni	Zn	Mn	Cd	Fe
Copper	Cu	–	●	●	●	●	●	●	●
Cromium	Cr	1065	–	◑	●	●	●	●	●
Cobalt	Co	948	286	–	◑	●	●	●	●
Nickel	Ni	107	445	265	–	●	●	⊕	●
Zinc	Zn	632	9·26	836	849	–	●	●	●
Manganese	Mn	148	1758	17·34	[illegible]	[illegible]	–	●	●
Cadmium	Cd	601	474	325	[illegible]	625	662	–	●
Iron	Fe	[illegible]	163	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	–

⊕ t< 2·8 , ◑ 2 8 ≤ t < 3 05, ● t ≥ 3 05

Trellis diagram for students t statistic to test the significance of the difference between trace meta. concentrations in algal species.

Fig.3.24

		Lp	Sg	Je	IGW	Sar	Cy	Mus
Laurencia papillonia	Lp	–	◑	⊕	⊕	◑	◑	◑
Seagrass	Sg	231	–	⊕	⊕	⊕	⊕	⊕
Jania	Je	061	214	–	⊕	⊕	◑	◑
IGW	IGW	210	052	191	–	⊕	◑	⊕
Sargassum	Sar	227	004	210	[illegible]	–	⊕	⊕
Cylindria	Cy	294	212	268	226	[illegible]	–	⊕
Musciform	Mus	262	602	248	[illegible]	[illegible]	[illegible]	–

⊕ t < 2·15 , ◑ 2 15 ≤ t < 2 98 , ● t ≥ 2 98

Trellis diagram for students t statistic to test the significance of the difference between alga species withrespect to concentration of trace metals

Fig. 3.25

SCLEROTHERMOMETRY

In 1979, Smith coined the term "sclerothemometry" to indicate the usefulness of Sr:Ca ratios of coral skeletons for the measurement of temperature or in short it is the thermometry based on the use of corals. An inverse relationship was found between Sr/Ca ratio and water temperature (Houck et al., 1977; Schneider and Smith, 1982; Shen and Boyle, 1988; Linn et al., 1990; Naqvi, 1991).

Variations in the Sr/Ca ratio of coral skeletons of reef building corals have the potential to be used as a recording thermometer, when combined with the chronological record preserved in coral density band (Naqvi, 1991). Incorporation of calcium into the coral mainly takes place organically but it goes into skeleton inorganically as well. The main site for strontium into the corals is in the aragonite lattice. It substitutes for calcium (Wolf et al., 1967). Magnesium occurs mainly in aragonite lattice but 25 % of it found in adsorbed sites and inorganic compounds (Amiel et al. 1973). XRD diagrams of the skeletons of the coral species are given in Fig. 3.26 which requires more investigations to elucidate conclusive statements.

Since carbonate fraction is a product of the environment, the variations observed in them will reflect the precipitation conditions prevailing in the lagoon (Naqvi, 1991). In shallow marine environments, precipitation of $CaCO_3$ can take place both organically and inorganically, in which aragonite precipitation is influenced by chemical processes (i.e. temperature, pH, CO_2)

Strontium is a major component of seawater present in concent 7.9 mg kg^{-1} and is the major constituent of Ca and Mg carbona positive correlation was reported between Sr and Ca in various sedime environments (Veeh and Turekian 1968; Goldberg, 1957; Paropkari Naqvi, 1991). Both strontium and calcium occur in similar valence sta they passes similar ionic radii (1.13 A^0 and 0.99 A^0 respectively, seawater temperature prevailing during the coral growth can be calcu using the equation (Smith, 1979),

$$\boxed{\mathbf{Sr/Ca \times 10^{-3} = 10.94 - 0.070\ T^{0}C}}$$

The resolution of this Sr thermometry is 1.5 ± ^{0}C.

The incorporation of Ca and Sr in the coral skeleton depend only seawater temperature, but also on various factors like light inte nutrient supply etc., This study is only a preliminary one i.e. an attemp been made to trace out the environmental record of temperature presen these coral skeletons during their growth. To assess the usefulness thermometry in recording seawater temperature, one must also take account the growth rate effect (Schneider and Smith, 1982). So we nee extended study to make it useful a recorder of environmental variations

Species Name	Sr/Ca x 10^{-3}	Calculated Temperature
Porites andrewsa	8.98	28.0^{0} C
Acropora formosa	8.86	29.7^{0} C

Environmental records preserved in the skeleton of massive *Porites* colonies have been retrieved previously using variations in chemical composition (Schneider and Smith 1982; Isdale, 1984; Shen et al., 1987; Lea et al. 1989; Linn et al., 1990) and isotopic ratio (Druffel, 1981; 1982; Druffel and Suess, 1983). These studies indicate that anthropogenic influences can override the natural rhythmic periodicity of climatic events (Rasmussen et al., 1992). Interruption to the natural, chemical and morphological structure of the skeleton chemistry, as well as changes to the internal and external architecture of the coral skeleton.

Aragonite forming in seawater, either biogenically or by inorganic precipitation. incorporates amounts of trace metals into its crystal structure. Because of their concentration in seawater, and their compatibility with the crystal structure of the aragonite, these include strontium, lead and barium. The extent of the uptake of the various elements by inorganic aragonite will be a function of trace element activity relative to calcium in the environment from which the skeleton is deposited, the temperature of the water in which the animal lives, a 'species" effect perhaps related to the microenvironment of the living organism, its feeding habits, and mode of skeleton construction and the salinity of the water column (Houck et al., 1977; Smith et al., 1979;

Shen et al., 1987; Linn et al., 1990; Rasmussen, et al., 1992; Esslem 1999); so that all fluctuations in the seawater column affecting the acti of the competing chemical species should be reflected in the chem composition of the aragonite skeleton.

Various trace elements (e.g., strontium, magnesium, sod potassium, iron, barium, cadmium and lead) incorporated into bioge carbonates at the time of deposition have been used as proxy conditions number of paleo-environmental parameters including oceanic temperat salinity, nutrient concentration, and rainfall timing and intensity (Druff 1981; 1982; Isdale, 1984; Druffel and Suess, 1983; Linn et al., 19 Bastidas and Garcia, 1997; Esslemont et al., 2000).

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Chapter 4

CHEMO-VARIABILITY IN ABIOTIC COMPONENTS – NUTRIENTS

INTRODUCTION

A nutrient element is defined as one that is functionally involved in the processes of living organisms (Parsons, 1975). Thus, anything besides water and CO_2 that is required by plants in the synthesis of organic matter or skeletal materials is regarded as a nutrient. Although nitrogen is usually considered to be the nutrient limiting primary production in marine and coastal systems (D'Elia et al., 1981; Thingstad et al., 1998), the evidence for this is meet as strong as the evidence that freshwater tends to be P-limited (Claudia et al., 2002).

Since the industrial revolution, the N and P contaminations of natural systems have been highly correlated with human activities - industrial, agricultural and sewage from population contributed to the enrichment in natural waters (La Jeunesse et al., 2002). Changes in both absolute and relative concentrations of nitrogen and phosphorous are good indicators of the intensity of eutrophication process and of disturbances in the cycling of these elements (Nixon et al., 1986; Lucena et al., 2002; [illegible], 2002) The excessive inputs of nutrients such as nitrogen and phosphorus to water bodies causes eutrophication. These accumulation to increase algal growth and disturb the natural balance that exists in water bodies (Diaz et al., 2001).

Human perturbations of the global nitrogen and phosphorus cy are widespread and dramatic. Through the production of fertilizers, hu have doubled the rate at which nitrogen enters the biogeochemical cycle land. Increasing transport of N and P in rivers has shifted many estua and coastal ecosystems to a condition of deficiency (Justic et al., 1995). these changes indicate the effect of a single species – the human upsetting a steady state in global nutrient cycling

Nutrients regulate biological processes by limiting or enhanc organic production in almost all types of aquatic environments (Redfield al., 1963). The study of nutrients in the dissolved and sedimented for would help in understanding the potential availability of life suppor elements in any particular region of the aquatic system (Klump and Marte 1983). Quantitative and qualitative studies on nutrients are important understanding the basic processes governing the distribution a biogeochemical cycling of nutrients (Nair, 1990; Khelifi et al., 2002).

From molecules to whole ecosystems, the movement of N, P and are strongly linked in biogeochemistry (Reiners, 1986). For both N and P small biogeochemical cycle with relatively rapid turnover is coupled t large global pool with relatively slow turnover (Moutin and Raimba 2002). For P, the large pool is found in unweathered rock and s (Gutschick, 1981). In general, the transformations of biologically essen nutrients depend on internal rates of organic production and subseque decomposition (Bloesch et al., 1977). Experimental evidences also indicate that non-biological reactions can also contribute to the control of nutrient distribution (Pomeroy et al., 1965; Liss and Spencer, 1970; Sholkovitz, 1976; Morris et al., 1981).

Nitrogen enters rivers estuaries, and coastal marine ecosystems from natural, and in many cases, anthropogenic sources throughout their water shed and air sheds (Seitzinger et al., 2002). Because nitrogen is the primary nutrient limiting resources for plant, algal and microbial production in many marine and some freshwater environments, increases in nitrogen inputs can markedly alter those ecosystems (Ryther and Dustan, 1971; Vitousek and Howarth, 1991; Cole et al.,1993; Caraco and Cole, 2001)

The most abundant form of nitrogen at the surface of the earth i.e. N_2 is the least reactive species. Nitrogen fixing species use most abundant in nitrogen-poor habitats, where their activity increases the availability of nitrogen for the biosphere. At the same time, denitrifying bacteria return N_2 to the atmosphere, balancing the overall stock of nitrogen available for life on earth. A large number of biochemical transformations of nitrogen are possible, since nitrogen is found at valence states ranging from –3 (in NH_3) to +5 (in NO_3^-). A variety of microbes capitalize on the potential for transformations of N among these states and use the energy released by the changes in redox potential to maintain these life processes (Rosswall, 1982; Anu Gopinath et.al., 2002). In living tissues, nitrogen is an integral part of enzymes, which mediate the biochemical reactions in which carbon is reduced (i.e. photosynthesis) or oxidized (respiration). The world's oceans receive about 36 x 10^{12} g N yr^{-1} in dissolved forms in rivers, about 15 x 10^{12}

g N yr^{-1} via biological N-fixation, and about 30 x 10^{12} g N precipitation (Duce et al., 1991).

The major processes by which nitrogen is brought to the se atmospheric precipitation, volcanic activity and continental dr whereas. the process involved for the nitrogen removal are loss marine sediments, migration of marine animals and loss of nitrogen atmosphere (Martin, 1970). In addition to the regeneration and diss processes involved in the nutrient cycles of phosphorus and nitrification, denitrification and fixation processes are also involved nitrogen cycle. The biogeochemical cycling of nitrogen is of a com nature because of varieties for chemical forms (species) in which nitrogen is available for biological unitization. These inputs comprehensively discussed in framework of the nitrogen cycle by V and Ryther (1960). All the species have significant role in the environment; nitrate and nitrite accounts for about 63 % of the combined nitrogen (Martin, 1970; Ryther and Dustan. 1971). Nitr formed as an intermediate in the oxidation of ammonia to nitrate or reduction of nitrate. The factors, which influence the availability of forms of nitrogen for biotic uptake is most important which in-turn de upon the concentration of the particular species of nitrogen. The n usually present in lower concentrations in the sea than the other fo combined inorganic nitrogen.

Nitrate is the most abundant and thermodynamically stable combined inorganic nitrogen in well oxygenated seawater Further, the final oxidation product of nitrogen compounds in seawater. In se

Nitrate is considered to be the micro-nutrient controlling primary production in the euphotic surface layers; concentration in these layers is governed by the advective transport of nitrate into the surface layer, the microbial oxidation of ammonia and the uptake by primary producers (Grasshoff et al., 1999). Denitrification is also observed in ocean sediments. Christensen et al. (1987a) estimate that over 50 x 10^{12} g N yr^{-1} may be lost from the sea by sedimentary denitrification in coastal regions. Phosphorous appears to be the limiting nutrient most often found in wetlands, estuaries and coastal areas (Bostrom, 1984; Harrison et.al.,1990; Pardo et al., 1998; Kleeberg, 2002; Pangatti and Maine, 2002; Qui et al., 2002).The global cycle of P is unique among the cycles of the major biogeochemical elements in having no significant gaseous component. The redox potential of most soils is too high to allow for the production of phosphine gas (PH_3) (Bartlett, 1986), except under very specialized, local conditions (e.g., Devai et al., 1988; Devai and De Laune, 1995). Unlike transfers in the global nitrogen cycle, the major source of reactive P in the global P cycle is mostly provided by microbial reactions. Nearly all the phosphorus in terrestrial ecosystem is originally derived from the weathering of calcium phosphate minerals, especially apatite ($Ca_5(PO_4)_3OH$). The main flux of P in the global cycle is carried by rivers, which transport about 21 x 10^{12} g P yr^{-1} to the sea (Meybeck, 1982).

Phosphorus is deposited in ocean sediments, which contain the largest phosphorus pool near the surface of the earth. About 2 x 10^{12} g P yr^{-1} is added to sediments of the open ocean – roughly equivalent to the delivery of reactive P to the oceans by rivers (Howarth et al., 1995). During sediment diagenesis, organic- and Fe- bound P are converted to phosphorite (authigenic apatite) and other minerals, which may ultimately dominate th P storage in sediments (Ruttenberg, 1993a; Filippelli and Delancy, 1996; Rasmussen, 1996). Phosphorite is formed when PO_4^{3-} produced from t mineralization of organic P combines with Ca and F to form fluroap (Ruttenberg and Berner, 1993). Only about 10 % of this flux is poten available to marine biota; the remainder is strongly bound to soil par that are rapidly sedimented on the continental shelf.

Relative to N, the global cycle of P turns very slowly. The [illegible] residence time for reactive P in the oceans, relative to the input in rive the loss to sediments, is about 25,000 years (Ruttenberg, 1993b; Filip and Delancy, 1996). Thus, each atom of P that enters the sea may com 50 cycles between the surface and the deep ocean before it is los sediments. All forms of buried phosphorus complete a [illegible] biogeochemical cycle when geologic process lift sedimentary rocks [illegible] sea level and weathering begins again.

The rate of transfer of phosphorus form sediment to water and [illegible] is controlled by numerous physical, biological and chemical factors: the [illegible] depends marginally on the concentration gradients between the two pha (Golterman, 1995). The surface sediments act as a "physical catalys [illegible] releasing or trapping phosphate depending on the phosphate concentr in overlying waters (Nair, 1990; Bonetto et al.,1994; Kleeberg, 2002)

Ever since Charles Darwin, the enigma of the existence of a [illegible] on coral reefs surrounded by surface oligotrophic oceanic waters deple nutrients became a point of heated discussions and investigations (Joha et.al..1984; Wiebe, 1988; Atkinson . 1992; Capone et al..1992; Atkins al., 1995; Szmant and Forrester, 1996; Miyajima et al., 2001; Suzumura et al., 2002). And, in fact, the photosynthetic primary production of the powerful reef autotrophic associations of plants and symbiotic animals approaches the highest level known for marine and terrestrial ecosystems: 5-[illegible] mg C m^{-2} day^{-1}; and sometimes even more, while the ambient concentrations of inorganic nutrients (NO_3^-, NO_2^-, NH_4^+, PO_4^{3-}) in waters of the surrounding ocean usually happens to be very low. But the very existence of the coral reef ecosystem a priori needs the positive balance of nutrients, while they actually exist and flourish, a positive balance of nutrients in their exchange between the reef and the ocean should be axiomatic (Sorokin, 1993).

The input of nutrients into the coral reef ecosystem, or the debit part of their balance, is provided by several interacting physical and biological mechanisms. The nutrients are brought to the reef with oceanic waters driven up the reef by the wind and by the geotrophic currents (Johannes et al., 1984).The importance of this source of input increases in areas where the surface waters are enriched with nutrients though their elevation from deeper layers in areas of quasi-permanent upwelling and divergences in the equational zone. On a smaller scale phophorites can be found in reef rocks of atolls. On being eroded, they release phosphates, which are driven out with ground waters and thus enrich the water column over the reef with phosphorus. An important role in the mobilization of the nutrients deposited in bottom sediments is their permanent resuspension by means of wave action (Entsch et al., 1982). In some reef areas a significant input of nutrients is produced by accumulation of masses of the floating wind-driven blue-green algae, *Trichodesmium* (Sorokin et al., 1993). The processes above provide a permanent flow of nutrients, both inorganic and orga their forms, from the external sources and from the deposits within a reef ecosystem. The consumption of nutrients from this flow, their rete and regeneration are accomplished by biological mechanisms.

The basic turnover of nutrients within the coral reef ecosys proceeds via their transformations in the food-webs. The processe nutrients turnover going on in the water column starts with the consump of their inorganic salts by the phytoplankton and bacterioplankton the dispersed dissolved nutrients are transferred into the concentra particulated matter, in the biomass of microorganisms, and in part int excreta by micro plankton dissolved, organic nutrients. Its larger por mineralized via respiratory decomposition, by planktonic and ben filterers and by bacteria of bottom sediments (Atkinson, 1987a; Suzum al., 2002).Corals excrete not only inorganic but also a significant amou organic nutrients. Besides the release of organic nutrients, corals also the organic N-P compound (Miyajima et al., 2001).

Coral reefs are unique for tropical environment and are associated with seagrass beds and mangroves with a perfect intera between them. Although, they are oligotrophic in nature, produc organic matter and turnover of nutrients results in high producti biodiversity. Especially the contribution from sediment seems to greater role in recycling and regeneration of organic matter and (Charpy et al., 1990; Harrison et al., 1990; Vinithkumar et al Harrison and Ward, 2001).

A baseline, which is needed to determine the future, if the natural and anthropogenic processes are changing the sedimentary environment of Lakshadweep Archipelago , has been attempted to formulate by assessing the nutrient characteristics of the study area The study focuses on six islands namely. Kavaratti, Kadamath, Agathy, Androth, Kiltan and Minicoy.

The surficial sediments have as important regulatory role in nutrient uptake and regeneration (Hesse, 1973). The fluctuations in the physical and chemical characteristics of surficial sediments will potentially influence the nutrient budget of the zone; this in turn will affect the biological processes.

MATERIALS AND METHODS

The details of methodology adopted are described in Chapter II. Table 4.1 gives the station numbers given to the different sampling sites to each islands.

Table No. 4.1. Station numbers used in Figs. (Chapter IV) are g parenthesis for identifying the respective sampling sites.

Kavaratti	Kiltan	Kadamath	Minicoy	Androth
Core (south)	**Lagoon Profile**	Sea-side Profile	Lagoon Profile	Seaside core
Surface(1)	Centre (11)	Land-soil south (1)	Lagoon (1)	Surface (1)
30 cm (2)	Low water mark (2)	high tide South (2)	Intermediate (2)	0.5m (2)
60 cm (3)	Intermediate (4)	low tide south (3)	Berm (3)	1m (3)
90 cm (4)	Berm (5)	North soil (4)	Land (4)	Land core
120 cm (5)	Land (6)	north high tide (5)	Lagoon Inner (5)	Surface (4)
Land (6)	Seaside Profile	north low tide (6)	NE boundary (6)	Soil 1(5)
Berm (7)	North-side St. 1 (7)	Lagoon - 1 (7)	Mangrove 1(7)	Soil (6)
Intermediate	North-side St. 2 (8)	Lagoon –2 (8)	Mangrove 2 (8)	Core - 15 cm
(8 Lagoon	North-side St. 3 (9)			Core - 30 cm
(9)	North-side St.4 (10)			Core - 50 cm
Core (North)	South-side St. 1 (11)	**Agathy**		Core - 90 cm
Surface (10)	South-side St. 2 (12)	Lagoon Profile		
30 cm (11)	South-side St. 3 (13)			
60cm (12)	South-side at.4 (14)			
90 cm (13)	Core Profile	Lagoon 1 (1)		
120cm (14)	Surface (15)	Lagoon 2 (2)		
	0.5 m (16)	Lagoon 3 (3)		
Ujrapally (15)	1.3 m (14)	Lagoon (4)		
		Intermediate 4(5)		
		Berm (6)		
		Land (7)		
		Land (8)		

RESULTS AND DISCUSSION

The analytical results of the general sedimentary characteristics pH, sedimentary organic carbon and grain size, used as supplementary data for the interpretation of spatial variability of nutrients are given in Fig. 4.1 to 4.3 respectively. The interrelationship between nutrients, org carbon, texture and pH are given in Tables 4.2 a & b and 4.3 a & b.

Forms of nitrogen

The apparent discrepancy between high rates of primary productivity and low nutrient stocks in coral reef ecosystems has stimulated an intense

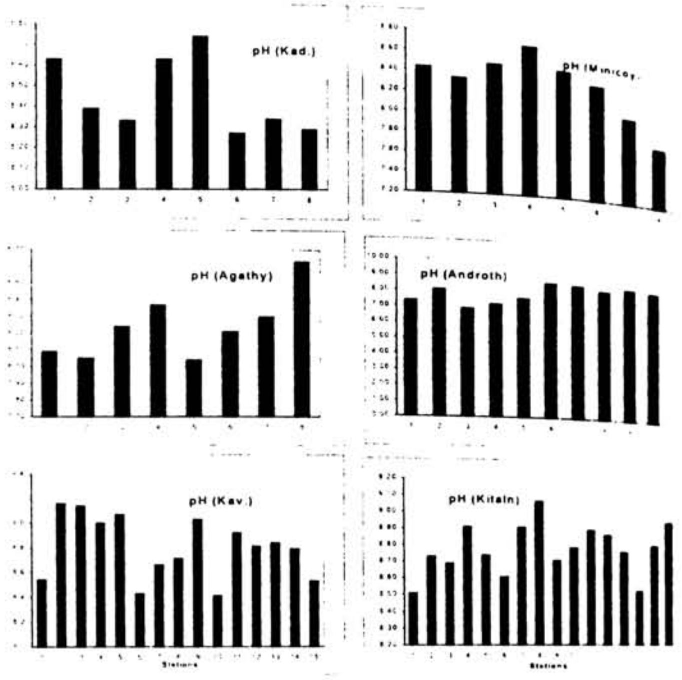

Fig. 4.1. Spatial variability of pH in six islands

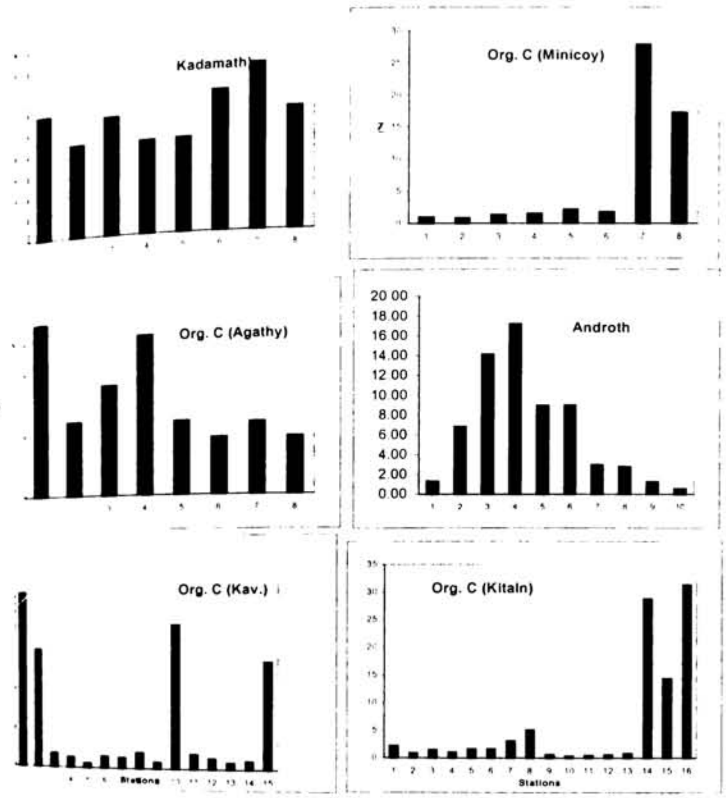

Fig. 4.2. Spatial variability of organic carbon (%) in six islands

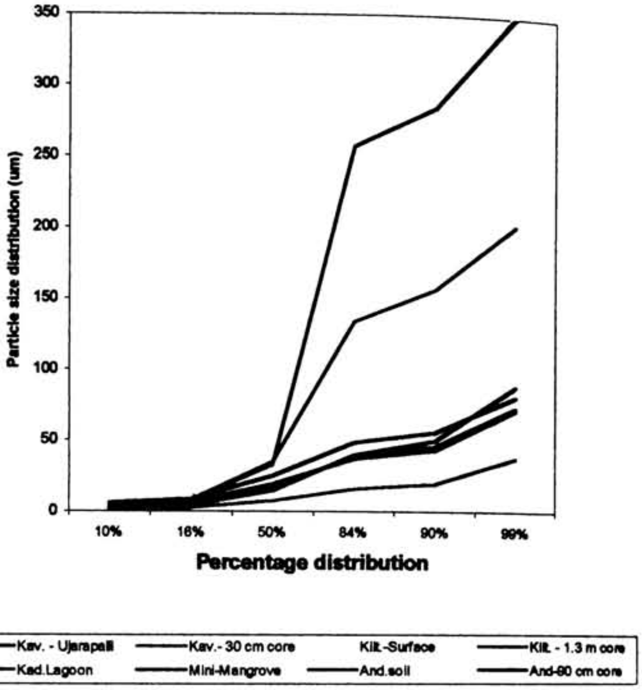

Fig.4.3. Percentage-wise particle size distribution of representative sediment samples taken on particle analyzer (SYMPATEC AAALYSER)

Table 4.2a. Correlations between nutrients, organic carbon and pH.

	pH	Nitrite	Nitrate	Total N	Exch. P	Ca-P	Inorg.	Org+R	Total P	N:P
Kavaratti										
pH	1.000									
Nitrite	-0.382	1.000								
Nitrate	-0.410	0.359	1.000							
Total N	-0.394	0.132	0.632	1.000						
Exch. P	-0.455	-0.102	-0.224	-0.152	1.000					
Ca-P	-0.437	-0.123	-0.243	0.141	0.519	1.000				
Inorg P	-0.506	-0.123	-0.260	-0.061	0.946	0.768	1.000			
Org+Res.P	-0.278	-0.129	-0.177	-0.130	0.911	0.332	0.808	1.000		
Total P	-0.291	-0.130	-0.182	-0.128	0.921	0.354	0.824	1.000	1.000	
N:P	-0.160	0.022	0.899	0.518	-0.343	-0.429	-0.419	-0.242	-0.252	1.000
O Carbon	-0.405	-0.057	-0.235	-0.077	0.770	0.375	0.719	0.607	0.618	-0.362
Kadamath										
pH	1.000									
Nitrite	0.278	1.000								
Nitrate	-0.231	-0.198	1.000							
Total N	-0.233	-0.663	0.784	1.000						
Exch. P	-0.422	-0.064	0.568	0.302	1.000					
Ca-P	0.209	0.350	-0.379	-0.505	0.057	1.000				
Inorg P	-0.077	0.239	0.027	-0.225	0.617	0.821	1.000			
Org+Res.P	-0.288	-0.467	-0.241	-0.157	-0.065	-0.182	-0.180	1.000		
Total P	-0.317	-0.373	-0.230	-0.243	0.173	0.135	0.206	0.925	1.000	
N:P	-0.339	0.392	0.294	0.077	-0.207	-0.352	-0.396	-0.334	-0.484	1.000
O Carbon	-0.555	0.050	0.066	0.046	0.411	0.512	0.638	-0.192	0.055	0.024
Minicoy										
pH	1.000									
Nitrite	-0.835	1.000								
Nitrate	-0.063	0.258	1.000							
Total N	-0.809	0.524	0.038	1.000						
Exch. P	0.443	-0.066	0.336	-0.184	1.000					
Ca-P	0.433	-0.110	0.364	-0.128	0.991	1.000				
Inorg P	0.439	-0.088	0.350	-0.156	0.998	0.998	1.000			
Org+Res.P	-0.373	0.049	0.071	0.798	-0.037	0.042	0.003	1.000		
Total P	0.122	-0.040	0.321	0.360	0.769	0.817	0.795	0.609	1.000	
N:P	-0.348	0.240	0.111	-0.040	-0.538	-0.536	-0.539	-0.448	-0.699	1.000
O Carbon	-0.777	0.490	0.088	0.995	-0.152	-0.089	-0.121	0.816	0.399	-0.066

Table 4.2b. Correlations between nutrients, organic carbon and pH

Agathy	pH	Nitrite	Nitrate	Total !	Exch. I	Ca-P	Inorg.	Org+R	Total I		
pH	1										
Nitrite	0.00058	1									
Nitrate	-0.2611	0.037	1								
Total N	-0.0008	0.451	-0.33	1							
Exch.P	0.30413	0.227	-0.36	0.394	1						
Ca-P	0.15589	-0.44	-0.57	-0.45	0.156	1					
Inorg.P	0.30699	-0.12	-0.6	-0.01	0.786	0.733	1				
Org+Res.P	-0.253	0.143	-0.61	0.745	0.17	0.024	0.132	1			
Total P	-0.1898	0.117	-0.69	0.715	0.3	0.151	0.301	0.985	.		
N:P	-0.1844	0.31	0.807	-0.02	-0.2	-0.57	-0.5	-0.5	-0.56		
Or. Carbon	-0.1641	-0.01	-0.57	0.543	0.524	0.038	0.384	0.459	0.508	[illegible]	
Androth											
pH	1										
Nitrite	-0.6064	1									
Nitrate	-0.8535	0.607	1								
Total N	-0.4743	0.181	0.471	1							
Exch.P	-0.7476	0.429	0.639	0.934	1						
Ca-P	-0.5514	-0.04	0.487	-0.09	0.148	1					
Inorg.P	-0.8397	0.225	0.74	0.487	0.695	0.814	1				
Org+Res.P	0.12791	0.588	-0.22	-0.36	-0.211	-0.39	-0.41	1			
Total P	0.11109	0.598	-0.2	-0.36	-0.198	-0.38	-0.39	1			
N:P	-0.3602	-0.01	0.312	0.967	0.861	-0.04	0.476	-0.41	-0.4		
Or. Carbon	-0.6475	0.449	0.707	-0.2	0.132	0.707	0.591	-0.08	-0.06	[illegible]	
Kiltan											
pH	1										
Nitrite	0.46813	1									
Nitrate	0.1467	0.391	1								
Total N	-0.533	-0.11	0.146	1							
Exch.P	0.07145	-0.25	-0.35	0.029	1						
Ca-P	0.05895	-0.33	-0.4	-0.04	0.041	1					
Inorg.P	0.08472	-0.4	-0.51	-0.02	0.511	0.88	1				
Org+Res.P	-0.4142	-0.02	-0.26	0.3	0.082	0.295	0.293	1			
Total P	-0.4107	-0.03	-0.26	0.298	0.09	0.308	0.308	1	.		
N:P	-0.3681	-0.1	0.165	0.712	-0.26	-0.16	-0.26	-0.25	-0.2		
Or. Carbon	-0.0142	-0.2	-0.5	0.006	0.129	0.907	0.842	0.565	0.57	[illegible]	

Table 4.3a Correlations between nutrients and grain size.

