UNRAVELING A BENCHMARK FOR SULPHUR AKIN IN THE COCHIN ESTUARINE SYSTEM

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NIFY BENNY

DEPARTMENT OF CHEMICAL OCEANOGRAPHY
SCHOOL OF MARINE SCIENCES
COCHIN UNIVERSITY OF SCIENCE AND TECHNOLOGY
KOCHI-682016

June 2009

Dedicated to my beloveds……

Dr. Sujatha C.H
Sr. Lecturer
Department of Chemical Oceanography

COCHIN UNIVERSITY OF SCIENCE AND TECHNOLOGY
SCHOOL OF OCEAN SCIENCE AND TECHNOLOGY
FINE ARTS AVENUE,
KOCHI 682 016,
KERALA,
INDIA

Certificate

*This is to certify that the thesis entitled "**Unraveling a benchmark for Sulphur Akin in the Cochin Estuarine System**" is a bonafide record of research carried out by Ms. Nify Benny, under my guidance in the Department of Chemical Oceanography, Cochin University of Science and Technology, in partial fulfillment of the requirements for the degree of Doctor of Philosophy of Cochin University of Science and Technology, and no part of these has been presented for the award of any other degree, diploma or associateship in any University.*

Kochi-16
June 2009

Dr. Sujatha C.H. (Supervising Guide)
Senior Lecturer
Department of Chemical Oceanography
Cochin University of Science and
Technology, Kochi-16

☎ (O) 91-484-2382131 (R) 91-484-2304722 (Mob) 9995991778
Fax : 91-484-2374164, 91-484-2532495
E-mail : drchsujatha@yahoo.co.in, ch_suji@yahoo.com

DECLARATION

I hereby declare that this thesis entitled "**Unraveling a Benchmark for Sulphur Akin in the Cochin Estuarine System**" is an authentic record of the research carried out by me under the supervision of Dr. Sujatha C.H, Senior Lecturer, Department of Chemical Oceanography, School of Marine Sciences, Cochin University of Science and Technology, and that no part of it has previously formed the basis of award of any degree, diploma, associateship or other similar title or recognition.

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June 2009.

Nify Benny

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CONTENTS

PREFACE

Sulphur is an important redox element and exists in wide range of oxidation states. Most of the sulphur added to the sea and oceans is dissolved from land areas and transported in rivers, mainly in the form of sulphate. Part of this sulphur comes from sedimentary rocks and ores exposed to weathering, atmospheric deposition, and to a lesser extent, volcanism. In addition to the natural sulphur flux, approximately the same amount of sulphur is discharged to the oceans by rivers as a result of anthropogenic processes. One further sulphur flux to the oceans is that resulting from submarine hydrothermal activity, which occurs primarily at mid-oceanic rift zones and other areas of tectonic activity.

In the ocean, sulfur is thermodynamically stable in the form of sulfate in the presence of oxygen, but under anaerobic conditions, sulphates can be largely reduced to sulfides by the common anaerobic respiration of marine sulphate reducing bacteria. The world oceans cover play a significant role in the transport of Volatile Sulphur compounds from marine, coastal and estuarine environments to the atmosphere.

The role of dissolved and sedimentary sulphur compounds (sulphate, sulphide , acid volatile sulphide in sediments and Total Sulphur) in determining the redox status of the marine environment is investigated with an attempt to reduce the amount of Sulphur in sediments by the application of phytoremediation. It is a new method for reducing the concentration of pollutants by using green plants. Though it is an environment-friendly method, no work has been yet reported in the Cochin estuarine System.

The present study area included the riverine zones of Periyar and Muvattupuzha. The study made an attempt to compare the hydrographical parameters and sediment characteristics of riverine and estuarine sites of the Cochin estuarine system.

The work presented in the Thesis is divided into following six chapters:

Chapter I: Introduction

Chapter II: Materials and Methods.

This chapter briefs the description of the study area, methodology adopted for the analysis of various parameters and results of the general hydrography.

Chapter III: Sulphur Compounds

This chapter deals with the determination of various inorganic sulphur species in the water and sediments of the estuary.

Chapter IV: Biogeoorganics in the sedimentary environment

This chapter holds the biogeochemistry of the sediments in the selected sites of the estuarine system. A correlation between hydrographical parameters, sulphur compounds and biogeoorganics is also discussed.

Chapter V: Application of Remedial Measure

This chapter is organized as two sections. Section I includes application of phytoremediation to the sediments and its results. Analysis of nutritional value of wheat grass is desribed in Section II.

Chapter VI: The salient features of the investigation are summarised in this chapter.

The references are given at the end of each chapter.

Chapter 1

INTRODUCTION

1.1 Sulphur and its analogues in the Marine Environment

1.1.1 Remedial Measures on Sulphur

1.2 Estuaries

1.2.1 Classification

1.2.2 Types of Estuarine Circulation

1.3 Cochin estuarine System

1.4 Scope of the present study

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1.1 Sulphur and its analogues in the Marine Environment:

The Chemistry of Sulphur and analogues in the environment has taken in a new significance in recent years due to its involvement in the formation of atmospheric aerosols and its impact on acid precipitation, human health, and in the radiation balance of the atmosphere. The world oceans cover approximately 70% of the surface of the earth, and may play a significant role in the transport of Volatile Sulphur compounds from marine, coastal and estuarine environments to the atmosphere.

Reduction and oxidation of sulphur compounds by bacteria play a supplementary role in the conversion of inorganic to organic carbon. The marine environment, constitutes by far the largest portion of the biosphere, is specifically characterized by a strong involvement of sulphur transformations in the production and decomposition of organic carbon (Jannasch, 1982). The oceans represent huge reservoirs of sulfur as dissolved sulfate, with typical concentrations around 29 mM (Strauss 1997; Pilson 1998). Sulphate acts as an additional electron acceptor when free oxygen is consumed. In this capacity, sulphate is quantitatively more important in the marine environment than nitrate or bicarbonate. Bacterial sulphate reduction occurs in the interstitial water of organically rich marine sediments or in stagnant estuarine waters where the dissolved oxygen has been consumed by decomposition processes (aerobic respiration). This reduction of sulphate to hydrogen sulphide by specific groups of bacteria is quantitatively by far more important in marine environments than the deamination of organic sulphur compounds (i.e. the release of HS from S-containing amino acids) during degradation processes. Deuser (1970) estimated, on the basis of ^{13}C determinations and the atomic ratio of sulphur to carbon in marine organic matter, that 95 to 97% of the sulphides in the Black Sea originate from bacterial sulphate reduction, the rest by decomposition of organic sulphur-containing compounds.

DMS is recognized as an important component of the biogeochemical Sulphur cycle and is now known as the second most important source of Sulphur in the atmosphere after anthropogenic SO_2 emissions from the fossil fuel combustion and industry. DMS is biologically produced in surface seawater by metabolic processes with variable abundance among certain phytoplankton species. The quantitatively most important source of DMS in nature is dimethylsulphionopropionate (DMSP), a compound which occurs in marine algae, which is produced in higher quantities in plankton groups such as Phaeocystis and Emiliania Huxley. DMS plays a very important role in the environment because its products contribute to the formation of sulphate aerosols that help in cloud formation and climate regulation.

The present study is an attempt to evaluate the effect of dissolved and sedimentary sulphur compounds (sulphate, sulphide, acid volatile sulphide and total sulphur) in determining the redox status of the selected sites in the Cochin estuarine system.

Most of the organic matter present in the upper waters of lakes and oceans originate from aquatic biota, yet a small percentage of materials escape remineralization during sinking and gets incorporated to the sediments. Organic matter transported to the lakes and oceans from anthropogenic and biological sources on land may behave differently from those of aquatic origin (Prahl et al 1980). Organic matter in sediments has to be regarded as the residue of organic life and this became more important and more abundant with the development and diversification of life. Sediment is a substrate for biological and chemical reaction; it plays a pivotal role in biochemical and geochemical processes. Sediment serves as a surface for bacterial activity. Sediments also act as a sink and a source of chemical components to the overlying water column.

A study of the dissolved and sedimentary organic components like proteins, carbohydrates and lipids is also incorporated for the better understanding of the biogeochemistry of the sedimentary environment of the Cochin Estuarine System.

1.1.1 Remedial measures on Sulphur:

Environmental pollution is a matter of greater concern today. The water bodies are subjected to heavy discharge of a variety of organic as well as inorganic substances by industries situated on its banks. Oil pollution from industries and other activities are hazardous to terrestrial and marine ecosystems. Metals are present in the Earth's crust at various levels. Though some metals are essential for cells, all metals are toxic at higher concentrations for the reason that they cause oxidative stress. Phenolic compounds are one of the most common types of organic soil contaminants. The widespread application of pesticides (alkyl and halogen substituted phenolic compounds) and their resistance to degradation have made the environment highly polluted with them. There exist various research findings on treatment of the polluted sites. Conventional methods for restoring contaminated sites include soil washing, excavation and reburial of soil and pump-and-treat systems for water.

Remediation is a developing technology that reduces the concentration and/or toxicity of various chemical substances such as petroleum products, aliphatic and aromatic hydrocarbons including poly aromatic hydrocarbons and polychlorinated biphenyls, industrial solvents, phenols, benzene, acetone etc., batter liquids, pesticides and metals. Among the remedial measures, the most accepted ones are bioremediation, phytoremediation and chemoremediation. The most pleasing and cost effective method is phytoremediation which uses green plants to remove/degrade pollutants from soils, sediments and groundwater. Plant species have a high biodiversity in uptake, metabolization and accumulation of sulfur so that there are potentials to use plants for phytoremediation of sulfur-enriched sites (Ernst, 1998). According to Marschner (1995), the effectiveness of phyto-extraction for remediation of sulfur enriched soils is highly dependent on the availability of sulfur for the plant. Roots can take up sulfate which is the most important source of sulfur for higher plants. The present study intended to find out the decrease in sulphur as a result of phytoremediation. Wheat grass was selected for this purpose. Since earlier studies have shown that wheat grass is effective in remediating pollutants particularly trace metals, reduction in the concentration of selected trace metals was also focussed.

1.2 Estuaries

An **estuary** is a semi-enclosed coastal body of water with a free connection with the open sea and within which seawater is measurably diluted with fresh water derived from land drainage (Prichard, 1967). The circulation pattern in an estuary is influenced to a considerable degree by its lateral boundaries. The definition also necessitates communication between the ocean and the estuary to transmit tidal energy and sea salts. An estuary is typically the tidal mouth of a river (*aestus* is Latin for tide), and estuaries are often characterized by sedimentation or silt carried in from terrestrial runoff and, frequently, from offshore. They are made up of brackish water. Some familiar examples of estuaries include San Francisco Bay, Puget Sound, Chesapeake Bay, and the New York/New Jersey Harbor. The estuaries serve a banquet of decaying plants, tiny floating plants and animals called plankton, and little fishes. Millions of sea animals get their start in life feeding in the quiet waters of the estuary. They can find shelter in salt marshes, beds of slender eelgrass, or wide mudflats. A range of coastal landforms fit this description, including bays, lagoons, harbours, inlets, sounds, fiords and swamps.

An estuary has very little wave action, so it provides a calm refuge from the open sea. Some of the animals, such as flounder, eels, and striped bass are just visitors to the estuary. Small fishes such as stickleback and mummichogs, mud snails, and oysters may spend their entire lives there. Flush with nutrients and inhabited by resilient organisms, estuaries are among the most productive ecosystems on earth. They provide rich feeding grounds for coastal fish and migratory birds, and spawning areas for fish and shellfish. They are also important in maintaining the quality of coastal waters. Estuaries and the lands surrounding them are places of transition from land to sea, and although influenced by the tides, they are protected from the full force of ocean waves, winds, and storms by such landforms as barrier islands or peninsulas.

Estuarine circulation is common in estuaries; this occurs when fresh or brackish water flows out near the surface, while denser saline water flows inward near the bottom. *Anti-estuarine* flow is its opposite, in which dense water flows out near the bottom and less dense water circulates inward at the surface. Estuaries are marine environments, whose pH, salinity and water level are varying; depending on the river that feeds the estuary and the ocean from which it derives its salinity (oceans and seas have different salinity levels). The time it takes an estuary to cycle completely is called flushing time. As ecosystems, the estuaries are under great threat from human activities. They are small, in demand, impacted by events far upstream or out at sea, and concentrate materials such as pollutants and sediments. (http://en.wikipedia.org/wiki/Estuary - cite_note-1#cite_note-1).

1.2.1 Classifications:

There are four primary subdivisions of estuaries:

a) Drowned river valleys: they are most commonly found along a coastline with a relatively wide coastal plain, and are generally confined to that geological regime. The Chesapeake Bay is a prime example of this type of estuary. Drowned river valleys are wide spread through out the world.

b) Fjords: Generally U-shaped in cross section, these coastal indentures have been gouged out by glaciers. They frequently have a shallow sill formed by terminal glacial deposits at their mouths. Some fjords along the British Columbia Coast have greater sill depths, and the estuarine layers do not extend down to the sill.

c) Bar built estuaries: when offshore barrier sand islands and sand pits build above sea level and extend between headlands in a chain, broken by one or more inlets, bar built estuaries are formed. Albemarle Sound and Pamlico Sound in North Carolina are examples of bar built estuaries.

d) Estuaries produced by tectonic processes: coastal indentures formed by faulting or by local subsidence, and having an excess supply of fresh water inflow, are covered by this category. San Francisco Bay is an example of this group of estuaries.

The main problems to be investigated in an estuary are the water movements, the mixing processes, and the distribution of salinity, which results from their combined action. The distribution of temperature is another factor which has less important effect on the density of water. Yet another type is concerned with the effect of circulation and mixing processes on the movement and dispersion of other substances introduced into the estuary in various ways. The rate of influx of fresh water from rivers varies greatly and the conditions in an estuary change with the variations in the volume of water discharged by the rivers flowing into it.

1.2.2 Types of Estuarine Circulation:

The basic factor in determining the type of circulation is the role played by tidal currents relative to that of river flow in the estuary in question. In the absence of other influences, the river water will tend to flow seawards as a layer of fresh water, separated by a fairly distinct interface from the salt water below. Based on the physical characteristics of estuarine circulation, estuaries can be classified as below.

Salt wedge estuary: River output dominates marine input. The steep density gradient at the interface, amounting to a discontinuity, reduces the turbulence and mixing to a very low level and thus a sharp contrast between fresh surface water and saline bottom water.

Slightly stratified estuary: River output is less than the marine input. Saline water circulates in at the bottom, mixes with fresh water, and then flows out at the top. Thus salinity increases with depth and out toward the sea.

Highly stratified estuary: This is similar to the slightly stratified type, but is limited to the upper layer of water above the outer sill of a fjord. River output and marine input are more even.

Vertically mixed estuary: River output is much less than marine input. Salinity, while constant from top to bottom at any site, increases from land to sea such that the freshwater contribution is negligible.

Inverse estuary: Located in regions with high evaporation, there is no freshwater input and in fact salinity increases inland; overall flow is inward at the surface, downwells at the inland terminus, and flows outward subsurface.

Estuarine environments are among the most productive on earth, creating more organic matter each year than comparably sized areas of forest, grassland, or agricultural land. The tidal, sheltered waters of estuaries also support unique communities of plants and animals, specially adapted for life at the margin of the sea. Many different habitat types are found in and around estuaries, including shallow open waters, freshwater and salt marshes, swamps, sandy beaches, mud and sand flats, rocky shores, oyster reefs, mangrove forests, river deltas, tidal pools, and sea grasses. Estuaries have long been the focal point for much human activity. As the meeting place of sea and river, they provide quite and sheltered waters for harbours and historically gave the easiest or the only access to the interior for trade or settlement. For people living in the interior, they use estuaries as route to the sea for trade, fishing and migration.

Unfortunately, this increasing concentration of people is upsetting the natural balance of estuarine ecosystems and threatening their integrity. Channels have been dredged, waters polluted, and marshes and tidal flats filled and shorelines reconstructed to accommodate human housing, transportation, and agriculture needs. Stresses caused by overuse of resources and unchecked land use practices have resulted in unsafe drinking water, beach and shellfish bed closings, harmful algal blooms, unproductive fisheries, loss of habitat, fish kills, and a host of other human health and natural resource problems. As our population grows, the demands imposed on our natural resources increase. So too does the importance of protecting these resources for all their natural, economic, and aesthetic values.

In India there are about 14 major, 44 medium and 162 minor rivers. Among them the most important major rivers are Ganga, Mahanadi, Godavari, Krishna and Cauveri on the east coast and Narmada and Tapti on the west coast.

1.3 Cochin Estuarine system:

The Cochin Estuarine System, approximately 320 km^2 in area, consisting of Vembanad Lake and the surrounding islands with six rivers flowing in to the estuary, is a very important and integral part of the estuarine ecosystem in Kerala (southwest coast of India). It is used extensively for fishing, transport of goods and also used as a dumping ground for industrial and domestic wastes. The estuarine system extends between 9^0 40'12" and 10^{0}10'46"N and 76^0 09'52" and 76^0 23'57" E with its northern boundary at Azheekodu and southern boundary at Thanneermukham bund. Two large rivers –Periyar and Muvattupuzha – discharge into this estuary. The Thanneermukham bund regulates flow from the other four rivers i.e., Meenachil, Manimala, Achankovil and Pamba. The major sources of sediments to the Cochin harbor are the two large rivers Muvattupuzha and Periyar and the four other rivers to a lesser extend.

The city of Cochin is situated on the western side of Vembanad Lake and is surrounded by a number of islands – the most important ones are Vallarpadam, Vyppin and Bolghatty in north and Nettoor, Kumbalam and Panangad in the south.

The area under study includes two zones- estuarine and riverine. Stations 1, 2, 7 and 8 belong to the riverine zone. Station 1 is in the Muvattupuzha River which is taken as a reference station, station 2 is in the Chitrapuzha River, stations 7 and 8 in the Periyar River. Stations 3, 4, 5 and 6 belong to the estuarine zone. These are closer to the Cochin bar mouth and shows estuarine characteristics in all the seasons.

1.4 Scope of the present study:

Cochin estuary, the largest estuarine system in the southwest coast of India, is a part of the Vembanad-Kol wetlands, which is a Ramsar Site (No.1214). The city of Kochi will be the fulcrum of development through out the country in the coming years. With the implementation of the Vallarpadam International Container Transshipment Terminal (ICTT), Kochi can accommodate the mother ships including many developmental activities in this region. With the need to maintain the outer channel as a passage for large vessels to port , and for the construction of container terminal and L N G terminal, enormous amount of sand has to be dredged out which has several detrimental effects on the environment. Dredging and subsequent dumping of the dredged material may impart drastic environmental problems due to dispersion of accumulated toxic substance in water column, depletion of dissolved oxygen content due to oxidation of organic matter, reduction in primary productivity and increase in temperature and nutrients in water column. The industries situated at the upstream region of Cochin backwaters are causing large scale environment pollution by way of industrial discharge. The industries include fertilizer, pesticides, radioactive mineral processing chemicals allied industries, petroleum refining, heavy metal processing and fish processing. Discharges from all the above industries are found to have a profound influence on the water quality and sediment characteristics of the estuary, especially the upstream region.

A number of multidisciplinary studies have been undertaken in the estuary during past five decades. The levels of trace metals in the water and sediments of Cochin estuary was reported by Nair et al 1990, Babukutty (1991) and Shibu 1996.

Suraj et al (1996) has study Clay mineralogy of Periyar river sediments and their role in the uptake of metals. Nutrient Chemistry of the Cochin estuarine System was investigated by Anirudhan (1988), Muraleedharan Nair (1990), Babu (1999) and Lizen Mathews (2000). The effect of significant pesticides on the water, sediment and biota of Cochin Estuarine System was studied by Sujatha (1992) and Babu (2001). Investigation on the biogeoorganics of the estuary was done by Vasudevan Nair (1992). Studies on the mangroves of Cochin Estuary were made by Geetha (2002), Rini (2002), Shaly John (2003) and Narayanan (2006). Beenamma Jacob (1993) studied the Sulphur Chemistry and Krishnakumar (1999) observed the variations in the surface active substances in the Estuary. All these studies describe the nature of the Cochin estuary. But no effort has been yet made in the direction of remediation. So the present study is an attempt to decrease the concentration of Sulphur and selected trace metals in the sediments of Cochin Estuarine System.

The objectives of the present study are:

- To evaluate the hydrographical parameters and sediment characteristics of selected sites of Cochin estuarine system
- To determine the various sulphur species present in the water and sediments of the system giving emphasis to redox condition
- To obtain a relationship between sulphur compounds and biogeoorganics of the estuary
- To evaluate the efficiency of phytoremediation in decreasing the pollution load
- To assess the nutritional value of wheat grass used for phytoremediation.

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Chapter 2

MATERIALS AND METHODS

2.1 Description of the study area:

The CES, one of the largest tropical estuaries in the Kerala State extends between 9°.40’ N - 10 °.12’ N and 76°.10’ E - 76°.30’ E. It has a length of about 70 km and width lies between a few hundred meters to about 6 km. The CES covers approximately an area of 300 km^2 and are highly dependent on the river basins draining into them. Two major rivers, the Periyar at the north and the Moovattupuzha at the south are the main sources of fresh water to this aquatic system. A channel of about 450m wide forming the entrance to the Cochin harbor and another opening located towards the north at Azhikode have linked the backwater permanently with the Arabian Sea **(Figure 2.1).** Not only the freshwater flow, but al The CES, one of the largest tropical estuaries in the Kerala State extends between 9°.40’ N - 10 °.12’ N and 76°.10’ E - 76°.30’ E. It has a length of about 70 km and width lies between a few hundred meters to about 6 km. The CES covers approximately an area of 300 km^2 and are highly dependent on the river basins draining into them. Two major rivers, the Periyar at the north and the Moovattupuzha at the south are the main sources of fresh water to this aquatic system. Not only the freshwater flow, but also the nutrient and sediment load into these water bodies depend on their drainage basins. The aquatic system is also delayering its quality by the introduction of a large variety of organic as well as inorganic substances including nutrients by the industries situated on its banks. The geochemistry of the sediments in the CES and the adjoining aquatic environment have been influenced by both natural and anthropogenic pollution loads (Arun, 2005; Balachandran et al, 2003; Lalu Raj et al, 2002; Madhu et al, 2007; Martin et al, 2008; Sujatha et al, 1999) and therefore there is an urgent need to the wise use of this aquatic system. So the nutrient and sediment load into these water bodies depend on their drainage basins. The aquatic system is also delayering its quality by the introduction of a large variety of organic as well as inorganic substances including nutrients by the industries situated on its banks. The geochemistry of the sediments in the CES and the adjoining aquatic environment have been influenced by both natural and anthropogenic pollution loads (Arun, 2005; Balachandran et al, 2003;

Lalu Raj et al. 2002; Madhu et al. 2007; Martin et al. 2008; Sujatha et al, 1999;) and therefore there is an urgent need to the wise use of this aquatic system.

Considering the geographic characteristics, eight Stations were identified for the sampling and the inturn analysis. The location of the studied area and sites are given in the **Figure 2.1**

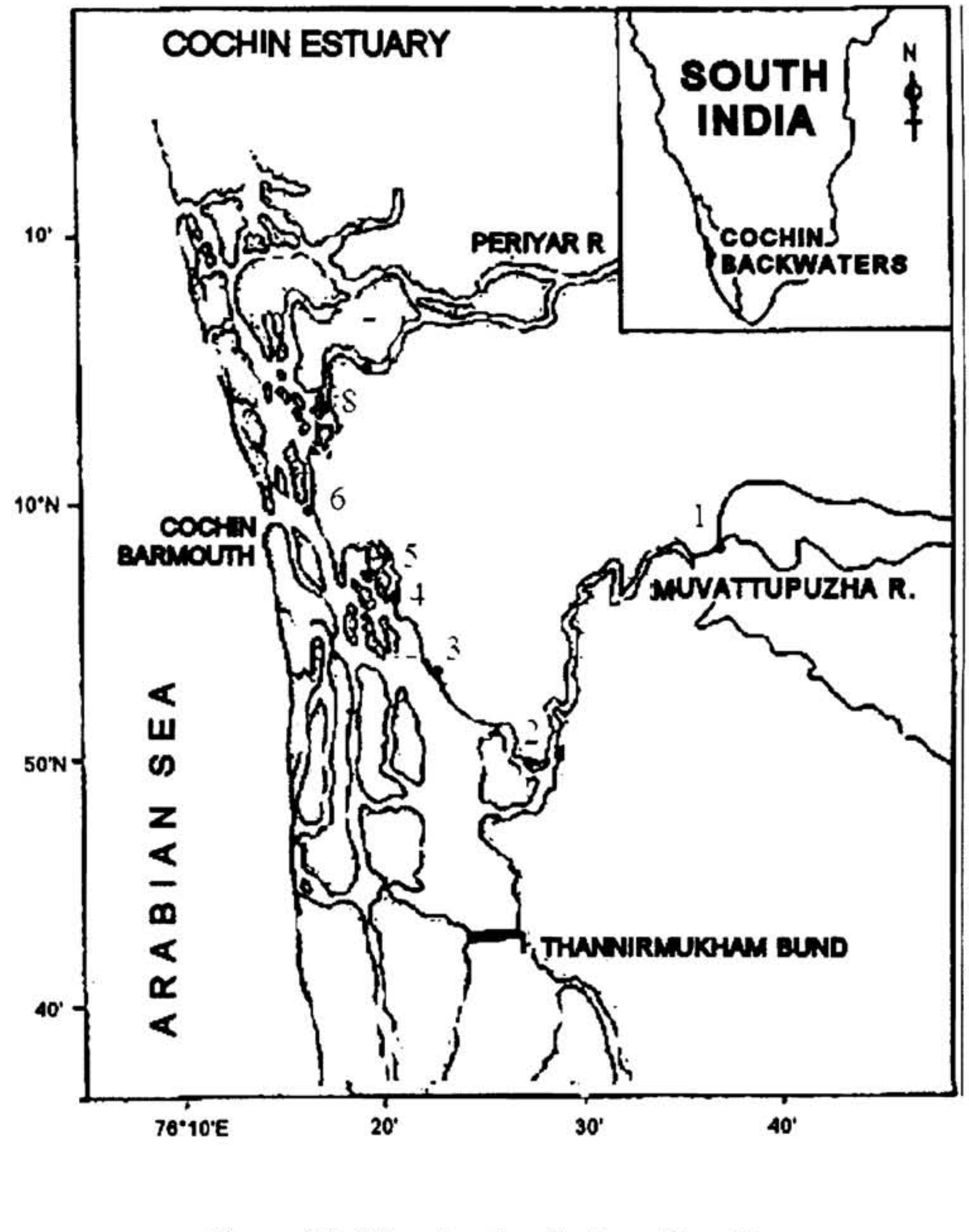


Figure 2.1: Map showing the Sampling sites

The Stations are

Station1: This station is in the Muvattupuzha River at the *Sangamam point.* The name 'Muvattupuzha' is made up of three Malayalam words: 'Moo', which stands for 'three', 'aaru' - small river, and 'puzha', which also means a river. The sampling site is the joining point of the three rivers- Kothamangalam River or *Kothayaar*, Kaliyar and Thodupuzhayar which merge to form a single river. Thus it is called *Thriveni Sangamam* or Centre Point in Malayalam. Muvattupuzha is comparatively less polluted.

Station 2: The sampling site is in the Chitrapuzha River which hosts diverse aquatic organisms and many areas have been transformed into breeding pools so as to increase fish production for commercial exploitation. Numerous industrial units including a diesel power project, fertilizer manufacturing unit and a petrochemical unit are located along the banks of the Chitrapuzha River. Effluents from these industrial units along with agricultural and other anthropogenic effluents find their way into Chitrapuzha River ultimately into Cochin backwaters. The lower reaches of this river became part of National water ways in 1993 and is now mainly used for transporting chemicals from Cochin port to the industrial units located on the banks of the river. The river Chitrapuzha is thus of considerable social and economic importance.

Station 3: This site is in the Champakkara canal nearer to the Champakkara fish market and is found to be highly polluted. The wastes from the fish market are drained to the canal. More over wastes from Cochin Corporation, urban and domestic wastes are also considered to affect the pollution status of the canal.

Station 4: This site is subjected to pollution from oil tankers and also the remains from the fishing industry. Wastes from the Fishing Harbour and fish processing units enter the estuary.

Station 5: This site is in the jetty nearer to the above site and is also polluted.

Station 6: Bolghatty Island also known as Ponjikara is one of the islands that make up the city of Kochi, Kerala, India. The island is a popular tourist haunt, and houses the Bolghatty palace. The palace was built by the Dutch during their reign of the

Kingdom of Kochi. The palace is today a heritage hotel, managed by the Kerala State Tourism Department. The island also has a golf course. Bolghatty Island has a local name Mulavukad. This island is on the western side of Ernakulam. The site is near the Bolghatty palace.

***Station** 7:* This site is in the Periyar river opposite to the location of FACT Caprolactum plant.

***Station** 8:* This station is at the Cheranellore ferry in the Periyar River. The ferry connects Cheranallore to Varapuzha and also to Eloor. One of the largest industrial manufacturing centres, the Udyogmandal Industrial Estate, is located around the branch of the Periyar which passes to the north of Eloor, an island in the upper tidal reaches of the Periyar. Here industrial chemicals, leather and other goods are manufactured. Many of the factories are located on the mainland, but several others are clustered on the north of the island, including FACT (Fertilisers and Chemicals Travancore), IRE (India Rare Earths), Merchem and HIL (Hindustan Insecticides Limited). Hence this site is highly polluted.

2.2 Sample collection and preservation:

The result of any testing method can be no better than the sample on which it is performed. Sample collection and preservation were done as per standard methods. (APHA 1997; Grasshoff et al., 1999). All the collecting scoops, bags and containers were acid washed and rinsed thoroughly with distilled water. Surface water samples were collected using a thoroughly cleaned acid washed plastic bucket and transferred to 5l clean pre washed plastic cans with tight fitting plug, which are rinsed initially with apportion of sample. Bottom samples were taken by Nansen bottle. Stations 2, 4 and 7 had no bottom samples in all the three seasons. Colour, odour, taste were noted first and pH was noted using pH meter. Water for determination of DO was collected first. Samples were siphoned off in a DO bottle, and adding Winkler A and B on the spot fix them for DO. All the samples were transported to the laboratory without any alteration and were refrigerated. The surface sediment samples were collected from each station using a plastic scoop in labeled plastic bags and were frozen.

2.3 Methodology

2.3.1 Hydrographical parameters:

pH of the surface and bottom water samples were measured using a pH meter and temperature using a sensitive thermometer. Salinity of the water samples was estimated by Mohr-Knudsen method (Muller, 1999). Modified Winkler method was used for the estimation of dissolved oxygen (Hansen, 1999). Alkalinity of the water samples was estimated by the method of Koroleff using Bromothymol blue as the indicator (Anderson et al, 1999). Nitrite was converted to an azo dye with sulphanilamide and NED. Formation of phosphomolybdate complex using ascorbic acid as reductant was used for phosphate determination. (Grasshoff, 1999). Phosphate and total nitrogen was also estimated spectrophotometrically using UV-Visible Genesys spectrophotometer.

2.3.2 Sedimentary Characteristics:

Texture analysis of the sediment was done based on Stoke's law using the method of Krumbein and Pettijohn (1983). Sediment samples were air-dried and finely powdered using agate mortar for the further analyses. Total phosphorus was estimated spectrophotometrically after digestion using a di-acid mixture (5:1 HNO_3: $HClO_4$). Sediment organic carbon was estimated on dry sediments by the procedure of El Wakeel and Riley modified by Gaudette et al (1974). Organic Nitrogen was estimated using Kjeldahl method and the distilled ammonia was determined by back titration with 0.01N HCl.

2.3.3 Proteins:

Proteins in water were hydrolysed with 1N NaOH at 80°C for 30 minutes. Colour developed using Copper reagent and Folin-Ciocalteu reagent (Lowry et al, 1951) was measured at 750 nm using UV- Visisble spectrophotometer. Proteins from the sediments were measured using Copper reagent and Folin-Ciocalteu reagent (Lowry et al, 1951).

2.3.4 Total Carbohydrates:

Carbohydrates were estimated by the phenol-sulphuric acid method (Dubois et al 1956). The samples were hydrolysed with 1N conc. H2SO4 in 1:1 ratio at 100o C for 1 hour and cooled aliquots at room temperature and filtered. To 1ml of the aliquots add 1ml of 5% phenol and concentrated H2SO4, cooled the test tube and measured absorbance at 490 nm using UV Visible spectrophotometer (Genesys 10uv). Blank and standards were also treated similarly analysed.

2.3.5 Total Lipids:

To 10 ml sample, 10 ml chloroform-methanol (2:1 v/v) mixture and 20 ml of aqueous NaCl were added in separating flask and after thorough shaking the preparation was allowed to stand for 30 minutes from the clean biphasic layer formed, the lower phase was removed and the same quantity of chloroform was added to makeup the volume. This extract was dried in a vacuum desiccator, over silica gel and added 0.5 ml concentrated H_2SO_4, boiled maintaining in a water bath at 60°C. After cooling to room temperature, 5ml vanillin reagent was added and allowed to stand for 30 minutes. The absorbance of pink color developed was measured at 520 nm using spectrophotometer. A standard was also run employing the same method using cholesterol. Blank was 10 ml of Chloroform-methanol mixture.

Lipids were extracted from the sediments and particulate matter according to the method of Bligh & Dyer 1959. A known amount of the sample is extracted with 2:1 (v/v) mixture of chloroform and methanol. The extraction was done four times. The extracts were pooled together and dried in vacuum desiccator over silica gel and developed the color using concentrated H_2SO_4 and vanillin reagent.

2.3.6 Sulphur Species:

2.3.6.1 Sulphate:

Sulphate from the sediment was extracted using 0.1 N LiCl and analysed gravimetrically(Grasshoff,1999).

2.3.6.2 Acid Volatile Sulphide:

Acid volatile sulphide in sediment was estimated by evolving the sulphide as hydrogen sulphide using HCl. The liberated hydrogen sulphide was trapped in 5% zinc acetate solution, the value was then determined spectrophotometrically using the Cline's methylene blue method (1969). The apparatus for evolving H_2S from sediments is given in **Figure 2.2**

2.3.6.3 Total Sulphur:

Total Sulphur was estimated gravimetrically after digestion using a diacid mixture (5:1 HNO_3: $HClO_4$)

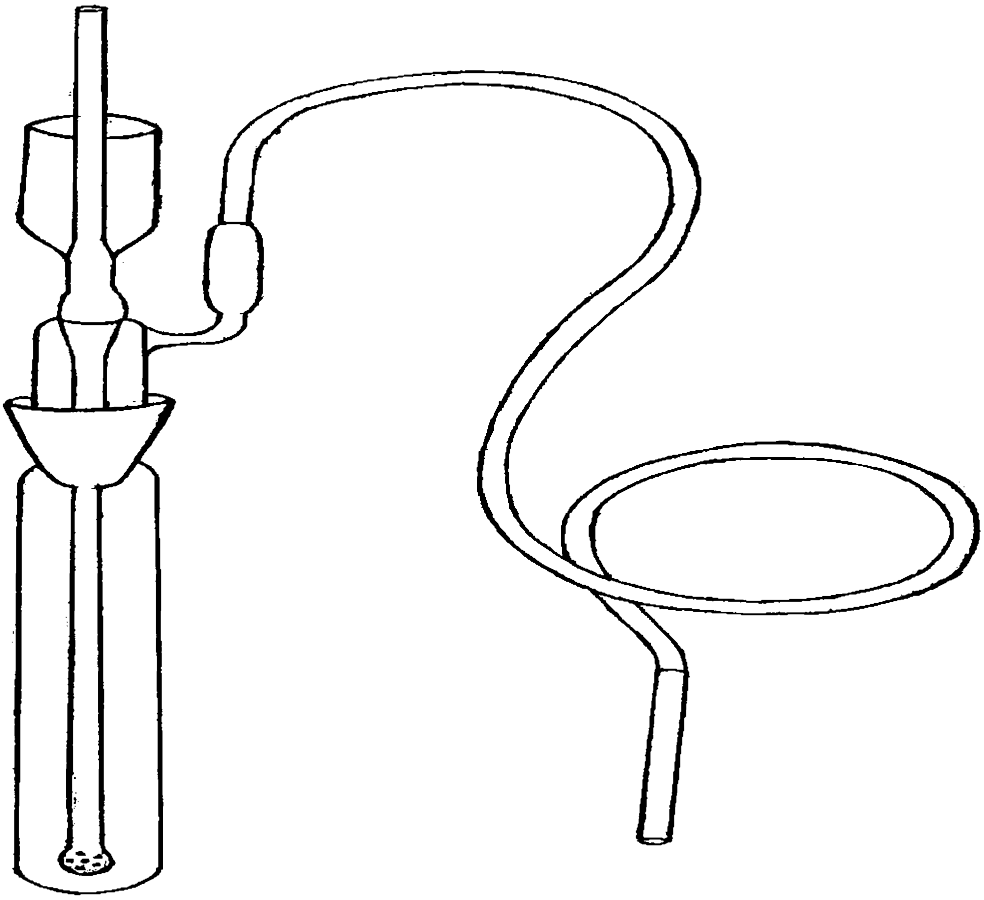


Figure 2.2: Apparatus for H_2S liberation

2.3.7 Application of Remedial Measures:

A remedial measure was trailed in the sediments of the above stations using wheat. Wheat grass was grown in these sediments for a period of two weeks. After the growth period, the grown wheat grass was cut and dried. The sediments were analyzed for various parameters (TOC, TN, TP, TS, sulphate, nitrite, phosphate etc.) before and after remediation. The decrease in the concentration of various nutrients and TOC, TN, TP, and TS are calculated.

2.3.8 Statistical Analysis:

The samples were collected during pre monsoon (Feb-May), monsoon (June – Sept) and post monsoon (Oct-Jan) inorder to establish reliable trends. Difference in parameters with station and season were tested using two way (station & season) ANOVA. Correlation analysis was carried out to find interrelation among different parameters.

2.4 Results and Discussion:

2.4.1 General Hydrography: (Appendix I)

The physiographic characteristics have always been the major constraints that affect the water resources adversely. Seasonal variations in the hydrographical parameters showed marked changes in the chemical constituents.

2.4.1.1 pH:

pH is a measure of acidity or alkalinity of water on a log scale from 0 (extremely acidic) through 7 (neutral) to 14 (extremely alkaline). It is the negative base-10 log of the hydrogen ion (H^+) activity in moles per litre. Hydrogen ions predominate in waters with pH less than 7; hydroxyl ions (OH^-) predominate in waters with pH greater than 7. The pH of marine waters is close to 8.2, whereas most natural freshwaters have pH values in the range from 6.5 to 8.0. Most waters have some capacity to resist pH change through the effects of the carbonate-buffer system. In this system, hydroxyl ions produced during the hydrolysis of bicarbonate neutralise H^+ ions, and maintain pH at a near constant level. Bicarbonate ions (HCO_3^-

) are acquired from the weathering of silicate or carbonate minerals as rainwater passes through the soil zone.

Most aquatic organisms and some bacterial processes require that pH be in a specified range. For example, the activity of nitrifying bacteria is optimal over a narrow pH range from 7 to 8.5 (Henriksen and Kemp 1988). If pH changes above or below the preferred range of an organism (including microbes), physiological processes may be adversely affected [ANZECC 2000) especially true for most organisms if the ambient pH drops to below ~7 or rises to above 9. Physical damage to the gills, skin and eyes can also occur when pH is sub-optimal for fish, and skin

damage increases susceptibility to fungal infections such as red spot desease. pH is driven more frequently to greater extremes under eutrophic conditions, allowing algal species with tolerance to extreme pH levels to grow and dominate communities, and to potentially form algal blooms (Hinga 2002).