	Very coars Sand >1000 µ	Coarse Sand 1000-500µ	Medium Sand 500-250µm	Fine Sand 250-125µm	Very Fine Sand 125-63µm	Silt + Clay <63 µm
uarts						
	-0.201	-0.295	0.165	0.103	0.008	-0.029
urite	-0.362	-0.442	0.115	0.490	-0.145	-0.228
urate	-0.498	-0.599	-0.081	0.196	0.070	0.233
tal N	0.214	0.243	0.139	-0.155	-0.020	-0.094
Exch P	0.106	-0.032	-0.197	0.071	-0.141	0.072
Ca P	0.204	0.173	0.031	-0.092	-0.069	-0.044
ru P	0.248	0.276	0.179	-0.171	-0.015	-0.128
rganic P	0.247	0.273	0.173	-0.169	-0.017	-0.125
tal P	-0.362	-0.429	0.087	0.570	-0.189	-0.281
N/P ratio	0.020	-0.042	-0.323	-0.479	0.564	0.540
rg C						
umulation						
	-0.671	-0.711	0.520	0.301	0.394	0.397
urite	0.551	0.228	-0.590	-0.230	0.276	0.279
Nitrate	0.705	0.365	-0.567	-0.352	0.055	0.059
tal N	0.669	0.418	-0.417	-0.217	-0.195	-0.202
Exch P	-0.156	-0.342	0.549	0.572	-0.333	-0.339
Ca P	0.260	-0.031	0.194	0.327	-0.374	-0.383
ru P	0.021	0.582	-0.313	0.082	-0.322	-0.322
rganic P	0.121	0.567	-0.236	0.207	-0.464	-0.468
tal P	-0.243	-0.520	-0.275	0.140	0.998	1.000
N/P ratio	0.219	-0.335	0.098	0.624	0.031	0.036
rg C						
gility						
	0.142	0.550	-0.447	-0.337	0.814	-0.569
Nitrite	0.867	0.454	-0.653	-0.854	-0.016	-0.299
Nitrate	0.643	0.627	-0.731	0.041	-0.331	-0.536
tal N	-0.843	-0.790	0.913	0.413	-0.211	0.666
Exch P	-0.711	-0.735	0.808	0.508	0.195	0.649
Ca P	-0.764	-0.779	0.862	0.521	0.151	0.684
ru P	-0.177	0.300	-0.182	0.787	-0.636	-0.375
rganic P	-0.342	0.117	0.015	0.879	-0.584	-0.212
tal P	0.923	0.511	-0.725	-0.799	0.368	-0.340
N/P ratio	-0.206	0.258	-0.142	0.806	-0.406	-0.331
rg C						

Table 4.3b. Correlations between nutrients and grain size

Androth	>1000 µ	1000-500µ	500-250µn	250-125µn	125-63µm	<63 µm
Nitrite	-0.009	0.084	0.085	0.052	0.063	-0.071
Nitrate	-0.086	-0.124	-0.125	-0.112	0.138	0.115
Total N	0.822	0.559	0.555	0.663	-0.631	-0.629
Exch P	0.601	0.288	0.283	0.406	-0.344	-0.368
Ca P	-0.680	-0.773	-0.773	-0.752	0.682	0.765
Inor. P	-0.260	-0.538	-0.541	-0.446	0.419	0.482
org+res P	-0.002	0.260	0.263	0.170	-0.091	-0.207
Total P	-0.007	0.252	0.256	0.163	-0.083	-0.200
N/P ratio	0.759	0.473	0.469	0.584	-0.572	-0.546
Org C	-0.877	-0.791	-0.790	-0.835	0.829	0.821
Nitan						
Nitrite	-0.175	0.072	-0.019	-0.126	0.044	0.169
Nitrate	0.414	0.833	-0.395	-0.376	-0.350	-0.242
Total N	0.217	0.194	-0.183	0.376	0.554	-0.400
Exch P	0.475	-0.129	-0.390	-0.213	-0.145	0.032
Ca P	-0.235	-0.687	-0.480	-0.031	0.280	0.767
Inor. P	0.011	-0.703	-0.637	-0.132	0.190	0.731
org+res P	-0.336	-0.482	-0.057	0.815	0.906	0.028
Total P	-0.335	-0.491	-0.065	0.811	0.906	0.038
N/P ratio	0.131	0.764	0.185	-0.337	-0.325	-0.367
Org C	-0.453	-0.800	-0.412	0.273	0.488	0.789

research effort to identify and quantify internal and external nutrient sources, especially those of fixed nitrogen (Webb et al., 1975). In this study, an effort has been made to document the concentration profiles of sedimental forms of nitrogen (nitrite, nitrate and total nitrogen) in the selected sedimentary environments of six islands of Lakshadweep archipelago.

Nitrite nitrogen and Nitrate nitrogen.

Nitrite is formed as an intermediate state in the oxidation of ammonia to nitrite or in the reduction of nitrate. The concentration of nitrite-nitrogen is found to be comparatively lower in the sea than the other forms of combined inorganic nitrogen. Nitrate – nitrogen is the final oxidation product of nitrogen compounds in seawater. This is the most abundant and thermodynamically the most stable form of combined inorganic nitrogen in well oxygenated seawater

In the present study the concentrations of nitrite nitrogen reported in the different sedimentary environments of the six islands were very low (Fig. 4.4). Among the six islands, the values were in the range : Kavaratti, 0.008 0.033 μ mole g^{-1} ; Kadamath, 0.001 – 0.033 μ mole g^{-1} ; Androth, 0.010 0.027 μ mole g^{-1} ; Kiltan 0.008 0.022 μ mole g^{-1} ; Minicoy 0.006 0.114 μ mole g^{-1} and Agathy 0.005 0.015 μ mole g^{-1}

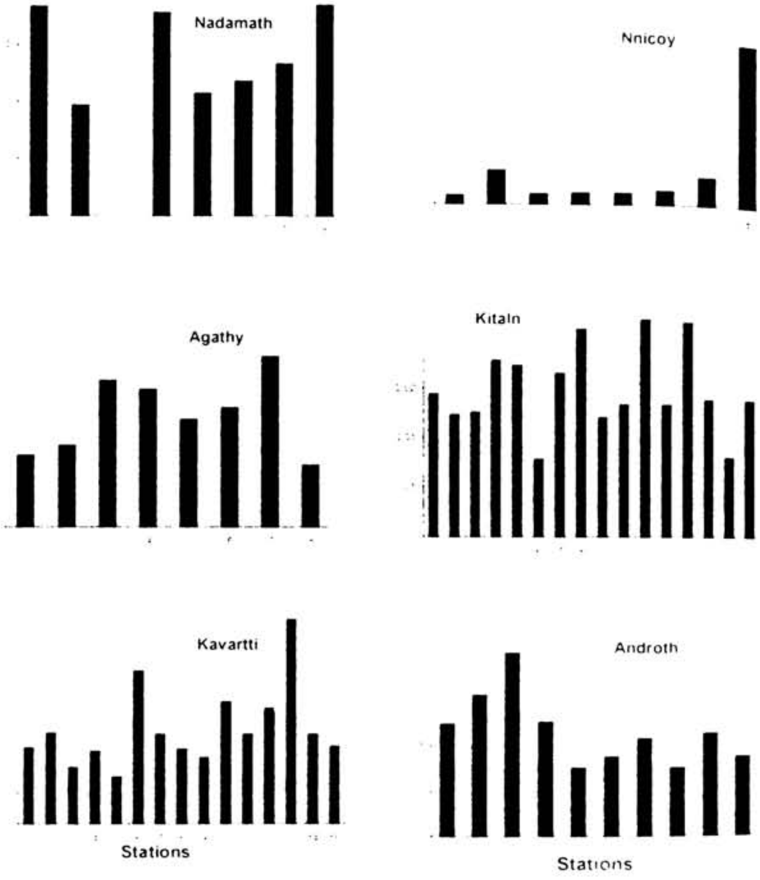

Fig. 4.4. Spatial variability of nitrite (μmole g) in six islands.

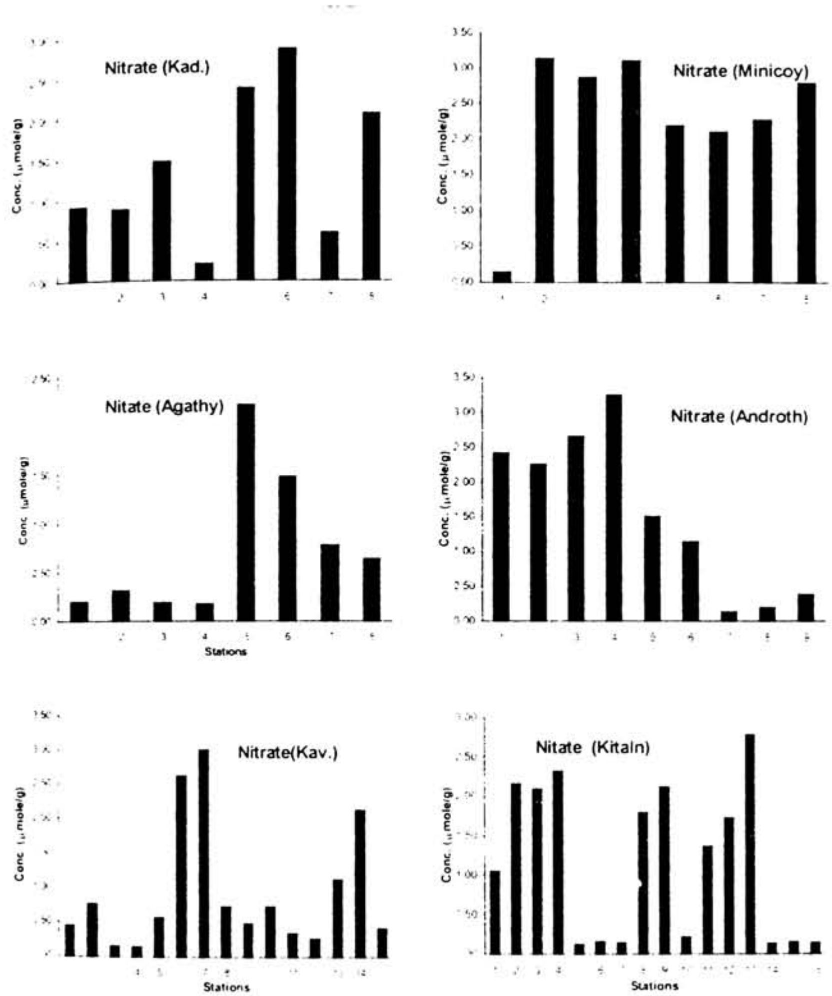

Fig. 4.5. Spatial variability of nitrate (µmole g^{-1}) in six islands.

The relatively low levels of intermediate nitrite, however, could b explained by the fact that ammonia oxidation (to nitrite) and nitri oxidation (to nitrate) are closely coupled (Webb and Wiebe, 1975).

In this study, the nitrate – nitrogen concentrations reported wer comparatively higher than that of nitrite nitrogen (Fig. 4.5).

Considering the variations of nitrate-nitrogen in Kavaratti core profiles, the concentration of nitrate-nitrogen in the core profile collected from southern part of Kavaratti island, varied between 0.150 (90 cm) 0.769 (30 cm) μ mole g^{-1} Towards the northern part, maximum concentrations were observed near to the lagoon, which decreased towards the land.

In Minicoy, comparatively higher concentrations were reported in the lagoon profile, as well as in the mangrove samples In Agathy island, towards the lagoon profile, highest concentrations were reported near to lagoon. Whereas in the seaside profile, concentration of nitrate decreased from land (2.0206 μ mole g^{-1}) towards the sea (0.637μ mole g^{-1}).

In Androth island, the core samples collected near the sea as well as the trough and crest soils recorded higher concentration of nitrate compared to the values recorded by the core samples collected from the land.

In Kiltan island, in the seaside profile samples were collected towards the northern as well as southern side of Dak bungalow in which a common trend was observed i.e., concentration of nitrate increased from land towards the seaside. The lagoon side profile in Kiltan island displayed comparatively higher concentrations towards the berm which slightly decreased in the land (0.129 2.320μ mole g^{-1}). The core profile collected upto 1.3 m depth also recorded very low values (0.129 - 0.150 μ mole g^{-1}).

It was pointed out that nitrate would have produced by bacterial nitrification in sediments using the available ammonia and oxygen released from mangrove roots or diffusion from sediment surface. Similar role of seagrass and mangrove plants are reported earlier (Jagtap and Untawale, 1984; Vinithkumar et al., 1999). Decreasing NO_3^- concentrations above and below a maximum result from vertical diffusion and microbial reduction.(Kemp et.al.,1990).Elevated concentrations of nitrate can be produced locally by groundwater discharge and surface run off (Marsh, 1977) and, therefore, can also be used as indicator of waste water contamination. This model of nutrient enrichment via ground water seepage is a plausible mechanism that can explain the eutrophication occurring in coral reef ecosystems on the northern coast of Bahia (Costa Jr. et al., 2000).

Various evidence suggests that, in many coastal environments, seasonal trends of denitrification are determined largely by NO_3^- availability (Koike and Sorenson, 1988), which, itself, tends to be controlled by rates of nitrification. Nitrifying activity is concentrated in the NH_4^+ rich region near the bottom of the oxygenated zone of sediments (Henriksen and Kemp, 1988). Low organic content of the sandy sediments in coral reefs accounts for the absence of nitrifiers thus leading to low nitrate concentrations. It is clear that coupled nitrification-denitrification can lead to removal of a substantial portion of the N inputs to coastal marine systems (Smith et.al., 1985; Seitzinger, 1988), thereby representing a natural mechanism for partial buffering against the global trend of coastal eutrophication (Christensen et al., 1987b; D'elia and Wiebe, 1990; Soonmo An, 2002).

Total Nitrogen

Fig. 4.6 represents the variation of total N among different sampl sites of each island. Discussing the variations of total N among the islands, in Kavaratti, the highest concentration of total nitrogen was in lagoon (34.29) whereas the lowest (3.91) was reported at 90 cm dept southern part of the island core profile. One of the characteri observations in this island was that, the samples collected from 1.2 m de on both sides of the island recorded higher concentrations compared other depths. The sample collected near the Ujra mosque also recorded higher concentration of total-N (20. 57 μ mole g^{-1}).

In Minicoy, the maximum value of the total nitrogen was recorded the lagoon (28.63 μ mole g^{-1}) which gradually decreased towards the land

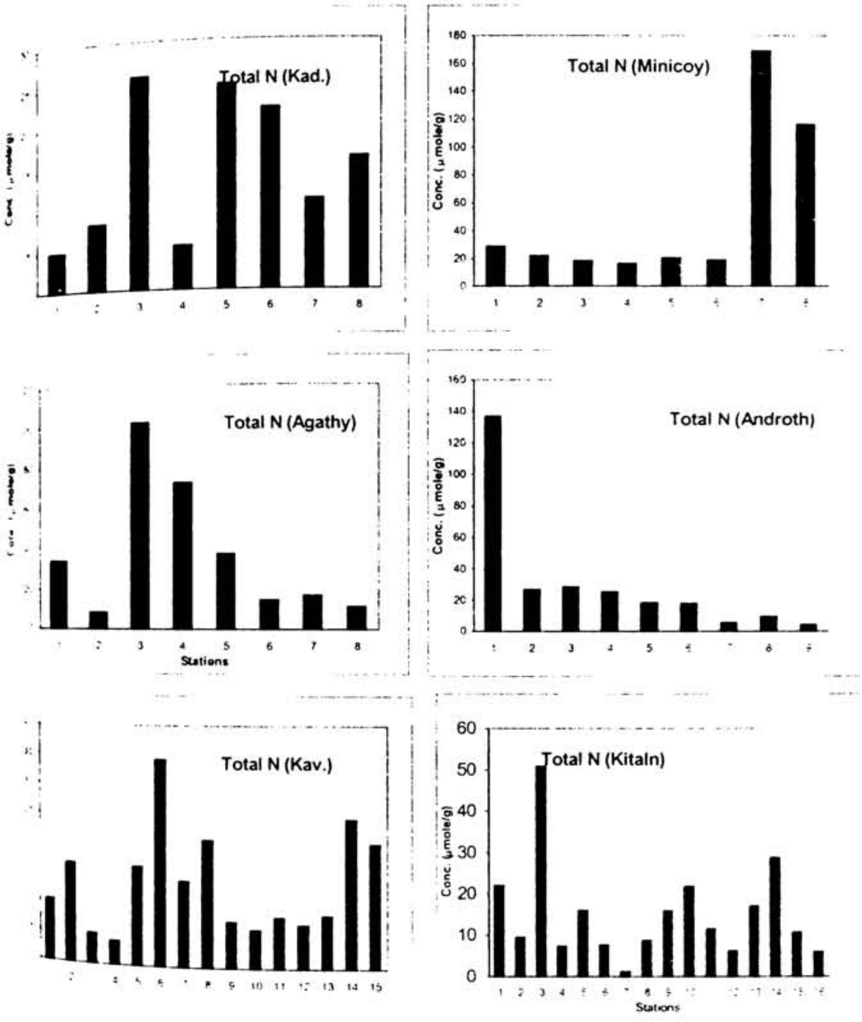

Fig. 4.6. Spatial variability of Total N (µmole g^{-1}) in six islands

(16.33 μ mole g^{-1}). The mangrove area of Minicoy recorded a very hig concentration of total N compared to the lagoon profile.

Illustrating the variations of total-nitrogen in Agathy island, contra to the behaviour of Kavaratti and Minicoy islands, the land soil recorde comparatively higher concentrations (72.25 μ mole g^{-1}) than the lagoo (33.86 μ mole g^{-1}). In the lagoon side profile of Agathy, maximum concentration of total N was reported at berm (101.81 μ mole g^{-1}). Toward the seaside, concentration of total nitrogen decreased from land (37.18 mole g^{-1}) towards the sea (11.38μ mole g^{-1}).

Regarding the variations of total nitrogen in Androth island maximum concentration of total nitrogen reported was in the surface sample collected from the seaside (136.68 μ mole g^{-1}). In this island, core samples were collected from the seaside and from the land

. and the observation was common in the sense that concentration decreased from surface towards 1 m depth. The trough soil and crest soil collected in Androth also recorded comparatively higher concentration of total N.

Discussing about Kiltan island, samples collected near the lagoon recorded higher values of total N (50.81 μ mole g^{-1}). Discussing about the seaside profile, towards the northern side samples towards the seaside recorded higher concentration of total N whereas in the southern part the land soil recorded higher concentration of total N (21.80 μ mole g^{-1} Regarding the variations in the core profile collected near 1.3 m depth. concentration decreased from surface (28.77 μ mole g^{-1}) towards maximum depth (5.99 μ mole g^{-1}).

Nitrifying potential (Henriksen and Kemp, 1988), which provides an index of nitrifying bacterial densities in natural sediments, exhibited consistent vertical distributions, with highest values in surface sediments and relatively low variance at each station depth.(Kemp et al.,1991; Devol, 1991)

For the purpose of discussion of total nitrogen variation among different environments of the islands, the classification scheme adopted was lagoon area, land, seaside and mangrove area. Within the island, again sampling was done to assess the variation of nutrient characteristics with depth (only for Kavaratti, Kiltan and Androth islands). The mangrove samples were collected only Minicoy, which is considered to be an artificial one.

Tracing the variations among the different environmental compartments of Kavaratti, the observed fact was that lagoon recorded higher concentrations of total N than land. Regarding the variations in core profile, no definite accumulation pattern was reflected . In Minicoy, the order of enrichment of total nitrogen in the different environments is Mangrove> lagoon > land > whereas for Agathy the order is, berm > land > lagoon > seaside. Concerning the variations in Androth, the order is land > trough soil > crest soil. Regarding the variations in Kiltan, lagoon > land > seaside. Except that in Agathy, the concentration of total nitrogen was higher in the lagoon than in the land.

Nitrogen fixation has been shown to occur in a variety of habitats within the reef. Fixation has been measured in beach rock zones, sandy lagoons, the reef flat, the reef slope and in certain fish territories. Various substrates have been associated with nitrogen fixation; sand, rubble, limestone, dead and living corals, beach rock and dead triclana shells (Larkum et al., 1988; Howarth et al., 1988; Capone et al., 1992), as well as other reef organisms such as sponges and zoanthids. The primary nitrogen fixing agents on coral reefs are cyanobacteria (Wiebe et al., 1975; Larkum et al., 1988). Comparing nitrogen fixation, rates in different parts of the reef shows that the sandy lagoon contributes the larger portion of the nitrogen to the reef community (Shashar et al., 1974). Upwelling acts as a major nutrient contributor to the offshore reef areas and only 10% of the total nutrient demand was estimated to come from external sources. In the inter-compartmental variations of total N, concentration found to be decreasing towards the seaside. This suggests that the inshore sources of nitrogen are not being transported offshore in measurable quantity or that they are metabolised before they can accumulate in the offshore sediments. In shallow coastal waters, nutrients regenerated in the sediments are an important source of nutrients that support shallow water benthic and water column productivity (Smith et al., 1981;1984; Nixon and Pilson, 1983; Entsch et al., 1983; Williams, 1884 a & b ; Williams et al., 1985; Furnas et al., 1993). Sediments are also a means of inshore/offshore nutrient transport during storms that resuspend sediments and make them susceptible to offshore tidal transport (Aller and Cochran, 1976; Zieman, 1982; Ullman and Sandstorm, 1987).

In the present study, concentration of total N was comparatively higher in the lagoon compared to land and seaside stations which can be due to the following reasons. The lagoons are shallow environments than the surrounding area. The rate of nitrogen fixation and the space and surface available for nitrogen fixation are comparatively higher in these zones. The amount of nitrogenous waste materials produced from the reefs and surrounding area, introduced into the lagoon will have limited exchange with the sea. The settlement and aggregation of organic matter through migratory fishes may contribute certain amount of total N (Meyer and Shultz, 1985). The major sources of nitrogen in sediments was attributed to the nitrogen fixation by benthic algal communities which are strongly influencing the nitrogen budget of coral reefs (Wiebe et al.. 1975). Coral reef flat are known to export dissolved organic N (Wiebe et al., 1975). The released nitrogen may be permanently lost from the system and exchange among the system and this could be the reasons for the changes observed in the inter-environmental variations of total nitrogen. Seagrasses play an important role in contributing aminoacids to the water and sediments which adds to the higher concentration of total N in sediments (Jagtap and Untawale, 1984).

Discussing he correlations of nitrogen forms with organic carbon, in Minicoy and Agathy total nitrogen displayed a positive correlation with organic carbon(r=0.995 and 0.543 respectively). In other stations no characteristic observations were made.

The total nitrogen in clayey sediments with carbon < 0.5% can be affected by fixed ammonium which is normally bound to illites (Muller and Mathesius, 1999; Muller, 2000). Generally, the marine organic matter contains less nitrogen relative to the freshwater or the terrestrial organic matter. The benthic biota play an important role in the uptake and retention of available nutrients (Laws and Redalje, 1979; Szmant – Froelich, 1983; Szmant, 1997).

Sediment feeders such as holothurians play an important role in supplying ammonia as a nitrogen source for benthic production (Uthicke and Klumpp, 1998). Nitrogen (N) fixation has been suggested as a major source of nutrient nitrogen in reef sediments (Capone et al., 1992; Miyajima et al ., 2001). Thus in the oligotropic ecosystems of reef carbonate sediment, where nitrogen fixation potentially supports the nitrogen requirement, phosphorus should be a limiting nutrient for primary production.

The C/N ratio provide information on the origin of organic matter, where higher ratios indicate terrigenous organic matter and lower ratios autochthonous organic matter(Redfield et. al.,1963; Muller and Mathesius, 1999). Organic matter in the basin is essentially autochthonous and associated with a minimum quantity of allochthonous matter. The organic nitrogenous compounds produced from the degradation of organic matter gets adsorbed onto sediments depending upon the temperature, electrical conductivity of the interstitial water, the concentration of organic matter and the porosity of sediments (Nasnolkar, et.al.,1996).Sediments with more percentage of sand were observed to be low in organic carbon and nitrogen(Jagtap and Untawale,1984).The biota, especially the benthic biota, play an important role in the uptake and retention of available nutrients(Laws and Redalje, 1979; Szmant-Froelich,1983; Hallock et.al.1993;Szmant,1997). In addition, the sediment evaluation (organic matter, carbon content, bacterial activity) should provide complementary information about the nitrification process, as the sediment constitutes the major nutrient source for benthic producers in shallow water systems (Szmant and Forrester, 1996; Szmant, 1997; Costa Jr. et al., 2000).

Low values of total nitrogen reported at some stations may be due to utilization of nitrogenous compounds and lower nitrogen fixation. Generally, the major source of nitrogen in sediments was attributed to the nitrogen fixation by benthic algal communities, which are strongly influencing the nitrogen budget of coral reefs. It was reported that transformation and fixation of nitrogen and effective utilization of phosphorous occurs efficiently in algal as well as in seagrass bed areas. Further influence of plant roots on nitrification in anaerobic sediments was also evidenced in seagrass beds.

Coral reef flats are known to export DON. Total nitrogen showed a negative correlation with organic matter, which reflects consumption of organic compounds from the sediments by macrophytes(Jagtap and Untawale,1984;Vinithkumar et.al., 1999).

Phosphorous forms.

The distributional characteristics of different forms viz. Exch. P, Ca-bound P, Inorg. P, Org. + Res. P and Total P among the six islands are given in Fig. 4.7 to Fig. 4.11 respectively. Among the various forms of Phosphorus fractions studied in the area, the order exhibited was. Total P > Org.+ Res. P > Inorg. P > Exch. / Ca-bound P. Regarding the variations of total phosphorus among the selected islands, the concentrations of all the forms of phosphorus exhibited higher values at the surface samples collected from southern side of Kavaratti island, this was highest reported values for Kavaratti island. The concentration of total P recorded in the lagoon area was very low compared to the values of total P indicating a high value of N/P ratio (139). Comparatively higher values are reported for N/P ratio ranging from 0.169 (reported near the southern part of Kavaratti) – 202 (reported for the lagoon area). The sample collected from 1.2 m depth on the southern and northern part of Kavaratti recorded 63 and 122 respectively indicating nitrogen enrichment and phosphorus depletion at the depths.

At some stations, org + residual P fractions amounted to be the major fraction of total P, when compared to other forms. For example, in the surface sample collected on the southern part of Kavaratti, org + residual fraction of total P was about 95 % of the total P estimated.