Changes in pH can also have indirect impacts on aquatic organisms. For example, changes in pH can alter the biological availability of metals, the speciation of nutrients and the toxicities of ammonium, aluminium and cyanide (ANZECC 2000). Increases in pH can also cause the electrostatic forces that bind viruses to particles to be overcome, thus facilitating their release to the water column (Miller, 2001). pH is important in calcium carbonate solubility (calcite or aragonite), which is important for shell-forming organisms. Shell growth (i.e. calcification) is inhibited if water becomes too acidic.

pH values in the present study ranged from 6.7 to 8.41, 6.33 to 7.92 and 5.77 to7.04 during pre-monsoon, monsoon and post-monsoon respectively [**Figure 2.3** and **Figure 2.4**] . The highest value being 7.94 at Station 6 bottom and lowest being 6.02 at Station 3 surface. There exist transitions of pH from acidic state in riverine sites to alkaline state in estuarine sites, which can be explained by the utilization and release of dissolved oxygen during the biological processes occurring in the estuary (Nasnolkar et al, 1996). In post monsoon, pH showed a lower value than the other two seasons, due to river discharges and mixing of surface runoff with tidal activity.

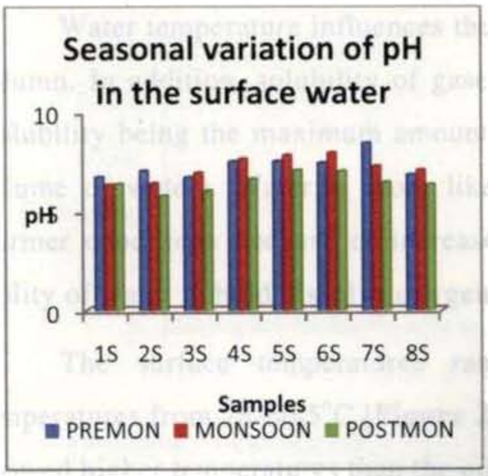


Figure 2.3

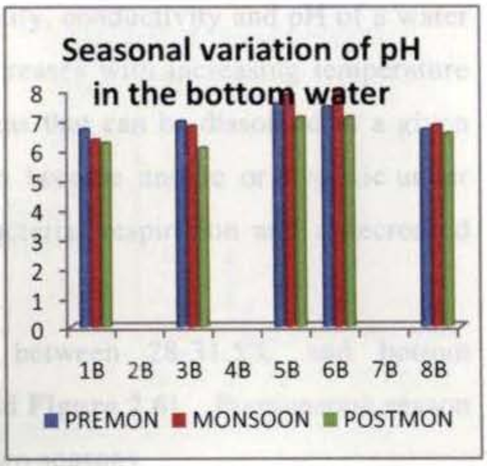


Figure 2.4

2.4.1.2 Temperature:

Water temperature is a measure of the degree of hotness or coldness of water (or the kinetic energy). Unnatural changes in water temperature are a suggested indicator of water quality ANZECC 2000)]. Changes in sea surface temperature in marine and coastal waters are also a suggested indicator for State of the Environment reporting (Ward et al 1998).

Water temperature regulates ecosystem functioning both directly through physiological effects on organisms, and indirectly, as a consequence of habitat loss [ANZECC 2000]. Photosynthesis and aerobic respiration, and the growth, reproduction, metabolism and the mobility of organisms are all affected by changes in water temperature. Indeed, the rates of biochemical reactions usually double when temperature is increased by 10°C within the given tolerance range of an organism (ANZECC/ARMCANZ (October 2000).

Aquatic organisms can only survive within a particular temperature range [Hoegh 1999]. Unnatural changes in water temperature impact indirectly upon biota through loss of supporting habitat such as coral reefs [Ward, 1998.], by changing the solubility of oxygen and calcium carbonate in water, or by influencing the extent to which metal contaminants (Luoma1983) and other toxicants are assimilated by physiological processes.

Water temperature influences the density, conductivity and pH of a water column. In addition, solubility of gases decreases with increasing temperature (solubility being the maximum amount of gas that can be dissolved in a given volume of water). Water is more likely to become anoxic or hypoxic under warmer conditions because of increased bacterial respiration and a decreased ability of water to hold dissolve oxygen.

The surface temperatures ranged between 28-31.5°C and bottom temperatures from 28-30.5°C [**Figure 2.5** and **Figure 2.6**]. Premonsoon season showed higher temperatures than the other two seasons.

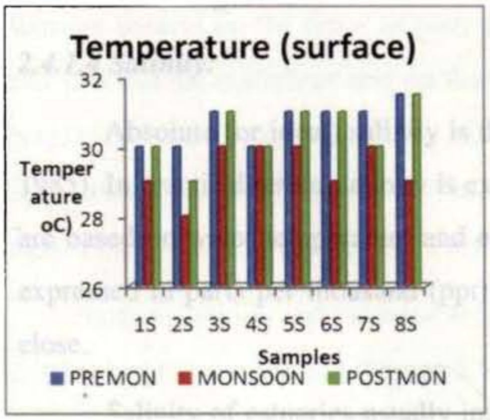


Figure 2.5

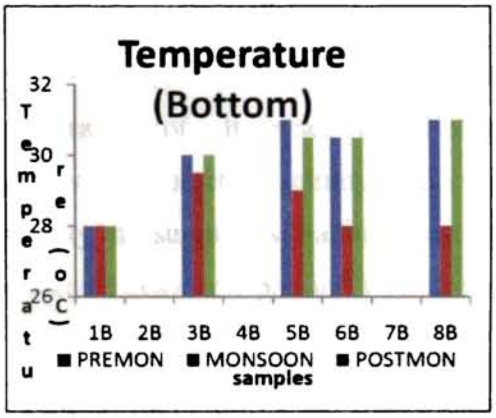


Figure 2.6

2.4.1.3 Conductivity:

Varying conductivity values were shown by the above stations [**Figure 2.7** and **Figure 2.8**]. Riverine stations (1, 2, 7 and 8) showed very lower values which is in agreement with salinity values. Estuarine stations (3, 4, 5 and 6) which are highly saline showed very high conductivity values and total dissolved solids. In surface water highest conductivity value was recorded station 6 during premonsoon.

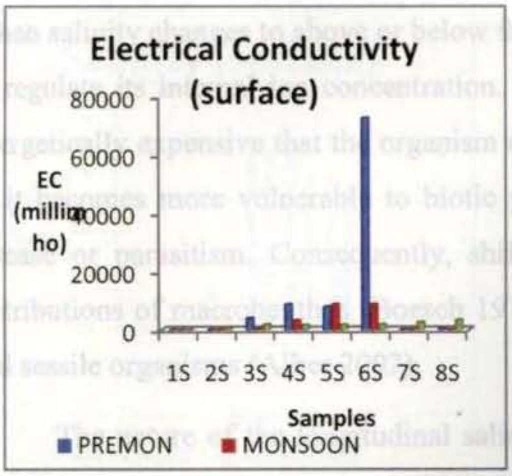


Figure 2.7

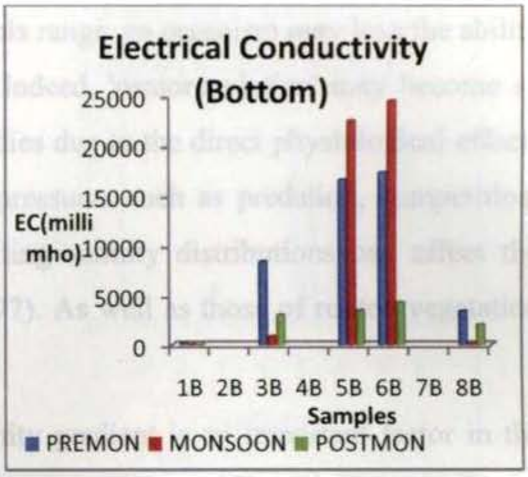


Figure 2.8

2.4.1.4 Salinity:

Absolute (or ideal) salinity is the mass fraction of salts in seawater (Fofonoff 1985). In practical terms, salinity is expressed as PSU (practical salinity units) which are based on water temperature and conductivity measurements. Salinity used to be expressed in parts per thousand (ppt). For oceanic seawater, ppt and PSU are very close.

Salinity of estuaries usually increases away from a freshwater source such as a river, although evaporation sometimes causes the salinity at the head of the estuary to exceed seawater. The vertical salinity structure and the nature of salinity variation along the estuary (i.e. how rapidly salinity varies in the vertical and horizontal) are the defining features of the salinity structure of coastal waterways. Salinity is a dynamic indicator of the nature of the exchange system. The salinity of the water within the estuary tells us how much fresh water has mixed with sea water.

Salinity is an important determinant of the mixing regime because of the density variation associated with salinity variation; salinity stratification tends to inhibit vertical mixing in an estuary; which can have important implications for dissolved oxygen concentrations. The circulation with estuaries and coastal regions can derive from or be strongly influenced by the density variation associated with salinity. In effect, dense saline water tends to flow under fresh water.

Most aquatic organisms function optimally within a narrow range of salinity. When salinity changes to above or below this range, an organism may lose the ability to regulate its internal ion concentration. Indeed, 'osmoregulation' may become so energetically expensive that the organism dies due to the direct physiological effects or it becomes more vulnerable to biotic pressures such as predation, competition, disease or parasitism. Consequently, shifting salinity distributions can affect the distributions of macrobenthos (Boesch 1977). As well as those of rooted vegetation and sessile organisms (Alber 2002).

The nature of the longitudinal salinity gradient is an important factor in the successful recruitment of larval and juvenile fish (Bulger, 1993). Salinity is also an important control on the types of pathogenic organisms and invasive species that can occur in a coastal waterway and on the activity of nitrifying and denitrifying bacteria (Rysgaard 1999). As a general rule, widely-varying salinity regimes tend to select for a low-abundance and low-diversity suite of species, which are adapted to a broad range of ionic concentrations (*e.g.* euryhaline species).

Surface salinity values were found to be lower than that of bottom in most of the Stations [**Figure 2.9** and **Figure 2.10**]. The influx of highly saline water and low discharge of fresh water by rivers caused high salinity during pre-monsoon and post-monsoon seasons. Low salinity during monsoon is due to the heavy rains that caused large freshwater influx into the system, while the differences in the surface and bottom salinity is due to the out flowing riverine water giving a two layered structure (Dehadrai and Bhargava, 1972). Similar results were reported by Nasnolkar et al, 1996. Riverine Stations showed comparatively lower salinity than others. This indicates the freshwater influx either through Muvattupuzha River or Vembanad Lake. Other Stations 3, 4, 5 and 6 close to the river mouth are much high saline in nature. This can be attributed to the sea water intrusion from Arabian Sea to the river water. During pre-monsoon, increased tidal activity brought in a vertical mixing; as a result the salinity increases from 0.08 to 18.55 psu in the studied sites. The salinity variation may be caused by semi-diurnal mixed tides as observed by earlier reporters (Srinivas et al, 2003; Martin et al, 2008).

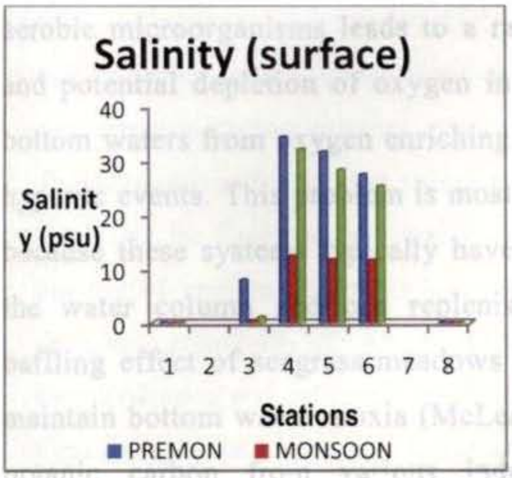


Figure 2.9

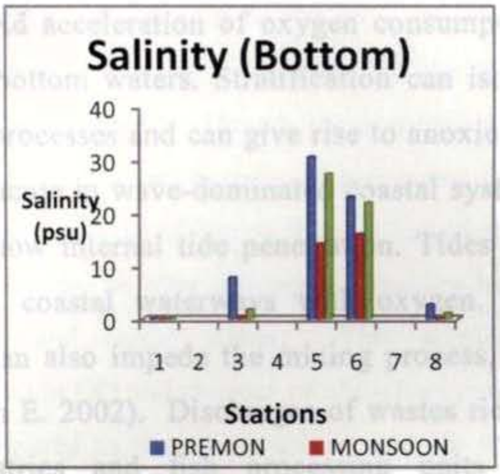


Figure 2.10

2.4.1.5 Dissolved Oxygen:

Measures of dissolved oxygen (DO) refer to the amount of oxygen contained in water, and define the living conditions for oxygen-requiring (aerobic) aquatic organisms. Oxygen has limited solubility in water, usually ranging from 6 to 14 mg L $^{-1}$ (Connell 1984). DO concentrations reflect an equilibrium between oxygen-producing processes (photosynthesis) and oxygen-consuming processes (*e.g.* aerobic respiration, nitrification, chemical oxidation), and the rates at which DO is added to and removed from the system by atmospheric exchange (aeration and degassing) and hydrodynamic processes (*e.g.* accrual/addition from rivers and tides vs. export to ocean) (Connell,1984). Oxygen solubility varies inversely with salinity, water temperature and atmospheric and hydrostatic pressure. Dissolved oxygen consumption and production are influenced by plant and algal biomass, light intensity and water temperature (because they influence photosynthesis), and are subject to diurnal and seasonal variation. DO concentrations naturally vary over a twenty-four hour period due to tidal exchange, and because there is net production of oxygen by plants & algae during the daytime when photosynthesis occurs. By comparison, plants and algae only respire at night time, and this process consumes oxygen. Highly productive systems are expected to have large diurnal DO ranges. Nutrient enrichment stimulates plant and algal growth (and algal blooms) and often results in a mass influx of particulate organic matter to the sediments (eutrophication). The decomposition of this labile organic matter by aerobic microorganisms leads to a rapid acceleration of oxygen consumption, and potential depletion of oxygen in bottom waters. Stratification can isolate bottom waters from oxygen enriching processes and can give rise to anoxic and hypoxic events. This problem is most acute in wave-dominated coastal systems because these systems typically have low internal tide penetration. Tides mix the water column and can replenish coastal waterways with oxygen. The baffling effect of seagrass meadows can also impede the mixing process, and maintain bottom water anoxia (McLean E. 2002). Discharges of wastes rich in organic carbon from various industries and fish processing units can substantially reduce dissolved oxygen concentrations. Most aquatic organisms require oxygen in specified concentration ranges for respiration and efficient metabolism, and DO concentration changes above or below this range can have adverse physiological effects.

The distribution of dissolved oxygen is found to be greatly related to salinity and has an inverse relation with it. DO values range from 1.28 to 5.77 ml/l, 0.9 to 1.96 ml/l and 2.8 to 5.49 ml/l during pre-monsoon, monsoon and post-monsoon respectively [**Figure 2.11** and **Figure 2.12**]. DO values showed a decrease during monsoon which arises from the consumption of oxygen for the oxidation of organic matter which reaches the estuary by land runs off. The sewage from the Kochi city and the neighboring areas and the heavy load of organic material find their way into Kochi backwaters and are responsible for the decrease in dissolved oxygen. Station 1, which is a riverine site, has the highest DO value. Station 8, which is also riverine, shows comparatively higher DO values than the estuarine sites. The lower DO values in the estuarine sites may be attributed to the low solubility of oxygen in saline waters and supports with the earlier studies conducted by Sankaranarayanan and Panampunnayil, 1979.

Phosphate concentration in the water ranges from 0·029-2·005 mg/l, 0·039-1·528 mg/l and 0·003-4·412 mg/l in the pre-monsoon, monsoon and post-monsoon period respectively **(Figure 2.15 and 2.16)**. Dilution of estuarine water with rainwater accounts for comparatively lower concentration in the monsoon months and liberation of phosphate from the bottom mud is responsible for the higher concentration during summer months (Arun, 2005). Though the construction of Thaneermukkom barrier has succeeded in its primary purpose of preventing saline water into the Kuttanad belt- which is the rice bowl of Kerala State, it has created a number of restrictions in the flushing action, thereby making the estuary into a dumping courtyard of agrochemicals and faecal matter. This accelerates eurtrophication and enhances the depletion in DO and increase of phosphate content. Concentration of nitrite was lower compared to that of phosphate and the values range from 0·015-0·436mg/l, 0·001-0·103mg/l and 0·002-0·043mg/l during pre-monsoon, monsoon and post-monsoon respectively (**Figure 2.17 and 2.18**). The lower values of nitrite in any season may be explained by the fact that nitrite is an essential nutrient required for phytoplankton growth and expected photosynthesis to be high in the photic zone due to the utilization of this nutrient for oxidation of organic matter. The CES is facing major threat from eutrophication and luxuriant growth of aquatic weeds, due to the excessive nutrients received either from natural or other artificial sources like sewage disposal sites.

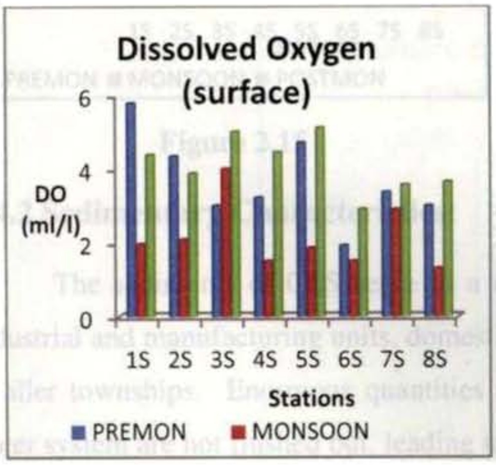
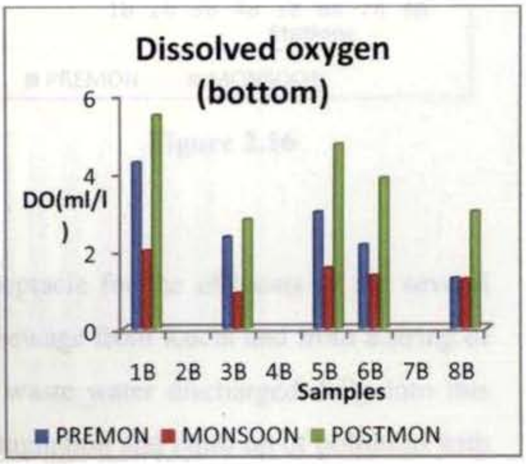


Figure 2.11



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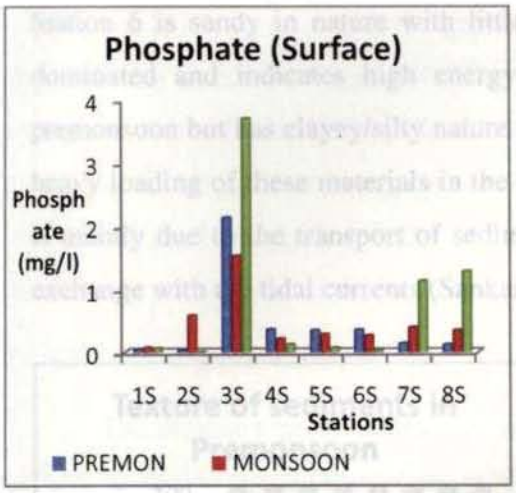

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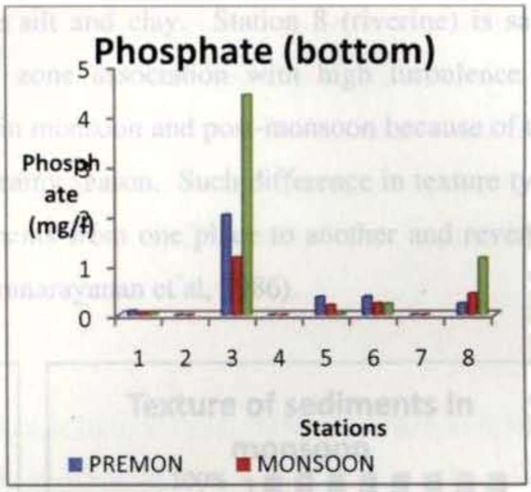

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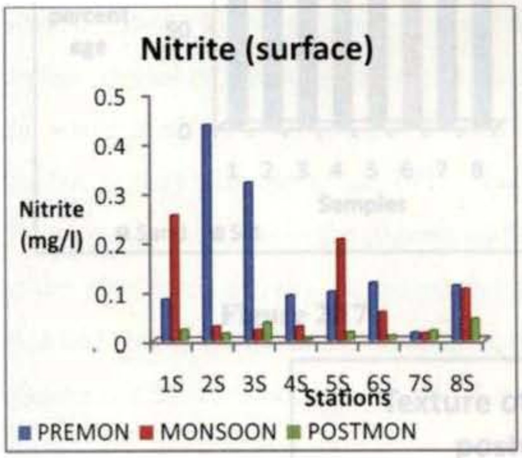

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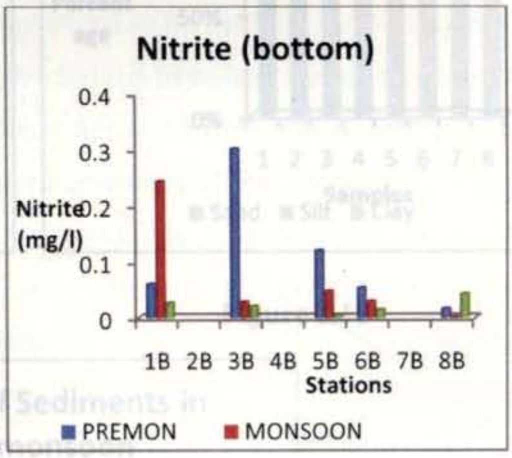

Figure 2.16

2.4.2 Sedimentary Characteristics:

The sediments of CES serve as a receptacle for the effluents of the several industrial and manufacturing units, domestic sewage from Kochi and from a string of smaller townships. Enormous quantities of waste water discharged daily into this water system are not flushed out, leading to stagnation and build up of pollution with high concentration of ammonia, phosphates etc.