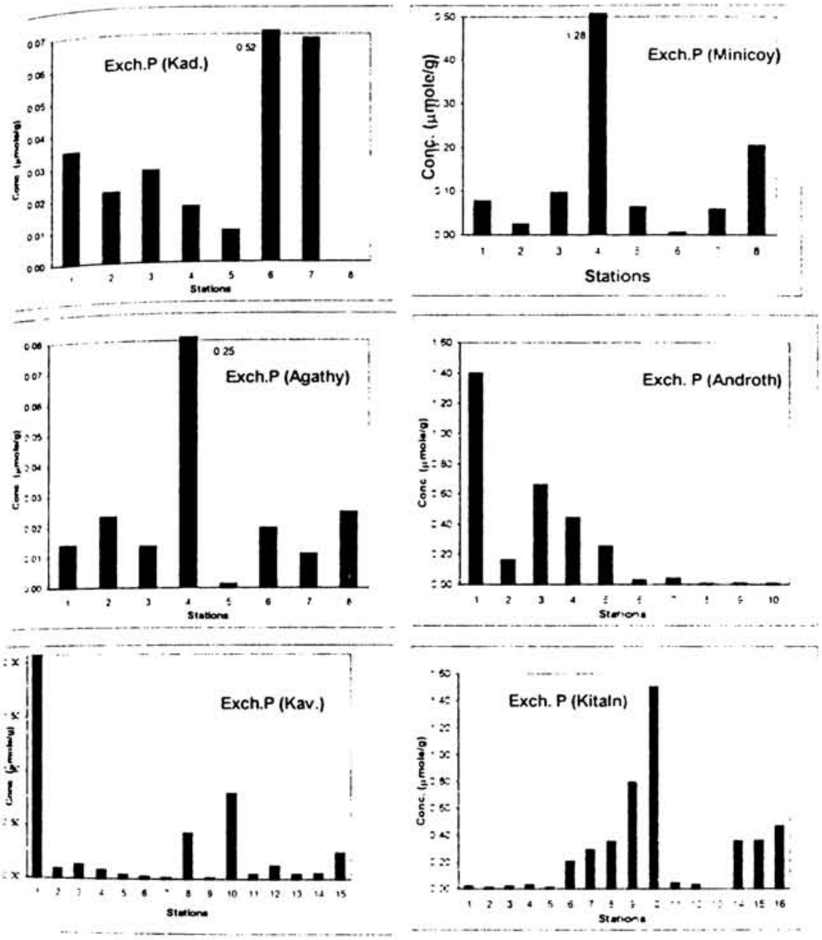

Fig. 4.7. Spatial variability of Exch. P (µmole g^{-1}) in six islands.

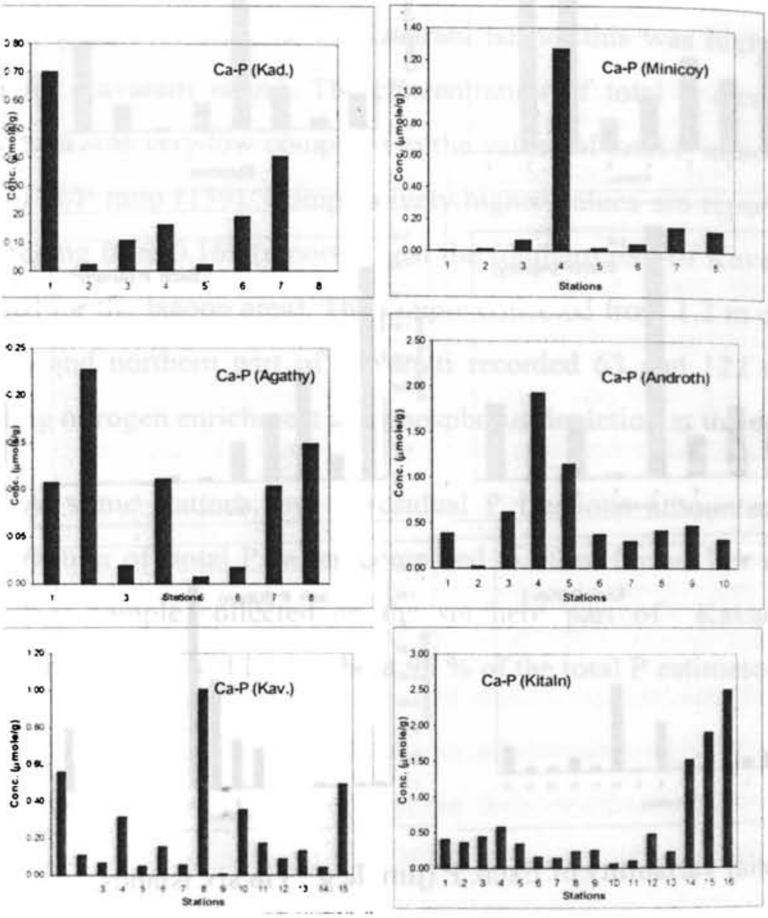

Fig. 4.8. Spatial variability of Ca- bound P (µmole g^{-1}) in six islands

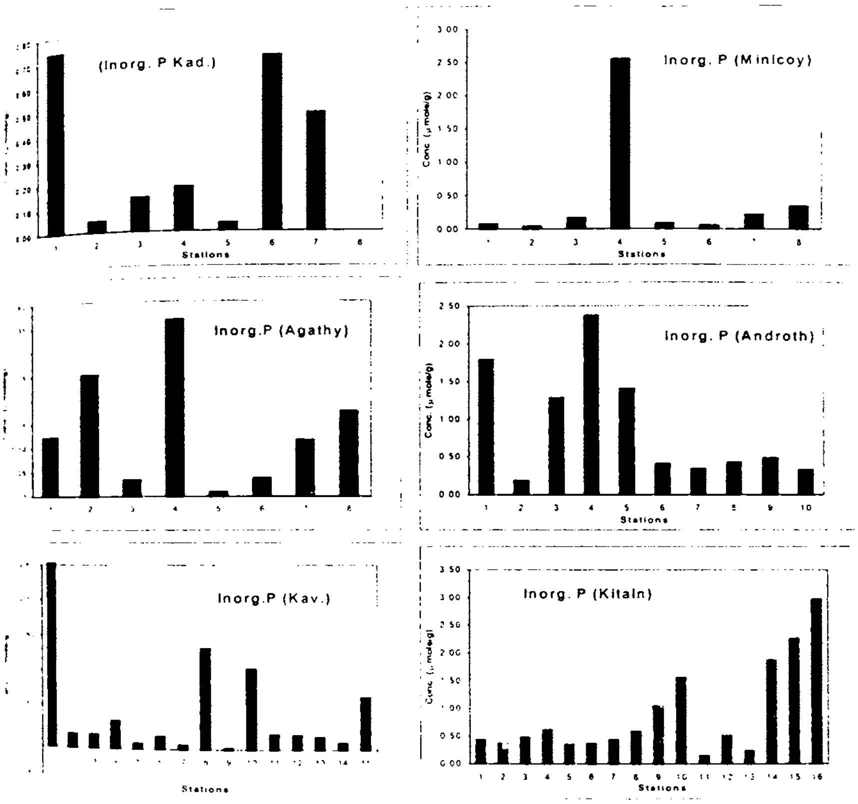

Fig. 4.9. Spatial variability of Inorg. P (μmole g^{-1}) in six islands

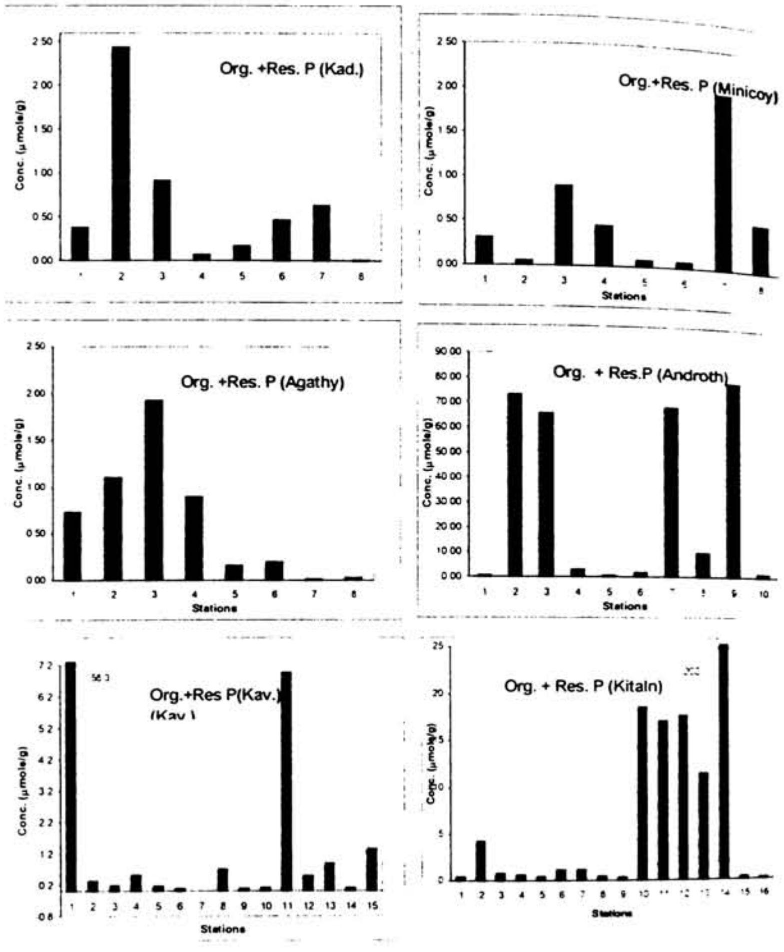

Fig. 4.10. Spatial variability of Org. + Res. P (μmole g^{-1}) in six islands

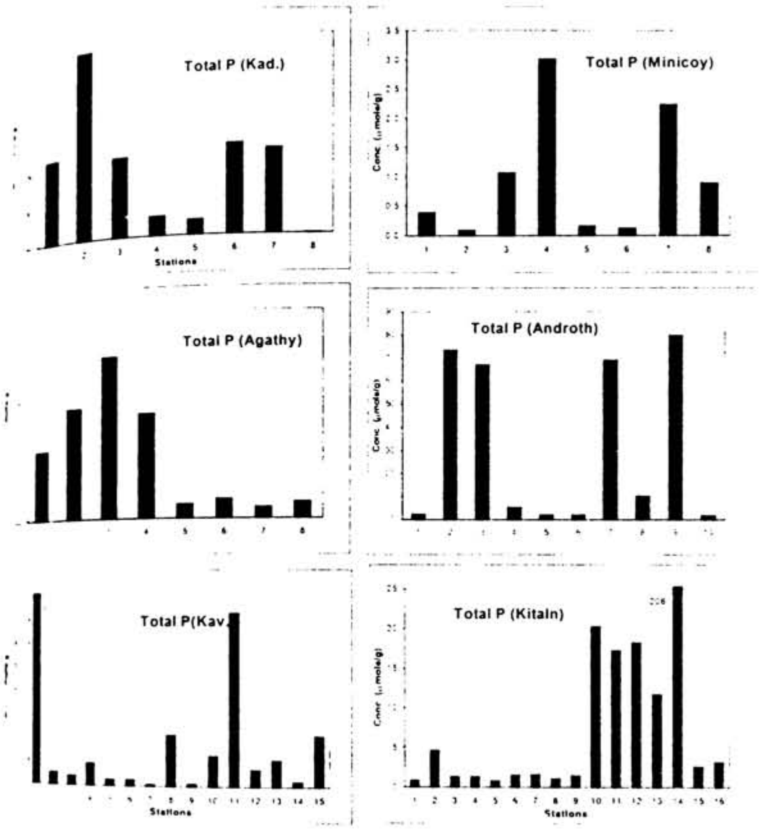

Fig. 4.11. Spatial variability of Total P (µmole g^{-1}) in six islands

samples collected at 1.2 m depths on the northern as well as southern side of Kavaratti, on an average, org + residual P amounted for about 60 % of the total P whereas in the lagoon side comparatively lower concentrations were recorded for org + residual P, which accounted for about 3 % of the total P. In Kavaratti, except that for Ca-bound phosphorus all other forms recorded highest values in the surface sample collected from the southern side of Kavaratti island.

In Minicoy island, the concentration of total P recorded were far less compared to the values of total N. This condition leads to high values of N P ratio in the range 5.43 – 250. In the mangrove environment, Org + Res P accounts for about 80 % of total P. In Minicoy island, though the values of total P recorded are very low in the lagoon environment, 79 % of contribution towards the total P in this region comes from the org + residual P fraction.

Regarding the variation in Agathy island, towards the lagoon profile, total P values ranged between 0.854 to 1.962 μ mole g^{-1} whereas for the seaside profile it was in the order, 0.132 – 0.234 μ mole g^{-1}. Here also the total phosphorus concentration was found to be increasing from lagoon to land and in the lagoon side org + residual fraction of total P comes around 80 % of the total P. Towards the seaside org + residual phosphorus fraction was very low, here on an average 86 % of the total phosphorus was from the Inorg. P fraction. In the seaside profile of Agathy island, concentrations of exchangeable, Ca-bound and inorganic phosphorus concentrations was very ow in the land, the major portion being the org + residual form of phosphorus (95%). In Agathy, the N/P ratio ranged from 6.07 – 221.54.

Discussing about Androth island, considering the variations in concentrations of total P in the core samples, concentrations recorded at depths were higher than that for surface. In the sea side core profile, high concentrations recorded at depths were higher than that for surface. In the land core profile, high concentrations were obtained at 0.5 m and 1 m depth (73 and 67 µ mole g^{-1}). Towards the northern side 0.3 m and 0.9 m depths recorded a very high connection (69 and 79 µ mole g^{-1} respectively). The N/P ratios recorded were not high in Agathy, except for the surface soil which recorded a value of 57.87. In Agathy, stations which recorded very high values for total P, also recorded a higher percentage of Org. + Res. P fraction – on an average 99% of total P is contributed by Org. + Res. P fraction.

In stations with comparatively lower total p content, the inorganic P made a major contribution towards total P content.

In Kiltan island, the values of total P were very low, except for the surface samples of the core profile which recorded a maximum value (205 µ mole g^{-1}). Considering the variations of total P, towards the seaside profile of Kiltan, the southern side recorded a higher concentrations of total P (11.7 – 20.19 µ mole g^{-1}) compared to the northern part (1.05 – 1.59 µ mole g). As observed for other islands, in stations reported to be having higher percentage of Total P, Org. + Res. P found the major component.

Concerning about lagoon side profile, which recorded higher concentrations of total N, the values reported for total P were very low, indicating N/P ratios in the range (2.07 – 39.16).

Phosphorus and organic constituents in sediments (ancient or modern) indicate the geochemical conditions wider which the deposits were laid down. While a study of the successive deeper layers of the deposits of a region reflects varying environmental conditions of the past, a study of the samples collected at the sediment – water interface, across the same region, reflects (i) the prevailing conditions under which the deposition is taking place, and ii) the relationship of the sediment with the overlying water mass, which in turn, is subject to movement of currents, oxygen content, upwelling, organic productivity etc.(Van Raaphorst et al., 1992; Van Den Broeck and Moutin, 2002).

Discussing the variations of different phosphorus fractions with other sedimentlogical parameters like texture, pH, organic carbon content the following generalizations were made. Interrelations of different nutrient forms among each other and also with pH and organic carbon are given in Table 4.2. Table 4.3 gives the correlations of different forms with grain sizes of sediments.

Considering the effect of organic carbon content on the distribution of nutrient forms, in all the islands different phosphorous forms displayed comparatively good positive correlations with organic carbon. Depending on the association of organic carbon with the grain size , different phosphorous forms also behaved accordingly. For example, In Agathy, total phosphorous displayed a significant positive correlation with fine sand(r= 0.879) and so also organic carbon(r=0.806).In Androth, the calcium bound and inorganic form of phosphorous showed an affinity towards silt – clay fraction in accordance with the behaviour of organic carbon. This occurred in Kiltan also, in which calcium bound and inorganic phosphorous fractions were associated with silt + clay form of sediment.

The organic carbon content is high in the silty ion of the sediment. The grain size of this fraction is considered to retard the organic carbon from rapid decomposition . Considered together, phosphorus and organic carbon fluctuate almost parallel to each other - wherever phosphorus values are high, the organic carbon contents are also high and vice versa. Lack of iron under aerobic conditions to fix phosphorus and phosphates results in low values of phosphates. The fine grain size of the calcareous or elastic clayey materials increases the phosphate values whereas coarseness of sediment inhibits the accumulation of organic carbon – resulting low values. The high organic content in the sediment is also a consequence of luxuriant organic productivity in the overlying water mass and the nutrients brought up by upwelling. Major fraction of phosphorous reported was the organic form which attests the fact that phosphorous may be deposited with organic matter possibly with the shells and bones of corals and molluscs (Atkinson,1990). In shallow environments nutrients contained in organic and inorganic particulate matter will not be lost o the system through sedimentation, but rather are readily stirred up and periodically recirculated (Rajendran and Venugopalan, 1973; Mach et al., 1987; Ramirez and Rose, 1992; Boucher et al., 1998). According to Pomeroy et al. (1965) t exchange rate and capacity of the sediments are ecologically impor factors in maintaining the phosphate concentration at an optimum level a that in minimum in the case of sandy sediments.

Depending on the actual loading and primary production, bo sorption and biotic uptake may play a role in the removal of phosphoro from the water. Biologically available is transported from water sediments in the form of dead organic matter leading to mineralization an adsorption. The phosphate binding power was shown to increase wi increase in calcium carbonate content of the sediments.(Istavanovics et a 1989).

P-release is the result of complex mechanisms includin mineralogical diagenesis, biotic and abiotic redox processes, biologica assimilation, and enzymatic and non-enzymatic hydrolysis reactions Macrophytes are essential not only as a source of organic matter but also as a phosphorous source. Bioturbation i.e. the disturbance of the sedimen surface by burrowing invertebrates and benthivorous fish . can have a greater effect on P release than any other physical or chemical factor (Holden and Armstrong, 1980; Bostrom et.al.,1982).

Characterizing the influence of pH on the distribution of phosphorous forms, the different fractions were found to be negatively correlated with pH , the level of significance varying among these islands In Androth, exchangeable, inorganic as well as calcium bound phosphorou forms displayed moderate negative correlations with pH. All phosphorou fractions displayed fairly good negative correlations pH in Kavaratt whereas in Kiltan, Org. + Res. P form and total phosphorous showed an inverse relationship with pH.

pH is an important factor in regulating rates of phosphorous release from sediments, rates increasing with increasing pH in the water column. A pH mediated phosphorous release can be significant in shallow productive water bodies where ph is often increased due to intensive primary production(Bostrom et.al.,1982). P-release from sediments increased with increasing pH , particularly above 8.5. In most natural waters, pH changes are the result of processes such as respiration by the biological community which can lead to a decrease in pH through the addition of carbon dioxide. Similarly, consumption of carbon dioxide through photosynthesis may rise pH through the production of OH^- ions (Rajamanickam and Setty, 1973; Venkatesh, 1981; Seitzinger, 1991). The latter mechanism is likely to be a controlling factor contributing to pH increase of these areas (Carpenter and Smith, 1985; Caraco et al., 1989).

The results presented here show that a sedimentary pool of P, in particular adsorbed P, is one of the most important sources for micro-phytobenthic community production in carbonate sediments. Even though the carbonate sediments have a relatively large source of this available P for maintaining productivity, there must be potential losses of P from the sediments through diffusional flux and desorption to the overlying seawater. However, laboratory and filed researches showed that there is no net liberation of P from undisturbed coral reef sediments (Atkinson, 1987b).

Although the diffusional flux of P from sediments might be minimized by micro-phytobenthic metabolism, potential losses of P must be considered through some other physical and biological processes, includ re-suspension and grazing by sediment feeders. Unfortunately, there is quantitative information regarding the removal of P flux from the carbon sediments of coral reefs through the processes (Suzumura et al., 2002).

One of the salient features observed in this study is the hi concentration of Org + residual P compared to inorganic P, particularly stations reported for higher total P concentrations. From the point of view availability as the P source for micro-phytobenthos production, organi phosphorus is the les important fraction compared to inorganic P, which ac as the major source to sustain micro-phytobenthos production in th carbonate sediments of coral reefs. The diffusional flux of P from th sediments might be minimized by microphytobenthic metabolism, potentia losses of P must be considered through some other physical and biologica processes, including resuspension and grazing by sediment feeders Sedimentation of suspended particles and aged marine plants is an importan source of supplying phosphorous to the sediments. The source materials o the carbonate sediments such as coral fragments and coralline alga skeletons are likely a significant phosphorous source in sediments as well. A large fraction of organic phosphorous remaining in the carbonate sediments was composed of refractory materials that withstand early diagenetic mineralization. Therefore, from the point of availability as the P source for microphytobenthos production, organic phosphorous is the less important fraction; hence inorganic fraction should be the major source to sustain microphytobenthos production in the carbonate sediments of coral reefs (Suzumura et al., 2002).

Contribution from high benthic biodiversity, besides death and decay of seagrass and seaweeds resulting higher release of organic materials and nutrients, which are retained according to the nature of the sediment texture also contributes towards the pool of organic plus residual form of phosphorous. Detritus formation and release during death and decay from the macrophytes have been viewed as a major source of organic carbon in the reef areas adjacent to grass meadows. Further aggregation of migrating fishes , crustaceans and molluscs and their excretory products could also seem to serve as another source of organic carbon in the reef areas(Vinithkumar et.al.,1999).

The inorganic association of P with the solid matrix may take place through adsorption on the surface of the particles or through precipitation as or with newly formed minerals (Apatites, Fe & Mn oxides and hydroxides). Both the adsorbed fraction and the fraction bound to the Fe & Mn oxides and hydroxides are considerably influenced by changes in the chemical and physical conditions. While they tend to participate under oxidizing conditions, they tend to enter into solution under reducing conditions and be recycled into the environment (Frascari et al., 2002).

The higher phosphorous content of offshore sediments either suggests that there is an offshore source of phosphorous to the area, or that phosphorous is less rapidly metabolised or more strongly absorbed offshore than inshore. Higher supply rate of N near shore could result in better utilization of P by algae and seagrasses in he nearshore sediments(i.e. nearshore plants are not nitrogen limited and can assimilate phosphorous). While low supply rates of nitrogen offshore results in the accumulation and absorption of phosphate in the sediments (e.g. offshore algae may nitrogen limited and unable to utilize phosphorous; thus it accumulates.

N/P ratio.

Spatial variation of N/P ratio in the study area is given in Fig. 4. Tracing the features of N/P ratio. except that in Androth. all other islan reported comparatively higher range. In Kavaratti, the highest value. 202 were observed for the lagoon sample. The variation observed for Kavaratti

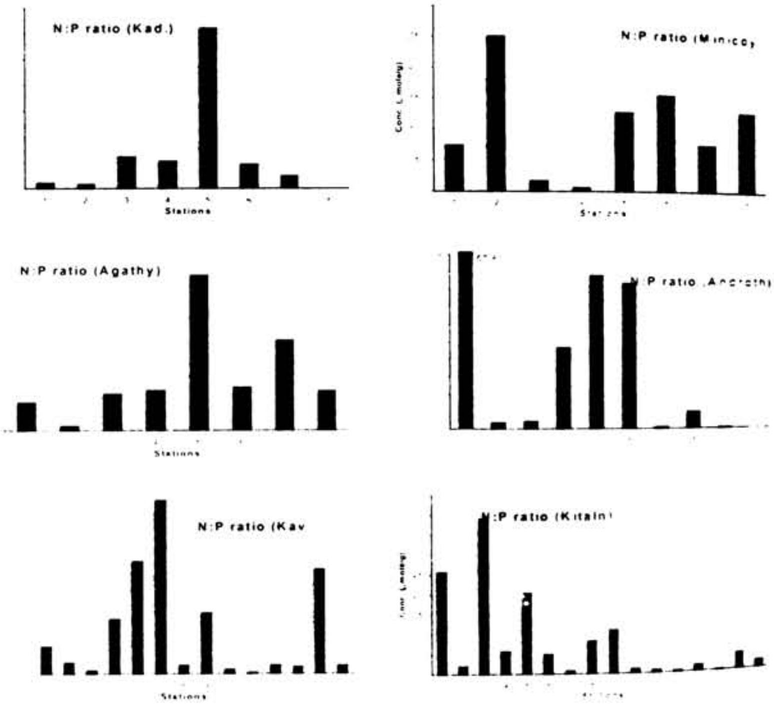

Fig. 4.12. Spatial variability of N P ratio in six islands

was. 0.69-202.59.In Kadamath high tide and low tide stations report comparatively higher values, the range of N/P for Kadamath was 3.3

124.34. in Minicoy, except for the sample collected from the land, all other stations recorded very high values in the range, 5.43(land)-250.84(lagoon).the variation observed for Agathy was, 6.07-221.54. In Androth except that in surface (57.87) all other stations reported very low values. In Kiltan also variations were observed only near the lagoon (25.74-39.16) and also in the land (20.43). For other station it varied from 0.14-10.96.

The high ratios indicate low phosphorous content of the sediments. Usually the contribution of phosphorous in sediments is from the organic matter as well as from the mineral matter. Here the sediments are very rich in sand and are mostly sandy with little silt or clay. Therefore apart from the organic matter, the contribution from the mineral phosphorous probably plays an important role in the variation of N: P ratios of these sediments. Significant positive correlation between nitrogen and phosphorous revealed that the concentration of one is dependent on the other and indicated a common source for both. Positive correlations with total nitrogen and total phosphorous represent increased nitrogen fixing activity from increased availability of phosphate as reported earlier (Smith and Atkinson, 1984; Vinithkumar et.al, 1999). Increase in concentration of phosphorous would increase the growth rate of certain algae (Atkinson, 1987a), particularly those tat are efficient in retaining and fixing sufficient amount of nitrogen. Higher accumulation of phosphorous fractions in shells and bones of animals may lead to lower N: P ratios, which were earlier reported by Shark Bay of Western Australia (Atkinson, 1987a). In the oligotrophic ecosystems of reef carbonate sediments, where nitrogen fixation potentially supports the

N requirement, phosphorous (P) should be a limiting nutrient for primar production. A supply of P maintaining microphytobenthic production canno be generated insitu like fixed N. (Suzumura et.al, 2002). The high values fo N/P ratios indicate low phosphorus content of the sediments. Apart from organic matter, the contribution from mineral phosphorus probably plays a important role in the variation of N:P ratios of these sediments

Trace Metals Nutrients Relationships

The correlation coefficient s of trace metal nutrient relation ship are given in Table 4.4. Although the biochemical mechanism responsible for Cd uptake by phytoplankton is not known, the consistent relationship between Cd & P has been elegantly exploited for the estimation of historical and paleochemical nutrients in the oceans (Noriki et al.,1999; Abe. 2002)

It is now well established that the geographical distribution of Cd in the deep ocean is similar to that of the labile micronutrient P (Boyle et al., 1976; 1977; 1981; Bruland et al., 1978; Bruland 1980, Bruland and Franks 1983; Hunter and Ho, 1991; Frew and Hunter 1992; 1995). Thus vertical profiles of Cd show nutrient like depletion in surface waters and enrichment at bottom. Early work tended to suggest that Cd could be regarded as close analogue since the rate of Cd and P concentration s in different regions of the oceans exhibited little variation particularly when comparing north Atlantic and north pacific data (Boyle et al., 1976; Bruland 1980; Bruland and Franks 1983). This would imply that Cd is taken up by surface level phytoplankton in a relatively constant Redfield type ratio (Redfield et al 1963) with respect to Carbon and the micronutrients. The mechanism of

Table 4.4. Correlations between nutrients and trace metals

Kavaratti isla	Cu	Cr	Co	Ni	Pb	Zn	Mn	Cd	Fe
Org. C	-0.345	-0.194	-0.511	-0.644	-0.640	-0.036	0.487	-0.377	0.568
Nitrite	0.110	-0.218	0.003	0.066	0.066	-0.097	-0.189	0.496	-0.239
Nitrate	0.224	-0.081	-0.024	0.064	0.040	-0.059	-0.079	0.098	-0.204
Total N	0.275	-0.143	0.065	-0.011	-0.002	0.206	0.119	-0.049	0.163
Exch. P	-0.709	-0.142	-0.856	-0.890	-0.894	0.110	0.326	-0.508	0.558
Ca-P	-0.151	-0.190	-0.219	-0.346	-0.317	0.789	0.345	-0.285	0.515
Inorg. P	-0.589	-0.179	-0.724	-0.798	-0.790	0.381	0.375	-0.488	0.613
Org+Res.P	-0.846	-0.089	-0.917	-0.955	-0.935	-0.114	0.230	-0.566	0.590
Total P	-0.841	-0.094	-0.916	-0.956	-0.936	-0.092	0.238	-0.567	0.596
N:P ratio	0.250	0.165	0.077	0.168	0.139	-0.186	-0.117	0.065	-0.241
Kadamath isl	Cu	Cr	Co	Ni	Pb	Zn	Mn	Cd	Fe
Org. C	-0.252	-0.400	-0.423	-0.363	-0.434	0.211	0.068	0.837	0.294
Nitrite	0.480	0.433	0.580	0.538	0.278	-0.494	0.033	-0.139	0.734
Nitrate	0.111	0.250	0.105	0.242	0.306	-0.085	0.710	0.640	-0.364
Total N	-0.242	-0.119	-0.219	-0.107	0.146	0.238	0.590	0.455	-0.761
Exch. P	0.235	-0.024	-0.138	-0.070	-0.133	0.054	0.062	0.906	-0.097
Ca-P	-0.504	-0.160	0.032	-0.058	-0.156	-0.396	-0.117	0.060	0.528
Inorg. P	-0.246	-0.137	-0.057	-0.086	-0.197	-0.271	-0.053	0.580	0.346
Org+Res.P	0.061	0.001	-0.267	-0.270	-0.318	0.240	-0.514	-0.253	-0.050
Total P	-0.032	-0.050	-0.288	-0.302	-0.392	0.138	-0.533	-0.035	0.081
N:P ratio	0.343	0.057	0.019	0.091	-0.032	0.218	0.164	0.017	0.424
Minicoy islan	Cu	Cr	Co	Ni	Pb	Zn	Mn	Cd	Fe
Org. C	0.876	-0.964	0.096	0.976	-0.987	0.975	0.262	-0.499	0.887
Nitrite	0.240	-0.620	-0.664	0.480	-0.537	0.547	0.495	0.242	0.825
Nitrate	0.221	-0.038	0.342	0.261	0.019	0.173	0.179	-0.039	0.199
Total N	0.847	-0.973	0.032	0.962	-0.995	0.963	0.304	-0.460	0.901
Exch. P	0.029	0.087	0.227	-0.062	0.295	-0.211	0.364	-0.082	-0.160
Ca-P	0.117	0.032	0.329	0.021	0.230	-0.145	0.366	-0.163	-0.129
Inorg. P	0.074	0.059	0.279	-0.021	0.263	-0.178	0.365	-0.123	-0.145
Org+Res.P	0.953	-0.720	0.430	0.807	-0.774	0.788	0.131	-0.894	0.519
Total P	0.644	-0.392	0.493	0.477	-0.257	0.336	0.382	-0.649	0.199
N:P ratio	-0.393	0.053	-0.136	-0.020	-0.010	-0.064	0.045	0.717	0.149

this relationship that is whether it is cellular incorporation (Walsh Hunter 1992) or by some adventitious associations like scavenging need be examined.