2.4.2.1 Texture:

Texture analyses of the sediments in the CES exhibited varying types of combinations- mixture of sand (Stations 1 and 2), clay/silt (Stations 3, 4 & 5) in all the three seasons [**Figure 2.14, Figure 2.15** and **Figure 2.16**]. In post-monsoon, Station 6 is sandy in nature with little silt and clay. Station 8 (riverine) is sand dominated and indicates high energy zone association with high turbulence in premonsoon but has clayey/silty nature in monsoon and post-monsoon because of the heavy loading of these materials in the rainy season. Such difference in texture type is mainly due to the transport of sediments from one place to another and reversal exchange with the tidal currents (Sankaranarayanan et al, 1986).

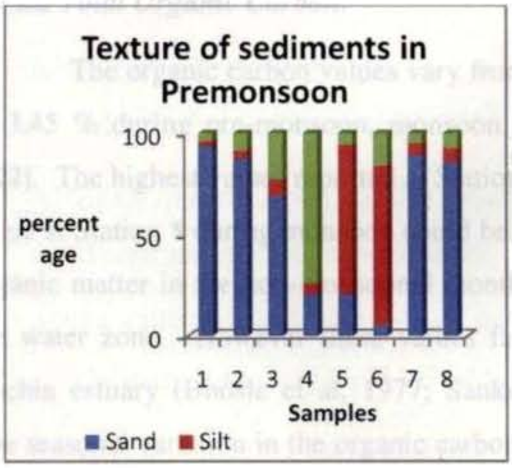

Figure 2.17

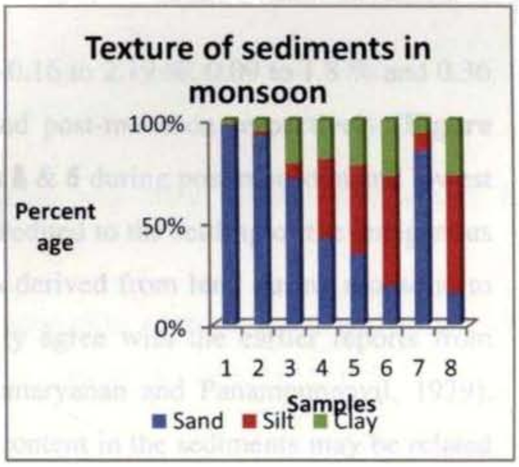

Figure 2.18

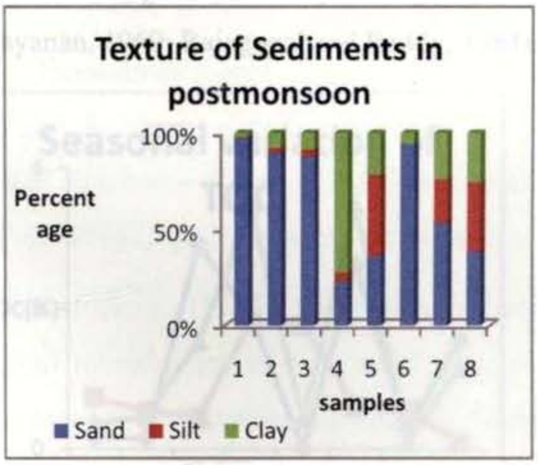

Figure 2.19

In Cochin Estuarine System, the bulk of the sedimentary material is being supplied by the two rivers, the Periyar on the north and the Muvattupuzha on south, mainly during rainy season. The sediments are transported as bed load as well as suspended load. The decreasing trend in grain size observed towards the lower reaches was in conformity with the general trend of progressive decrease in size in a current in the direction of transport. The settling of finer fractions of the sediments took place preferentially during the non-monsoonal months. The increase noted in the case of finer fractions during the non-monsoonal period could be attributed to the low fluvial discharge and a better mixing of saline and freshwater that facilitated flocculation and settling of suspended particles.

2.4.2.2 Total Organic Carbon:

The organic carbon values vary from 0.16 to 2.19 %. 0.09 to 1.8 % and 0.36 to 3.45 % during pre-monsoon, monsoon and post-monsoon respectively [**Figure 2.22**]. The highest values reported at Stations 4 & 6 during post monsoon and lowest value at Station 5 during monsoon could be credited to the settling of the terrigenous organic matter in the non-monsoonal months derived from land during monsoon to the water zone. However these values fairly agree with the earlier reports from Cochin estuary (Bhosle et al, 1977; Sankaranaryanan and Panampunnayil. 1979). The seasonal variation in the organic carbon content in the sediments may be related to the planktonic activity in the overlying water, the humic material brought from land and also to the oxidation of organic matter by the organisms living in the bottom (Qasim and Sankaranarayanan. 1969; Rajagopal and Reddy. 1984).

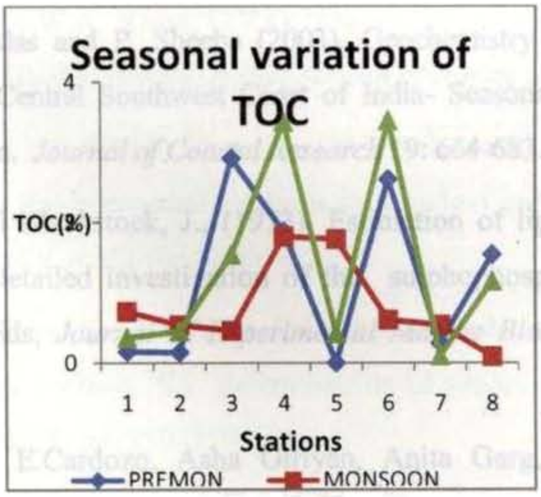

Figure 2.20

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Chapter 3

DISSOLVED AND SEDIMENTARY SULPHUR COMPOUNDS

3.1 Introduction:

Sulphur is an important redox element and exists in wide range of oxidation states. Most of the sulphur added to the sea and oceans is dissolved from land areas and transported in rivers, mainly in the form of sulphate. Part of this sulphur comes from sedimentary rocks and ores exposed to weathering, atmospheric deposition, and to a lesser extent, volcanism. In addition to the natural sulphur flux, approximately the same amount of sulphur is discharged to the oceans by rivers as a result of anthropogenic processes. The total flux of sulphur to the oceans is estimated to be 339.2 TgS per year, half of this from anthropogenic sources. One further sulphur flux to the oceans is that resulting from submarine hydrothermal activity, which occurs primarily at mid-oceanic rift zones and other areas of tectonic activity.

The important biogeochemical processes into which sulphur can enter involve Sulphate reduction, pyrite formation, metal cycling, formation of important resources like petroleum hydrocarbons and coal, atmospheric sulphur emissions, metal corrosions, acid rain and regulation of global climate. Sulphate reduction has gained much attention due to its pivotal role in anaerobic respiration and the resultant production of sulphide minerals. In the +6 oxidation state, chemistry of sulphur is dominated by sulphuric acid and sulphate, which are rather involatile chemical species. As only this oxidation state is stable in the presence of oxygen, sulphate is the predominant form of sulphur in seawater, freshwater and soils. Therefore the reduction of sulphate to a more reduced species is a necessary pre requisite for the formation of volatile sulphur species and their emission to the atmosphere. In the global geochemical cycle, there are two types of biochemical pathways which lead to sulphate reduction: 1) assimilatory sulphate reduction which results in the biosynthesis of organic sulphur compounds which are used for various purposes by the cell (Michel Droux, 2004) and 2) dissimilatory Sulphate reduction which involves the use of Sulphate as a terminal electron acceptor to support respiratory metabolism in the absence of molecular oxygen.

Dissimilatory sulphate reduction is the major pathway for the production of H_2S in an oxygen depleted environment. When the supply of organic matter exceeds the availability of oxygen, which is the most favourable electron acceptor, other electron acceptors (nitrate/sulphate are used) for the oxidation of organic matter. Dissimilatory sulphate reduction is most commonly observed in marine environments where water circulation, and consequent oxygen availability is limited, but where sulphate is easily available because of its relatively high concentration in sea water. This pathway is used by prokaryotes, fungi and photosynthetic organisms (Kredich 1996; Marzluf 1997; Thomas and Surdin-Kerjan 1997; Leustek et al. 2000).

Sulphur is an essential element in the form of organosulphur compounds for biological organisms. All organisms except animals and protozoans are able to carry out assimilatory sulphate reduction for their sulfur requirement. The assimilation of sulphate to cysteine, the first organosulphur metabolite produced, is a complex, multistep process. Cysteine serves as the starting compound for the biosynthesis of all other sulphur metabolites, especially the sulphur containing aminoacids homocystein and methionone.

Sulphate reduction may also be important in salt marsh soils due to the effects of sulfide on plant production. Concentrations of sulphide in marsh soils affect soil redox, metal concentrations, and oxygen availability, all of which may feed back to control plant growth (Howes et al. 1981; Mendelssohn et al. 1981). Sulphate reducers also have other important functions in aquatic environments, such as reduction of intermediate sulphur compounds, iron, manganese, nitrate and oxygen; ethylation and demethylation of metals and metalloids; fermentation of organic compounds; disproportioning of inorganic sulphur compounds and oxidation of reduced sulphur compounds (King et al. 1982).

3.1.1 Sulphur Cycle:

Sulphur is one of the components that make up proteins and vitamins. Proteins consist of amino acids that contain sulphur atoms. Sulphur is important for the functioning of proteins and enzymes in plants, and in animals that depend upon plants for sulphur. Plants absorb sulphur when it is dissolved in water. Animals consume these plants, so that they take up enough sulphur to maintain their health.

Most of the earth's sulphur is tied up in rocks and salts or buried deep in the ocean in oceanic sediments. Sulphur can also be found in the atmosphere. It enters the atmosphere through both natural and human sources. Natural sources can be volcanic eruptions, bacterial processes, evaporation from water, or decaying organisms. When sulphur enters the atmosphere through human activity, this is mainly a consequence of industrial processes where sulphur dioxide (SO_2) and hydrogen sulphide (H_2S) gases are emitted on a wide scale. When sulphur dioxide enters the atmosphere it will react with oxygen to produce sulphur trioxide gas (SO_3), or with other chemicals in the atmosphere, to produce sulphur salts. Sulphur dioxide may also react with water to produce sulphuric acid (H_2SO_4). Sulphuric acid may also be produced from dimethylsulphide, which is emitted to the atmosphere by plankton species.

All these particles will settle back onto earth, or react with rain and fall back onto earth as acid deposition. The particles will than be absorbed by plants again and are released back into the atmosphere, so that the sulphur cycle will start over again.

The principal volatile sulphur species found in seawater are dimethyl sulphide (DMS), carbonyl sulphide (COS) and carbon disulphide (CS_2). Of these, DMS is the most abundant and widespread in its distribution. The predominant oceanic source of DMS is dimethylsulphoniopropionate (DMSP), synthesized by phytoplankton for osmoregulation and cryoprotection. Phytoplanktons differ in their ability to produce DMSP; diatoms generally produce little, whereas prymnesiophytes and some dinoflagellates make significantly larger amounts. Death or predation of the plankton releases much of the DMSP and DMS. Oxidation of DMS to dimethyl sulphoxide (DMSO) is an important process in the water column, and considerable internal cycling in the DMSP/DMS/DMSO system occurs in the euphotic zone. A fraction of the DMS crosses the sea surface and enters the atmosphere where it is oxidized by radicals such as OH^- and NO_2^- to form products such as methane sulphonate (MSA), DMSO and non-sea salt sulphate (NSSS) particles. These particles are the main source of cloud condensation nuclei (CCN) over oceanic areas remote from land. A schematic representation of the sulphur cycle is shown in **Figure 3.12**

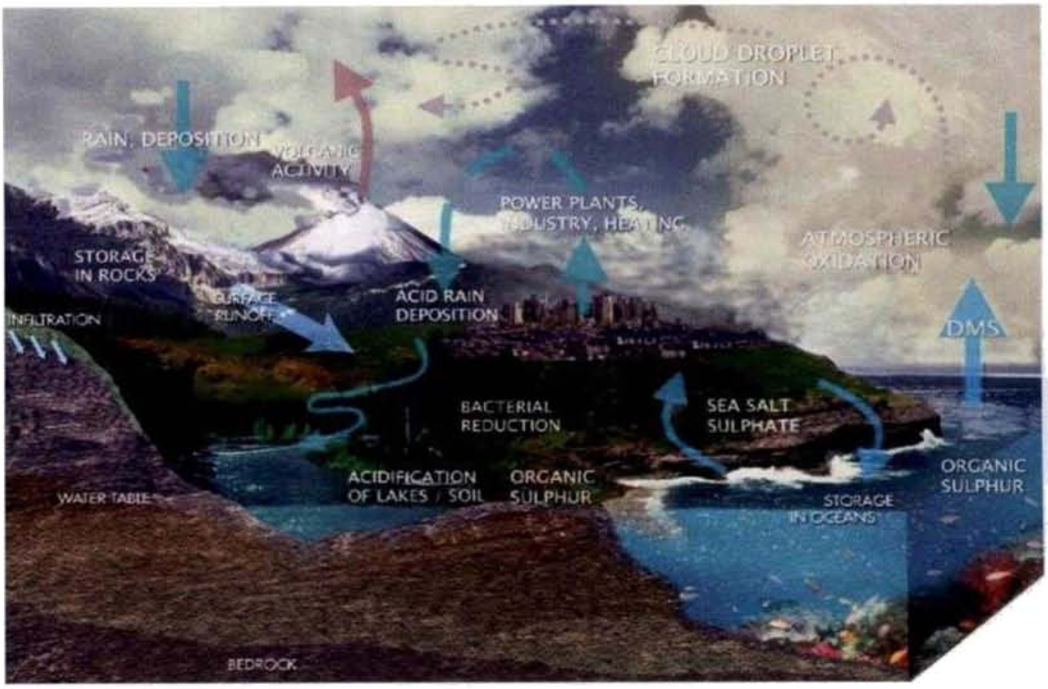

Figure 3.12 Schematic representation of Sulphur cycle

Source: http://www.atmosphere.mpg.de/enid/Nr_6_Feb__2__6_acid_rain/C__The_sulphur_cycle_5i9.html

3.1.2 Estuarine Sulphur Dynamics:

Sulphur is most stable in the form of sulphate and it is a major dissolved constituent in sea water. Sulphate-ion amounts to 7.68% of the total dissolved salts and its concentration varies with changes in total salinity. Dissolved sulphates are partially bound in ion pairs, predominantly $NaSO_4^-$, $MgSO_4^0$, $CaSO_4^0$ and KSO_4^-. Free sulphate ions account for 39-59% of the total sulphate in seawater. In the marine environment, Sulphate is originated from the volatiles which have distilled from the interior of the earth under the influence of radioactive heating (Riley and Chester, 1971). It can come from dissolution of soluble sulphate minerals in sedimentary rocks, oxidation and leaching of sedimentary sulphides mostly pyrite), directly from the atmosphere and soil, or from anthropogenic sources like acid rains and organically-bound sulphur (e.g., Moncaster et al., 2000). Weathering of sulphide minerals also results in the release of Sulphate in to the sea. In the presence of molecular oxygen, organic decomposition is dominated by organisms using oxygen (Goldhaber and Kaplan, 1974). All of these sulphates are mixed in rivers, and may be partly absorbed by plants, partly reduced by anaerobic bacteria in the bottoms of stagnant waters and reformed by oxidation processes. These different sulphate-forming processes will become active at different times according to varying conditions during the year (e.g., Krouse, 1980; Krouse and Grinenko, 1991; Krouse and Mayer, 2000). Most aqueous sulphate is formed by biochemical processes such as dissimilatory reduction which enriches them in the heavy isotopes of both sulphur and oxygen (Nemeck et al; 2006). Sulphate reduction was found to occur more frequently in the overlying sediments (Goldhaber and Kaplan, 1974) than in the water column. In either case, availability of organic matter is a criterion for sulfate reduction.

In marine environment, sulphate reduction depends on three factors: 1) concentration of sulphate, 2) availability of organic matter and nutrients and 3) size and density of bacterial population. In the case of abundance of organic matter and nutrients, the rate of sulphate reduction is limited by concentration of sulphate. If the population of sulphate reducing bacteria is limited by organic matter and nutrients, rate will be controlled by either nutrient and sulphate concentration or both. Sulphate is reduced to a number of sulphur species with the formation of intermediate oxidation states. These includes sulphite ($SO_3{}^{2-}$), thiosulphate ($S_2O_3{}^{2-}$), sulphide(S^{2-}) and solid sulphur in colloidal or orthorhombic form. Sulphide exists as H_2S (aq.), HS^- or S^{2-}. Their relative stabilities depend on physico chemical parameters (Field, 1972). HS- is the major sulphur species found in sea water at a pH of 8, followed by H_2S and S^{2-} in minor quantities. (Richard 1965). H_2S is found to be the most stable in highly acidic anoxic environment (Garrel and Christ, 1965; Krauskopt, 1967). Thus the major sulphur species in oxygenated water is SO_4^{2-} and in anoxic bottom water is S^{2-}. In estuaries, importance of sulphate lies in the fact that it is present in higher concentrations in these systems and is used as an electron acceptor for the oxidation of huge amounts of organic matter which accumulates in estuaries as a result of anthropogenic actions. (Pfenning & Widdel, 1982).

In stagnant water, some sulphur may be present in the form of dissolved sulphide. Sulphide is also found in the waters of inland seas, lagoons, depressions, fjords, and upwelling areas. Often its appearance is a recurrent phenomenon, which is governed by seasonal and climatic conditions. The bulk of dissolved sulphide in seawater and pore fluids of marine sediments is in the form of HS^{-1} ions. The contribution of dissolved sulphide to sulphur balance is negligible, even in regional cycles. During the oxidation of sulphides in the presence of dissolved oxygen, HS- is again oxidized to sulphate (Richards, 1965) and different intermediate species like $S_2O_3^{2-}$, SO_3^{2-} etc are formed. Hydrogen sulphide may be photosynthetically oxidized to sulphur. In anoxic waters, sulphide may be removed by large amounts of trace metals by precipitation as the metal sulphide or anaerobic oxidation of bisulphide ion as reported by Luther and Church (1988) with the production of hydrogen peroxide by micro organisms. Tuttle and Jannasch, (1973) have reported the occurrence of sulphide oxidizing bacteria in the anoxic waters and sediments of Black Sea.