One of the characteristic observations of this study is the correlat exhibited by total N with trace metals in some islands namely Andr Agathy, Minicoy and Kadamath islands. In Minicoy, significant posit correlations were observed with Cu, Ni, Zn, Fe and organic carbon cont (p > 99.9%), whereas with Cr and **Pb** significant negative correlations w displayed (r = -0.973 and -0. 995 respectively). Another moderate posit correlation was reflected with organic plus residual phosphorous fract (P>99%). A similar pattern was observed in Agathy island also with exception of correlation with Ni in which a negative correlation w observed. Relationship with iron was not significant in this case whereas negative correlation was observed with Mn which was absent in Minic As in the case of Minicoy, here also total N exhibited a positive correlat with organic + residual phosphorous.

Tracing the correlations in Kadamath, a negative correlation wa observed between total N and Fe (p = 99 %). Characterizing correlations in Androth, entirely different pattern was observed in which the metals display fairly good negative correlations with total N, where highly significant positive correlation s are observed with exchangeable inorganic forms of phosphorous. Positive correlation s of total N and metals indicates similar pattern of remineralization and deposit behaviour involved in their accumulation pattern.. The negative correla s reflects selective removal of trace metals or denitrification mechan operating with microbial assistance – both of which acting opposition to one another. In other words the rate of occurrence of one of these two may be far exceeding the other and which is acting in opposition to one another in trace metal and total N variations. The organic nitrogenous compounds produced from the degradation of organic matter gets adsorbed on sediments depending upon the temperature, electrical conductivity of the interstitial waters, the concentration of organic matter and the porosity of sediments (Rosenfeld 1979; Nasnolkar et al., 1996).

In the present study one of the salient features observed was that the relationship between Cd and P content of the sediments. Discussing about these correlations in Kadamath island exchangeable as well as inorganic P fractions display significant positive correlations with Cd (P>99.9%) and P > 90% respectively,. Concerning about Agathy, the inorganic as well as Calcium bound P fractions display P moderate positive correlation with Cd.

Contrary to the relationship observed for Agathy and Kadamath islands in Kavaratti total P display a fairly good negative correlation with Cd (P 99%) This was true for other forms of P namely exchangeable inorganic as well as organic + residual forms of P. This was the observation made at Minicoy also, in which total P as well as org. + residual phosphorus fractions displayed negative correlations with Cd (p>95% and 99.9% respectively). Characterizing the correlations in Androth, only the exchangeable phosphorus fraction displayed significant negative correlation with Cd (p>99%).

The positive correlations exhibited indicates almost a parallel mechanism involving the enrichment and remineralization processes through the sinking biogenic organic matter. The negative correlation indicate relative enrichment of Cd due to anthropogenic input. In the upwelling region at the north of New Zealand, Cd responds inversely to P, showing an increasing selectivity for Cd, at higher P concentrations. In the extensive Challenger Plateau region, however, the Cd-P relationship is significantly perturbed by an excess of Cd relative to P that may be a consequence of terrestrial inputs (Hunter and Ho, 1991). Generalizing the observation, high nutrient concentrations promote productivity coupled with high concentrations of biologically-active trace metals like Cd – leading to positive relationship between the two. Contrary to this observation, differences in the rate of uptake and recycling of trace metals and nutrients leads to an inverse relationship between the two.

Discussing the relationships of various P fractions with other trace metals, in Kavaratti, total phosphorus displayed negative correlations with Co, Ni, Pb and Cu (p>99.9 %). A positive correlation was observed only in the case of Fe (p>99%). The behaviour of different forms were more or less the same, except the fact that Ca-bound P displayed significant positive correlation with zinc (p>99.9%). Tracing the features of Agathy, total as well as org – residual P fraction, displayed positive correlation with Cu and Zn. These all forms of phosphorus displayed a moderate negative correlation with iron (p <95% for total P, for other P > 95 %).

Inorganic as well as Ca-bound P fractions displayed moderate positive correlations with Cr, Co, Ni, Pb and Mn. Illustrating the interrelationships in Minicoy, Org + residual P fractions displayed a correlation with almost all metals, the significant ones are with Cu, Ni, Zn (

= + ve, p>99.9% for Cu, 99% for Ni and Zn) and for Cr and Pb (r = -ve, p>98 %). Characterizing the features of Agathy, total as well as organic + residual from of P were strongly correlated with Mn (r = 0.91), Fe (r = 0.99), Cr (r = -0.95), Pb (r = -0.90) and Cr (r = -0.85) whereas for Androth only the exchangeable p fraction displayed moderate negative correlation with various metals except that with Zn.

Metals that are positively correlated with total as well as org + residual P fractions were formed to be positively interrelated with organic carbon content. Little is known about the nature of phosphorus and metals bound to organic matter in sediments and their roles in biogeochemical cycling. Naturally occurring P and metal – organic complexes could be expected to cover a wide range of polarity, molecular weight, lability and thermodynamic stability (Mantoura and Riley, 1975; Hirata, 1979; 1982; 1983; 1985; Mackey, 1982; 1983). Sediments consist of detritus derived from suspended particulate matter, plankton, microorganisms, fecal pellets etc. and the early diagenesis of the sediments is considered to be modified by microbial activity. The source of organically bound P is considered to be marine plankton and is thought to have been formed by the rapid deposition of relatively non-degraded planktonic organic matter into the sediments (Nissenbaum, 1979), and may be derived from phospholipids and phosphoproteins (Schnitzer and Khan, 1978). Organically bound P is decomposed in the early diagenesis of sediments. Organically bound Ca and Zn may be derived in a similar manner as marine planktonic organic matter, and are also decomposed in the early diagenesis of sediments. Moreover, positive correlation between metals and organic carbon contents occurs when metal ions interact with dissolved organic matter in seawater, both are concentrated by adsorption onto particulates such as clay minerals and sedimented to be bottom, as pointed out by Curtis (1966).

Several workers have reported on the relationship between iron and phosphorus in rivers and estuaries and a variety of reactions have been proposed to explain their relationship and it is clear that many processes involving flocculation, specific adsorption and precipitation of iron and phosphate are possible (Curtis, 1966; Windom et al., 1991; Sundby et al 1997; Frankowski et al., 2002).

In this study, a positive as well as negative correlation was displayed by iron with various phosphorus fractions. Among these the significant ones observed were in Kavaratti and Agathy in which total as well as org-residual P fractions exhibited positive correlation with iron (both the elements co-vary with each other to very significant extent in these sediments. Iron in the marine environment may be associated with the sediments i) as iron located in the lithogeneous minerals ii) as iron incorporated in the marine sediments directly from seawater, iii) as iron derived through biological processes and iv) as iron associated with the clay minerals either as an essential constituent or as a major constituent within the crystal lattice or as iron oxide on the surface of the mineral platelets (Martynova, 1984; Koop et al., 1990; Sonderguard, 1988; Sundby et al., 1997; Frankowski et al., 2002). Similarly phosphate also apart fro being associated with the sediments in the form of primary chemical precipitates or as incomplete replacement product formed from pre existing carbonate material (Sundby et al., 1997; Frankowski et al., 2002).

Therefore the possibility of phosphate being associated with these sediments to some extent in the chemical precipitate form cannot be excluded. The significant relationship obtained between phosphorus and iron indicates that it occurs to some extent as ferric compound also.

Tracing the characteristics of zinc, it was found to be exhibiting significant positive correlations with various fractions in Kavaratti, Agathy, Minicoy and Androth islands. This formulate the fact that uptake and remineralization of zinc takes place in harmony with the uptake and regeneration of phosphorus. In estuaries, zinc removal seems only to be observed where nutrients are removed to a significant degree by biological processes (Paulson et al., 1993). The near simultaneous decomposition of hard silicates parts and soft organic matter allows us to use phosphate as parameter that reflects regeneration of both hard and soft biological matter.

Concerning the behaviour of copper, it displayed negative correlation with total P in Kavaratti whereas those with the org + residual P fraction in Minicoy was found to be positive ($p > 0.001$ in both cases). Marine organisms excrete dissolved organic ligands that complex Cu (Sundby et al., 1992). The complexation of Cu by such excreted dissolved organic ligands has been shown to contribute to the low affinity of dissolved Cu for marine particulate matter in laboratory experiments (Paulson, 1993).

Summarizing the behaviour of nutrients among the six islands, higher values of both total and total phosphorous are reported for Androth Island. In all other islands, concentrations of total nitrogen was far exceeding that of total phosphorous attesting the role of nitrogen fixation towards the nitrogen requirement of the environment where phosphorous acts as a limiting nutrient for primary production.

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Chapter 5

CHEMO-VARIABILITY IN ABIOTIC COMPONENTS – TRACE METALS

INTRODUCTION

Human activities have been altering the land ever since hunting began to give place to agriculture, while in freshwater, pollution, initially largely from sewage, has been a matter of concern for centuries, increasing with the spread of urbanization. When we did begin to expand over horizons and eventually to complex and chart the global oceans, the only adverse effects we were likely to cause were inflicted directly on ourselves, through piracy and war. Before considering the present state of the marine environment, and how humans have affected it, it may be useful to look back a little, if only to place the problems in perspective. In doing this, perhaps the most striking point is just how relatively recast our awareness of anthropogenic impact on the seas turns out to be recent, that is, in comparison with terrestrial and freshwater environments.

By the middle of the century, it became clear that we could indeed contaminate on the oceans can alter their chemical composition in a measurable way, but as often happens, the production began to swing too far. It was not until the second half of the present century that marine pollution became of in dispread concern, but having been alerted to the potential problem of seafood contamination, the scientific community directed a great deal of research to the distribution and fate of metals in the sea. The most toxic became a focus of attention, and mercury and cadmium were built into the black lists of several international conventions developed in the 1970s.

The continual development of agricultural, industrial and urban activities has given rise to a number of environmental problems. Heavy metal contamination in aquatic environments is of critical concern, due to the toxicity of metals and their accumulation in aquatic habitats. Heavy metals, in contrast to most pollutants, are not biodegradable, and they undergo a global ecological cycle in which natural waters are the main pathways (Tam and Wong, 1995). Heavy metal enrichments of surficial sediments have been noted in numerous coastal environments (Chow et al., 1973; Bruland et al., 1974; Goldberg et al., 1977; 1978; 1979; Skei and Paus, 1979; Katz and Kaplan, 1981; Lyons et al., 1983). Most authorities have assumed that such enrichments above a baseline concentration represent as anthropogenic presence and, furthermore, patterns of enrichment have been used to describe the variations in chronology of contamination of an environment.

In the majority of studies of coastal and non-marine environments emphasis has been placed on anthropogenic inputs, particularly the burning of fossil fuels, as the cause of Cu, Pb and Zn enrichment (Bruland et al., 1974; Erlenkeuser et al., 1974; Suess and Erlenkeuser, 1975; Goldberg et al., 1977; 1978). Present anthropogenic inputs of heavy metals into the environment far exceed natural inputs (Nriagu and Pacyna, 1988); the former may pose health risks in areas where metals accumulate. The impact of heavy metal pollution to coastal and estuarine areas. Physical, chemical and biological effects may be seen in estuarine and coastal environments (Ellis, 1987) and sediments are a medium of transport, accumulation and storage of pollutants (Forstner and Schoer, 1984). indicators of environmental quality (Literathy et al., 1987), and a benthic biota damage agent (Litlepage et al., 1984).

Marine sediments can be a sensitive indicator for both spatial and temporal trend monitoring of contaminants in the marine environment (Larsen and Jensen, 1989) and as a result they have formed an essential component in many international monitoring programmes (North Sea Task Force, 1993). The impact of heavy metal pollution to coastal and estuarine areas could be substantial because of the variety of inputs to these areas; potential sources include riverine inputs, land runoff (both include treated and untreated sewage (Galloway, 1979) and industrial effluents (Gross, 1978) atmospheric deposition and coastal waters (Callaway et al., 1998). Further concentration of heavy metals in sediments reflects both logical mineralogy and the origin and nature of sediments (e.g. grain size, clay, organic content etc.,). Sediments have been used extensively as indicator of chronological pollution of coastal areas, including both subtidal sediments (Santschi et al., 1984; Schmidt and Reimers, 1991; Swartz et al., 1991; Velette-Silver et al., 1993) and intertidal wetland sediments (Griffin et al., 1989; Bricker, 1993).

Modern society drives us to couple industrial and agricultural practice to the increasing use of a wide range of chemicals. These chemicals, their break down products and by-products generated as part of their production will often end up in the final reservoir of many of the waters of our wastes of our society, the sea. The issue that arises in these circumstances is whether the presence of residual concentrations of these compounds represents a risk to man and to biota in the marine environment (Michael et al., 2002). Heavy metals are introduced into the marine environment in a number of ways. They may be deposited in the sea "naturally" as a consequence of erosion from ore bearing rock, wind blown dust, volcanic activity and forest fires. Increasing however, they are introduced via contaminated rivers, marine out falls and through the deliberate dumping of wastes in coastal waters (Gregory et al., 2002).

Potential impacts from heavy metals are generally restricted to locations adjacent to major cities or industrialized areas on the coastal fringe and to site draining areas of intensive agriculture. Once introduced into the marine environment, heavy metals have the potential to affect sediment nutrient cycling, cell growth and regeneration as well as reproductive cycles and photosynthetic potential of marine organisms (Bricker, 1993; Burton and Liss, 1976). Results of Australian studies of marine environmental metal contamination indicate that surficial sediments adjacent to most urbanized and industrialized estuaries are contaminated with metals, particularly Pb and Zn.

Coastal reef areas are being heavily impacted by increasing sediments from terrestrial origin, including run-off and river inputs (Batley, 1996). The detrimental effect of sediments on the structure of coral reef communities is well documented. However, these effect on specific coral species have been more variable depending on the type and size of sediment, frequently of the load, clearing ability, colony morphology and species resistance (Batley, 1995; 1996; Esslemont, 2000; Elizalde et al., 2002).

The biggest problems with heavy metals are that they are persistent (remain in the environment unchanged for years), and they bioaccumulate (increase in concentration as they go up the food chain). So, in addition to posing a thread to the health of coral reefs around the world, toxic metals also pose a long-term public health risk, especially for those human population hat rely on fish for protein .

In an area like Lakshadweep, where people have lived depending on their primary links to the ecosystem and productivity pattern were not so energy intensive, the concept of pollution is very new. An evaluation is necessary to assess whether pollution from different sources is taking its toll on the ecosystem inspite of being declared as the 'no industry zone'.

In this study an attempt has been made to pattern of enrichment of nine metals (Cu, Cr, Co, Ni, Pb, Zn, Cd, Mn and Fe) in the different sedimentary environments of six inhabited islands - namely, Kavaratti, Kadamath, Minicoy, Androth and Kiltan – belonging to Lakshadweep archipelago. To assess inter-environmental variations of trace metals, study area of each island is geographically located into several compartments as land profile, lagoon profile and seaside profile. An artificial mangrove ecosystem of Minicoy Island is also selected for an inter ecosystem comparison (i.e., between reefs and mangroves).

MATERIALS AND METHODS

The materials and methods adopted are detailed in Chapter II. The station numbers indicating the different environmental compartments of each islands are given in Table 5.1.

Table No.5.1. Station numbers used in Figs. (Chapter V) are given in parenthesis for identifying the respective sampling sites.

Kavaratti	Kiltan	Kadamath	Minicoy	Androth
Core (south)	**Lagoon Profile**	Sea-side Profile	Lagoon Profile	Seaside core
Surface(1)	Centre (1)	Land-soil south (1)	Lagoon (1)	Surface (1)
30 cm (2)	Low water mark (2)	high tide South (2)	Intermediate (2)	0.5m (2)
60 cm (3)	Intermediate (3)	low tide south (3)	Berm (3)	1m (3)
120 cm (4)	Berm (4)	North soil (4)	Land (4)	Land core
Land (5)	Land (5)	north high tide (5)	Lagoon Inner (5)	Surface (4)
Berm (6)	Seaside Profile	north low tide (6)	Mangrove 1(6)	Core - 15 cm
Intermediate(7)	North-side St. 1 (6)	Lagoon - 1 (7)	Mangrove 2 (7)	Core - 30 cm
Lagoon (8)	North-side.St. 2 (7)	Lagoon –2 (8)		Core - 50 cm
Core (North)	North-side St. 3 (8)		Agathy	Core - 90 cm
Surface (9)	South-side St. 1 (9)		Lagoon Profile	
30 cm (10)	South-side St. 2 (10)		Lagoon 1 (1)	
60cm (11)	South-side St. 3 (11)		Lagoon 2 (2)	
90 cm (12)	Core Profile		Lagoon 3 (3)	
120cm (13)	Surface (12)		Intermediate 4(4)	
Ujrapally (14)	0.5 m (13)		Berm (5)	
	1.3 m (14)		Land (6)	

RESULTS AND DISCUSSION

Spatial variability in the distributions of trace metals except iron for the islands, Kavaratti, Kadamath, Agathy, Androth, Kiltan and Minicoy are give respectively in Fig. 5.1 to Fig.5.6. The spatial distribution of iron is given separately in Fig. 5.7 for better a graphical presentation.

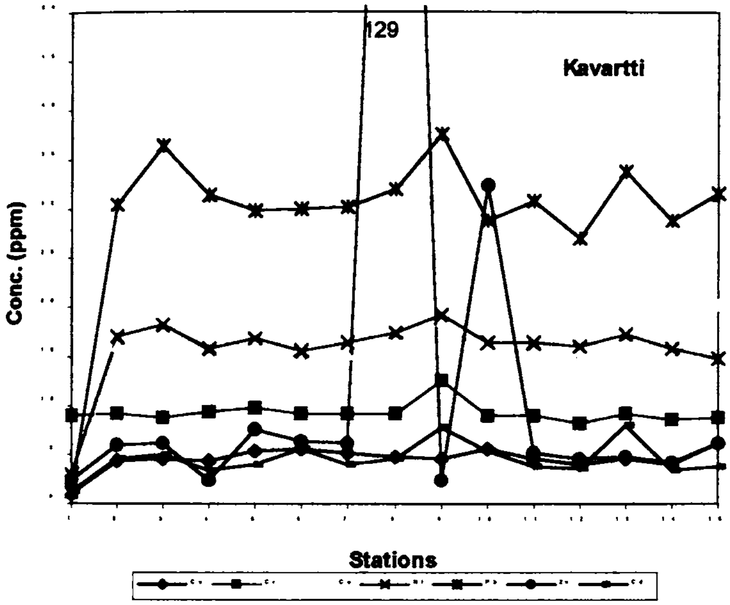


Fig.5.1 Spatial variability in the concentrations of trace metals in Kavaratti

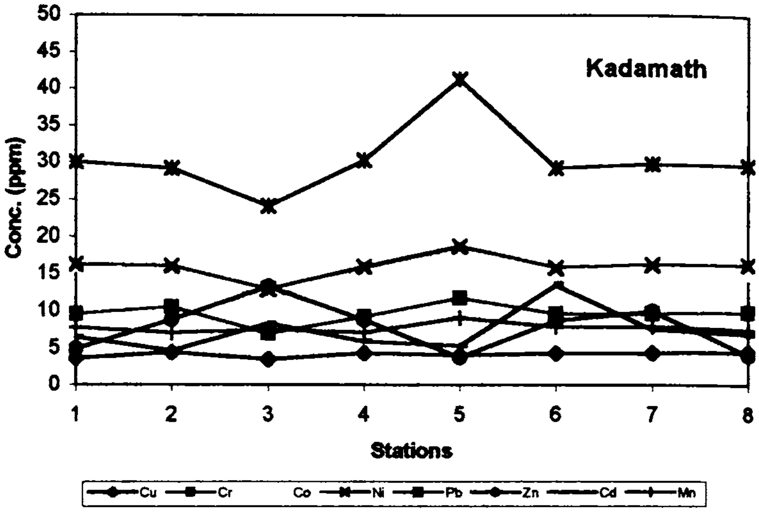


Fig.5.2. Spatial variability in the concentrations of trace metals in Kadamath

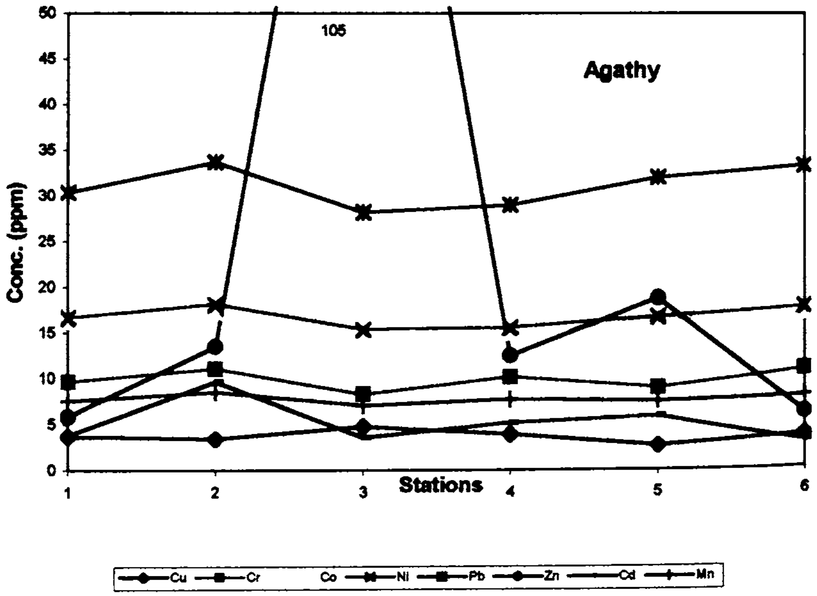


Fig.5.3 Spatial variability in the concentrations of trace metals in Agathy.

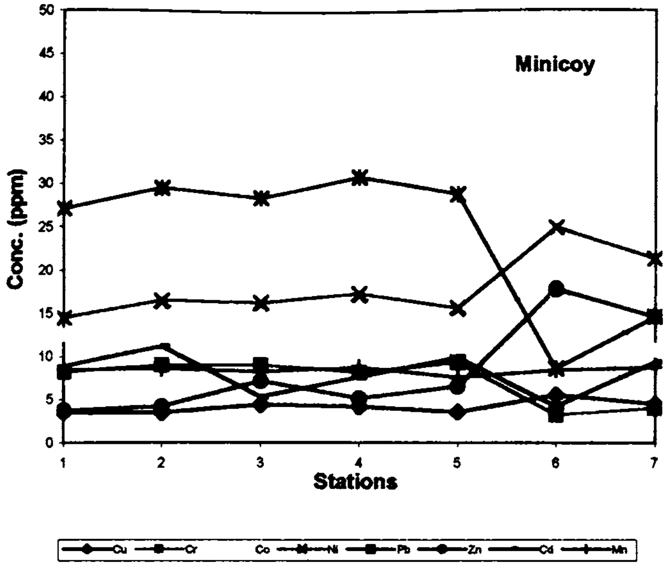


Fig.5.6 Spatial variability in the concentrations of trace metals in Minicoy.

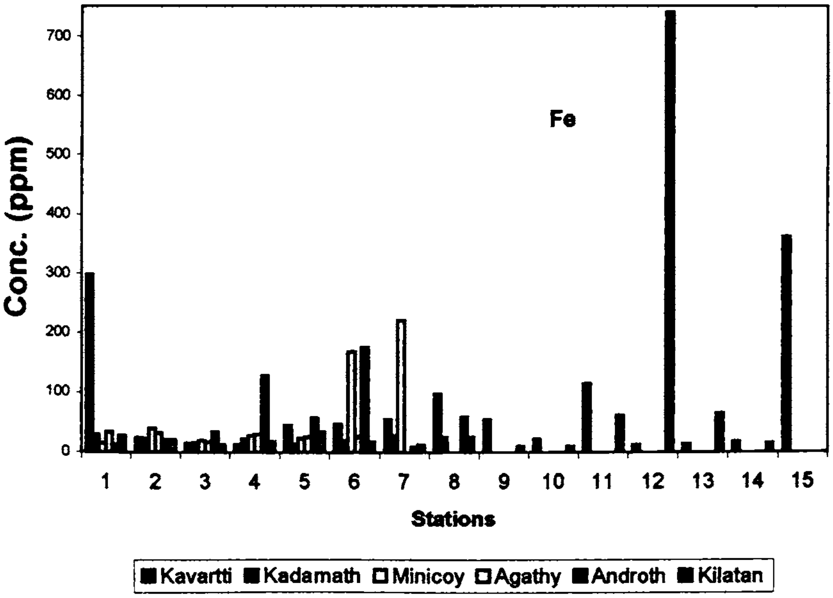


Fig.5.7. Spatial variability in the concentrations of Fe among the stations in the six islands.

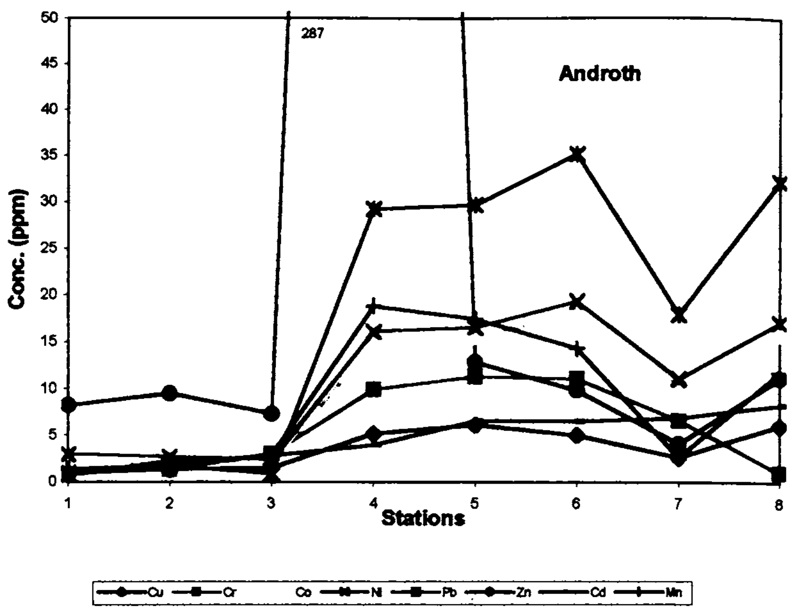


Fig.5.4 Spatial variability in the concentrations of trace metals in Androth

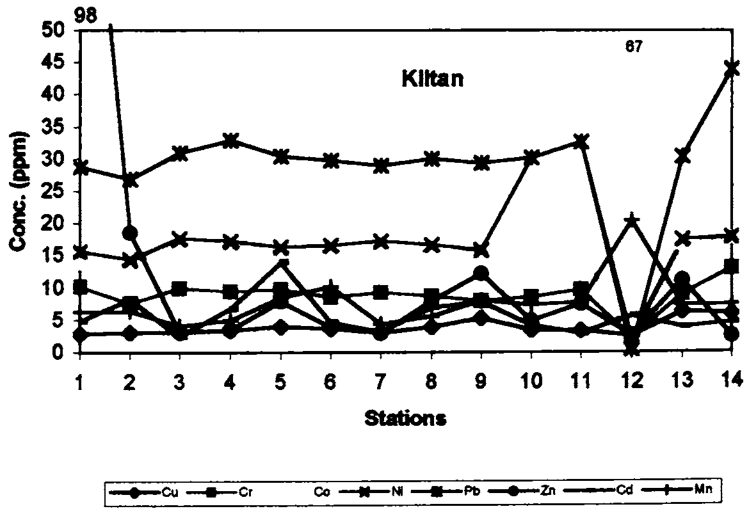


Fig.5.5 Spatial variability in the concentrations of trace metals in Kiltan.

Copper

Copper is an essential element for all living organisms as it acts as a catalyst for many enzyme systems, and is also important as an electron carrier in intracellular structures (Depledge and Rainbow, 1990). Copper is required in relatively low concentrations compared with other essential elements such as zinc. Higher concentrations of copper are the basis for common fungicides and molluscicides, and it is thought that their higher concentrations disrupt protein – binding system and interfere with metabolism (Depledge and Rainbow, 1990).

Copper concentrations in seawater ranges from 8 x 10^{-4} $\mu g\ l^{-1}$ in pristine open ocean, upto 29.2 $\mu g\ l^{-1}$ at highly polluted sites (Sadiq, 1992). The water quality guidelines generally state the copper concentrations in marine waters should not exceed 5 $\mu g\ l^{-1}$. The toxicity of copper to marine organisms is fairly well documented, as a result of its widespread use in anti foulant coatings as well as its presence in industrial, urban and agricultural discharges (Philips, 1995).

Considering the variations of copper among the core profiles of six islands, no definite pattern was observed for the enrichment of metals. The core samples collected from the southern part of Kavaratti island as well as the core profile of Androth island (sea side) showed almost similar distribution pattern in which lowest concentration was at the surface and highest at maximum depth of the selected core (1.2 m and 1 m respectively). The core profiles of northern side of Kavaratti island, Androth and Kiltan land samples displayed similar pattern by observing maximum concentration at the surface and minimum at intermediate depth of the cores

(≈ 0.5 meters). In the lagoon profile of Kavaratti island, even though no significant variations were observed, the highest concentration was reported for lagoon sediments and lowest for land samples – in which a decreasing order of metal concentration was observed on tracing from lagoon to land. The soil sample collected near Ujra mosque, recorded a copper concentration of (6.15 mg kg^{-1}) which was slightly higher than that reported for core as well as seaside profile. Concerning the variations of copper in the lagoon profile of Minicoy, no significant variations were observed in the metal concentrations among the sampling sites. The five stations recorded the following order of metal enrichment. Discussing about Kadamath, lagoon samples recorded comparatively higher value than those collected during high tide and low tide stations, though they have-not shown any remarkable concentration range.

In Kiltan Island, tracing the behaviour of copper in the lagoon profile, concentrations gradually increased from lagoon (2.83 mg kg^{-1}) towards the back-slope (3.97 mg kg^{-1}). In Agathy Island, as in the case of other islands, no wide differences in concentrations were observed between stations. Among the selected stations, lagoon sample recorded the highest value (4.77 mg kg^{-1}), whereas lowest was in the berm (2.61 mg kg^{-1}).

The spatial variability of copper recorded here 0.96(Kavaratti)-6.21(Kiltan) mg/kg are below the limit of pollution. This is comparable with the values reported by Anandaraj (2002) for Kavaratti (0.3-2.8mg/kg) and Minicoy (3.3-6.2mg/kg) islands. Since copper has a strong affinity for clays, iron and manganese oxides, and carbonate materials, residues are often elevated in sediments in both fresh and marine sediments. In Great lake.

Mudroch et.al. (1988) reported copper values in the range 109-206,5-207.3-8,15-54 and 30-173 mg/kg from the depositional basin of Ontario, Erie, Huron, Michigan and Superior respectively. Highly polluted parts of Chesapeake Bay (USA) contain copper in the range, 250-1500 mg/kg dry weight (Sinex and Wright, 1988). Mohapatra and Rengarajan (2000) recorded copper concentration 1.6μg/g for Mandapam coast and 8.7mg/kg for Tuticorin Bay (stations significant as near to coral reef ecosystem). Copper concentration in the coastal sediments of bay of Bengal was reported to be 26mg/kg (Sasamal et.al.,1987). Important sources of copper towards the aquatic environment include sewage, coal combustion, mining, fertilizers, copper fungicides, petroleum refining and paper and pulp mills..

Iron

Iron is the most abundant element in the planet earth, and fourth most plentiful in the lithosphere, where O, Si, Al are present at higher concentrations. It occurs in a variety of minerals, including oxides, sulphides, carbonates and silicates. In most aquatic ecosystem, however the concentrations of dissolved iron are very small, with that in oceanic waters being about $3\ \mu g\ l^{-1}$, and that in freshwater averaging slightly more (Bowers and Huang, 1987; Balls et al., 1997). Though some polluted waters, notably aired more drainage, may contain much greater concentrations of Fe. The best-documented mechanism for Fe cycling is via oxido-reduction and is most readily observed in environments where oxic and anoxic sites are in close proximity or juxtaposition, such as freshwater and marine sediments, and clay soils (Langston and Bebianno, 1998).

Discussing the variations of Fe in the core samples, in Kavaratti, the core profile of the southern part of the island showed maximum (297.64 mg kg^{-1}) at the surface and minimum at 0.9 m depth (13.15 mg kg $^{-1}$) whereas in the northern side, maximum was at 0.3 m depth (114. 46 mg kg $^{-1}$) and minimum at 0.6 m (12.58 mg kg $^{-1}$).

In the core profile of Androth island, the seaside recorded lowest value at the surface which gradually increased towards 1 m depth. In the land profile, comparatively higher concentrations were for the surface and 0.3 m depth samples. The lowest concentration (8.82 mg kg $^{-1}$) was reported at 0.5 m depth. Regarding Kiltan core profile, concentration decreased from surface (739.81 mg kg $^{-1}$) towards 1.3 m depth (15.55 mg kg $^{-1}$). Tracing the features of Kadamath, in the southern side, soil samples from land recorded maximum concentration (29.09mg/kg) and the lowest was for low tide samples (16.45mg/kg) ,whereas, towards the north high tide samples recorded the lowest concentration (14.04mg/kg). The lagoon side of Kadamath displayed concentration comparable to that of land.

The sediment collected near Ujra mosque in Kavaratti, showed highest concentration of iron (361.98 mg kg $^{-1}$). In the lagoon profile. concentration of iron gradually increased from lagoon towards the berm. In Minicoy island, the concentration of iron in the sea side profile was in the order; lagoon intermediate > land > lagoon inner > berm > lagoon. a similar trend was also displayed in the Fe concentration of Agathy island.

Concerning the behaviour of Fe in the lagoon profile of Kiltan. though wide fluctuations in variations were not observed, the land (back-slope) recorded the maximum value. In the seaside profile of Kiltan.

sampling was from the northern and southern side ; on both sides samples collected near the beach rock recorded the maximum value.

The concentration range of iron reported for this study 8.82(Androth)-739.81(Kiltan) mg/kg, is not in the level of pollution. The most important sources of iron being various industrial activities (chemical, dye, iron and steel industry etc.,) and they are absent in this "no industry zone" region of Lakshadweep. The values reported by Anandaraj (2002) for Kavaratti was in the range 13.2-196 ppm ,whereas, for Minicoy it was 26-668ppm. Rao (1996) has given a high range of Fe(212-4435ppm)for the bulk sediments of the modern carbonate. High concentrations (0.7-1.8%) was reported for offshore areas of the Arabian Gulf (Samhan et. al.,1987), the Ganges estuary(1.2-4.6%)(Subramanian et. al.,1989) and Bombay Harbour(6.2-7.6%) (Mohapatra and Rengarajan, 2000).

Chromium

Chromium is one of the least toxic of the trace elements on the basis of over-supply and essentiality (Forstner and Wittmann, 1983). Total anthropogenic discharges of chromium to surface water ranges from 45×10^{3} to 239×10^{3} MT year (Nriagu and Pacyna, 1988). The anthropogenic sources of chromium include domestic waste water discharges from central and non-central sources, atmospheric fallout, input from rivers, damping of sewage sludge and industrial waste etc.

Discussing the behaviour of chromium among the six islands, no definite accumulation patterns were observed. In the core profile of Kavaratti, no wide fluctuations were observed among various depths, among these, lowest values were at 0.6 m depth.

In Androth island, seaside core profile concentration of chromium increased from surface towards 1 m depth, whereas in the land core profile concentration decreased from 0.15 m towards 0.90 m where minimum value was observed. In Kiltan, observation was similar to that of Androth lagoon core profile, in which maximum concentration (12.97 mg kg^{-1}) was observed at 1.3 m depth.

The sample collected near Ujra mosque recorded a value of 8.74 mg kg^{-1} . In Minicoy Island, the maximum concentration was in the inner part of the lagoon. No wide fluctuations or regular distribution pattern were observed for chromium concentrations in the seaside profile of Kiltan and Kadamath islands.

The concentrations of chromium reported for this study 0.92 (Androth)-12.97 (Kiltan) mg/kg are very low, indicating insignificant contribution of this metal form various sources like coal burning, fertilizers and petrochemicals. Studies on the sedimentary environment of Kavaratti and Minicoy islands recorded values in the range 0.8-5.8ppm and 0.4-6.8ppm respectively (Anandaraj. 2002).

Cobalt

Cobalt is widely distributed throughout the human body. without excessive concentration in any particular organ or tissue (Forstner and Wittmann. 1983). Cobalt is relatively scarce in the earth's crust. but is required by human body in vitamin B_{12} which is a cobalt (III) complex to form hemoglobin. Cobalt in uncontaminated freshwater sediments is generally found at 1-10 µg g^{-1} dry weight, increasing 25-50 µg l^{-1} in anthropogenically contaminated areas.

No regular trend was observed for the distribution of cobalt in the core profiles of Kavaratti island. This was also true for Androth island in which no periodic trend was observed to explain the metal enrichment phenomena of core profile whereas in Kiltan island, cobalt concentration showed an increasing trend from surface (1.11mg kg^{-1}) towards 1.3 m depth (17.66 mg kg^{-1}).

In the lagoon profile of Kavaratti, the concentration of cobalt gradually decreased from land towards the lagoon, even though, vast differences in concentrations were not observed among stations. The maximum cobalt concentrations recorded in Kavaratti island was near Ujra mosque (20.11mg kg).

Discussing the features of Kiltan, no regular pattern was observed for cobalt variations in the lagoon profile. In the sea side profile, towards the northern and southern profiles, no large variations were observed in metal concentrations among the stations and so also no characteristic distribution pattern. In Kadamath, except the low tide samples towards south (11.74mg/kg) and high tide samples towards north (18.35mg/kg) , all other stations displayed uniform concentration.

The range of concentration recorded for cobalt in the present study was 1.11(Kiltan)-18.58 mg/kg (Kavaratti) very low indicating insignificant sources of metal input. Anandaraj (2002) observed concentrations in the range 1.2-13ppm and 3.3-6.2 ppm respectively for Kavaratti and Minicoy islands. Appreciably higher residues, averaging 37 $\mu g g^{-1}$ were found in Thane creek, which receives industrial wastes from the city of Bombay (Mohapatra and Rengarajan, 2000). Most important sources of Co are alloys, high-speed tools and turbines making and none of them is prevailing in the area of study. Cobalt in uncontaminated fresh water sediments is generally found at 1-10dry weight, increasing to 25-50 in anthropogenically contaminated areas.

Nickel

The major source of discharges of nickel is municipal wastewater followed by smelting and refining of non-ferrous metals (Nriagu and Pacyna, 1988). The anthropogenic sources of nickel include mining and smelting of nickel bearing ores, use of fossil fuels particularly coal, use of crude oil and its products. The toxic action of Ni is due to its ability to replace essential metals in the metallo-enzymes resulting in the disruption of metabolic pathways. Total nickel residues in sediments typically range upto 100 µg g^{-1} dry weight, but may fall below 1 µg g^{-1} in some unpolluted coastal waters. Enrichment factors (concentration in sediment concentration in earth's crust) typically range form 1 to 12 (Sinex and Wright, 1988).

Illustrating the variations of Ni in the core profiles of various islands, as in the case of other metals no generalization can be done in the metal enrichment pattern, particularly in Kavaratti island. In the seaside core profile of Androth, concentration slightly decreased from surface towards 1 m depth whereas, in the core profile of Kiltan, concentration gradually increased from surface towards 1.3 m depth. In Kiltan island no definite pattern or wide variations were observed in the metal concentrations lagoon profile as well as northern side seaside profile. Two important sources of Ni in this region can be automobile paints and the use of fertilizers. Tracing the features of Kadamath, the low tide samples recorded the lowest concentrations towards the northern as well as southern side, whereas, highest was reported for high tide samples towards north (18.82mg/kg). No wide differences were observed between land and lagoon samples.

The proposed variation of nickel in this study was in the range,2.27-33.49mg/kg(both for Kiltan). Total nickel residues in sediments typically range upto 100 µg/g dry weight, but may fall below 1 µg/g in some unpolluted coastal waters. Maximum residues are typically associated with nickel-bearing geologic formations and with the discharge of industrial and municipal wastes. The Indian average of total nickel in river bed sediments is only 37 µg/g . Values in the range 2.5-16.9ppm and 0.2-19.4ppm were reported respectively for Kavaratti and Minicoy islands (Anandaraj, 2002).

Lead

Lead is a non-essential and potentially toxic – element which is present in the tissue and organs of mammals. In fresh water, lead forms a number of complexes of low solubility with many of the major anions, including hydroxides, carbonates, sulphides and (less commonly) sulphates. The average concentration of lead in river and ocean waters is 0.1 and 0.003 $\mu g\ l^{-1}$ respectively (Martin and Fitzwater, 1988). The main sources of input of lead include atmosphere fallout, smelting operations and automobiles. Although maximum residues are often associated with poorly treated industrial or mining effluents, the impact of lead into remote waters is primary due to atmosphere deposition (Evans and Dillon, 1982; Mortimer and Rae, 2000).

In the distribution pattern of lead among the six islands, a regular pattern was observed only in Kiltan in which concentration gradually increased from surface towards 1.3 m depth. In the core profiles of Kavaratti and Androth islands no wide fluctuations or characteristic patterns were observed in the distribution of lead. In the seaside profile of Kavaratti, as in the case of Cr, Co and Ni, concentration of lead also decreased. Similar pattern of distribution was observed in the lagoon profile of Minicoy and Agathy islands where lead behaved similar to that of Co and Ni. Discussing about Kiltan, the pattern of distribution of lead in the seaside as well as in the lagoon side profile was highly monotonous in which neither regularity in distributions nor considerable variations among stations was observed. In Kadamath, among the nine metals studied, lead displayed higher concentration than for other metals. The values were in the range24.11-41.26mg kg.

The overall range of this study was 0.75(Androth)-43.91(Kiltan) mg/kg. Approximately 99% of the lead entering the oceans with the suspended load of rivers is deposited in the sediments of estuaries and continental shelves(Craig, 1980). Residues in the 15-50µg g dry weight range were frequently reported for coastal/estuarine sediments (Samhan et.al.,1987; Araujo et .al.,1988; Subramanian et.al.,1989), and may exceed 400µg/g near waste outfalls (Stull and Baird, 1985): Stull et al., 1986 Luoma and Phillips, 1988).extremely high concentrations are reported for fresh water sediments receiving industrial or municipal wastes. The important sources of lead in the study area are exhaust of ships and aircrafts fertilizers, paints, oil refinery process and the user of leaded petrol.

Zinc

Zinc is an essential element for all biological systems (Depledge and Rainbow, 1990) and zinc requirements for organisms are usually higher than for copper. Zinc can also be more abundant in the environment than other trace metals; therefore organisms have developed several metabolisms for bioregulation (Depledge and Rainbow, 1990). Zinc concentrations recorded throughout the world's open oceans average 5 µg l^{-1} (Riley and Chester, 1971).

Considering the variations of zinc among the profiles of six islands, in Kavaratti, no significant variations were observed in the concentrations of Zn at various depths in the southern side core profile. In the northern part of the surface samples reported the maximum (32.48 mg kg^{-1}) whereas minimum was at 1.2 m (4.21 mg kg^{-1}). In Androth island, in the seaside core profile, the distribution pattern of zinc was highly monotonous depicting no significant change with depth, whereas in the land core profile the surface samples recorded a very high value of (28.71 mg kg^{-1})) compared to other depths. In Kiltan, lowest concentration was reported at maximum core depth, 1.3 m (2.39 mg kg^{-1}). In the seaside profile of Kavaratti, though wide fluctuations were not observed among stations, a comparatively higher concentration was at berm (129.59 mg kg^{-1}). The concentration recorded near Ujra mosque was 6.25 mg kg^{-1} . Almost contrary behaviour was observed for lead in the lagoon profiles of Minicoy and Agathy islands. In Minicoy, no wide fluctuations were observed among stations, the highest in the berm and lowest in the lagoon. In Agathy, the lagoon samples recorded a comparatively higher concentrations (104.89 mg kg^{-1}) whereas lowest was in the land (6.02 mg kg ^{1}). In Kiltan island, no characteristic trend was displayed by zinc in the lagoon as well as seaside profiles, pattern of distribution was highly in random. Discussing about Kadamath, in the northern side concentration were more or less uniform. In the southern part, soil samples recorded the lowest concentration (4.83mg/kg) and the low tide samples recorded the highest concentration (13.26 mg kg ^{1}).

Considering the range of zinc concentration in the study area, it was found to be 2.33 mg kg ^{1} (Kavaratti)-287.09 mg kg ^{1} (Androth). Relatively high concentrations of zinc can be found near major municipalities and coal burning power stations. Poulton (1987), for example, reported that a core sample from Hamilton Harbour(a major steel-producing region in Canada) contained 5,700 µg/g of zinc. Sediments from uncontaminated waters contain 5-50 µg/g range of zinc. The concentration of zinc reported for Mandapam coast and Tuticorin Bay was 3.0 and 4.9 µg/g respectively (Mohapatra and Rengarajan, 2000). The values recorded by Anandaraj (2002) were in the range 1.4-12.5 ppm for Kavaratti and 0.6-38.6ppm for Minicoy.

The major sources of zinc in relation with activities of island are combustion of coal, pesticides, and automobiles, domestic and agricultural wastes.

Manganese

After Fe, Mn is the most abundant heavy metal in the lithosphere. Whilst its average concentration is only 1/50th that of Fe, local concentrations of Mn can vary widely. In freshwater, the average concentration of soluble Mn is about 8 µg l^{-1}, whereas in seawater is less than 0.2 µg l^{-1} . The major processes involved in the manganese cycling in aquatic systems are oxidation and reduction. The reactivity of manganese in aquatic system exhibits a complex behaviour with conservative and non conservative nature depending upon a number of factors such as the concentration in sediment, water and suspended particles, ionic strength , pH, Eh etc. (Burton and Liss, 1976; Graham, et al.. 1976; Duinker et al ., 1977; Evans et al., 1977; Langston and Bebianno, 1998).

Considering the variations of manganese in the core profiles, as in the case of most other metals no regular pattern was depicted to explain their variations. This was true for the lagoon side profiles of Kavaratti, Minicoy and Agathy Islands; all these islands recorded no significant changes in concentrations. In Kiltan, the trend was highly randomness, so it was difficult to formulate a definite trend. Concerning the variations in Kadamath, concentrations were more or less uniform, the highest(9.03mg/kg) was recorded by the high tide sample(north).

The present study showed a variation of 1.31(Androth)-20.44mg/kg (Kiltan). The values reported by Anandaraj (2002) for Kavaratti was higher than this study (28.2-73.5 ppm) whereas he reported values in the range (8.8-35.8 ppm) for Minicoy. Rao (1996) has given a wide range of manganese content in the sediments of modern carbonates. Manganese in the sediments of North sea near Belgium averaged 261µg/g dry wts and was enriched (438µg/g) in the clay/silt fraction (Araujo et.al.,1988); the corresponding values for the Scheldt Estuary (The Netherlands) were reported by Araujo et.al. (1988) to be 117-434µg/g, respectively. Samhan et.al. (1987) reported values in the range 216-528 µg/g in bulk samples from

Arabian Gulf. Sasamal et al., (1987) observed manganese concentration 529µg/g from Bay of Bengal.

The important contribution of manganese is from iron and steel industries, glass and ceramic industries and paint industry. Since none of these processes are active in this zone, we can justify the relative low concentrations recorded for manganese in this area.

Cadmium

Cadmium is one of the most intensively studied heavy metals with regard to its interaction with marine biological activity (Abe, 2002). Cadmium is a relatively rare element, with concentrations in seawater ranging from 2 x 10^{-4} to 2.9 µg l^{-1} (Sadiq, 1992). However, in polluted estuaries or harbours and ports, values upto 50 µg l^{-1} has been reported (Grasshoff et al., 1999). The water quality guidelines normally suggest that cadmium in marine waters should not exceed 2 µg l^{-1}. Cadmium is appreciably enriched in coastal marine sediments. Cadmium is of considerable environmental and health significance because of its increasing mobilization and toxicity to man life forms. The anthropogenic sources of cadmium include – photographic industries, manufacture of storage batteries, glass ceramics, pigments, biocides, electro plating and alloy industry.

Except that in the Androth island land core profile, highly irregular distribution pattern with depth was observed in all other core samples. This was true for the seaside profiles also, where it was very difficult to formulate a regular trend. In Kadamath, lagoon as well as land soils recorded a uniform concentration range. Regarding the variations with tide.

in the southern side highest was reported at low tide (8.29 mg kg^{-1}) and lowest at high tide(4.61 mg kg^{-1}) and towards the north the reverse thing happened in which low tide samples recorded the highest value(13.51 mg kg^{-1}).

The range of values reported for this study was, 0.91(Androth)-15.31 mg kg^{-1} (Kiltan). Cadmium is appreciably enriched in coastal marine sediments and waters. Cadmium in uncontaminated freshwater sediments is generally detected to be 0.1-1.0 µg/g dry weights, increasing to 4-10µg/g in contaminated areas (Mohapatra and Rengarajan, 2000; Mudroch et.al.,1988). Among the nine elements studied in these islands, comparatively higher values were recorded for cadmium, which is found to be exceeding the limits of permissible concentrations. This requires a detailed assessment based on contamination factor and pollution load index, which are discussed later. It has been reported that cadmium in sea water is regulated by marine geochemical processes that include an uptake by phytoplankton in surface waters, consequential decomposition and remineralization in deep waters, and physical mixing of different water masses.

In an attempt to picturize the distributional characteristics of metals among the selected core profiles, the results can be summarized as follows.

In this study core samples were collected from three islands, namely, Kavaratti, Kiltan and Androth leading to the possibility of discussion on the basis of inter-island and intra-island variations. In Kavaratti, two cores were collected, one from the northern end and other from the southern part, and so also for Androth, in which one core was collected from the land and the near the sea. In Kiltan, only one core was collected upto 1.3m depth within the central part of the island.

In Kavaratti, distinct variations were observed in the behaviour of metals towards the northern as well as southern part of the island. In the northern side, Fe, Mn, Cu, Zn concentrations displayed maxima at the surface, whereas, for the other metals Cr. Co, Ni, Pb and Cd. maximum enrichment was at 90cm depth. Towards the southern side, only iron and manganese displayed surface maxima, while, the other metals. Ni, Pb, Zn. Cd, Co and Co were found to be minimum at the surface. In Kiltan Island, Mn, Fe and Cd displayed maximum surface concentrations. For other elements, i.e. Cu, Cr, Co, Ni and Pb surface minima were displayed followed by maximum enrichment at 1.3 m depth. Discussing about Androth, remarkable differences were displayed by the core profiles of land and seaside samples. In the land core, metals like Co, Ni, Pb, Fe, Zn and Mn exhibited maximum concentrations in the surface and was found to be minimum at 0.5m depths. Contrary to this behaviour, towards the seaside, except nickel, other metals i.e., Cu, Cr, Mn, Cd and Fe displayed maximum concentrations at 1m depths, whereas these metals displayed minimum values towards the surface.

Justifying these observations, in Kavaratti, the surface samples are characterized by higher percentage of medium sand content and organic matter enrichment (22.27%), compared to other depths. pH was slightly reducing; which can be the reason for surface enrichment of metals like Fe and Mn. In Kiltan Island, organic carbon content of surface as well as 1.3 m depth samples was very high (28.69% and 31.33% respectively). Here also the surface samples are characterized by high amount of iron and manganese, whereas, at 1.3 m depth maximum concentration of Cu, Cr, Co, Ni and Pb was found. Compared to other depths, pH of the surface samples was slightly reducing. Regarding the textural characteristics, surface samples were sandy (fine sand), whereas, at 1.3 m depth, it was predominantly silty-clay. This pattern was reflected in Androth Island also, here, Cu, Cr, Mn, Cd and Fe showed maximum enrichment at 1m depths which was characterized by high organic carbon content (14.10%) and a reducing pH.

The redox sensitive iron and manganese hydroxides and oxides under oxidation condition, constitute significant sink of heavy metals in aquatic systems (Wittmann, 1983). This hydroxide and oxide readily sorb or co-precipitate cations and anions; even a low percentage of $Fe(OH)_3$ has a controlling influence on the heavy metal distribution in aquatic system. Iron oxide coating is an important factor responsible for the concentration of trace elements in the aquatic environment (Burton and Liss, 1976). Chemically mobile elements are concentrated in fine particles than coarser bed sediments. Several investigations repeatedly advocated that metal scavenging ability of clastic sediments increases as the particle size decreases (Gibbs, 1973; Panigrahy et al., 1997; Unnikrishnan, 2000; Balachandran, 2001). Increased organic carbon levels in the fine particulates catalyze the metal scavenging ability (Jayasree and Nair, 1995; Unnikrishnan, 2000).

Synoptic relations

The salient features of the spatial distributional characteristics of trace elements among the six islands can be intercorrelated as follows,

Metal–metal interrelation – highlighting similar sources of input or chemo behavioural pattern

- Metal – pH relationships – reflecting redox sensitive metal ad/desorption from sediments.
- Metal – organic carbon co-variability –focusing on metal webbing into biorhythm
- Metal particle size/nature connectivity – indicating the particle surface area/nature control on metal loading.