Sulphur in modern ocean sediments exists in various forms. Deposition of organic matter in large quantities converts the sediment to a strongly reducing environment in the estuary, especially in the surface. During sedimentation some dissolved sulphate is entrapped in pore-water. In addition, sulphates can occur in the solid phase of sediments as clay mineral sulphate, as sulphate in the carbonate skeletons of organisms, and as anhydrite, gypsum and barite. In addition to sulphate, various amounts of soluble sulphide, thiosulphate, and sulphite are found in pore-waters of reduced sediments. Insoluble reduced sulphur in reducing sediments include acid-soluble iron sulphides, pyrite, elemental sulphur and organically bound sulphur. The total amount of reduced sulphur in sediments can be taken to be a measure of the intensity of bacterial sulphate reduction which occurs particularly in sediments with a high content of organic matter. In the majority of the cases, the amounts of soluble sulphide, thiosulphate, and sulphite in pore waters are negligible compared to those of reduced forms of sulphur in the solid phase of sediments and are usually ignored.

3.2 Dissolved sulphur compounds: (Appendix II)

3.2.1 Sulphate:

The investigations of the sulphate origin in rivers by means of isotopic techniques are widely documented (Morrison et al., 1999; Soler et al., 1999; Bottrell et al., 2000; Haubrich and Tichomirowa, 2002; Otero and Soler, 2002; Soler et al., 2002). .

Many workers reported conservative behavior for sulphate in various aquatic systems. Morris and Riley (1966) suggested a steady value for Sulphate/chlorinity ratio of 0.14+- 0.002 in the major oceans and seas of the world except for Baltic. Hosokawa et al (1970) found that sulphate behaved conservatively in Chikugogawa Estuary. Gupta and Naik (1981) suggested that sulphate behaved in a purely conservative manner in Mandovi and Zuari river systems. In the Cochin Estuarine System, Beenamma Jacob (1993) studied the various Sulphur species in the water and sediments and found that sulphate showed deviation from conservative behavior.

The seasonal distribution of dissolved sulphate in surface and bottom water samples are presented in **Figures 3.1** and **3.2**. The concentration of sulphate in premonsoon varied from 0 to 109.5 mmols/l in surface and from 0.01 to 3.35 mmols/l at the bottom. In monsoon, the values ranged from 0.42 to 32.77 mmols/l at the surface and from 0.01 to 0.99 mmols/l at the bottom. In postmonsoon, sulphate concentration varied from 2.45 to 98.16 mmols/l in surface and from 0.05 to 2.43 mmols/l in bottom. The concentration of sulphate is found to be higher at stations closer to the barmouth. The highest sulphate concentration was recorded at station 5 surface (109.5 mmols/l) where the salinity is 15.67 psu. Station 1 which lies in the riverine zone recorded lowest values. Highest values were recorded in the pre monsoon season and the lowest in the monsoon season. Earlier Burton and Liss (1976), reported that the average concentration of sulphate in river water is 0.116 mmol/l with a high sulphate/chloride ratio.

In the present study, sulphate concentration showed deviation from conservative behavior in certain stations and this could be due to the change in the pattern of biogeochemical activities of sulphate in the estuary. The distribution pattern of sulphate showed a general decreasing trend towards the upstream. The highest values for sulphate observed in station 5 & 6 are due to the nearby marine conditions. Lowest sulphate concentrations were recorded at station 1 which is the farthest from bar mouth. This station is in the Muvattupuzha River and is characterized by low sea water influx.

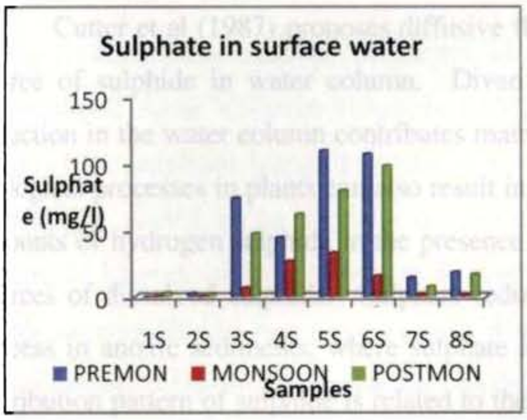

Figure 3.1

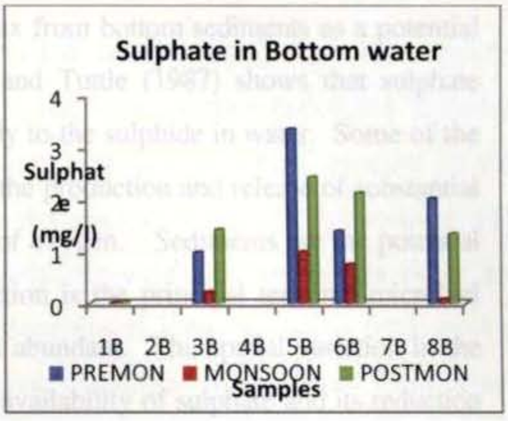

Figure 3.2

3.2.2 Dissolved Sulphide:

The seasonal variation of dissolved sulphide concentration in surface and bottom water samples at various stations are graphically represented in **Figures 3.3 and 3.4.** During the period of study, the sulphide concentration varied from 0.019 to 0.534 mg/l in the surface water and from 0.097 to 0.421 mg/l in the bottom water. In pre monsoon, sulphide concentration varied from 0.036 to 0.534 mg/l in surface water and 0.11to 0.221 mg/l in bottom water. In most of the stations, monsoon season recorded lowest values which ranged from 0.019 to 0.497 mg/l in surface waters and from 0.097 to 0.317 mg/l in bottom waters. Post monsoon exhibited higher sulphide concentrations than other two seasons which ranged from 0.222 to 0.442 mg/l in surface and from 0.325 to 0.421mg/l in bottom waters. Dissolved sulphide content was found to be high in bottom water samples than surface except in few cases.

Though sulphide was believed to exist in anoxic waters, recent studies have found wide distribution of H_2S in oxic surface waters (Cutter & Krahforst 1988, Andreae et al, 1991).

Maximum concentrations of sulphide observed in the stations 4, 5 and 6 during postmonsoon season may be due to the heavy loads of organic matter in these sites drained from domestic sewage, fishing and coconut retting industries which is accounted for the high rate of sulphate reduction.

Cutter et al (1987) proposes diffusive flux from bottom sediments as a potential source of sulphide in water column. Divan and Tuttle (1987) shows that sulphate reduction in the water column contributes mainly to the sulphide in water. Some of the biological processes in plants can also result in the production and release of substantial amounts of hydrogen sulphide in the presence of oxygen. Sediments are the potential sources of dissolved sulphide. Sulphate reduction is the principal terminal microbial process in anoxic sediments, where sulphate is abundant. The spatial variation in the distribution pattern of sulphide is related to the availability of sulphate and its reduction and transport from sediments. Thus decrease of sulphide concentration observed at different stations could be due to low sulphate reduction rate. This inturn depends on the availability of sulphate and abundance of organic matter. The low intensity of sulphate reduction, low organic input from sewage and retting grounds etc. showed low sulphide values at station 1 in the Muvattupuzha River. The high sulphide concentration in the bottom water in almost all the stations may be due to reduction of sulphate taking place in the anoxic bottom waters (Burner, 1970). The distribution of sulphide is influenced by the mixing of sea water with freshwater during tidal action and this could be the reason for the high surface values than the bottom values observed in some cases. The oxides of Fe and Mn may also be responsible for the turnover of H_2S in deep waters (Millero, 1991). The comparatively lower values for sulphides recorded in surface water samples in all the stations during pre monsoon might be due to the extreme hot condition which facilitates the escape of H_2S gas from water.

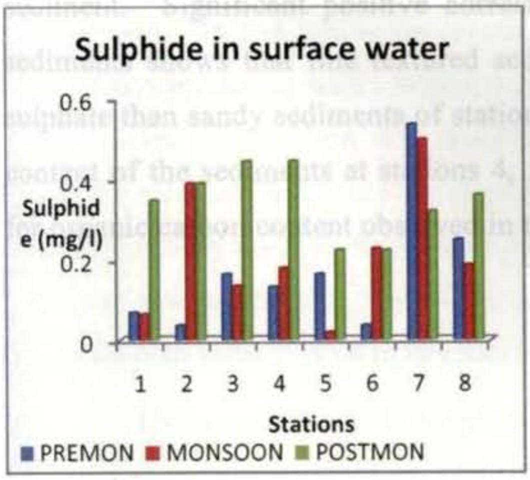

Fig. 3.3

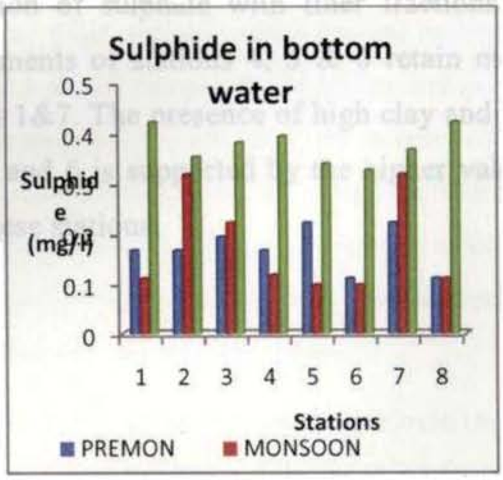

Fig. 3.4

3.3 Sedimentary Sulphur Fractions:

Sedimentary sulphur fractions identified in this study include sulphate sulphur and Acid Volatile Sulphide (AVS). Sulphate sulphur estimated includes mainly the sulphate trapped in the sediments and any traces of gypsum in the sediments. AVS is so termed inorder to distinguish between the soluble and insoluble phases of iron sulphide in hydrochloric acid. In sediments there are many monosulphide compounds with divalent metal ions including iron, nickel and copper. Upon acidification, hydrogen sulphide is released from these monosulphides and hence this sedimentary sulphur fraction is called Acid Volatile Sulphide (Cutter and Oatts, 1987).

3.3.1 Sulphate in sediments:

Supply of sulphate from the water column to the sediment is one of the factors which decides the amount of sedimentary sulphur fractions (Nriagu, 1968). Seasonal variation of sedimentary sulphate at different stations are represented in **Figure 3.5**. Sedimentary sulphate concentration varied from 0.83 to 10.88 mg/g, 0.57 to 31.85mg/g and 1.45 to 20.98mg/g during premonsoon, monsoon and postmonsoon respectively. The sulphate content was comparatively high in the estuarine zone than in the riverine zone. Highest value was recorded at station 5 during monsoon and lowest at station 1 during premonsoon. The concentration of sulphate in the sediment depends largely on the nature of the sediment. Significant positive correlation of sulphate with finer fractions of sediments shows that fine textured sediments of stations 4, 5 & 6 retain more sulphate than sandy sediments of stations 1&7. The presence of high clay and silt content of the sediments at stations 4, 5 and 6 is supported by the higher values for organic carbon content observed in these stations.

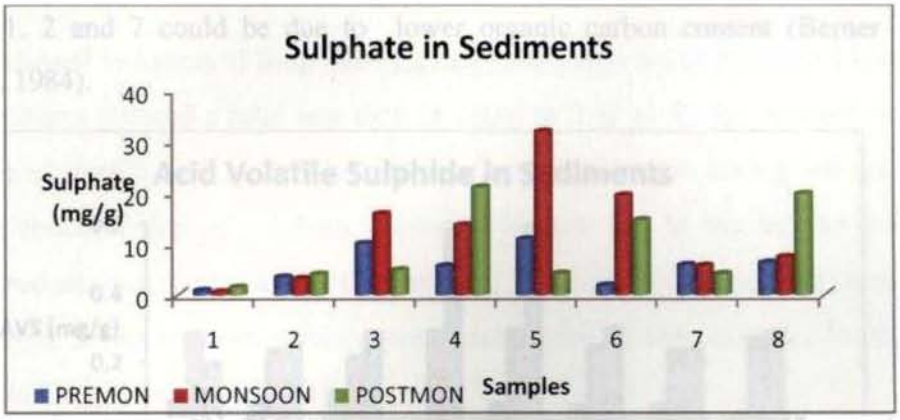

Figure 3.5

3.3.2 Acid Volatile Sulphide:

The seasonal distribution of Acid Volatile Sulphide(AVS) in the sediments of different stations are graphically represented in **Figure 3.6**. During the period of study, the concentration of AVS among the stations varied from 0.003-0.097 mg/g, 0.199-0.277 mg/g and from 0.23-0.577mg/g during premonsoon, monsoon and postmonsoon respectively. The lowest value was recorded at station 4 during premonsoon and highest value at station 5 during postmonsoon. Organic carbon content in Stations 4,5 and 6 were found to be the maximum during the course of the study which suggest high degree of sulphate reduction at these stations. The decrease in the concentration of dissolved sulphate in the bottom water samples during premonsoon and monsoon suggests an increased supply of sulphate to the sediments. This in turn in the presence of huge organic carbon content undergoes reduction producing AVS. Station 4 and 5 shows comparatively higher amounts of AVS in the postmonsoon. The dissolved oxygen in the bottom water samples of this station was low and hence the organic matter brought by the land runoff during monsoon, may undergo decay in the anoxic conditions liberating hydrogen sulphide, a large amount of which may go into the sediments as FeS and MnS thus accounting for the high value of AVS in this station (Boesen and Postma, 1988).

The variation in the distribution of AVS in sediments may be attributed to the variation in the amount of organic matter. Thus the low values for AVS found in

Stations 1, 2 and 7 could be due to lower organic carbon content (Berner and Raiswell, 1984).

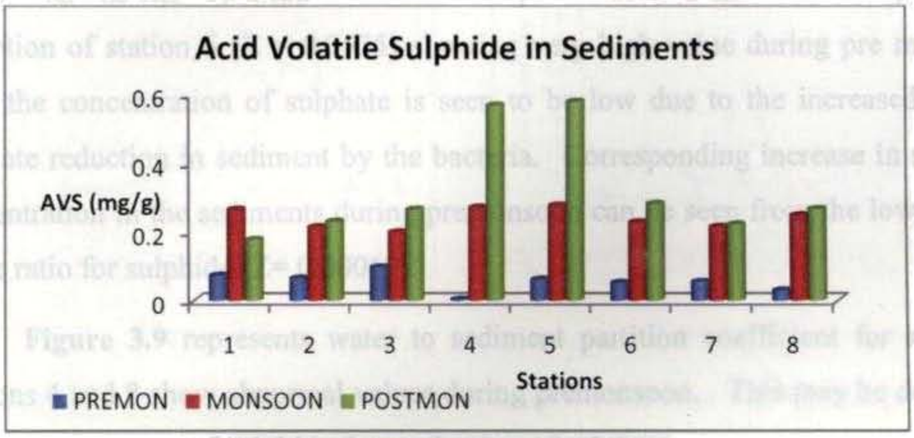

Figure 3.6

3.3.3 Total Sulphur:

Seasonal variation in Total sulphur in sediments are depicted in **Figure 3.7.** Total sulphur in the sediments of selected sites ranged from 1.98-42.09 mg/g, 0.881-47.37 mg/g and 1.99-40.66 mg/g during pre monsoon, monsoon and post monsoon respectively. The highest concentration was reported at station 5 (47.37) during pre monsoon and lowest at station 1 (0.881 mg/g) during pre monsoon. Station 1 showed the lowest TS concentration at all the three seasons. Station 5 recorded the highest values. This station is located at the Cochin Port Jetty, where the transportation of Sulphur to the factories (FACT) is taking place. Station 5 is followed by station 4 (Cochin Port near Taj Malabar Hotel) and station 6 (Bolghatty).

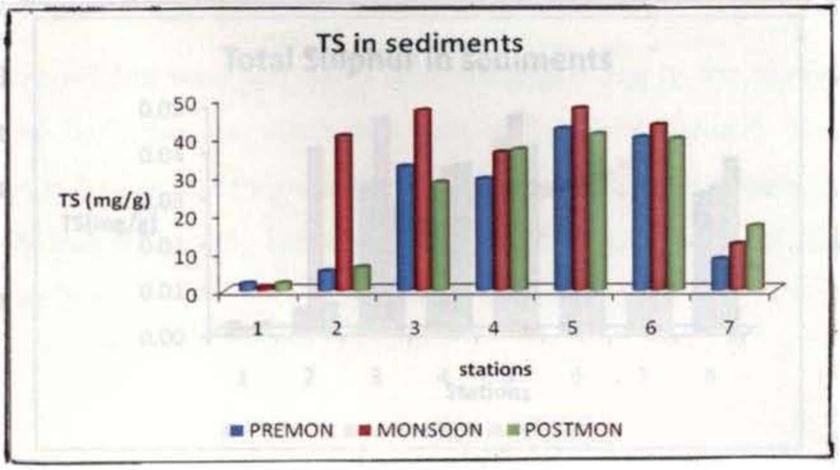

Figure 3.7

3.4 Water to Sediment Partition Coefficient:

Seasonal variation of Sulphate $_{\text{water}}$/Sulphate $_{\text{sediment}}$ are depicted in **Figure 3.8**. All the stations showed a ratio less than or equal to 0.02 at all the seasons, with the exception of station 6 (Z = 0.0575) showing very high value during pre monsoon. Here the concentration of sulphate is seen to be low due to the increased rate of sulphate reduction in sediment by the bacteria. Corresponding increase in sulphide concentration in the sediments during premonsoon can be seen from the lower value of the ratio for sulphide (Z= 0.00069).

Figure 3.9 represents water to sediment partition coefficient for sulphide. Stations 4 and 8 show abnormal values during premonsoon. This may be due to the increased oxidation of sulphide than reduction of sulphate.

3.5 ANOVA

Table 3.1 Two factor ANOVA for Total Sulphur

Source	Sum of Squares	df	Mean Square	F	Sig.
Intercept	206.535	1	206.535	5243.578	.000
Season	.072	2	.036	.912	.424
Station	23.866	7	3.409	86.561	.000
Error	.551	14	.039		
Total	231.024	24			

Here we can seen that the p-value corresponding to the seasonal factor is greater than 0.05, then the effect of season on the Total Sulfur is not statistically significant at 0.05 level of significance. Also the p-value corresponding to different stations is less than 0.05, hence the factor Station significant at .0.05 level of significance.

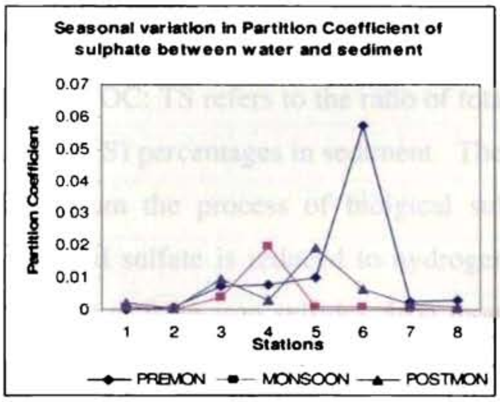

Figure 3.8

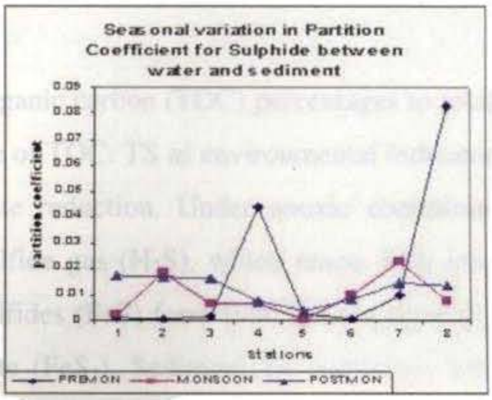

Figure 3.9

Table 3.2 Water to Sediment Partition Coefficient for Sulphate

STATIONS	PREMON	MONSOON	POSTMON
1	0.0000	0.0007	0.0021
2	0.0008	0.0001	0.0006
3	0.0074	0.0042	0.0098
4	0.0079	0.0196	0.0030
5	0.0101	0.0010	0.0191
. 6	0.0575	0.0008	0.0067
7	0.0025	0.0003	0.0019
8	0.0029	0.0002	0.0009

Table 3.3 Water to Sediment ratio for Sulphide

STATIONS	PREMON	MONSOON	POSTMON
1	0.0009	0.0024	0.0173
2	0.0006	0.0185	0.0169
3	0.0017	0.0067	0.0164
4	0.0437	0.0066	0.0078
5	0.0027	0.0007	0.0038
6	0.0007	0.0099	0.0079
7	0.0097	0.0226	0.0145
8	0.0830	0.0074	0.0133

3.6TOC: TS ratio

TOC: TS refers to the ratio of total organic carbon (TOC) percentages to total sulfur (TS) percentages in sediment. The use of TOC: TS as environmental indicator arise from the process of biolgical sulphate reduction. Under anoxic conditions dissolved sulfate is reduced to hydrogen sulfide gas (H_2S), which reacts with iron minerals to form iron sulfides. Iron monosulfides (FeS) form first, but are typically unstable, and are usually converted to pyrite (FeS_2). Sediment TS comprises iron monsulfides and potentially a very small amount of elemental sulfur (S^0). TOC:TS ratios reflect the importance of sulfide reduction in the decomposition of organic matter, and thus give a qualitative indication of the redox status of the environment of deposition **(Figure 3.10)**

Aerobic marine sediments typically have TOC:TS ratios greater than 5.0. Marine sediments undergoing sulfate reduction under euxinic/inhospitable bottom conditions (*e.g.* anoxic bottom waters with high H_2S concentrations) typically have TOC: TS ratios lower than 1.5 [Berner, 1983; Craft et al., 1991]. Marine sediments undergoing sulfate reduction below an oxygenated water column typically have TOC:TS ratios in the range from 1.5 to 5.0 [Berner, 1983].