Discussing the above facts, significant correlations were formulated by evaluating Pearson correlation coefficients for the dependent variables (Table 5.2 a, b, & c; Table 5.3). In this attempt, copper displayed significant positive

Fig.5.2a. Correlations among metals and between organic carbon.

kavaratii	Cu	Cr	Co	Ni	Pb	Zn	Mn	Cd	Fe	)rg. C
Cu	1.000									
Cr	0.066	1.000								
Co	0.843	0.209	1.000							
Ni	0.760	0.268	0.914	1.000						
Pb	0.783	0.287	0.958	0.975	1.000					
Zn	0.120	-0.038	0.107	0.159	0.103	1.000				
Mn	0.225	0.043	0.025	-0.212	-0.123	0.103	1.000			
Cd	0.460	0.537	0.589	0.683	0.697	0.060	-0.108	1.000		
Fe	-0.220	-0.103	-0.301	-0.636	-0.515	0.010	0.708	-0.463	1.000	
Org.C.	-0.345	-0.194	-0.511	-0.644	-0.640	-0.036	0.487	-0.377	0.568	1.000

Kadamath	Cu	Cr	Co	Ni	Pb	Zn	Mn	Cd	Fe	)rg. C
Cu	1.000									
Cr	0.552	1.000								
Co	0.414	0.932	1.000							
Ni	0.459	0.957	0.988	1.000						
Pb	0.255	0.864	0.921	0.937	1.000					
Zn	-0.077	-0.799	-0.904	-0.870	-0.820	1.000				
Mn	-0.075	0.543	0.584	0.655	0.794	-0.578	1.000			
Cd	0.034	-0.327	-0.397	-0.316	-0.332	0.310	0.069	1.000		
Fe	0.180	-0.030	0.018	-0.028	-0.337	-0.067	-0.420	-0.069	1.000	
Org.C.	-0.252	-0.400	-0.423	-0.363	-0.434	0.211	0.068	0.837	0.294	1.000

Minicoy									
Cu	1.000								
Cr	-0.829	1.000							
Co	0.311	0.091	1.000						
Ni	0.902	-0.945	0.194	1.000					
Pb	-0.836	0.969	0.040	-0.940	1.000				
Zn	0.889	-0.939	0.025	0.958	-0.968	1.000			
Mn	0.244	-0.454	-0.188	0.356	-0.275	0.193	1.000		
Cd	-0.824	0.418	-0.461	-0.510	0.459	-0.519	0.009	1.000	
Fe	0.690	-0.941	-0.268	0.882	-0.908	0.908	0.444	-0.192	1.000

Fig.5.2b. Correlations among metals and between organic carbon

Agathy										
Cu	1.000									
Cr	-0.274	1.000								
Co	-0.730	0.670	1.000							
Ni	-0.547	0.743	0.964	1.000						
Pb	-0.674	0.693	0.970	0.971	1.000					
Zn	0.698	-0.727	-0.713	-0.590	-0.610	1.000				
Mn	-0.418	0.925	0.746	0.820	0.782	-0.645	1.000			
Cd	-0.435	0.430	0.450	0.497	0.489	-0.246	0.730	1.000		
Fe	-0.037	-0.303	-0.284	-0.469	-0.416	-0.232	-0.565	-0.769	1.000	
Org.C.	0.002	-0.151	0.090	0.013	-0.139	-0.180	-0.184	-0.176	0.335	1.000

Androth										
Cu	1.000									
Cr	0.608	1.000								
Co	0.940	0.716	1.000							
Ni	0.945	0.703	0.999	1.000						
Pb	0.954	0.685	0.998	0.999	1.000					
Zn	0.302	0.378	0.287	0.291	0.298	1.000				
Mn	0.921	0.753	0.865	0.870	0.874	0.552	1.000			
Cd	0.784	0.420	0.833	0.826	0.832	-0.115	0.527	1.000		
Fe	0.621	0.680	0.724	0.723	0.719	0.458	0.762	0.323	1.000	
Org.C.	-0.113	0.193	-0.257	-0.269	-0.256	0.268	0.100	-0.310	-0.007	1.000

Kiltan isl	Cu	Cr	Co	Ni	Pb	Zn	Mn	Cd	Fe	Org. C
Cu	1.000									
Cr	0.419	1.000								
Co	0.430	0.881	1.000							
Ni	0.094	0.541	0.668	1.000						
Pb	0.498	0.959	0.950	0.618	1.000					
Zn	-0.209	0.136	-0.048	-0.084	-0.004	1.000				
Mn	-0.138	-0.777	-0.881	-0.525	-0.803	-0.138	1.000			
Cd	0.065	-0.103	-0.077	-0.291	-0.066	-0.012	0.119	1.000		
Fe	-0.294	-0.826	-0.961	-0.612	-0.898	-0.115	0.914	-0.012	1.000	
Org.C.	0.358	-0.165	-0.473	-0.466	-0.252	-0.178	0.577	-0.146	0.607	1.000

Fig.5.2c. Correlations between trace metals and pH

Kavatti	Cu	Cr	Co	Ni	Pb	Zn	Mn	Cd	Fe	pH
pH	-0.266	-0.166	0.294	0.310	0.365	0.141	-0.368	0.063	-0.404	1.000
Kadmath										
pH	0.110	-0.010	0.173	0.110	-0.060	-0.066	-0.196	-0.444	0.713	1.000
Minicoy										
pH	-0.487	0.809	0.417	-0.737	0.817	-0.807	-0.011	0.025	-0.456	1.000
Agathy										
pH	0.089	0.521	0.249	0.293	0.315	-0.343	0.215	-0.471	0.278	1.000
Androth										
pH	0.666	0.405	0.731	0.725	0.725	-0.231	0.454	0.793	0.285	1.000
Kiltan										
pH	-0.404	0.041	0.523	0.412	0.448	-0.533	-0.687	-0.434	-0.304	1.000

Table 5.3. Correlations between metals and sediment particle sizes

Kavarti	Cu	Cr	Co	Ni	Pb	Zn	Mn	Cd
>1000 µm	-0.365	-0.114	-0.316	-0.305	-0.266	-0.202	-0.529	-0.478
1000-500 µm	-0.418	-0.227	-0.325	-0.274	-0.225	-0.269	-0.457	-0.421
500-250 µm	-0.220	-0.150	-0.285	-0.124	-0.112	-0.132	-0.195	-0.013
250-125 µm	0.120	0.554	0.091	0.279	0.190	0.472	-0.041	0.477
125-63 µm	-0.070	-0.162	0.023	0.011	-0.055	-0.137	-0.080	-0.055
<63 µm	0.318	-0.279	0.313	0.007	0.071	-0.173	0.528	-0.129
Kadamath	**Cu**	**Cr**	**Co**	**Ni**	**Pb**	**Zn**	**Mn**	**Cd**
>1000 µm	-0.398	-0.559	-0.620	-0.583	-0.396	0.548	0.033	0.797
1000-500 µm	-0.287	-0.283	-0.401	-0.442	-0.275	0.551	-0.239	0.314
500-250 µm	0.049	0.358	0.596	0.512	0.446	-0.291	0.264	-0.483
250-125 µm	0.074	0.225	0.164	0.212	0.008	-0.236	0.157	-0.183
125-63 µm	0.407	0.052	-0.059	0.061	-0.080	-0.445	-0.110	-0.053
<63 µm	0.421	0.076	-0.037	0.085	-0.057	-0.456	-0.089	-0.064
Agathy	**Cu**	**Cr**	**Co**	**Ni**	**Pb**	**Zn**	**Mn**	**Cd**
>1000 µm	0.714	-0.773	-0.786	-0.692	-0.683	0.998	-0.881	-0.196
1000-500 µm	0.189	-0.800	-0.686	-0.824	-0.789	0.498	-0.758	0.514
500-250 µm	-0.415	0.893	0.804	0.870	0.848	-0.748	0.906	-0.295
250-125 µm	-0.394	0.404	0.513	0.411	0.263	-0.738	0.421	0.023
125-63 µm	-0.687	-0.362	0.311	0.183	0.409	0.021	-0.105	0.627
<63 µm	-0.045	0.693	0.578	0.751	0.715	-0.311	0.623	-0.613
Androth	**Cu**	**Cr**	**Co**	**Ni**	**Pb**	**Zn**	**Mn**	**Cd**
>1000 µm	-0.623	-0.714	-0.549	-0.523	-0.548	-0.547	-0.613	-0.926
1000-500 µm	-0.631	-0.732	-0.565	-0.554	-0.562	-0.570	-0.633	-0.813
500-250 µm	-0.630	-0.731	-0.565	-0.554	-0.561	-0.570	-0.633	-0.811
250-125 µm	-0.640	-0.740	-0.570	-0.553	-0.568	-0.573	-0.638	-0.870
125-63 µm	0.538	0.649	0.463	0.446	0.460	0.466	0.537	0.807
<63 µm	0.645	0.744	0.577	0.562	0.574	0.580	0.645	0.856
Kiltan	**Cu**	**Cr**	**Co**	**Ni**	**Pb**	**Zn**	**Mn**	**Cd**
>1000 µm	0.330	0.101	0.305	0.324	0.153	0.453	-0.495	-0.149
1000-500 µm	-0.309	0.244	0.309	0.373	0.188	0.848	-0.545	0.079
500-250 µm	-0.314	-0.142	0.020	0.018	-0.103	-0.385	0.167	0.587
250-125 µm	-0.601	-0.846	-0.813	-0.823	-0.835	-0.403	0.930	-0.012
125-63 µm	-0.385	-0.861	-0.883	-0.891	-0.891	-0.340	0.902	0.013
<63 µm	0.388	0.401	0.093	0.056	0.359	-0.277	-0.004	-0.280

correlations with Fe, Mn, Co, Ni, Pb, Cr and Cd. Positive correlations of Cu with Fe and Mn, indicates a redox control in the distribution pattern, diagenetic mobility being controlled by redox cycles of Fe and Mn. These interrelations suggest that they are introduced from similar sources and behave in a chemically similar manner.

Studies on metal distributions in sediments (intertidal or subtidal) have also found high inter metal correlations (Santschi et al., 1984; Zwolsman et al., 1996; Basaham and El-Sayed, 1998). The surface enrichment of Cu appears to be controlled by diagenetic process in the sediments. During early diagenesis, P, Cr and Cu are released near the sediment – water interface (Bruland et al., 1974; Nair and Balchand, 1993), where they are likely adsorbed to the Fe-oxyhydroxides. While anthropogenic sources may be important in supplying Cu to the basins (Bruland et al., 1974), some Cu is clearly associated with the Fe-rich face. Since Cu – profiles are strongly influenced by diagenesis, they do not reflect the history of anthropogenic input.

Another important factor elucidated was the significant positive correlations of Fe and Mn with other metals, in additions to the significant positive correlations exhibited among these two. In Androth island, Fe and Mn displayed significant positive correlations with all other metals, but this is not true for other islands because some negative correlations were also observed for other elements with Fe and Mn. For example, in Kiltan except that with Fe, Mn displayed negative correlations with all other metals and with Fe it displayed a positive correlation (r = 0.914). In Minicoy island, considering the relationship of Fe with other trace metals on the basis of

Pearson correlation coefficient, it was significantly negatively correlated with Cr and Pb ($p>0.001$). In Kadamath and Agathy islands, contrary to the behaviour of other islands, Fe and Mn were negatively interrelated.

The behaviour of metals exhibiting positive values for Pearson coefficients are exhibiting similar source of anthropogenic inputs or the sedimentary environment (for example pH, particle size etc.,) affecting the deposition of these metals are more or less the same.

Fe and Mn oxides play a major role in the distribution of almost all trace metals. Iron and manganese are extremely important elements in aquatic geochemical processes because their various oxide and hydroxide species act as scavengers for a variety of trace metals (de Groot, 1976) by adsorption or lattice substitution processes. The positive correlations of Cr and Pb with Fe and Mn suggest their association with Fe-Mn oxides (Unnikrishnan, 2000; Panigrahy et al., 1997). Cobalt displayed significant positive correlations with Fe and Mn attesting the fact that cobalt occurs in association with Fe-Mn oxides, which are believed to be its common carriers (de Groot, 1976; Mohan, 1997).

The levels of significance of correlations exhibited were different for different metals in which low correlations indicate that these two metals behave differently from Fe and Mn, which are most strongly influenced by redox conditions. Griffin et al., (1989) found a higher correlation between Ni and Fe than for other metals; whereas, Zwolsman et al. (1996) indicated that Ni was co-precipitating with Mn not Fe, in salt marsh sediments from the Western Scheldt. Some of the metals exhibited Pearson correlation coefficient with Fe, the value being less than that of Mn and vice versa which may reflect their distribution rather than anthropogenic enrichment. Considering the positive correlations exhibited by Ni with Fe and Mn in some islands, it was found to be co-varying more strongly with manganese than with iron. ii) precipitation by sulphide ions in local regions of low oxidation potentials iii) adsorption by materials such as ferrous sulphide, hydrated ferric oxide, hydrated manganese

Other positive interrelationships observed during this study are between Cr/Co, Cr/Ni, Cr/Pb, Co/Ni, Co/Pb, Co/Cd, Ni/Pb, Ni/Zn etc. These relationships may not be true throughout the study area. There are some instances in which some of the relationships mentioned above turned to be negative on the basis of inter-island comparisons. For example, Agathy and Minicoy, coppér exhibited positive correlation with Pb. This was true for Ni-Pb relationship also which was found to be negatively correlated ($r = -0.940$) only in Minicoy. Such contradictory behaviour of trace metals can be explained by considering the sedimentary environment of the respective islands.

Interrelating the metal distribution with organic carbon content, except with some anomalies, metals were negatively correlated with organic carbon content. In Minicoy island, Cu, Fe, Ni and Zn exhibited significant positive values for Pearson correlation coefficient ($p>0.001$). This was true for Cu, Mn and Fe in Kiltan Island, which showed significant positive correlations with organic carbon content. Except that in Minicoy, the negative interaction of organic carbon content with metals was highly significant as indicated by this Pearson correlation coefficients.

This attests the fact that organic carbon content alone cannot be a decisive factor in the mechanism of metal accumulation in sediments. The surface area of the sediments, presence or absence of reducing environment etc are all equally important regarding the metal enrichment capacity of sediments.

Generally, considering the variations of organic carbon content among the islands, enrichments were found only at some selected stations. Mangrove samples of Minicoy, soil surface samples of various islands showed organic carbon enrichment compared with the lagoon and seaside profiles. The core sample of Kiltan (upto 1.3 m depth) and Androth (upto 1 m depth) showed increasing trend for organic carbon with depth Considering the horizon-wise description of soil profiles by Mannadiar (1977), it is divided into four horizons i) horizon A – uppermost layer with considerable organic matter about 20 cm thickness ii) horizon B – here the leached product of horizon A are deposited and this represents the sub-soil. The colour of this soil is white. iii) horizon C – represents the immediate weathered parent material having texture of unbound soil particles, purely white or colour. iv) horizon D is the solid parent rock.

The higher organic carbon content of the surface soils corresponds to decrease in the content of $CaCO_3$ due to its dissolution by organic acids. The increase in organic carbon content with depth may be considered due to root accumulation in these zones. Regarding the variations of pH with this organic carbon content are characterized by a decrease in pH. The lowering of pH is due to the acids released during the decomposition of accumulated organic matter. The chemical nature of bottom sediments and organic matter associated with sediments, play a major role in the cycling and concentration of many elements in the oceans.

The variation in concentrations and inter-island differences in correlation may be due to the differences in sources of the heavy metals and complex reactions of various trace metals studied such as adsorption, flocculation, ion-exchange etc. taking place in the sediments.

As in the case of metal-metal and metal-organic interrelations, metal-pH relations also displayed inter-island variations. Discussing only the significant ones, in Kadamath island iron displayed positive correlations with pH (r=0.713). Another important observations were made in Minicoy, Cr and Pb displayed moderate positive correlations with pH, whereas Ni, Zn and Fe displayed fairly good negative correlations. In Androth islands, except Zn, all the elements displayed positive correlations with pH whereas, for Kiltan, Cu, Zn, Mn, Cd and Fe exhibited fairly good negative correlations with pH.

Interrelating the variations of metal – pH relationships with variations in organic carbon, among the significant ones, those, which exhibited positive correlations with pH, displayed negative interactions with organic carbon content and *vice versa* with some exceptions.

Aquatic organisms are well known for their ability to take up trace elements from solution and particulate form (Riley and Chester, 1971; Ridgway and Price, 1987). Correspondingly, the underlying sediments are rich in organic matter content (Murty and Veerayya, 1972; Mortimer and Rae, 2000). It is therefore, possible that the elements are incorporated into the sediments in association with organic web to a certain extent.

Iron may be the most redox sensitive element in aquatic systems to pH changes, forming new solid phases capable of scavenging other trace elements from solution with a rise in pH (Boyle et al., 1977; Mayer, 1982, Unnikrishnan, 2000; Balachandran, 2001). The redox sensitive iron and manganese hydroxides under oxidizing conditions constitute significant sinks of heavy metals in aquatic systems. These hydroxides readily adsorb or co-precipitate cations and anions. The reactivity of manganese in aquatic systems exhibits a complex behaviour with conservative and non-conservative nature depending upon number of factors such as the concentration in sediment, water and suspended particles, ionic strength, pH, Eh etc., (Burton and Liss, 1976; Duinker et al., 1977). In aquatic environment, the behaviour of copper differs from that of iron and manganese. The major portion of copper in tropical seawater has been found to be associated with organic matter (Lee and Hoadley, 1967; Slowey et al., 1967; Meade and Parker, 1985). One of the characteristic observations regarding the behaviour of Ni in Minicoy was the significant positive correlation exhibited with organic carbon and a negative correlation with pH.

The seasonal production of biogenic particles only tends to influence particle composition and partitioning when suspended loads are low and for those metals with a tendency to concentrate in organic phases e.g., Cd and Cu. The Fe enrichment most likely results from reduction of Fe in the sediments during the oxidation of organic matter

(Macdonald et al., 1991) followed by upward diffusion and precipitation as amorphous oxyhydroxides near the sediment water interface. Diagenetic processes associated with the breakdown of organic carbon also influence the sedimentary metal profiles. Down core profiles of metals such as Co and Cu are strongly influenced by this process (Lowe, 1970; Luoma, 1990; Unnikrishnan, 2000).

Sinking of organic particles also scavenge trace metals from surface waters. Some of the essential trace elements are consumed by phytoplankton. The subsequent sinking of live cells or fecal matter will transport a portion of the biogenic metal from surface waters. Considering the behaviour of iron., it may sorb to colloidal organic matter which is abundant in surface waters (Bruland et al., 1974; Katz and Kaplan, 1981; Izquierdo, et al., 1997; Hema Achyuthan et al., 2002). The extremely large colloidal surface area combined with the particle reactive nature of iron suggests that aggregation of organic colloids could be important for removing ions. Strong correlation between metals and organic carbon may result in part from the presence of sewage particles, which are enriched in organic carbon, Pb, Zn and Cr (Bruland et al., 1974; Galloway, 1979; Katz and Kaplan, 1981).

Except for Cd, Zn and Pb, the concentrations of trace elements recorded for the sedimentary environment of Lakshadweep islands studied was not in the limit of pollution. Sediments with high organic carbon content, develops a reducing environment resulting in an increase in pH, which is very much effective in removing or desorption of number of elements from the precipitate.

In this study, the pH of the sedimentary environment was alkaline, and generally alkaline conditions react and leached the minerals such as chlorite, ilmenite, magnetite etc. as bicarbonate but deposited in the form of organic and inorganic colloids, finely divided into detrital grain and oxidative precipitation of Fe^{2+} as $Fe(OH)_3$. Boyle et al. (1977), Schor (1985), Bowers and Huang (1987) and Unnikrishann (2000) have also suggested that similar factors play an active role in the enrichment of iron content in estuarine environment.

Unnikrishnan (2000) suggested that anoxic conditions leads to enrichment of dissolved Mn in the seawater. In the case of near shore, even though the pH was almost similar to that estuarine alkaline environment, but due to the constant turbulent nature of water by wave action, nearshore environment becomes more oxic in turn increases the deposition of precipitation along with adsorption of different elements.

Discussing the effect of particle size on the distributional behaviour of trace elements, in Kadamath Co, Cu. Mn and Fe were found to be associated with silt + clay fraction (<63 µm) as evidenced by the positive value of Pearson correlation coefficients between the metals and silt + clay fraction of sediment. Metals like Cr, Ni. Zn and Cd showed associate-ship with the fine sand fraction (250-125 µm).

In Kadamath and Agathy islands. Cr. Co, Ni, Pb and Mn displayed positive correlations with the medium sand fractions. In Kadamath island. Zn and Cd displayed an affinity towards very coarse sand. Here Cu was found to be associated with the silt + clay fraction whereas Fe was associated with the fine sand (r = 0.683). In Agathy. Cu and Zn was correlated with the very coarse sand fractions. In addition to medium sand. Cr. Co. Ni. Pb and Mn in this island showed affinity towards the silt + clay faction. Considering the behaviour of iron, it was strongly correlated with the fine sand fraction (r = 0.925) whereas for Cd affinity was towards coarse sand as well as very fine sand fractions. Concerning about Androth, all the metals displayed association with silt + clay as well as very fine sand fractions whereas negative correlations were displayed by other fractions (very coarse sand - fine sand)

Characterizing the correlations of Cu, Cr and Pb with sediment texture, they displayed correlations with silt + clay. Very fine as well as fine sand fractions acted as the major scavengers of Fe and Mn in this island. While the affinity of Cd was towards medium sand, zinc was associated with coarse sand.

Metals displayed positive correlations with the organic carbon content, in accordance with the fact that, clay minerals act as scavengers for trace metals by adsorbing and subsequently getting settled in the bottom sediments under reducing environmental conditions. The surface area of the adsorption sites is an important factor regarding metal enrichment by sediments. Clay and silt fractions with large surface area bind metals more effectively than the sand fractions with less adsorptive capacity on the basis of small surface area.

In Lakshadweep archipelago, most of the elements showed increase in accumulative pattern with decrease in particle size. This is evidenced by the fact that most of the metals exhibited affinity towards <63 µm size fractions followed by very fine and fine sand fractions. This is well characterized in Androth in which all the metals displayed moderate negative correlations with sand fractions ranging from very coarse sand to fine sand.

Comparatively higher elemental concentrations of elements like Fe, Mn etc. in the clay fraction compared to that in the bulk fractions is due to the fact that these elements get precipitated on the surface area of silt + clay which is comparatively flat and also flocculates along with organic carbon which can hold more amount of precipitate. The fine size silt + clay particles held in the precipitates and formed as a floc in the alkaline environment and deposit (Mohan, 1997).

Comparing the enrichment pattern of different elements with that of Fe and Mn in different size fractions, highlights the fact that similarity in metal enrichments is being controlled by Fe and Mn hydroxide phases in alkaline environment. Fine-grained sediments with low carbonate content are characterized by higher concentrations of trace elements than coarse grained sediments with higher carbonate content (Padmalal, and Seralathan, 1995; Padmalal et al., 1997; Unnikrishnan, 2000; Balachandran, 2001).

An inter-comparison between mangrove and coral reef ecosystems of Minicoy.

In Minicoy island an artificial mangrove habitat is created which is considered to be a virgin area. This is in the formative stage and is free from serious human interaction.

Mangrove ecosystems are one of the major types of natural wetlands in tropical and subtropical region, flooded by fresh river water as well as by salty oceanic water. Salt marshes, particularly those located near or along estuaries such as mangrove forests, are often polluted by river-borne and marine derived particles and pollutants (Tam and Wong, 1995). As in other coastal marshes, mangrove sediments are reduced and act as either as sources or sinks of heavy metals (Lacreda et al, 1987; Silva , 1998; George Thomas and Fernandez, 1997). Knowledge of the levels of such contaminants in mangrove sediments is important for understanding the degree of heavy metal pollution in aquatic systems, throwing light on the degree and sources of metal pollution, the transport, fate and bioavailability of the metals concerned.

Comparing the trace element concentrations reported for these mangrove samples with the lagoon profile of Minicoy, except for Fe, Ni and Zn, they recorded lower values or more or less equal concentrations as that of lagoon samples. The sedimentary organic carbon content and pH values reported for mangrove stations 1 and 2 were 17.29 – 27.86 % and 7.81-8.07 respectively.

The concentrations of iron reported for these samples are 221.82 and 169.27 mg kg^{-1} respectively. The concentrations of Ni (21.35 and 24.89 mg kg) reported for these stations were slightly higher than that of Zn (14.64 and 17.83 mg kg^{-1}). Comparatively higher values of Fe may be due to the precipitation of Fe as iron sulphides which is common in mangrove ecosystem. It is generally described as the principle metal that precipitates with sulphide compounds in anaerobic sediments and these sulphides form a major sink for heavy metals in the mangrove area. According to Lacreda et al (1987), trace metals precipitate with iron forming polysulphide minerals in particular Cu, Zn and Pb. Comparing the elemental composition of Minicoy island with three mangrove ecosystems from Kerala coast *viz*.

Kumarakam (less contaminated), Veli and Quilon (contaminated with respect to industrial effluents). we can attest the fact that Minicoy island remain to be virgin with regard to trace metal pollution.

Table 5.4. . Concentration of trace metals along the three mangrove ecosystems of Kerala coast (George Thomas and Fernandez, 1997) and the mangrove ecosystem of Minicoy island (this study).

Mangrove Location	Cu (mgkgl^{-}	Co (mgkg^{-1})	Pb (mg kg^{-1})	Zn (mg kg^{-1})	Mn (mg kg^{-1})	Fe (g kg^{-1})
Kumarakam	10 – 44	159-261	1100-1300	31-155	318-1089	46 – 121
		148-248	1800-1950		198-1124	
Quilon	652-845	91-144	1250-1475	1550-2372	150-456	116 – 146
	62-256			223-370		
Veli			8.67-31.33		7.58-8.79	99 – 149
(Trivandrum)		10.74-				
	3.48-5.57	17.71		14.6-17.8		
Minicoy island						0.22-0.17
(This study)						

Pollution Load Index (PLI).

Metal pollution in estuarine, harbour and coastal environment is usually caused by land run off, mining activities, stripping and dredging activities and anthropogenic inputs. Sediments in such affected domains not only record its history, but also indicates the degree of pollution. The extent of contamination of aquatic sediments has been earlier quantified by comparing with an uncontaminated natural background for a specific constituent (Turekian and Wedephol, 1961; Forstner and Muller, 1973; Nikoforova and Smirnova, 1975). The factors that influence the mechanism of pollutant accumulation in sediments are the nature of the substrate as well as the physicochemical conditions controlling dissolution and precipitation (Panigrahy et al., 1997). An assessment based on pollution load index (PLI) has been employed to assess the extent of pollution by metals in estuarine sediments as suggested by Tomlinson et al. (1980).

According to this, pollution load index can be evaluated using the equation,

$$\text{PLI} = n\sqrt{\text{Product of n number of CF values}}$$

Where CF = contamination factor,

N = number of metals

$$\text{The contamination factor (CF)} = \frac{\text{Metal concentration in sediment}}{\text{Back ground value of the metal}}$$

Table 5.5. Back-ground values of trace metals on the basis of World Shale Average. (Turekian and Wedephol, 1961)

Element	World Shale Average
Fe	4.6 %
Mn	0.08 %
Cu	45 ppm
Co	19 ppm
Ni	68 ppm
Zn	95 ppm
Pb	20 ppm
Cd	0.3 ppm
Cr	90 ppm

Geo-accumulation index (I_{geo}) , a pollution indicator, which takes into account of natural background as well as variation with rock types (lithogenic effect), is calculated using the equation,

Geo-accumulation index (I_{geo}) = $\log_2 C_n / 1.5B_n$

Where, C_n = the measured concentration

B_n = the background value (World Shale Average) of element 'n'

In an attempt to summarize results of this study, contamination factors, pollution load index and geo-accumulation index has been evaluated for all the metals studied both in the lowest and highest ranges of concentrations . The CF, PLI and I_{geo} values of the trace metals studied in 6 islands are given in Table 5.6 to Table 5.8 respectively.

Table 5.6. Contamination factors calculated for 6 islands .

Islands	Cu	Cr	Co	Ni	Pb
Kavaratti	0.02 - 0.23	0.09 - 0.14	0.09 - 1.06	0.04 - 0.28	0.06 - 1.88
Kadamath	0.08 - 0.10	0.08 - 0.13	0.62 - 0.97	0.19 - 0.28	1.21 - 2.06
Minicoy	0.08 - 0.12	0.03 - 0.10	0.57 - 0.93	0.21 - 0.37	0.43 -1.53
Agathy	0.06 - 0.11	0.09 - 0.12	0.75 - 0.90	0.23 - 0.27	1.41 -1.69
Androth	0.02 - 0.14	0.01 - 0.13	0.09 - 0.97	0.04 - 0.29	0.04 - 1.76
Kiltan	0.02 - 0.21	0.01 - 0.14	0.06 - 0.93	0.03 - 0.48	0.02 - 2.20

	Zn	Mn	Cd	Fe
Kavaratti	0.02 - 1.37	0.005 - 0.153	3.7 - 26.7	0.00027-0.0353
Kadamath	0.04 - 0.14	0.009 - 0.011	15.37 -45.03	0.00031-0.00063
Minicoy	0.04 - 0.19	0.009 - 0.012	14.03 - 37.1	.00033-0.0.0095
Agathy	0.06 - 1.09	0.009 - 0.011	9.77 - 32.16	0.00039-0.00074
Androth	0.04 - 3.02	0.002 - 0.024	3.03 - 27.87	0.00019-0.0038
Kiltan	0.02 - 1.04	0.005 - 0.026	3.7 - 51.03	0.00020-0.0160

Table 5.7. Pollution load index calculated for 6 islands .

Island	Pollution load index (PLI)
Kavaratti	1.7×10^{6} - 0.536
Kadamath	3.6×10^{4} - 5.1×10^{3}
Minicoy	1.3×10^{4} - 2.03×10^{2}
Agathy	4.6×10^{4} - 1.11×10^{2}
Androth	3.2×10^{7} - 7.4×10^{2}
Kiltan	2.1×10^{6} - 0.227

Table 5.8. Geo-accumulation index calculated for 6 islands .

Geo-accumulation Index (I_{geo})

	Cu	Cr	Co	Ni	Pb	Zn	Mn	Cd	Fe
Kavaratti	-0.001	0.022	0.026	0.015	0.011	0.009	0.002	0.335	0.0000520
	0.051	0.027	0.152	0.042	0.174	0.049	0.006	6.671	0.0001546
Kadamath	0.026	0.021	0.125	0.036	0.153	0.014	0.002	4.899	0.0000552
	0.032	0.026	0.147	0.042	0.179	0.026	0.003	8.347	0.0000704
Minicoy	0.027	0.013	0.120	0.038	0.104	0.013	0.002	4.608	0.0000666
	0.037	0.024	0.145	0.045	0.165	0.029	0.003	7.725	0.0001270
Agathy	0.021	0.023	0.134	0.039	0.161	0.018	0.002	3.446	0.0000604
	0.033	0.026	0.144	0.041	0.169	0.047	0.003	7.268	0.0000737
Androth	0.002	-0.001	0.032	0.013	-0.014	0.014	0.000	-0.302	0.0000435
	0.039	0.026	0.147	0.042	0.171	0.057	0.004	6.808	0.0001081
Kiltan	-0.001	0.002	0.005	0.012	-0.048	0.009	0.002	0.335	0.0000469
	0.048	0.027	0.145	0.049	0.182	0.046	0.004	8.748	0.0001381

An evaluation based on pollution load index formulates the fact that the values of PLI recorded for all these islands were less than 1.

Among the highest contamination factors of elements recorded for each islands the results were as follows. For metals Cu, Co, Mn and Fe highest values of contamination factors are reported for Kavaratti islands. The contamination factors recorded for Ni, Pb and Cd were higher in Kiltan island. Considering the behaviour of zinc, Androth island displayed highest contamination factor. For Cr, even though no wide differences were observed among islands, highest values were for Kavaratti and Kiltan.