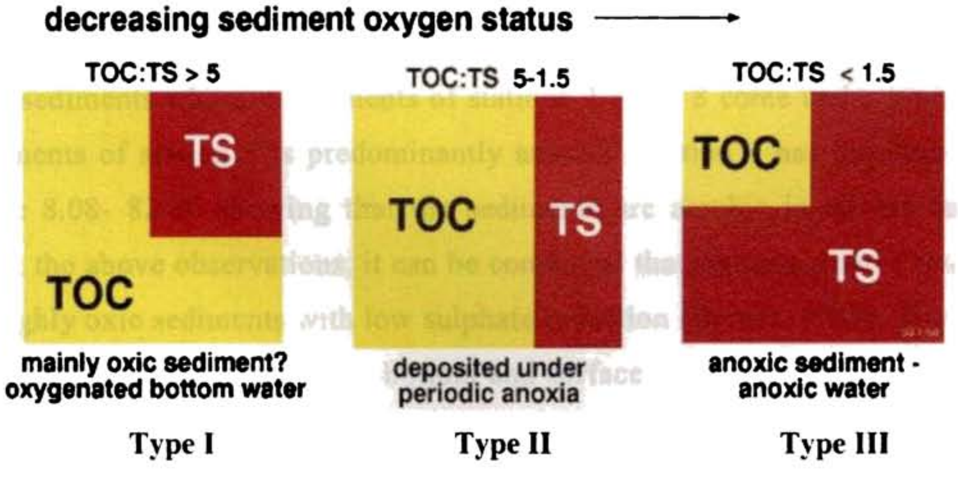

Figure 3.10 As dissolved oxygen status decreases, TS concentrations (S) in sediment increase and TOC contents (C) decrease

(Source: http://www.ozcoasts.org.au/)

Table 3.4 TOC: TS ratio in the present study

STATIONS	PREMONSOON	MONSOON	POST MONSOON
1	8.08	82.86	18.06
2	4.71	19.35	4.32
3	8.99	**0.98**	5.46
4	6.43	5.00	9.35
5	NA	3.72	**1.03**
6	6.56	**1.42**	8.74
7	4.30	2.32	3.11
8	5.08	**0.28**	3.07

On the basis of TOC: TS ratio, the sediments of the present study can be classified into three types. Seasonal variation of TOC: TS ratio in the present study is shown in the **Table 3.4**. It ranges from 4.30 – 8.99, 0.28 - 82.86 and 1.03 – 18.06 during premonsoon, monsoon and post monsoon respectively. During premonsoon, the sediments of almost all the stations come under type I category with the exception of stations 2 and 7 both coming under type II. During Monsoon, sediments of stations 1 and 2 are highly aerobic sediments, sediments of stations 4, 5 and 7 come under type II and sediments of stations 3, 6 and 8 are anoxic. During post monsoon, sediments of stations 1,3,4 and 6 are oxic sediments whereas sediments of stations 2,7 and 8 come under type II, but sediments of station 5 is predominantly anoxic. Station 1 has the ratio in the range 8.08- 82.86 showing that the sediments are aerobic in all the seasons. From the above observations, it can be concluded that stations 1 and 2 comprise of highly oxic sediments with low sulphate reduction (Berner, 1983). The higher dissolved oxygen values in the bottom and surface waters of this station further clarifies. Sediments of Station 3 is anoxic (TOC:TS = 0.98) during monsoon undergoing sulfate reduction under anoxic bottom waters with high H_2S concentrations (Craft et al., 1991) but is predominantly oxic during premonsoon and postmonsoon. Station 5 sediments with TOC:TS ratio between 1.5-5 of station 7 (2.32 – 4.3) shows that these sediments undergo sulfate reduction below an oxygenated water column (Hedges and Keil, 1995). Sediments of station 6 are anoxic during monsoon but oxic dring premonsoon and post monsoon. Monsoon season shows comparatively lower TOC:TS ratio than premonsoon and post monsoon seasons. Lower the TOC:TS ratio, greater the TS concentrations and Lower the dissolved oxygen values. The lower dissolved oxygen values in the monsoon season supports this fact.

3.7 Correlations:

Pearson Correlation coefficient for various sulphur species and hydrographical parameters is shown in **Table-3.5, 3.6 and 3.7** Correlation analysis was done between sulphur compounds in water and sediments in all the seasons. No significant correlation was found between these species during premonsoon except that between TS and sulphate in bottom water. During monsoon, significant positive correlations are found between sulphate in sediment and sulphate in water, TS and sulphate in sediment, sulphate bottom and sulphate surface, sulphide bottom and sulphide surface whereas significant negative correlation exist between AVS and sulphide bottom. During post monsoon season, TS exhibits significant positive correlation with sulphate in water, sulphate in sediment and AVS.

Table 3.5

Pearson correlation for Sulphur compounds and hydrographical parameters (Pre Monsoon)

	PH	TEMP	DO	SALINITY	HARDNESS	SULFATE S	SULFATE B	SULFIDES	SULFIDEB	SULPHATE	AVS	TS
PH	1.000	.139	.549	.963**	.187	.113	.597	.673	.447	.090	-.313	-.016
TEMP	.139	1.000	-.116	-.183	-.036	.413	.055	.473	-.113	.489	.087	.569
DO	.549	-.116	1.000	-.263	-.493	-.463	.840	.680	.684	-.020	.173	-.635
SALINITY	.963**	-.183	-.263	1.000	.977**	.696	.471	-.286	.260	.206	-.420	.620
HARDNESS	.187	-.036	-.493	.977**	1.000	.788*	.219	-.332	-.015	.257	-.369	.751*
SULFATES	.113	.413	-.463	.696	.788*	1.000	.208	-.232	.047	.456	.100	.885**
SULFATEB	.597	.055	.840	.471	.219	.208	1.000	.281	.438	.421	-.370	.539
SULFIDES	.673	.473	.680	-.286	-.332	-.232	.281	1.000	.457	.330	-.095	-.163
SULFIDEB	.447	-.113	.684	.260	-.015	.047	.438	.457	1.000	.549	.358	-.182
SULPHATE	.090	.489	-.020	.206	.257	.456	.421	.330	.549	1.000	.145	.548
AVS	-.313	.087	.173	-.420	-.369	.100	-.370	-.095	.358	.145	1.000	-.188
TS	-.016	.569	-.635	.620	.751*	.885**	.539	-.163	-.182	.548	-.188	1.000

** Correlation is significant at the 0.01 level (2-tailed).

* Correlation is significant at the 0.05 level (2-tailed).

Table 3.6:
Pearson correlation between Sulphur compounds and hydrographical parameters (Monsoon)

	PH	TEMP	DO	SALINITY	HARDNESS	SULFATE S	SULFATE B	SULFIDE S	SULFIDE B	SULPHATE	AVS	TS
PH	1.000	.549	-.036	.900*	.864**	.782*	.913*	-.139	-.442	.794*	.273	.765*
TEMPERATURE	.549	1.000	.519	.369	.347	.526	.407	-.234	-.167	.509	.186	.547
DO	-.036	.519	1.000	-.418	-.077	.044	-.212	-.460	-.081	.277	-.277	.470
SALINITY	.900*	.369	-.418	1.000	.982**	.906*	.972**	.096	-.470	.698	.380	.497
HARDNESS	.864**	.347	-.077	.982**	1.000	.935**	.989**	-.395	-.574	.845**	.492	.675
SULFATES	.782*	.526	.044	.906*	.935**	1.000	.959**	-.487	-.531	.856**	.589	.678
SULFATEB	.913*	.407	-.212	.972**	.989**	.959**	1.000	-.160	-.362	.934*	.228	.659
SULFIDES	-.139	-.234	-.460	.096	-.395	-.487	-.160	1.000	.816*	-.488	-.626	-.468
SULFIDEB	-.442	-.167	-.081	-.470	-.574	-.531	-.362	.816*	1.000	-.450	-.746*	-.490
SULPHATE	.794*	.509	.277	.698	.845**	.856**	.934*	-.488	-.450	1.000	.281	.857**
AVS	.273	.186	-.277	.380	.492	.589	.228	-.626	-.746*	.281	1.000	.097
TS	.765*	.547	.470	.497	.675	.678	.659	-.468	-.490	.857**	.097	1.000

* Correlation is significant at the 0.05 level (2-tailed).

** Correlation is significant at the 0.01 level (2-tailed).

Table 3.7
Pearson correlation between Sulphur compounds and hydrographical parameters (Post Monsoon)

	PH	TEMPERATURE	DO	SALINITY	HARDNESS	SULFATE S	SULFATE B	SULFIDE S	SULFIDE B	SULPHATE	AVS	TS
PH	1.000	.484	.118	.817*	.805*	.757*	.580	-.744(*)	-.024	.275	.573	.645
TEMPERATURE	.484	1.000	.303	-.217	.217	.507	.653	-.326	-.279	.372	.181	.758(*)
DO	.118	.303	1.000	-.035	.221	.253	.183	.226	.398	-.137	.534	.231
SALINITY	.817*	-.217	-.035	1.000	.996**	.822*	.641	-.365	.174	.322	.827(*)	.594
HARDNESS	.805*	.217	.221	.996**	1.000	.853**	.685	-.397	-.035	.463	.856(**)	.705
SULFATES	.757*	.507	.253	.822*	.853**	1.000	.519	-.456	-.120	.359	.633	.798(*)
SULFATEB	.580	.653	.183	.641	.685	.519	1.000	-.527	.268	.245	.914(*)	.814
SULFIDES	-.744*	-.326	.226	-.365	-.397	-.456	-.527	1.000	.022	.156	-.107	-.281
SULFIDEB	-.024	-.279	.398	.174	-.035	-.120	.268	.022	1.000	-.659	.260	-.224
SULPHATE	.275	.372	-.137	.322	.463	.359	.245	.156	-.659	1.000	.365	.667
AVS	.573	.181	.534	.827*	.856**	.633	.914(*)	-.107	.260	.365	1.000	.657
TS	.645	.758*	.231	.594	.705	.798*	.814	-.281	-.224	.667	.657	1.000

* Correlation is significant at the 0.05 level (2-tailed).

** Correlation is significant at the 0.01 level (2-tailed).

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Chapter 4

BIOGEOORGANICS IN THE SEDIMENTARY ENVIRONMENT

4.1 Introduction

The hydrosphere is an enormous structure of vibrant balance between the salty solution, the liquid and solid contribution from land, the atmosphere, the marine organisms, dissolved and suspended matter and bottom sediments. Therefore studies made on the environment are mainly focused on the hydrosphere in order to understand the importance of reclamation and use of its nutritive, mineral and power resources. Owing to the incomparable complexity and the versatile character, the investigations on hydrosphere fundamentally necessitate a blending of different disciplines of science like chemistry, physics, geology, biology and geography. **Biogeochemistry** is one such branch which integrates the areas of biology, geology and chemistry to explore the various roles of the biosphere, particularly the hydrosphere. Organisms and organic matter are believed to have a principal role in the biogeochemical processes occurring in the hydrosphere. Biogeochemistry is basically designed to evaluate the alteration, cycling and fate of various forms of organic matter in the hydrosphere. It is a vital means in alleviating the burning tribulations that disturb the human race.

Sediments, which ought to be the major contributors for the transport and storage of contaminants, play a prominent role in the biogeochemical reactions. Sediments faithfully record and time-integrate the environmental status of an aquatic system. Contaminant concentrations are high in sediments, and thus they are ease, cheap and accurate to be analyzed. It can be an important secondary source of pollutants and their quality influences the nature of overlying and interstitial waters through physical, chemical and biological processes. They are important in identification of contaminant sources and determining dispersion pathways.

Organic matter in the nature is that which arises from the degradation of plants and animals in the environment. Natural Organic Matter (NOM) is a collective term, assigned to the kingdom of all of this broken down organic matter which includes cellulose, tannin, cutin, and lignin, along with proteins, lipids and sugars. NOM plays a very important role in the movement of nutrients in the environment. In the marine environment, organic matter occurs in the dissolved form in water, in the sedimentary phase and in aquatic organisms.

4.1.1 Dissolved organic matter:

Dissolved Organic Matter (DOM) is an ever-present constituent of sedimentary pore waters. It takes part in various reaction processes occurring in chemical, biological and even physical oceanographic behaviours. DOM interacts with trace metals or radio nuclides and controls their dynamics. DOM in natural waters is generally considered to originate from three key sources:

1. Natural source- by the decomposition of plant and animal matter, organic substances including humic substances are produced in the sedimentary environments (Nakane et al. 1997; Uchida et al. 2000; Volk et al. 1997);
2. Anthropogenic sources- agricultural, industrial and human activities result in the liberation of organic compounds comprising of fluorescence whitening agents and detergents, organo-chlorine pesticides, herbicides etc (Azevedo et al. 2000; Derbalah et al. 2003; Mostofa et al. 2005a); and
3. Autochthonous production inside the lake environment which includes carbohydrates, amino acids, proteins, lipids etc. (Benner and Kaiser 2003; Hayakawa 2004; Ogawa and Tanoue 2003).

The biogeochemical cycling of carbon and nitrogen is illustrated by the involvement often motivated by DOM in different phases of the system; therefore an understanding of the real sources and fate of DOM is required for exploring biogeochemistry of aquatic ecosystems. (Meyer et al. 1988).

In estuaries, the amount of organic matter, living or dead, is usually greater than in the open ocean. Estuarine organic matter consists of an autochthonous contribution resulting from primary production within the estuary and allochthonous content from adjacent ecosystems. The decomposition of organic matter in estuaries can lead to anoxic conditions if the water exchange is poor or if large amount of organic pollutants are introduced. Dissolved organic matter has a lot of significance in estuarine ecosystems. It affects the acid-base chemistry and control pH of many wetland waters (McKnight, 1985), because natural dissolved organic matter is acidic and is a powerful agent for complexation of metals. It plays an important role in the mineral weathering; metal toxicity and metal export (Mierle and Ingram, 1991) influencing the cycling of metals such as copper and mercury which inturn can effect concentration of trace metal found in aquatic organisms. It is a major mode of export of nitrogen and phosphorus (Hedin et al 1995, Qualls et al, 2002) in many ecosystems. It is a potential source of energy and nutrients to the microbial growth (Travink, 1992) and a source of energy and nutrients to the microbial food chain. Dissolved organic carbon protects aquatic organisms from harmful effects of UV radiation. It restricts the depth of euphotic zone, stabilizes the depth of thermocline and depresses primary productivity in lakes (Quinby, 2000).

The major fraction of the dissolved organic carbon in the sea consists of a complex material, which is very resistant to bacterial attack. Minor fraction is composed of more labile compounds such as amino acids, carbohydrates, lipids and vitamins. The concentration of these substances are low and must reflect a balance between the rates at which they are produced and that which they are used by micro organisms.

4.1.2 Sedimentary organic matter:

Organic matter constitutes an important fraction of lake sediments. It originates from the complex mixture of lipids, carbohydrates, proteins, and other biochemicals produced by organisms that have lived in the lake and its watershed. The primary source of organic matter to lake sediments is from the particulate detritus of plants; only a few percent come from animals. The organic matter in the sediments is derived from terrestrial and estuarine or marine sources. Primary production is an important factor controlling the distribution of the organic molecule in sediment. Moreover rivers can bring about distribution of larger quantities of terrestrially derived organic matter to the sediments. Atmospheric transport of land derived natural compounds to the estuarine sediment can also take place. Organic matter exist as a particulate and dissolved form within the water column, the initial input of organic matter consist of all major classes of naturally occurring organic compounds such as carbohydrates, proteins, amino acids pigments, phenolic substances, lipids and other constituents of living organisms (Premuzic et al, 1982). Studies on lipids (Wakeham and Canuel, 1986) aminoacids and sugars (Ittekot et al, 1984, Muller et al, 1986) indicated that biochemical decomposition and transformation processes acted on rapidly sinking particles throughout the water column. However these reactions were dominant in relatively shallow depths (Suess, 1980). The survival of the individual organic constituents during sedimentation depends on a number of factors including their chemical stability, biochemical usefulness, oxygen concentration and their interaction with the clay minerals. Thus the vertical transport of organic matter in the water column in particulate material is an important source of carbon to surface sediments. After reaching the sediments significant modification of organic matter take place due to the activities of benthic organisms. The physical and chemical properties of sediments such as retention capacity, porosity and compressibility are controlled, to a great extent by the amount of organic matter within sediments. Organic matter supports microbial metabolism which inturn influences the organic chemical reactions by regulating Eh and pH.

In the CES numerous studies related to the dynamics of both inorganic and organic species had been conducted earlier (Balachandran et al, 2003; Arun, 2005; Madhu et al, 2007; Martin et al, 2008). Studies were concentrated on the biogeoorganics of mangrove ecosystem of Cochin Estuary. Rini Sebastian (2002) and Geetha (2002) studied the organic content in the mangrove sediments of Cochin estuary. Zeena P. (2003) noted the distribution of amino acids in the mangrove sediments of Cochin Estuarine System. Investigations on the sterols of the mangrove ecosystem of CES was done by Narayanan (2006). The abundance and temporal variation of organic matter in the sediments of Cochin estuary was studied by Vasudevan Nair (1992). The present study was conducted to express the relation of the organic matter in the estuary with the Sulphur compounds and hydrographical and sediment parameters. Also the partition coefficient for the proteins, carbohydrates and lipids between water and sediments are illustrated.

4.2 Proteins: (Appendix IV)

Proteins occupy an essential position in the structure and performance of living organic matter. They are the main materials of the animal tissue. They are the important biological macromolecules and also the important components of organic matter in lake sediments. Their variations are closely related to biological processes, microbial activities, mass cycling and early diagenesis (Xiaobing et al, 2002). Protein components seem to be resistant to bacterial decay, thus accumulating in water. Owing to the close connection of proteins with other macromolecules like polysaccharides, they are subjected to geochemical modification resulting in refractory proteins (Keil & Kirchman, 1994). Proteins are widely distributed in the sediments, which arise from the residues of plants, animals and microorganisms. Proteins are easily hydrolysable compounds and so they are preferentially utilized. Proteins and Carbohydrates commonly represent a significant portion of the sedimentary organic matter and assume vital importance, since organic matter of water and sediments has been established as forming a strong link between several known and unknown phenomena. The abundance of protein was seen to be influenced by the substratum as well as the season and the anthropogenic inputs. Proteins and their constituent amino acids are typically the most abundant substance in phytoplankton and mangrove litter and represent an important source of Carbon and nitrogen in the Aquatic system. The large amount of protein in phytoplankton (upto 75% of particulate Nitrogen Nguyen & Harvey 1994) is rapidly recycled in the water column (Harvey et al 1995). The preservation of organic matter in aquatic system may be attributed to the presence of inherently refractory biomolecules, condensation reaction that make compounds refractory (Ishiwatari 1992) and slower rates of decay under anoxic conditions (Cowie et al 1995; Harvey et al 1995). It has been suggested that protein adsorption to plant detritus may sterically protect the peptide bond from proteolitic bacterial exoenzymes (Samuelson & Kirchman 1990). In addition, during degeradation, proteins and polypeptides may undergo chemical transformation including Schiffs-base condensation with sugars to become insoluble and resistant to attack (Kiel and Kirchman 1993). Recent evidences suggest that one mechanism for preservation of labile organic matter, such as protein may be through chemisorptive attachment to mineral surfaces or sorption in the small pores of minerals (Mayer, 1994) which presumably protects the linkage of biomolecules from the hydrolytic action of enzymes. The proteins were strongly and rapidly adsorbed by the clay minerals and sediments and much of the adsorbed protein was not really desorbed (Ding and Henrichs 2002).

The quantity of protein delivered to sediments through water columns transport the same relative quality and quantity of proteins to sediments and its fate is to be essentially demineralised (Keil and Fogel 2001). Most organic matter present in the sediments is found in the form of aggregates that are surrounded by clay plates. There is a positive correlation between proteins in clay to organic rich aggregates and the degradation state of organic matter. Proteins in clay rich aggregates are more fragmented and partially degraded than those in organic rich aggregates (Armarson & Keil 2001; Keil et al 2000; Keil & Fogel 2001; van Mooy et al 2002). The budget of Nitrogen and carbon contained in the sediment proteins account for a large proportion of the total nitrogen and organic carbon. In the marine sediments distributed along the coastal areas the nitrogen in protein accounts for 40-60 % of the total (Xiaobing et al, 2002). Proteins contain large amount of N and S. Their release and accumulation in the form of protein will influence the contents and their variations, as well as the cycling of N and S.

The seasonal variation of proteins in surface and bottom water are graphically represented in **Figures 4.1 & 4.2**. There was no bottom water sample for stations 2, 4 and 7. Protein concentration in surface water ranged from 1.11 to 9.54 mg/l, 2.44 to 10.78 mg/l and from 0.99 to 8.76 mg/l during premonsoon, monsoon and postmonsoon respectively. The highest concentration was reported at station 3 during monsoon and lowest at station 6 during post monsoon. At Station 8, surface water also showed higher protein concentration. In bottom water, protein concentration varied from 3.11 to 7.32 mg/l, 1.45 to 12.66 mg/l and 2.11 to 4.21 mg/l respectively. Station 5 reported maximum value and station 1 showed the minimum value both during monsoon season.

Sedimentary protein concentrations range from 60 to 1285 mg/kg, 536 to 2452 mg/kg and from 70 to 1667 mg/kg during premonsoon, monsoon and postmonsoon respectively **(Figures 4.3)**. Maximum protein concentration was found in the sediments of Station 8 and minimum in the sediments of station 2. There was no seasonal variation in the estuarine stations. Station 1 whose sediments are sandy in nature reported very low protein concentration (60-536 mg/kg). (Appendix IV)

Proteins of the Cochin estuary were studied earlier by Vasudevan Nair (1992) and Rini Sebastian (2002). Vasudevan Nair (1992) focused on the biogeoorganics in the sedimentary environments and found that the northern part of the estuary where the Periyar River drains was polluted with high organic matter and phosphorus. The study revealed that the organic matter is mostly of terrestrial origin and make profound influence in the biogeochemical processes. Sedimentary proteins were found to vary in the range 0.24 to 46.07 mg/g. Biogeoorganics in the mangrove sediments of Cochin estuary was studied by Rini Sebastian (2002). Joseph et al (2008) worked on the biogeochemistry of surficial sediments in the mangrove and estuary and found that protein concentrations ranged from 702-4608 µg/g and from 205-1924 µg/g in mangrove and estuarine sediments, respectively. This was in well agreement with the present observation. Bhosle, (1988) reported that the protein values in the sediments of Bay of Bengal varied from 0.25 to 3.4 mg/g of the dry sediment and accounted for 5.05 to 20.34 % of carbon of the total organic carbon. The monthly as well as seasonal values of protein observed in the sedimentary environment of Cochin was higher than that of Bay of Bengal. The high turn over of protein and other organics such as lipids and carbohydrates in the sediments could be due to the decomposition of organic matter in phytoplankton and in domestic waste water. The wastes from fish peeling and processing units housed on the banks of the estuary, are dumped into the estuary and these animal tissues undergo decomposition and liberate proteins which are adsorbed into the sediments. A decrease in the concentration of proteins at stations 4, 5 & 6 during premonsoon may be due to the preferential utilization of protein by the benthic organisms and biological activity and similar explanations were also printed out by earlier workers (Bhosle, 1988).

Clayey silt and silty clay sediments were capable of adsorbing more organics than the sandy ones. Estuarine sediments were mainly composed of silty clay or clayey silt whereas riverine sediments were always sandy. This could be the reason for the low protein in sediments in station1.

4.2.1 Partition Coefficient:

Partition coefficient for proteins between water and sediments are depicted in **Table 4.1.** Water to sediment partition coefficient for proteins were found to be less than or equal to 0.02 with some exceptions. Station 1 showed abnormally high value for the partition coefficient, especially during pre monsoon and post monsoon. This may be attributed to the poor capacity of the sandy sediments of this station to hold organics. So water of this station was found to have more protein concentration than sediments. The lowest value for partition coefficient was found to be at station 6 whose sediments are having highest percentage of silt, which is found to have more holding capacity for organics.

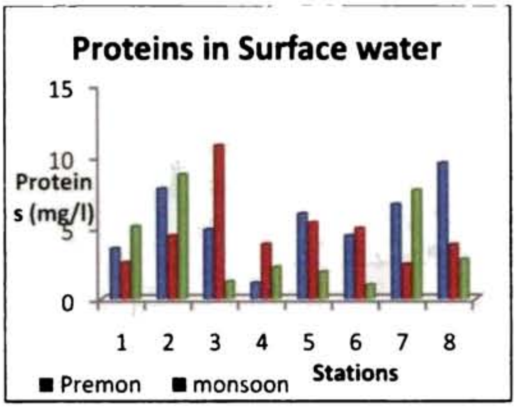

Figure 4.1

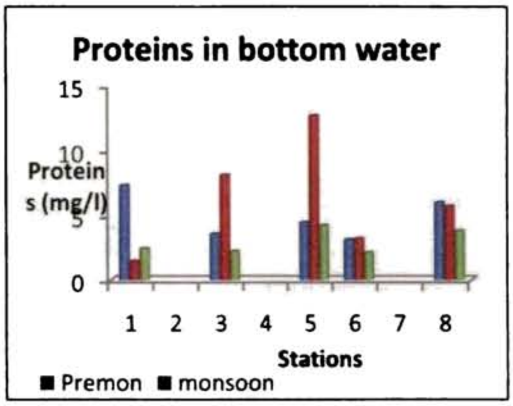

Figure 4.2

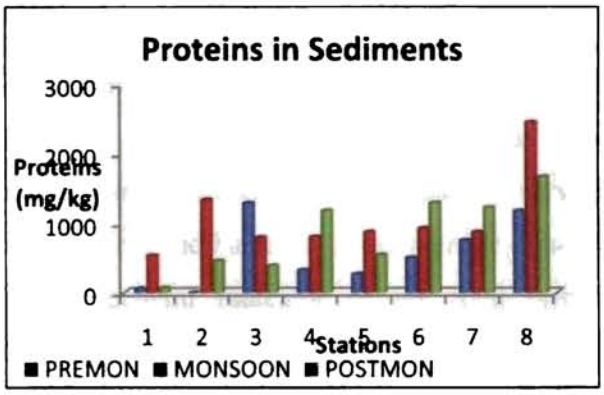

Figure 4.3

Table 4.1

Partition Coefficient (Protein $_{water}$/Protein $_{sediment}$) for the three seasons:

Stations	Premonsoon	Monsoon	Postmonsoon
1	0.058717	0.004774	0.072714
2	NA	0.003333	0.019224
3	0.003798	0.013532	0.003124
4	0.003432	0.004793	0.001875
5	0.022429	0.006142	0.003481
6	0.008864	0.005345	0.000767
7	0.008845	0.002803	0.006256
8	0.008118	0.001558	0.001661

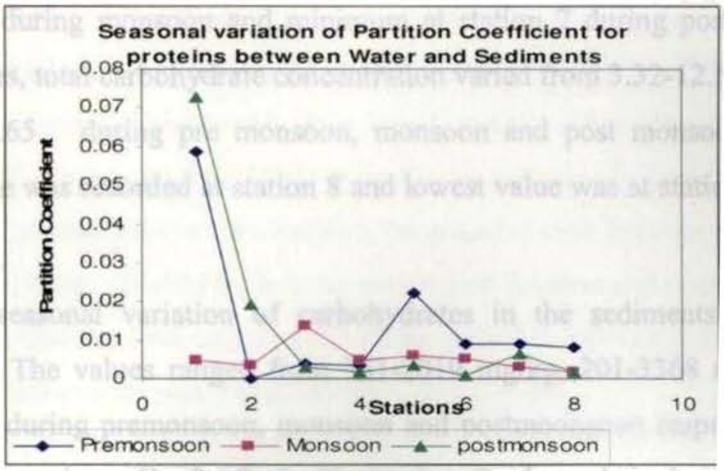

Figure 4.4

4.3 Carbohydrates:

Carbohydrates are simplest organic molecules and protein is the most complex. They are important constituents of dissolved organic matter. Distribution of dissolved and particulate carbohydrates in the ecosystem is very important as they serve as energy source for plants and bacteria. Moreover the dissolved carbohydrate content. also serves as a general indicator of the total primary productivity (Sankaranarayanan et al., 1982). Majority of carbohydrates in fresh water originate from terrestrial system, i.e. from death and dry out and may release 30% organic matter into water (Dham, 1981). Leachates of plant material are an important source of carbohydrates in water. Leaf materials from Vascular plants are source of organic carbon in coastal and estuarine ecosystem (Valets et al., 1984). Distribution of dissolved and particulate carbohydrates in the ecosystem is very important as they serve as energy source for plants and bacteria. Moreover the dissolved carbohydrate content also serves as a general indicator of the total primary productivity. They belong to the labile fraction of marine DOM and are directly associated with biogeochemical processes taking place in the marine environment (Bada and Lee, 1977).

Figure 4.5 & 4.6 represents the seasonal variation of total carbohydrates in the surface and bottom waters. Total carbohydrate concentration in surface waters varied from 2.91-13.09 umols/l, 1.76-32.53umols/l and 0.45- 9.23 umols/l during premonsoon, monsoon and postmonsoon respectively. Maximum concentration was at station 8 during monsoon and minimum at station 7 during post monsoon. In bottom waters, total carbohydrate concentration varied from 3.32-12.55 , 2.14-20.64 and 6.39-15.65 during pre monsoon, monsoon and post monsoon respectively. Highest value was recorded at station 8 and lowest value was at station 1 both during monsoon.

The seasonal variation of carbohydrates in the sediments is depicted in **Figure. 4.7.** The values ranged from 381-2019 mg/kg, 201-3368 mg/kg and 354-1755 mg/kg during premonsoon, monsoon and postmoonsoon respectively. Out of the riverine stations (1, 2, 7 & 8), station 8 showed high concentration of carbohydrate especially during monsoon. The effluents from the industrial units have influenced the carbohydrate concentration to increase in great extent in this station. Out of the estuarine station (3, 4, 5 & 6), station 3 showed maximum value during premonsoon, due to the discharge of wastes from the nearby fish market.

Grain size of the sediment plays a pivotal role in determining the distribution of organic compounds. The riverine stations 1 & 2, where the sediment was sandy, showed low concentration levels of carbohydrates as compared with estuarine stations 3, 4, 5 & 6 where the sediment was fine grained. High surface area and the high adsorptive capacity of the fine grained sediments may be the reason for such features.

A lot of works have been carried out on carbohydrate concentration. Amy and George (2002) studied total carbohydrate concentration in unfiltered sea water in U.S. middle Atlantic Bight and Delaware estuary. They found that 4.8-31.3 uMC/L for free monosaccharides and 15.6-67.2 uMC/L for total dissolved carbohydrates. Benedict and David (2001) gives the idea of formation and degree of DOC, combined neutral sugars and amino acids during phytoplankton blooms. Bulk sugar concentrations measurements in estuarine environment shows that relationship between chlorinity and total dissolved carbohydrates and were dependent on seasons. Some of the Indian researchers also carried out works on the concentration level in estuaries and also in Oceans. Kamat (1976) has undergone a study about the concentration of Carbohydrates in estuarine water of Goa and concluded that soluble carbohydrates in shore water of

Goa is the order of magnitude is 3-4 times higher than that of estuarine water and also found the total dissolved carbohydrates have much been contributed by bacterial action on polysaccharides of planktonic origin. Previous studies (Anirudhan, 1988; Beenamma Jacob, 1992; Vasudevan Nair, 1992) in the Cochin Estuarine System have reported high concentration of organic wastes reaching the estuarine sites from the fishery industries, sewage works etc. Studies made in the mangrove ecosystem and estuary by Joseph et al (2008) demonstrates total carbohydrates of the range 505-2458 µg/g, and 250-1229 µg/g, in the mangroves and estuary respectively.

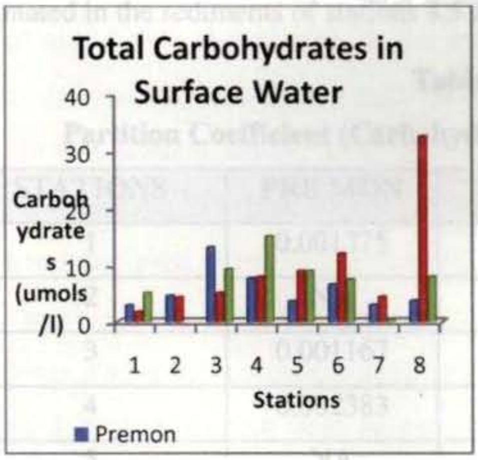

Figure 4.5

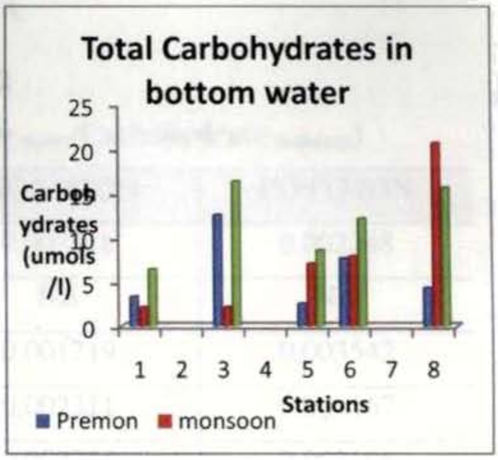

Figure 4.6

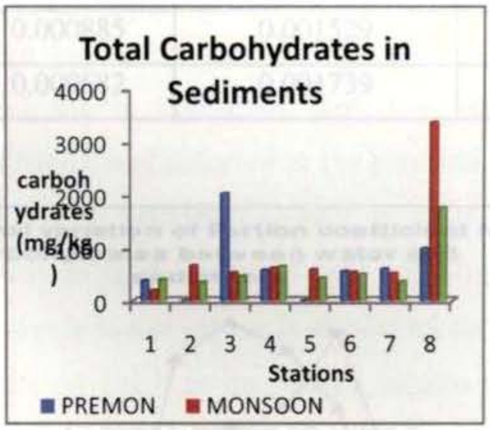

Figure 4.7

4.3.1 Partition coefficient:

Water to sediment partition coefficient(Z) for carbohydrates is represented in **Table 4.2.** In premonsoon, partition coefficient showed the lowest values (less than

0.0025). monsoon also showed similar values except station 6 (Z=0.0039). Water sample of this station showed higher concentration of carbohydrates than other stations. This may be due to the higher organic content brought by land run off during monsoon. There is no specific seasonal variation in the partition coefficient for station 1. Stations 7 and 8 also showed similar values in all the seasons. The varition in partition coefficient was shown by the estuarine station 3, 4, 5 and 6. The variation in the texture of the sediments in these stations may be the reason for this. Sand dominated in the sediments of station 3 in all the seasons but clay and silt dominated in the sediments of stations 4,5 and 6.

Table 4.2

Partition Coefficient (Carbohydrate $_{water}$/Carbohydrate $_{sediment}$)

STATIONS	PRE MON	MONSOON	POSTMON
1	0.001375	0.001576	0.002248
2	NA	NA	NA
3	0.001167	0.001719	0.003542
4	0.002383	0.002311	0.004167
5	NA	0.002714	0.003696
6	0.002113	0.003976	0.00268
7	0.000885	0.001529	0.000223
8	0.000682	0.001739	0.000811

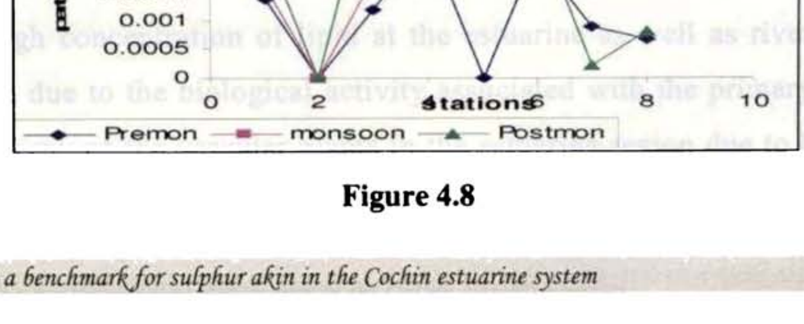

Figure 4.8

4.4 Lipids:

Lipids are heterogeneous substances of biological origin, insoluble in water but soluble in fat solvents such as ether, benzene or chloroform. They are classified as simple, compound and derived. All the forms are widely distributed in the sediments. The obvious sources of lipids are plant and animal tissue and the microbial population.

Seasonal variation of total lipid concentration in surface water, bottom water and sediments are represented in **Figures 4.9, 4.10 and 4.11** respectively. Lipids are widely distributed in the s sediments and its abundance depends on the environmental conditions such as primary production, anthropogenic inputs etc. In the present study, total lipid concentration in the surface water varied from 0 -5.54 mg/l, 0.156 - 6.23 mg/l and 1.76 - 9.3 mg/l during pre monsoon, monsoon and post monsoon respectively and in bottom water, it ranged from 0 - 3.96 mg/l, 0.546 - 5.84 mg/l and 2.67 - 25.54 mg/l during pre monsoon, monsoon and post monsoon respectively. Maximum value was reported at station 3 bottom during post monsoon and minimum value at station 1 during pre monsoon. Post monsoon season showed higher values than the other two seasons. Stations 1 & 2 reported very low values during pre monsoon and monsoon seasons. Protein and carbohydrate concentrations are also very low at these two stations which are in agreement with low organic carbon values. Lower concentration of lipids was reported at the riverine stations compared to estuarine stations. Station 8 sediments though riverine, showed abnormally high values of total lipids as in the case of total carbohydrates. Premonsoon season showed comparatively lower values in almost all the stations. This could be due to the utilization of lipid as an energy source by the heterotrophic organisms (Gagosian & Lee, 1981; Ittekkot et al; 1984).

High concentration of lipid at the estuarine as well as riverine stations should be due to the biological activity associated with the primary production and the decay of the vascular plants in the estuarine region due to high salinity intrusion and subsequent transformation of organic matter by micro organisms, high rate of sedimentation and subsequent preservation. The grain size of the sediments also influences the adsorption of organics into the sediments. Fine grained sediments adsorbed and preserved lipids from the surroundings, this being controlled by the content of indigenous matter such as humic acid (Mayers and Quinn, 1973).