The geo-accumulation index (I_{geo}) also was in agreement with contamination factors recorded for the elements.

Generalizing the behaviour of trace elements in Lakshadweep archipelago, contamination factor greater than one was reported for Pb, Zn and Cd, which is very high in the case of Cd (51.03 recorded at Kiltan). In the case of Co, contamination factor greater than 1 was recorded at Kavaratti, for all other elements the values were less than unity.

Regarding the geo-accumulation index of heavy metals in the study area, elements except Cd can be included in I_{geo} class zero, the geo-accumulation index of cadmium was fond to be very high ranging from 0.30 to 8.75. Contamination factor less than one indicates the insignificant role of anthropogenic inputs such as industrial effluents, domestic sewage, mining activities and land run-off towards the metal incorporation in sediments. Relatively higher values of PLI have been reported for Vishakapattanam harbour(1.45-1.78: Panigrahy et.al.,1997), Vishakapattanam inner harbour (PLI=3.82, Satyanarayana et.al.,1994), indicating gross pollution.

Summarizing the results, the following points can be abstracted,

- The six islands selected for study in Lakshadweep archipelago remain unpolluted with respect to the six metals, viz. Cu, Cr, Co, Ni, Mn and Fe.
- Based on the contamination factors for Pb, Zn and Cd as well as the geo-accumulation index of Cd, it can be generalized that these islands remain polluted with respect to these elements – the severe effect is from cadmium as evidenced by high values of contamination factors and geo-accumulation index of this element.

Looking into the justification for this observation, one important thing is oil based power generation prevailing in these islands. For this, large quantity of crude oil is being used as a fuel source which contributes a larger proportion of associated pollutants like Pb, Cd and Zn. Another thing is shipping activity which contributes in two ways - one is contamination of these metals through oil and another is from antifouling coatings of ships the major ingredient of which is lead. The major contribution towards pollution is from cadmium, compared to that of Pb and Zn and this is very high in Kiltan. Lead is known to form colloids in seawater, and such colloids could have settled down after gaining weight by adsorbing onto the surface of planktonic debris which consequently resulted in higher concentration in sediment. If the sediment is very fine in nature, the lead fixed in the lattice between the fine sand grains could remain unaffected by physical processes like turbulence, currents etc (Palanichamy and Rajendran, 2000). The values of cadmium reported by Sanzgiry and Braganca (1981) were in the range 0.5-2ppb and values in the range 0-4.33 ppm was reported for Gulf of Mannar by Palanichamy and Rajendran (2000). The cycle of cadmium should be considered in connection with other factors, such as terrestrial input or regeneration from the dissolution by biogenic hard parts, such as calcium carbonate (Noriki et al., 1999; Abe, 2002).

Kiltan Island lies along the international shipping route. In 1974 September, an American oil tanker "Transhuron", owned by Hudson Waterways Corporation and chartered by the U.S. Navy, ran aground on Kiltan. The tanker got badly damaged and its oil began to spill. It was carrying about 18, 500 tones of furnace oil from Bahrain to the Philippines. Nearly 3000 tones of oil leaked from the tanker into the sea creating oil pollution in a wide area. This incident made a significant contribution towards the enrichments of persistent inorganic pollutants like Pb, Zn and Cd.

Correlating the contamination factor with the population size of the island, Androth is the most populated island (17.6%) followed by Kavaratti (16.8%). The highest contamination factors of Cu, Co, Mn and Fe was reported for Kavaratti, Androth comes in the 3rd position – indicating that there can be some contributions from human activities towards the metal concentrations in these islands. With the exception of Kiltan, other islands displayed contamination factor in accordance with their population size.

Regarding the influence of agriculture on pollution, coconut contributes 99 % of net sown area, and it is the main stay in agriculture and economy of Lakshadweep. In addition to this there is cultivation of vegetables, banana, rice and others. The use of fertilizers used for there makes a contribution though not significant towards the pollution load index of metals in Lakshadweep archipelago.

Evaluating the role of industries towards metal contribution, Lakshadweep is considered as a "no industry zone". There are certain minor industrial units working under the public and private sectors. In 1993-94, there are 29 units under the public sector, the majority of which were related to coir, coir processing and printing. Small establishments like saw mills, general workshops, carpentry units etc., also function in Lakshadweep.

In addition to the activities of local inhabitants, anthropogenic introduction of pollution can also come from tourist activities. The multihued, shallow, placid lagoons with its myriad life forms are a feast to the eye and a life long experience not easily matched. Being a centre of tourist attraction, activities related to tourism for e.g., contribution of buildings, mode of transportations (boats/vessels) among these islands play a significant role in the pollution load of some of the metals.

Considering the role of transportation, Lakshadweep had remained either as guide to the sailing vessels passing by or a temporary halting anchorage place for the vessels from the western world. The traditional means of transport in the territory has been the sailing vessels. There are two types of vessels - quare-rigged Minicoy Odies and the lateen sailed odams of other islands. The importance of odams as a large carrier is declining as a result of the introduction of the steamer service and motor vessels later on. The major transportation sources can be classified as i) mechanized boats for transporting men and materials between islands ii) cargo cum passenger ships for transportation between islands and the mainland iii) air craft services to main land.

The major sources of input of Cd, Pb and Zn into the aquatic environment reviewed from the literature of elsewhere (Anderson et al., 1983; Forstner and Wittmann, 1983; Barcellos et al. 1991; Dorr et al., 1991; Mohapatra, and Rengarajan, 2000; Elizalde et.al., 2002) are summarized hereunder:

- Cd – metal industry, refining of zinc, lead . copper, electroplating, alloying, pesticides, fly-ash, petrochemicals, fertilizers, textile, printing, photography, protective coating of iron, copper, steel, cigarettes, paint, plastics, batteries, domestic waste water, leather tanning.

- Pb – leaded petrol, exhaust of motor vehicles, pulp and paper bound mills, oil refineries, inorganic and organic chemical industries, steel industries, fly ash, combustion of coal, dredging of harbours, battery plates, paints, lead-oxides, ship breaking industry, photography, mining, smelting, alloys, roadside soil and dust.
- Zn – electroplating, fly-ash, combustion of coal, dredging of harbour, pulp nd paper mill waste, petrochemicals, organic chemicals, fertilizers, steel hook foundries, Zn, Cu and Pb smelting industries, brass alloy manufacturing, galvanizing iron and steel, dry batteries, domestic wastes, pesticides, automobiles, fungicide, pigments, printing.

Concluding the effect of all these activities, Lakshadweep archipelago remains as unpolluted with respect to many of the elements selected in this study. An exception to this was for cadmium and to a limited extent for Pb and Zn. According to the latest report on Union Territory of Lakshadweep by the Department of Environment and Forest published in May 2002, the surrounding of the islands including the lagoon was getting polluted with oil and metallic contents from ships and barges and pollution from boats was also severe. They also projected diesel as the source from which electricity is generated in the islands. Right from the point it is unloaded from the barges to the jetty the diesel drums leave a trail of destruction. Switching over to coconut plantation recorded a loss in soil fertility and a subsequent increase in the usage of chemicals which can contribute towards a slight excess of zinc and lead.

Statistical Approach

Statistical Methods applied are 3 way ANOVA 1) for testing the difference in the concentration of trace metals with respect to south and north, between core depths and between metals at Kavaratti Island and Kiltan Island. (2) for testing the difference in the trace metal concentration with respect to south and north, between stations and between metals at Kiltan Island and (3) between islands, between land lagoon variations and between metals based on the trace metal concentration at Kavaratti, Minicoy, Agathy and Kiltan Island using original data and standardized data.

Having found significant differences, student-t test in applied to test difference between metals, between core depths at Kavaratti and Kiltan Island, between stations at Kiltan Island and between various lagoon features at Kavaratti, Minicoy, Agathy and Kiltan Island.

Multivariate factor analysis by Q-mode and R-mode for grouping of locations/stations/depths and for grouping metals after variance rotation to simple structure for uniqueness of the factor loadings.

Results and Discussions

At Kavaratti Island on comparing the south & north and core depths and trace metals after standardizing the data for row and columns it is observed that there is high difference between north and south ($F_{(1,32)}$ 11651.4, $P<0.01$), ($F_{(4,32)} = 2.1346, P<0.05$) and also between core depths and metals ($F_{(8,32)} = 7715.9$, $P<0.01$). Also the interaction between direction and depths ($F_{(4,32)} = 3.18$, $P<0.05$) and between direction and metal concentrations ($F_{(8,32)} = 3725.9$, $P<0.001$) were highly significant (Table 5.9) The distribution with respect to core depth showed that in north at surface it is only less than half of that at south where as at 30cm depth at south it was nearly ½ of that at north. At deeper core depths (>60cm) not much significant difference was observed between north and south for the average quantity as well as for the variation in the distribution (Table 5.10 a & b) with respect to metals high difference was observed between iron and other metals and also between lead and other metals. The order of occurrence could beginning as iron> lead> nickel> cobalt> chromium> manganese> zinc> copper and cadmium in the south with a lead for zinc and manganese over chromium in the north (Table 5.10 c & d). Distribution was more stable in the north for copper, cobalt, nickel, lead, cadmium and iron at north than at south.

Q-mode factor analysis based on raw normalization and variance rotation to simple structure grouped the core depths >60 at south and north together with high negative loading for final factor. This factor explains anent 64.25% of the spatial variability and it forms the differential factor group at this island indicating that it gives sufficient information on the trace metal distribution.

R-mode factor analysis based on column normalization and variance rotation to simple structure has grouped the metals copper, chromium, cobalt, nickel, lead, manganese and cadmium together into factor group 1 explaining about 62.99% of the spatial variation it forms the differential factor groups indicating that additional metals considered do not add. Significantly to the information of the trace metal distribution at this island for the pollution aspect. Manganese and iron are grouped together in second factor groups and zinc in the third (Table 5.11 a & b) solving the difference in the distribution of the latter two group elements and association of manganese with iron applied.

At Kiltan island 3 way ANOVA after row and column standardization showered that there is significant difference between south and north stations, between stations as well as between metals ($P<0.001$) all the first order interactions are also highly significant ($P<0.05$, Table 5.12). Average distribution of the trace metals at south are all greater than that of north at all stations and there is an increasing trend towards the sea side from the land at both south and north regions. At south there is less heterogenety in the metal distribution land ward than seaward where as in north the distribution is with same pattern of variation at all stations.

Regarding the distribution of the metal, individually, the average metallic content at south is greater than that at north. With highest value for iron at south and lead in the north the order of concentration is Iron>lead>nickel>cobalt> chromium>zinc> manganese> cadmium>copper at south where as the order is, Lead> iron> nickel> cobalt> chromium> manganese> zinc> cadmium> copper in the north. In the south, iron is more unevenly distributed while cobalt most informally in the north, the zinc is most highly dispersed while cobalt most uniformly (Table 5.13 a, b, c & d)

Q-mode factor analysis applied for grouping of stations delineated 3 distinct factor groups, first containing stations at 50m, 100m seaside both at south and north with high negative values. The second factor group is unique with the only land on station of south with high negative loading. Factor group 3 contains stations of north mostly, but with moderate positive factor loading. The grouping shows that north sea ward station has characteristics of both factor group 1 and factor group 3 stations. The three factor groups explain respectively 47.46%, 22.34% of the spatial variation and these two together form the differential factor group. Thus again implies that almost all the important informations abut the trace metal distribution could be galleried only if the stations of factor groups 1 and 2 are considered (Table 5.14a).

R-mode analysis applied grouped the trace metals into 3 distinct factor groups containing the elements copper, chromium, cobalt, nickel, lead and iron with high negative factor loading, with zinc and manganese with very high negative factor loading in factor group 2, cadmium and iron with high positive factor loading in factor groups 3 and 4 respectively. Moderate loading for iron in factor 1 resembles its distribution with that of other metals of this group and its high loading for factor group 4 spelling out its unique characteristic of being moderately abundant at north and highly abandoned at south justifying its interaction with geographical reference. In this case all the metals except cadmium distribution are important in the study of pollution aspect, since the first two factor groups together explain (47.17 + 28.04 = 75.21) >50% of the variability in the spatial distribution (Table 5.14 b). 3 way ANOVA applied for the lagoon features at Kavaratti, Minicoy, Agathy and Kiltan islands showed significant island wise differences ($F_{(3,72)} = 2377.26$, $P<0.001$) and between metals ($F_{(8,72)} = 28033.7$, $P<0.001$) (Table 5.15) Lagoon features – Station interaction was moderately significant ($F_{(9,72)} = 2.7803$, $P<0.05$), so also the station – metal interaction was highly significant ($F_{(24,72)} = 8150.0$, $P<0.001$) indicating that the distribution of metals differs with respect to island characteristics.

Average metal distribution has the order;

Kiltan>Agathy>Kavaratti>Minicoy at Lagoon 1.

Kavaratti>Minicoy>Agathy>Kiltan at the station intermediate between lagoon and land.

Kavaratti>Agathy>Minicoy>Kiltan at berm and

Kavaratti>Kiltan>Agathy>Minicoy in the land area.

Variation in the metal distribution also follows almost the same ordering for the islands (Table 5.16 a, b, c & d).

Regarding the metal distribution in the lagoon area of the 4 islands at Kavaratti, Iron is most abundant followed by zinc and lead with maximum variation for zinc and least for Manganese (Table 5.16e). At Minicoy, lead is most abundant-followed by iron and nickel with maximum variation for iron and least for manganese (Table 5.16 f). At Agathy island, zinc and cadmium are equally distributed, lead by iron with maximum variation for zinc and least variation for Manganese (Table 5.16 g). At Kiltan island, lead occurs the maximum followed by zinc and then by iron with high spatial heterogeneity for zinc and high uniformity for chromium (Table 5.16h).

The order of occurrence for the various metals could be given as :

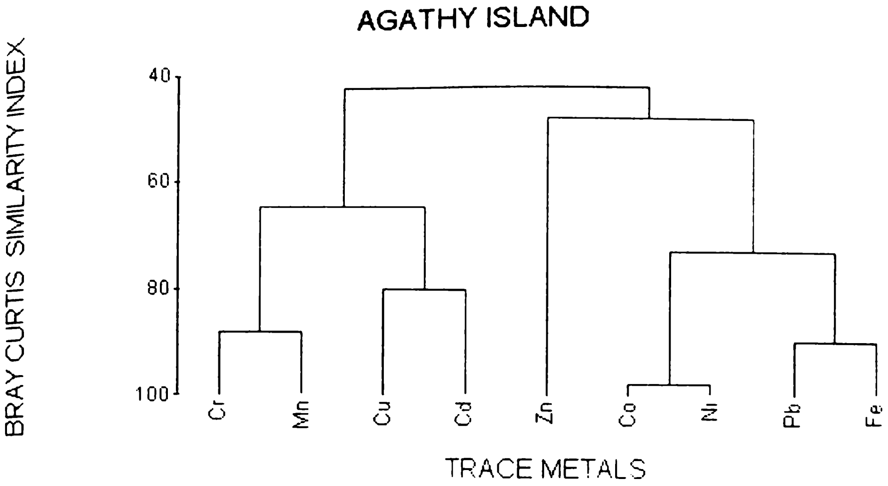
1)	for Copper,	Ka>Mi>Ag>Ki
2)	for Chromium,	Ka>Ki>Ag>Mi
3)	for Cobalt,	Ka>Ki>Ag>Mi
4)	for Nickel,	Ka>Ki>Mi>Ag
5)	for Lead,	Ka>Ki>Mi>Ag
6)	for Zinc,	Ka>Ki>Ag>Mi
7)	for Manganese,	Ka>Mi>Ki>Ag
8)	for Cadmium,	Ag>Mi>Ki>Ka
9)	for Iron,	Ka>Ag>Mi>Ki

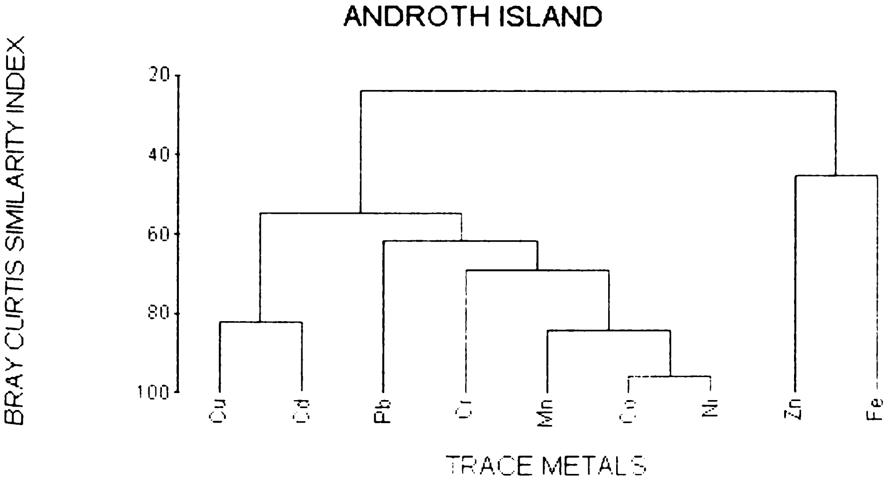
where Ka = Kavaratti, Ki = Kiltan, Ag = Agathy and Mi = Minicoy.

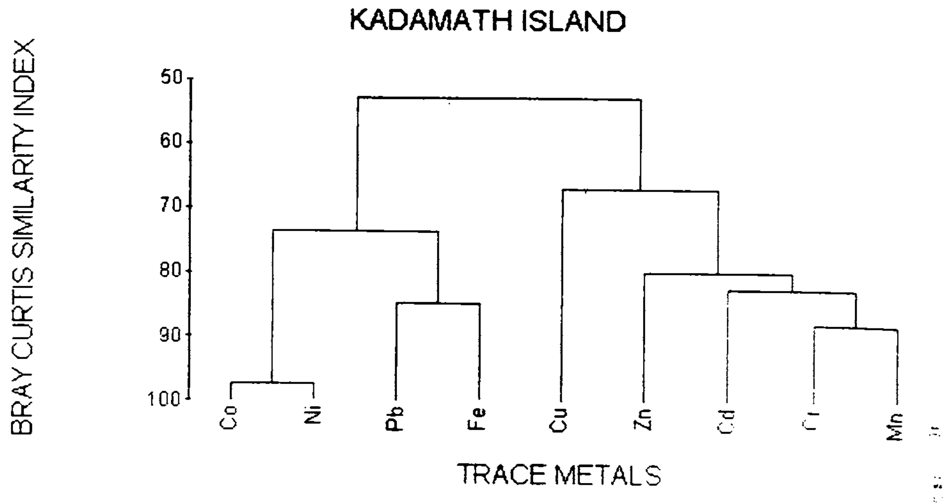
Trace metal distribution was more consistent at Minicoy and more variation at other islands. Q-mode factor analysis applied for grouping of lagoon features at the 4 islands, it showed 3 factor groups with the first two being statistically significant factor group and the first factor group is the differential factor group explaining 50.02 % of the spatial variability in the lagoon area. The first factor group contains invariability in the intermediate, berm and land area of the islands of Minicoy, Agathy and Kiltan, and all the factor loadings are highly moderately negative. Factor group includes lagoon of Agathy and Kiltan and berm area of Kavaratti sharing the similarity in the metal content of these spots with high positive factor loading. Factor group 3 is exclusively of the areas of Kavaratti (except that of berm Kavaratti). Minicoy intermediate and Kiltan land area also show some features common to Kavaratti island (Table 5.17a).

R-mode analysis applied for grouping of trace metals in the lagoon area, delineated 3 significant factor groups with factor group 1 containing all metals except zinc (forming factor group 2) and manganese (forming factor group 3). Factor group 1 is the differential factor group explaining 63.01% of the spatial variation. This further indicates that factor group 1 metals extract almost all the information regarding the pollution aspects of the lagoon area of these islands (Table 5.17b).

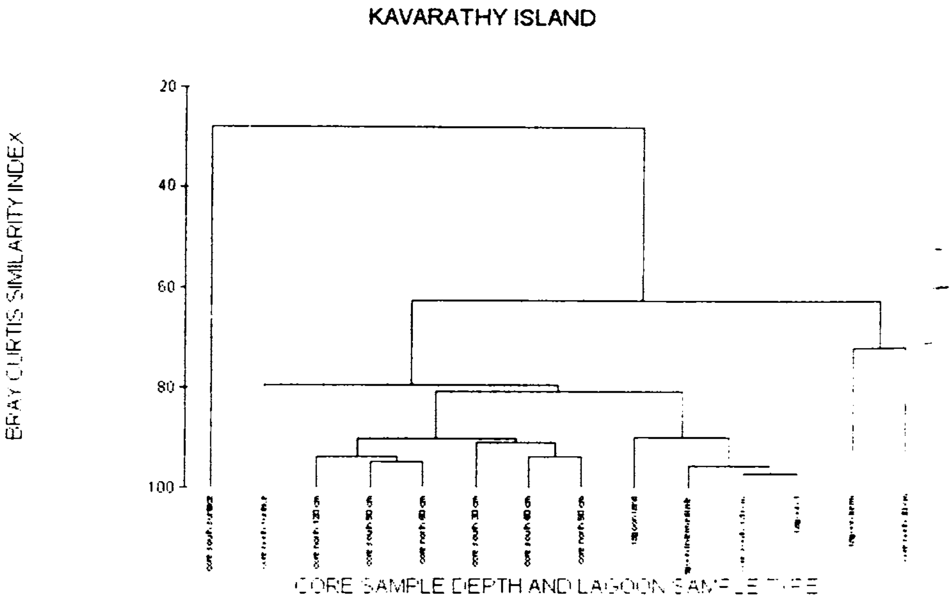
Dendrograms are drawn for studying the similarity between metals at each island for station characteristics at each island, and also for metals at different lagoon features of the 4 islands (Kavaratti, Agathy, Kiltan and Minicoy) and for the lagoon features using group linkage cluster analysis of Bray Curtis coefficient of similarity and are representatively given below.


AGATHY ISLAND
BRAY CURTIS SIMILARITY INDEX
40
60
80
100
Cr
Mn
Cu
Cd
Zn
Co
Ni
Pb
Fe
TRACE METALS


ANDROTH ISLAND
BRAY CURTIS SIMILARITY INDEX
20
40
60
80
100
Cu
Cd
Pb
Cr
Mn
Co
Ni
Zn
Fe
TRACE METALS

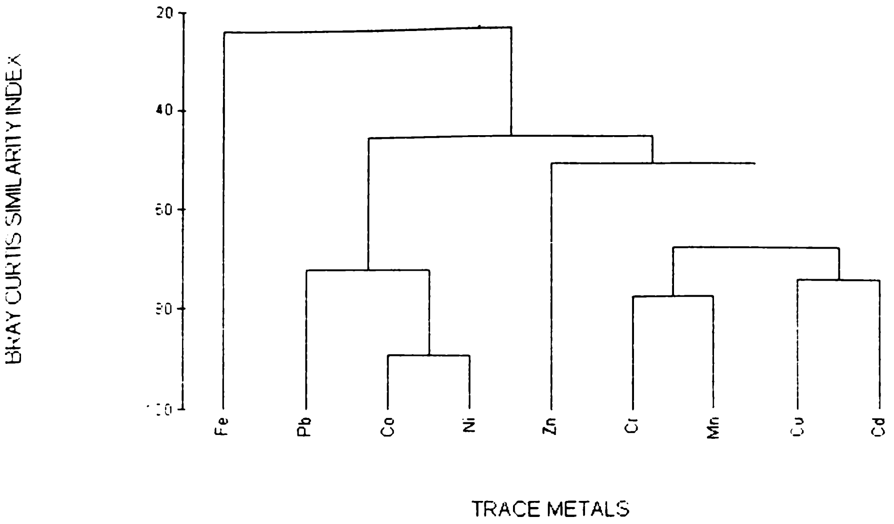


KADAMATH ISLAND

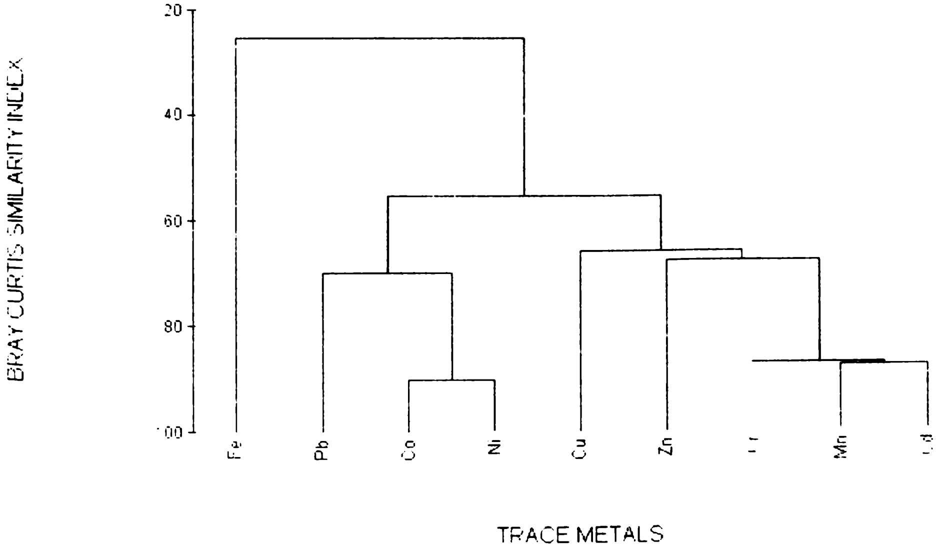


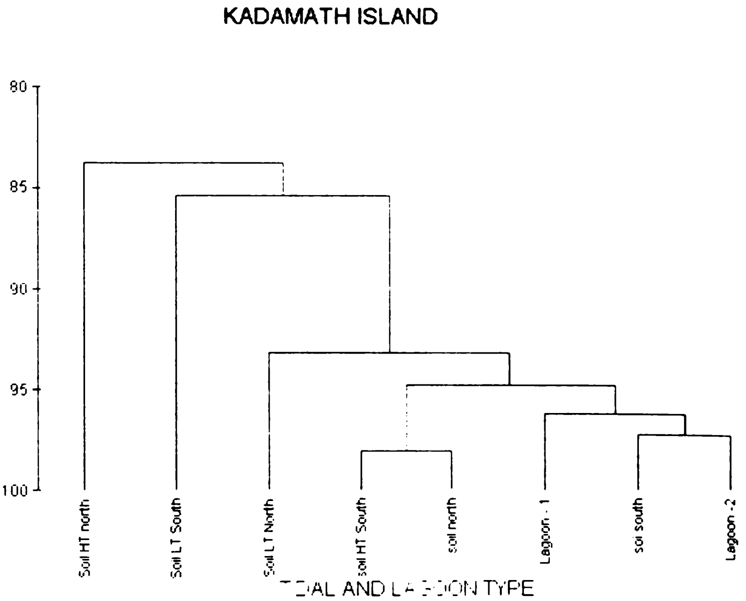
KAVARATHY ISLAND

KILTAN ISLAND

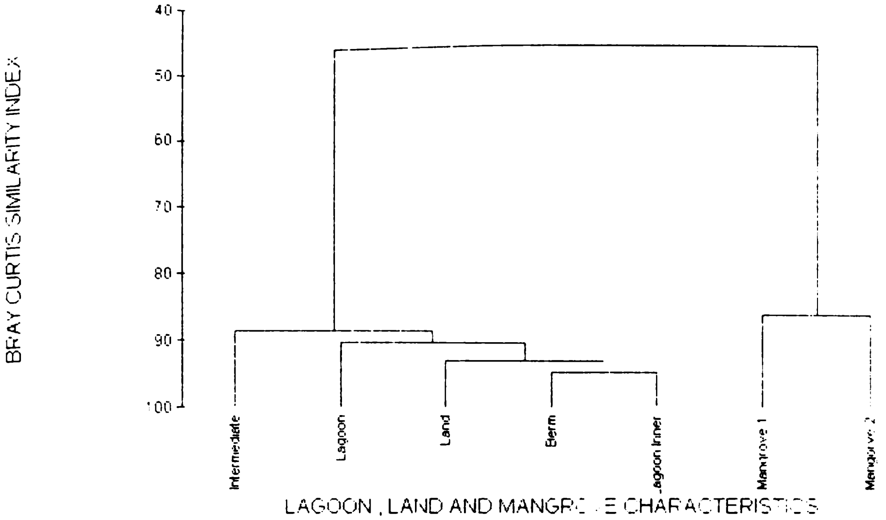


MINICOY ISLAND

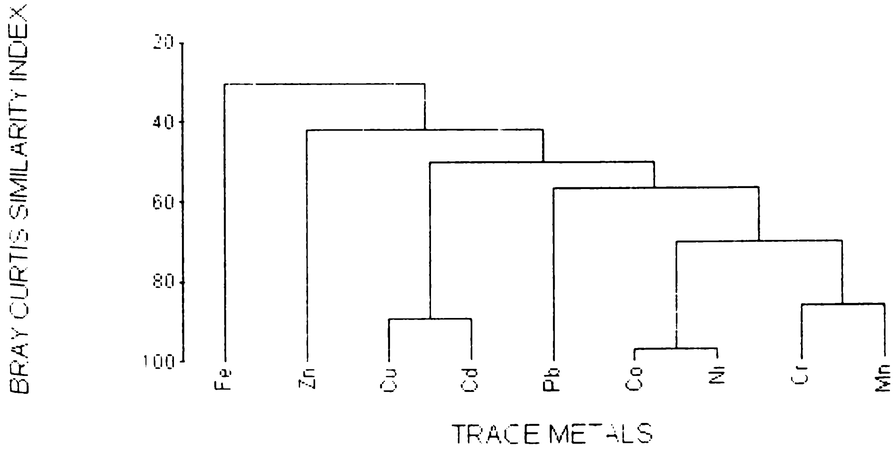


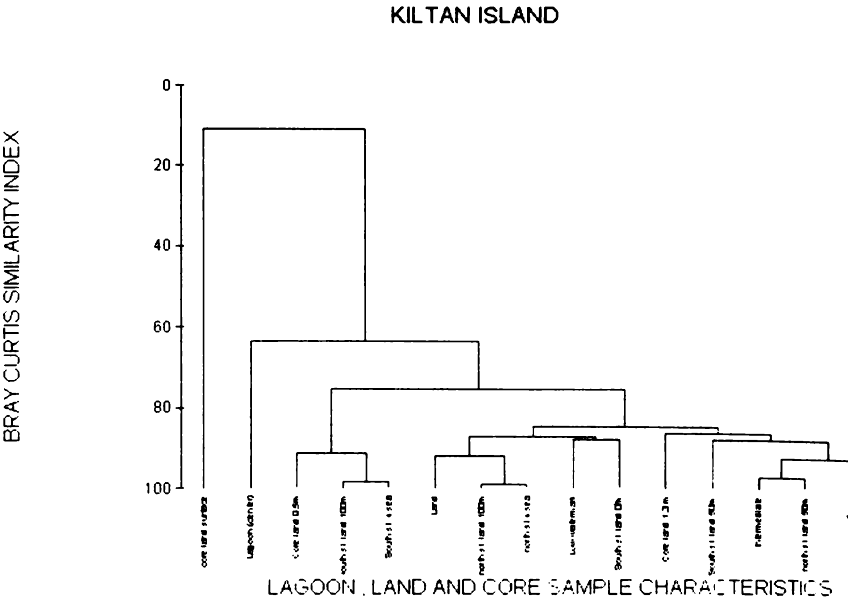

KADAMATH ISLAND
80
85
90
95
100
Soil HT north
Soil LT South
Soil LT North
Soil HT South
soil north
Lagoon - 1
soi south
Lagoon - 2
TIDAL AND LAGOON TYPE

MINICOY ISLAND



KAVARATHY ISLAND




KILTAN ISLAND
BRAY CURTIS SIMILARITY INDEX
0
20
40
60
80
100
LAGOON , LAND AND CORE SAMPLE CHARACTERISTICS

Statistical tables:

Table 5.9 :Distribution of Trace Metals at Kadamath Island

Region	Mean	Standard Dev.	Coeff. Of Variation
(a) Sea side South			
Soil	13.71	9.44	68.81
Soil High Tide	13.20	8.03	60.85
Soil Low Tide	11.61	5.79	49.86
(b) Sea side North			
Soil	13.33	8.18	61.32
Soil High Tide	14.05	11.02	78.45
Soil Low Tide	13.85	7.17	51.81
(c) Metal South			
Copper	3.79	0.38	10.15
Chromium	8.99	1.54	17.16
Cobalt	14.34	1.86	12.96
Nickel	15.09	1.52	10.08
Lead	27.76	2.61	9.39
Zinc	8.97	3.44	38.38
Manganese	7.36	0.29	3.88
Cadmium	6.45	1.50	23.31
Iron	22.84	5.17	22.61
(d) Metal North			
Copper	4.19	0.12	2.96
Chromium	10.23	1.15	11.20
Cobalt	16.29	1.50	9.23
Nickel	16.91	1.35	7.99
Lead	33.64	5.40	16.05
Zinc	7.11	2.34	32.89
Manganese	7.98	0.80	10.05
Cadmium	8.25	3.72	45.12
Iron	19.10	3.67	19.22

Table 5.10 : Distribution of Trace Metals in Kiltan Island

Region	Mean	Standard Dev.	Coeff. Of Variation
(a) Sea side South			
Station 1/land 0 m	12.48	6.89	55.25
Station 2 50 m	12.70	10.00	78.75
Station 3 100 m	19.30	18.24	94.51
Station 4 Sea	19.97	18.83	94.30
(b) Sea side North			
Station 1 land 0 m	12.28	8.05	65.52
Station 2 50 m	10.84	8.36	77.10
Station 3 100 m	13.41	8.67	64.63
Station 4 Sea	13.59	8.70	64.03
(c) Sea side South			
Metals	3.89	0.81	20.83
Copper	8.98	0.74	8.21
Chromium	16.18	0.32	2.00
Cobalt	28.06	7.12	25.38
Nickel	31.60	1.90	6.02
Lead	8.14	2.64	32.48
Zinc	7.84	0.32	4.08
Manganese	4.51	1.98	43.88
Iron	35.84	26.19	73.07
(d) Metals Sea side North			
Copper	3.62	0.38	10.47
Chromium	8.91	0.29	3.26
Cobalt	15.75	0.13	0.84
Nickel	16.72	0.35	2.09
Lead	29.75	0.43	1.44
Zinc	5.79	2.37	40.92
Manganese	6.51	2.18	33.41
Cadmium	5.45	1.61	29.57
Iron	20.27	5.58	27.52

Table 5.11: **Distribution of Trace Metals n Lagoons of various Islands**

Region	Mean	Standard Dev.	Coeff. Of Variation
(a) Kavarathy Island			
Lagoon	16.07	13.27	82.61
Intermediate	16.86	15.53	92.12
Bern	35.77	42.99	120.20
Land	18.59	16.10	86.61
(b) Minicoy Island			
Lagoon	11.35	6.80	59.93
Intermediate	15.40	11.56	75.06
Bern	12.59	7.46	59.27
Land	13.97	9.21	65.91
(c) Agathy Island			
Lagoon	22.71	29.95	131.88
Intermediate	14.35	9.03	62.91
Bern	15.06	9.28	61.65
Land	14.00	10.01	71.49
(d) Kiltan Island			
Lagoon Centre	23.19	28.04	120.89
Intermediate	11.17	8.97	80.26
Bern	12.53	9.13	72.87
Land	15.72	9.87	62.78
(e) Kavarathy Island Metals			
Copper	5.05	0.42	8.35
Chromium	10.08	1.49	14.78
Cobalt	16.33	1.44	8.80
Nickel	17.17	1.30	7.27
Lead	32.42	3.09	9.54
Zinc	36.17	5.93	149.09
Manganese	9.94	0.14	1.40
Cadmium	5.48	1.41	25.70
Iron	63.73	19.81	31.90
(f) Minicoy Island Metals			

Copper	3.90	0.39	9.97
Chromium	8.55	0.41	4.76
Cobalt	14.98	1.49	9.96
Nickel	16.03	0.97	6.05
Lead	28.83	1.31	4.53
Zinc	5.06	1.29	25.52
Manganese	8.47	0.19	2.28
Cadmium	8.24	2.11	25.66
Iron	25.88	9.60	37.12
(g) <u>Agathy Island Metals</u>			
Copper	3.74	0.77	20.57
Chromium	9.54	0.98	10.28
Cobalt	15.56	1.09	7.00
Nickel	6.05	0.90	5.52
Lead	4.53	2.05	6.70
Zinc	25.53	40.29	113.38
Manganese	2.28	0.31	4.13
Cadmium	25.66	1.18	27.05
Iron	37.12	4.57	17.86
(h) <u>Kiltan Island Metal</u>			
Copper	3.31	0.42	12.78
Chromium	9.84	0.24	2.47
Cobalt	15.76	1.18	7.51
Nickel	16.75	0.80	4.77
Lead	30.74	1.52	4.95
Zinc	28.26	40.58	143.59
Manganese	5.95	1.69	28.38
Cadmium	6.99	4.29	61.45
Iron	23.31	8.81	37.78

Table 5.12: 3 way ANOVA for Kavarathy Island

Source	Mean sum of Squares	d-f	F. Ratio
(a) Directions N and S	1038.09	1	11651.4 **
(b) Core depths	0.19019	4	2.1346 **
(c) Metals	687.456	8	7715.90 **
(AxB)	115.554	9	
(BxC)	125.065	44	
(AxC)	540.791	17	
AB interaction	0.2833	4	3.1800 *
BC interaction	0.0764	32	0.8577
AC interaction	331.963	8	3725.9 **
Error	0.08910	32	

* F significant at 5% level. ** F significant at1% level.

Table 5.13: 3 way ANOVA for Kadamath Island

Source	Mean sum of Squares	d-f	F. Ratio
(a) Direction (N,S)	42.3862	1	394.465 **
(b) Soil Depth .	0.3061	2	2.8492
(c) Metals	403.761	8	3757.58 **
(AxB)	8.6695	5	
(BxC)	124.423	26	
(AxC)	299.788	17	
AB interaction	0.1746	2	1.6225
BC interaction	0.2686	16	2.4993
AC interaction	227.99	8	2121.78 **
Error	0.1075	17	

** calculated F is significant at 5% level.

Table 5.14 :3 way ANOVA for Kiltan Island

Source	Mean sum of Squares	d-f	F. Ratio
(a) Direction (S,N)	5932.58	1	108805.0 **
(b) Station	0.9544	3	17.5045 **
(c) Metals	5364.45	8	98385.7 **
(AxB)	847.983	7	
(BxC)	1226.45	35	
(AxC)	3652.73	17	
AB interaction	0.14714	3	2.6985 *
BC interaction	0.3039	24	5.5731 **
AC interaction	1656.04	8	30372.2 **
Error	0.05452	24	

* Calculated F is significant at 5% level. ** calculated F is significant at 1% level.

Table 5.15 :3 way ANOVA for (3) lagoons in Islands

Source	Mean sum of Squares	d-f	F. Ratio
(a) Stations	172.568	3	2377.26 **
(b) Lagoon features	0.05534	3	0.7623
(c) Metals	2035.00	8	28033.7 **
(AxB)	34.6457	15	
(BxC)	465.221	35	
(AxC)	885.615	35	
AB interaction	0.2018	9	2.7803 *
BC interaction	0.10831	24	1.4922
CA interaction	591.62	24	8150.00 **
Error	0.07259	72	

Table 5.16 a to h: Factor analysis for Kavarathy Island

Q – mode for grouping of Core Depths

Factor	Depth	Maximum F-L	Eigen Value	V (%)	V (%)
1	South 30	-0.8734	8.349	6.4251	64.25
	South 60	-0.9501			
	South 90	-0.9662			
	South 120	-0.7056			
	North Surface	-0.6892			
	North 60	-0.9519			
	North 90	-0.9565			
	North 120	-0.9225			
2	South Surface	0.9913	1.399	2.8337	28.34
	North 30 cm	0.9010			

R – mode for grouping of metals

Factor	Metals	Maximum F-L	Eigen Value	V. Value	V (%)
1	Copper	-0.9013	7.417	5.669	62.993
	Chromium	-0.8551			
	Cobalt	-0.9434			
	Nickel	-0.9356			
	Lead	-0.9491			
	Manganese	-0.6773			
	Cadmium	-0.8951			
2	Manganese	0.5564	0.9948	1.6288	18.097
	Iron	0.9866			
3	Zinc	0.8978	0.4927	1.5987	17.763

Table 5.17 a and b : Factor analysis for Kiltan Island

Q – mode for grouping of stations based on distance from sea using trace metal concentration

Factor	Distance	Maximum F-L	Eigen Value	V. Value	V (%)
1	South 50 m South 100 m South Sea North 50 m North 100 m	-0.6646 -0.9385 -0.72667 -0.9475 -0.5512			

Q – mode : Factor analysis for Kiltan Island

Factor	Distance	Maximum F-L	Eigen Value	V. Value	V (%)
1	North Sea	-0.7363	6.826	3.7998	47.45
2	South Land O M	-0.9418	0.9518	1.7875	22.3432
3	South 50 m North Land o m North 100 m North Sea	0.6256 0.7670 0.6685 0.5899	0.2049	2.3937	29.92

R – mode : Factor Analysis for Kiltan Island

Factor	Metals	Maximum F-L	Eigen Value	V. Value	V (%)
1	Copper Chromium Cobalt Nickel Lead Iron	-0.07703 -0.8528 -0.8416 -0.7982 -0.9780 -0.6625	6.475	4.2452	47.17
2	Zinc Manganese	-0.9757 -0.9376	1.358	2.5236	28.04
3	Cadmium	0.9528	0.7576	1.3058	14.51
4	Iron	0.7276	0.2870	0.7714	8.57

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Chapter 6

PREDICTIVE REGRESSION MODEL

In the study of impact of environmental parameters on the ecosystem as whole, a number of factors are jointly controlling the bioactivities at a point of time or space. Pederson et al., (1995) has given a method for choosing the minimal set of environmental variables that explain the variation in the affected parameters.

Multiple regression model fitted is of the form $Y = a_0 - {}_{i=1}\Sigma^k a_k X_k - {}_{i=1}\Sigma^k {}_{j=1}\Sigma^k (X_i * X_j) b_{ij}$ where a_i b_{ij}, $i,j = 1,2,\ldots\ldots k$, $i<j$ are the regressive coefficients (Jayalakshmi, 1998). Among these the model which explains the maximum variability is considered as the best predictive multiple regression model.

Multiple regression model using step up method is developed for predicting manganese and iron concentration from nutrient values in the study area after pooling all the data ignoring their differences.

Multiple regression analysis applied ranked the parameters based on their relative importance as

(Exch. P* Org C) > (Exch. P * Total P) > (Inorg. P * Org C)> (Total N & Org C) > (Inorg. P * Total P) > (Total N. * Total P) > (pH * Org C) > (pH * Total P) > (Total P) being the first 9 relatively most important factors controlling the iron distribution in the study area and for manganese the relatively important parameters are;

(Exch. P * Org c) > (Exch. P & Total P) > (Inorg P * Org C) > (Total P) > (Inorg P & Total P) > (Org & Res P) > (Total N * Org C) > (Total N * Total P) > (Exch. P & Org & Res P) among the first 28 parameters. The above ranked parameters are highly significant as indicated by test statistic t for testing the significance of the regression coefficients (Table 6.1).

Multiple Regression model for predicting concentration variation of trace metal, iron from the parameters pH (X_1), Total Nitrogen (X_2), Exchange P (X_3), Inorganic P (X_4), Organic + Residential P(X_5), Total P (X_6) and organic carbon (X_7) and the first order interaction effects of these 7 parameters is fitted. The best predictive model from a collection of 512 x 5 = 2560 model fitted, is selected and it is the model for predicting square root transformed and standardized [Standardized by subtracting the arithmetic means and dividing by the standard deviation, X-M/σ)] values of dependent variable, trace metal concentration of iron on the square root transformed and standardized values of the independent variable X_1, X_2, X_3, X_4, X5, X_6 and X_7 given above is obtained as;

$Y = 0.8332 + 0.5406\ X_1 + 0.8328\ X_2 - 1.2504\ X_3 - 0.8297\ X_4 - 5.1108\ X_5 +$

$6.2027\ X_6 + 2.0940\ X_7 - 1.4368\ (X_1X_2)$

$+0.9795\ (X_1X_3) - 0.9718\ (X_1X_4) + 0.07281\ (X_1X_5)$

$-10.5256\ (X_1X_7) + 11.5018\ (X_1X_7) - 1.3373\ (X_2X_3)$

$+0.1328\ (X_2X_4) - 1.3986\ (X_2X_5) - 22.1389\ (X_2X_6)$

$+24.3386\ (X_2X_7) - 0.3679\ (X_3X_4) + 03.7613\ (X_3X_5)$

$+43.5286\ (X_3X_6) - 48.4101\ (X_3X_7) - 1.2107\ (X_4X_5)$

$-24.2638\ (X_4X_6) + 25.3410\ (X_4X_7) - 1.52203\ (X_5X_6)$

$-1.0725\ (X_5X_7) + 1.6705\ (X_6X_7)$

Variability explained = 59.9440%

$F(28,28) = 3.9930$, $(P<0.05)$

Multiple regression model for predicting concentration of trace metal manganese, from the parameters, pH (X1), Total Nitrogen (X2), Exchange P(X3), Inorganic P (X4), Organic and Residual P(X5), Total P(X6) and organic carbon (X7) and their first order interaction effects found to be the best-model from among a collection of 2560 models fitted with Y(manganese) and Xi is (given earlier) treated as in the case of iron. The model equation is;

$Y = 0.8676 + 0.3315\ X1 + 0.3483\ X2 - 0.9132\ X3 - 1.0207\ X4 -$ 11.74387

$X5 + 2.8308\ X_6 + 1.4982\ X_7 - 0.86419\ X_1X_2$

$-0.85129\ X_1X_3 - 0.08014\ X_1X_4 + 0.1342\ X_1X_5 +$

$1.12428\ X_1X_6 - 0.63566\ X_1X_7 - 0.98707\ X_2X_3 +$

$0.5485\ X_2X_4 - 0.89674\ X_2X_5 - 7.26416\ X_2X_6$

$- 8.29618\ X_2X_7 - 0.35976\ X_3X_4 + 2.03856\ X_3X_5$

$-22.3978\ X_3X_6 - 25.3967\ X_3X_7 + 0.4346\ X_4X_5$

$-12.17649\ X_4X_6 + 13.5952\ X_4X_7 - 0.7297\ X_5X_6$

$-1.1333\ X_5X_7 + 1.13626\ X_6X_7$

Variability explained = 56.84%, $F_{28,28} = 3.634$, $P < 0.05$)

Table showing the standard error and test statistics for the regression coefficients in the 28 parameter regression model fitted for iron and manganese on the parameters pH(X_1). Total Nitrogen (X_2). Exchange P(X_3). Inorganic P (X_4), Organic and Residual P(X_5). Total P(X_6). organic carbon (X_7).

Table 6.1. Regression model fitted for 28 parameters.

X_6X_7 Parameter	0.4656 **Manganese Std. Error**	2.4403 **t statistic**	0.4486 **Iron Std. Error**	3.7242 **t statistic**
PH (X_1)	0.1863	1.7791	0.1795	3.0115
Total Nitrogen (X_2)	0.2740	1.2713	0.2639	3.1553
Exchange P (X_3)	0.3441	-2.6542	0.3315	-3.7722
Inorganic P (X_4)	0.5923	-1.72321	0.5706	-1.4541
Organic and Residual P (X_5)	7.2962	-1.6096	7.0289	-0.7271
Total P(X_6)	7.7920	1.6467	7.5066	0.8263
Organic Carbon (X_7)	0.3986	3.7582	0.3840	5.4525
X_1X_2	0.4855	-1.7799	0.4677	-3.0718
X_1X_3	0.2760	3.0848	0.2659	3.6843
X_1X_4	0.4760	-0.1684	0.4586	-2.1191
X_1X_5	0.6059	0.2215	0.5837	0.1247
X_1X_6	6.7711	0.1660	6.5231	-1.6136
X_1X_7	7.1510	-0.0889	6.8891	1.6696
X_2X_3	0.3030	-3.2579	0.2919	-4.5817
X_2X_4	0.3735	1.4687	0.3598	0.3690
X_2X_5	0.8182	-1.0959	0.7883	-1.7742
X_2X_6	9.3714	-0.7751	9.0282	-2.4522

X_2X_7	9.7011	0.8552	9.3458	2.6042
X_3X_4	0.1822	-1.9740	0.1756	-2.0957
X_3X_5	0.7615	2.6770	0.7336	5.1271
X_3X_6	9.1793	2.4400	8.8431	4.9233
X_3X_7	10.0071	-2.5379	9.6406	-5.0215
X_4X_5	0.3545	1.2261	0.3415	3.5455
X_4X_6	8.0608	-1.5106	7.7655	-3.1246
X_4X_7	8.1516	1.6678	7.8530	3.2269
X_5X_6	0.4662	-1.5650	0.4492	-3.3886
X_5X_7	0.3446	-3.2889	0.3320	-3.2309

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Chapter 7

PERSPECTIVES AND SAFEGUARDS OF CORAL ECOSYSTEMS

Many coral reefs around the world are under as immediate threat of devastation. Other reefs are showing considerable signs of degradation, and virtually the only reefs that are still in excellent health are those remote from human activities or under active management (Wilkinson, 1992).

During the last two decades coral reefs have experienced an increase in the number of environmental disturbances associated with global level-changes in temperature and light. (Goreau et al., 2000; Mc Clanahan, 2000). Many recent changes in reefs have been associated with localized phenomenon of nutrification, diseases, and heavy fishing. (Mc Clanahan, 2000) one of the most recent global-level disturbance to coral reefs was the 199701998 El Nino event (Wilkinson et.al., 1999; Goreau et.al., 2000). This large scale warming probably represents one of the biggest large scale disturbances to coral reefs in recent history (Goreau et.al., 2000; ISRS statement on Bleaching). The out come of these temperature fluctuations is of concern to the future of coral reefs as they may be indicative of future climate patterns associated with global warming.

The important stress which produce a threatening effort on the existence for coral reefs are anthropogenic-namely-organic and inorganic pollution from sewage, agricultural and industrial waters, sediment damage from excessive land cleaning, and over exploitation particularly through destructive fishing methods. In addition these one other more localized or less service anthropogenic stress : Pollution by oil and other hydrocarbons, complex organic molecular and heavy metal pollution, and destructive engineering practices.

Threats to Indian Reefs.

1.Palk Bay and gulf of Mannar

Exploitation of fishery resources in the inshore waters has been the sole occupation of hundreds of fishing families along the coast for centuries. The reefs are used to carry out reef fishery, chanks and pearl fishery, ornamental shell trades and illegal mining of coral (Mulaev et al., 2000). The distribution of reefs and reef associated organism in the history of environmental damage to nature and natural resources in the recent past .

Some of the islands are totally submerged and vanished may be due to quarrying . The most affected species were the branching corals such as Acropora species, Pocillopora species and Montipora species.

2. Anadaman and Nicobar Islands

Today, among all the reefs in India, many areas in Andaman and Nicobar remains to be in near pristine condition (56-65% live coral exist as per the studies conducted by ZSI, UNDP. Mass mortality of corals was also observed in and around Port Blair probably due to siltation, sand mining, collection of coral reef associates, invasion of crown of thorn starfish (Acanthaster planchi) and White Band disease are reported in many reefs in Andaman and Nicobar Islands (Mulaey et al., 2000). A recent survey conducted in the Little Andaman and Great Nicobar Islands revealed mean live coral cover of 56 %, dead coral cover of 22 % and coral rubble of 11 %

3. Lakshadweep

Black and white band diseases have been observed in shallow coral areas and these are reported of pink band disease . In addition to beaching, coral mining, dredging of navigational channels, unsustainable fishing practices, coastal development activities, souvenir collection and other population associated pressures also contribute to the loss of reef biodiversity (Koya et al., 2000).

The bleaching event of 1998 destroyed much of the living coral cover around Lakshadweep. These are varying reports on loss of live coral and the impact of bleaching estimated between 43-87 % and 60-80 % (Muley et al., 2000).

4.Gulf of Kutch

The major impacts on the coral reef ecosystem come from industrial development, including cutting of mangroves, development of ports and offshore moorings and pollution from large cities. Anthropogenic impacts due to human activities have degraded the coral reef habitats and reduced the coral cover by more than 50 % of most reefs. They have also reported that 70 % of live corals were destroyed during the 1998 bleaching event.

Management Strategies.

Based on the assessment of global reef resources by UNEP / IUCN (1998). other published material, as well as anecdotal evidence and personal observations, Wilkinson (1992) classified the coral reefs of the world into three category.

1. Critical :- Reefs that are severely damaged and is imminent threat of collapse or extermination unless the current levels of anthropogenic stress are removed or ameliorated.

2. Threatened:- Reefs that currently show signs of stress and will come under greater threat of collapse if populations and associated stresses continue to increase at current rates.

3. Stable reefs: reefs with no imminent threat of collapse through anthropogenic damage, which should remain healthy in the immediate future unless events like global climate change introduce unforeseen impacts and stress.

The development strategies for the management of reefs must be viewed on the basis of the above classification as critical, threatened and stable reefs.

A major impediment to management of coastal resources in many countries, is that they are part of the commons; they are not owned by any individual, family or tribal group. Therefore, the traditional mechanisms for sustainable exploitation and protection of land resources are usually absent or have been lost in the fare of increasing economic and population pressure (Wilkinson, 1992).

Considering the need of immediate action, the prime importance must be given to reefs that are in a critical state. Complete removal of anthropogenic sources of pollution must be complemented with the help of local population; the principle users of reef resources.

For reef that are in the threatened category control measures much be taken to prevent destructive exploitations of reefs and their resources. Measures must be taken for the sustainable development of this ecosystem and there is a need for the establishment of marine protected areas. Reefs in the stable category must remain unaffected by the impacts of human populations, economic pressures and global climatic changes.

There is a vast difference between developing and developed counties in their attempt for the management reef resources. In developed countries, the government can legislate for the declaration of marine protected areas and they obtain backing of the local people, scientific community they emphasize on the aesthetic values of the reefs.

In developing countries the mechanisms for enforcing government legislation are inadequate and for the sustainable use practices to proper information must be given to the local population who exploit reef as a way of life.

International agencies like UNESCO, IOC, UNEP, WMO, ASPES, CARICOMP, SCOR, IUCN and the World Bank etc. have potential roles in developing sustainable coral reef use plans.

Global efforts to conserve coral reefs

The international community responded to alarm calls on the status of coral reefs in the early 1990s by initiating major initiatives. The international Coral Reef Initiative (ICRI) was catalyzed by the USA in 1994 with participation of Australia, France, Jamaica, Japan, the Philippines, Sweden, UK and major agencies like UNEP (united nations environmental programme), the Intergovernmental Oceanographic Commission (IOC/UNESCO), the World Bank, ICLARM (International Center for Living Aquatic Resources Management), and SPREP (South Pacific Regional Environment Programme). For more information the date of the status of the reefs – Global Coral Reef Monitoring Network (GCRMN) was formed under the sponsorship of IOC/UNESCO, UNEP, IUCN (the world Conservation Union), and the World Bank. A parallel monitoring programme involving volunteers – Reef Check, joined the GCRMN to broaden global monitoring to include user communities. Reef check has built up a strong following among scientists and recreational divers, and achieved a major goal in raising awareness among the public and governments about the need for coral reef conservation.

CARICOMP (Caribbean Coastal Marine Productivity Program) is an environmental programme that includes reefs, which will co-ordinate monitoring in smaller Caribbean countries and states for the CRMN. A coral reef mapping called AGRA (Atlantic and Gulf Reef Assessment) was launched by scientists at the University of Miami in Florida in 1998, to map reef health. Another programme, AQUANAUT has been developed by ICLARM to train dive-masters to lead reef assessment teams.

Efforts taken for the conservation of Indian reefs

In 1986 Ministry of Environment and Forests (MoEF) launched a scheme for the conservation and management of Indian coral reefs. On the recommendations of the National Committee on Mangrove and Coral Reefs. all the four major coral reefs in the county have been identified for intensive conservation and management. State level steering committees will monitor the progress of implementation in identified reef areas which again be assessed by National Committee consisting of members from various line Ministries Department as well as experts and the representatives of the implementing agencies. In the coral reef areas identifying thrust areas has encouraged research. Government of India has developed adequate policy framework so as to protect coral reefs in India. So as to regulate the on shore developmental activities affecting the coastal environment. Government of India issued a Coastal Regulation Zone (CRZ). Notification in 1991 and amendments in the subsequent years (Mulaey et al., 2000). Environmental Protection Act (1986) and the National Conservation Strategy and Policy Statement on environment and development (1992) as well as the action plan of the Ministry of Environment and Forest have given the consideration this effort.

Certain marine species have been protected under the Wild Life Protection Act (1972). In addition to the national efforts related to conservation of coral reef, the Ministry and Environment is collaborating through various international agencies like UNDP/GEF DPFB programmes. Ministry is also represented on the Global Coral Reef Monitoring Network

(GCRMN), south Asia and in this scheme the Ministry has established Indian Coral Reef Monitoring Network (ICRMN).

Recommendations for protection

Development and implementation of integrated coastal zone management strategies are needed for the effective management of coral reef ecosystems of the world. They must involve combination of the following factors

- Public education
- Community development
- Economic incentives and alternative income generation
- Global or regional legal instruments
- Institutional restructuring
- Well-managed marine protection areas
- Management of tourism and recreational activities
- Management of land-based activities and coastal development
- Coral reef ecosystem monitoring

In addition to the above, a scientific management information is also needed for the protection of coral reefs which includes,

- Understanding the relationship of natural to anthropogenic impacts
- Conducting damage assessments
- Understanding coral recruitment and the maintenance and renewal of reefs

- Understanding water circulation pattern to determine the distribution of reefs and the fate of pollutants
- Developing an improved scientific concept of what constitutes a healthy reef

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