Very few studies are reported on the concentration of lipids in the aquatic system. The abundance and temporal variation of lipids in the sediments of Cochin estuary was studied by Vasudevan Nair (1992). Rini Sebastian (2002) studied the lipid content in the mangrove sediments of Cochin estuary. Investigations by Joseph et al (2008) showed that total lipids ranged from 804-6816 μg/g in mangroves and from 312-2815 μg/g at estuarine sediments. Bhosle and Dhople (1988) studied the biochemical compounds in the sediments of Bay of Bengal and reported that lipid constitutes 1.91 to 4.28% of the organic matter. Cranwell (1976) found that changes observed in the relative distribution of lipids in the surficial sediments could be explained either by early diagenesis by the bacterial activity or by changes in lipid contribution. They also gives the information that the higher content of lipid level in the sediment might be due to the influence exerted on the composition of organic matter by the bottom fauna which was capable of resynthesis of lipid from organic matter during the course of their vital activity.

4.4.1 Partition coefficient for lipids:

Water to sediment Partition coefficient was low compared to proteins and carbohydrates **(Table 4.3).** This may be due to the low solubility of lipid compounds in water. There is no seasonal variation in the partition coefficient for stations 1 and 8, which is similar to that for proteins and carbohydrates. Estuarine stations show large variation in the partitioning of lipids, especially during premonsoon and postmonsoon. Station 5 showed very high value during postmonsoon.

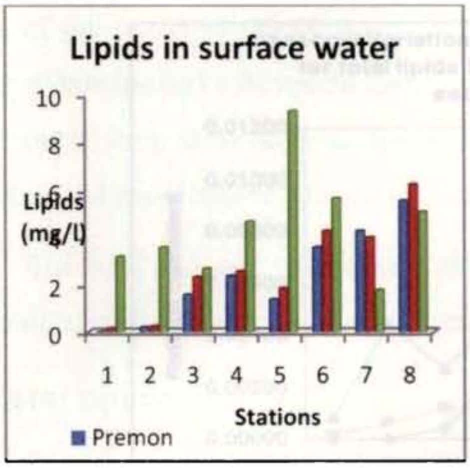

Figure 4.9

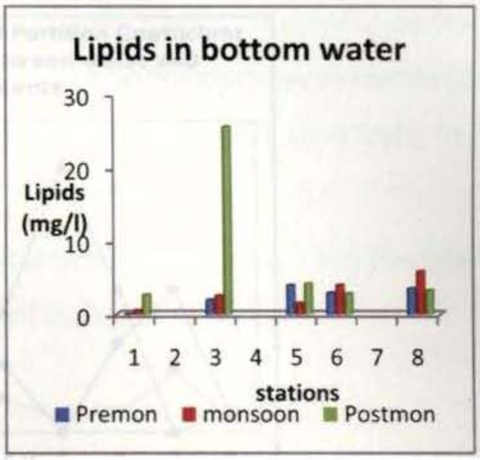

Figure 4.10

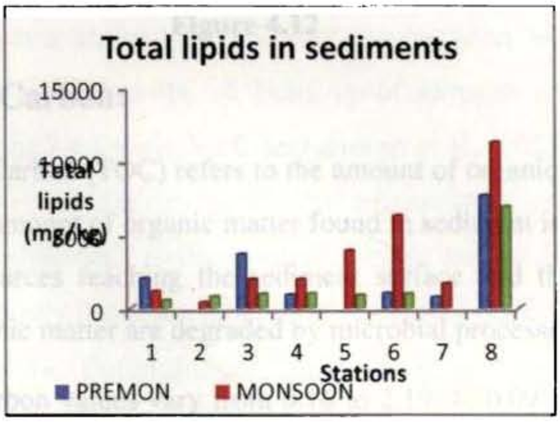

Figure 4.11

Table 4.3

Partition Coefficient (Lipid $_{water}$/Lipid $_{Sediment}$) for the three seasons:

SAMPLES	PREMON	MONSOON	POSTMON
1	0.00000	0.00013	0.00083
2	0.00000	0.00060	0.00441
3	0.00043	0.00117	0.00271
4	0.00256	0.00129	0.00462
5	0.00000	0.00047	0.01028
6	0.00341	0.00067	0.00557
7	0.00554	0.00235	0.00000
8	0.00072	0.00055	0.00073

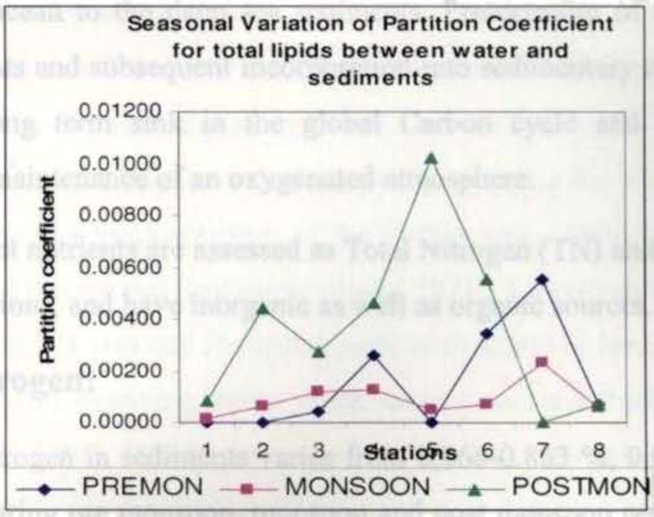

Figure 4.12

4.5 Total Organic Carbon:

Total Organic Carbon (TOC) refers to the amount of organic matter preserved within sediment. The amount of organic matter found in sediment is a function of the amount of various sources reaching the sediment surface and the rates at which different types of organic matter are degraded by microbial processes during burial.

The organic carbon values vary from 0.16 to 2.19 %, 0.09 to 1.8 % and 0.36 to 3.45 % during pre-monsoon, monsoon and post-monsoon respectively (**Figure 2.20**). The highest values reported at Stations 4 & 6 during post monsoon and lowest value at Station 5 during monsoon could be credited to the settling of the terrigenous organic matter in the non-monsoonal months derived from land during monsoon to the water zone. However these values fairly agree with the earlier reports from Cochin estuary (Bhosle et al, 1977; Sankaranaryanan and Panampunnayil, 1979). The seasonal variation in the organic carbon content in the sediments may be related to the planktonic activity in the overlying water, the humic material brought from land and also to the oxidation of organic matter by the organisms living in the bottom (Sankaranarayanan and Qasim, 1969; Rajagopal and Reddy, 1984). In oceanic environments, particulate organic matter (POM) is mostly derived from phytoplankton. POM serves as an important source of food for aquatic organisms. POM is of considerable biogeochemical and oceanic importance because it serves as a vehicle for the transport of organic matter produced in the upper sunlit surface waters of the ocean to the deep sea sediments. Preservation of organic carbon in marine sediments and subsequent incorporation into sedimentary rocks represent the predominant long term sink in the global Carbon cycle and contribute to the formation and maintenance of an oxygenated atmosphere.

Sediment nutrients are assessed as Total Nitrogen (TN) and Total Phosphorus (TP) concentrations, and have inorganic as well as organic sources.

4.6 Total nitrogen:

Total nitrogen in sediments varies from 0.068-0.863 %, 0.0254-0.428 % and 0.05-0.334% during pre monsoon, monsoon and post monsoon respectively (Fig. 6). Earlier studies in Cochin backwaters by Sankaranarayanan and Panaampunnayil, (1979) agree with the above results. A build up of nitrogen and phosphorus after 1975 was reported in the backwater by Balachandran et al, (2003). The lower value at Station 1 (the sandy riverine zone) reveals that adsorption is mainly affected by the finer fraction of the sediments. Hydrographic changes are minimum in this station, and there may be relatively lesser accumulation of organic materials in the sediments from the overlying waters. Determination of nitrogen and phosphorus species in the coastal and shelf waters of south eastern North Carolina, Mid Atlantic US Coast shows that all areas with high values of total dissolved nitrogen also have high total dissolved phosphorus values. TDN ranged from 7.87-139.22 micromoles and TDP ranged from 0.5-4.98 micromoles. Concentration of nitrogen and phosphorus species decrease in the direction from inshore to the shelf water simultaneously with increasing salinity. Accumulation of Nitrogen and phosphorus species was attributed to loading from agricultural and urban sources to the coastal watersheds, transported to receiving estuaries.

4.7 Total Phosphurus:

Phosphorus is one of the major nutrient components sustaining the aquatic life and is strongly influenced by physical, chemical and biological processes operating in the system. The major phosphorus forms in natural waters are inorganic and organic phosphorus (Babu et al., (2000).

Total phosphorus values were much higher during post-monsoon (7.99-30.38%) compared to the other two seasons (in pre-monsoon 1.16-2.42% and in monsoon 2.14-5.61%). These higher values point to the large quantities of organic matter brought into the estuary by land runoff during monsoon and settled in the sediments in the nonmonsoonal periods. Highest values at Station 4 reveal the greater adsorption of phosphate by the silty sediment type of the studied area. Similar earlier works also support this trend (Qasim and Sankaranarayanan, 1972). Lower values were reported by earlier workers in this area and illustrated some environmental leaching of Phosphorus from the mud to the overlying waters (Sankaranarayanan and Panaampunnayil, 1979; Jyothibabu et al, 2006). Sankaranarayanan and Qasim, 1969 have reported the total phosphorus variation in the detritus of the Cochin backwater between 1.3- 1.9 mg/g owing to the effect of domestic waste, which is emptied in the region through canals.

4.8 Correlation

Pearson correlation coefficient for sedimentary parameters are given in **Table 4.4, 4.5 and 4.6**. Sedimentary sulphate is in significant correlation with carbohydrates during premonsoon and with TOC and proteinduring post monsoon. Total Sulphur is in high positive correlation with TOC in premonsoon, with clay and total nitrogen in monsoon. Only significant correlation for AVS is with Total phosphururs during postmonsoon

Significant linear variations with clay and silt components were exhibited by the sediments in different locations of the designated sites. There is a profound relationship of carbon and nutrients with sediment texture. TOC has significant correlation only with sand in pre-monsoon and with total nitrogen in post-monsoon. In monsoon total nitrogen is in significant correlation with silt and clay, which shows that nitrogen is more adsorbed by the finer fractions of the sediments. Significant negative correlation with sand proves above findings. Pattern of variation of Nitrogen and Phosphurus is different from one another in all the seasons; total nitrogen has its maximum value in pre-monsoon where total phosphorus has the lowest values. Total Phosphorus has its highest values in post-monsoon. Correlation analysis also shows that total nitrogen and total phosphorus have a strong positive relation only in monsoon deriving the conclusion that concentration of one is independent of the other.

Table 4.4

Pearson correlation for sediment parameters during pre monsoon

	SULPHATE	AVS	TS	TOC	TN	TP	SAND	SILT	CLAY	PROT	CARB	LIPID
SULPHATE	1.000	.144	.548	.474	.237	.650	-.172	.146	.067	.438	.850(*)	.421
AVS	.144	1.000	-.188	-.016	-.383	.071	.356	.041	-.617	.210	.530	.804
TS	.548	-.188	1.000	.948(**)	.694	-.067	-.785(*)	.698	.262	.220	.418	.035
TOC	.474	-.016	.948(**)	1.000	.603	-.384	-.681	.518	.418	.463	.621	.371
TN	.237	-.383	.694	.603	1.000	.004	-.298	.304	.045	.578	.243	-.308
TP	.650	.071	-.067	-.384	.004	1.000	.384	-.181	-.353	.277	.214	-.096
SAND	-.172	.356	-.785(*)	-.681	-.298	.384	1.000	-.780(*)	-.486	.355	.155	.208
SILT	.146	.041	.698	.518	.304	-.181	-.780(*)	1.000	-.168	-.300	-.187	-.193
CLAY	.067	-.617	.262	.418	.045	-.353	-.486	-.168	1.000	-.125	-.013	-.081
PROT	.438	.210	.220	.463	.578	.277	.355	-.300	-.125	1.000	.822(*)	.304
CARB	.850(*)	.530	.418	.621	.243	.214	.155	-.187	-.013	.822(*)	1.000	.762
LIPID	.421	.804	.035	.371	-.308	-.096	.208	-.193	-.081	.304	.762	1.000

* Correlation is significant at the 0.05 level (2-tailed).

** Correlation is significant at the 0.01 level (2-tailed).

Table 4.5

Pearson correlation for sediment parameters during monsoon

	SULPHATE	AVS	TS	TOC	TN	TP	SAND	SILT	CLAY	PROT	CARB	LIPID
SULPHATE	1.000	.282	.857(**)	.581	.556	.616	-.610	.559	.672	-.181	-.131	.193
AVS	.282	1.000	.097	.680	-.023	.477	-.345	.431	.110	-.044	.093	.179
TS	.857(**)	.097	1.000	.319	.728(*)	.548	-.760(*)	.668	.904(**)	.043	.144	.424
TOC	.581	.680	.319	1.000	-.106	.105	-.164	.196	.071	-.497	-.435	-.332
TN	.556	-.023	.728(*)	-.106	1.000	.664	-.918(**)	.883(**)	.911(**)	.546	.561	.819(*)
TP	.616	.477	.548	.105	.664	1.000	-.754(*)	.755(*)	.680	.417	.483	.742(*)
SAND	-.610	-.345	-.760(*)	-.164	-.918(**)	-.754(*)	1.000	-.988(**)	-.931(**)	-.468	-.550	-.822(*)
SILT	.559	.431	.668	.196	.883(**)	.755(*)	-.988(**)	1.000	.864(**)	.478	.557	.823(*)
CLAY	.672	.110	.904(**)	.071	.911(**)	.680	-.931(**)	.864(**)	1.000	.396	.480	.741(*)
PROT	-.181	-.044	.043	-.497	.546	.417	-.468	.478	.396	1.000	.960(**)	.784(*)
CARB	-.131	.093	.144	-.435	.561	.483	-.550	.557	.480	.960(**)	1.000	.861(**)
LIPID	.193	.179	.424	-.332	.819(*)	.742(*)	-.822(*)	.823(*)	.741(*)	.784(*)	.861(**)	1.000

** Correlation is significant at the 0.01 level (2-tailed).

* Correlation is significant at the 0.05 level (2-tailed).

Table 4.6

Pearson correlation for sediment parameters during post monsoon

	SULPHATE	AVS	TS	TOC	TN	TP	SAND	SILT	CLAY	PROT	CARB	LIPID
SULPHAT	1.000	.365	.667	.749(*)	.155	.241	-.529	.073	.656	.797(*)	.677	.562
AVS	.365	1.000	.657	.359	.208	.894(**)	-.731(*)	.372	.701	.127	-.017	-.154
TS	.667	.657	1.000	.591	.370	.585	-.569	.442	.429	.600	.424	.340
TOC	.749(*)	.359	.591	1.000	.616	.121	-.099	-.419	.451	.434	.113	-.074
TN	.155	.208	.370	.616	1.000	-.147	.164	-.360	.052	.219	-.460	-.472
TP	.241	.894(**)	.585	.121	-.147	1.000	-.692	.557	.507	.005	.141	.013
SAND	-.529	-.731(*)	-.569	-.099	.164	-.692	1.000	-.678	-.830(*)	-.534	-.434	-.410
SILT	.073	.372	.442	-.419	-.360	.557	-.678	1.000	.153	.345	.469	.571
CLAY	.656	.701	.429	.451	.052	.507	-.830(*)	.153	1.000	.456	.228	.121
PROT	.797(*)	.127	.600	.434	.219	.005	-.534	.345	.456	1.000	.647	.698
CARB	.677	-.017	.424	.113	-.460	.141	-.434	.469	.228	.647	1.000	.988(**)
LIPID	.562	-.154	.340	-.074	-.472	.013	-.410	.571	.121	.698	.988(**)	1.000

* Correlation is significant at the 0.05 level (2-tailed).

** Correlation is significant at the 0.01 level (2-tailed).

4.9 ANOVA

Three factor ANOVA was carried out for Proteins, Total Carbohydrates and Total Lipids.

Table 4.7 ANOVA Table for Proteins

Source	Sum of Squares	df	Mean Square	F	Sig.
Intercept	599.675	1	599.675	1668.421	.000
Spatial	322.402	2	161.201	448.495	.000
Season	1.627	2	.814	2.263	.115
Station	7.203	7	1.029	2.863	.014
Error	17.971	50	.359		
Total	1095.424	62			

It can be seen that the p-values corresponding to Spatial factor and Station is less than 0.05 and therefore the Protein data vary significantly with these factors and the difference between different seasons is not significantly different.

Table 4.8 ANOVA Table for Total Carbohydrates

Source	Sum of Squares	df	Mean Square	F	Sig.
Intercept	666.750	1	666.750	2347.813	.000
Spatial	257.665	2	128.833	453.655	.000
Season	.178	2	.089	.314	.732
Station	9.170	7	1.310	4.613	.001
Error	13.631	48	.284		
Total	1083.386	60			

It can be seen that the change in the total carbohydrates data between various seasons are not statistically significant at 0.05 level of significance.

Table 4.9 ANOVA Table for Total Lipids

Source	Sum of Squares	df	Mean Square	F	Sig.
Intercept	596.095	1	596.095	1367.761	.000
Spatial	450.736	2	225.368	517.115	.000
Season	1.002	2	.501	1.150	.326
Station	7.417	7	1.060	2.431	.033
Error	20.048	46	.436		
Total	1232.974	58			

For Total Lipids, since the p-value corresponding to various seasons is greater than 0.05, we conclude that the impact of seasons on the Total Lipid data is not statistically significant at 0.05 level. Also, as the p-value corresponding to various spatial levels and at various stations are less than 0.05 we conclude that these factors influence the data significantly.

Two factor ANOVA was carried out for Total organic carbon, Total Nitrogen and Total phosphorus.

Table 4.10 ANOVA Table for Total Nitrogen

Source	Sum of Squares	df	Mean Square	F	Sig.
Intercept	1.579	1	1.579	147.553	.000
Season	.051	2	.025	2.377	.129
Station	.258	7	.037	3.445	.023
Error	.150	14	.011		
Total	2.038	24			

For Total Nitrogen, the p-value corresponding to different seasons is greater than the significance level 0.05 and the p-value corresponding to different stations is less than the significance level 0.05, hence the impact of station is statistically significant on the Total Nitrogen at 0.05 level of significance and the impact of season is not significant.

Table 4.11 ANOVA Table for Total Phosphorus

Source	Sum of Squares	df	Mean Square	F	Sig.
Intercept	64.260	1	64.260	493.014	.000
Season	8.530	2	4.265	32.722	.000
Station	1.944	7	.278	2.130	.108
Error	1.825	14	.130		
Total	76.558	24			

For Total Phosphurus, since the p-value corresponding to the factor Season is less than 0.05, the factor Season is different at 0.05 level of significance. In addition, the p-value corresponding to the factor Station is greater than 0.05, which means there is no difference in the Phosphorous data between various Stations at 0.05 level of significance.

Table 4.12 ANOVA Table for Total Organic Carbon

Source	Sum of Squares	df	Mean Square	F	Sig.
Intercept	10.159	1	10.159	72.184	.000
Season	.178	2	.089	.631	.548
Station	2.724	7	.389	2.765	.054
Error	1.830	13	.141		
Total	15.002	23			

The p-values of both the two factors Season and Station are greater than the level of significance 0.05; we can conclude that both the factors are not significance at the same level of significance for Total Organic Carbon.

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Chapter 5

APPLICATION OF REMEDIAL MEASURES

5.1 Introduction:

Environmental pollution is a matter of greater concern today. The major sources of land and water pollution in recent times are petroleum products, metals and organic compounds. The water bodies are subjected to heavy discharge of a variety of organic as well as inorganic substances by industries situated on its banks. Oil pollution from industries and other activities are hazardous to terrestrial and marine ecosystems. Mining, industry and agriculture lead to accelerated release of metals into ecosystems, causing serious environmental problems and posing a threat to human health. Phenolic compounds are one of the most common types of organic soil contaminants. The widespread application of pesticides (alkyl and halogen substituted phenolic compounds) and their resistance to degradation have made the environment highly polluted with them. There exist various research findings on treatment of the polluted sites. Conventional methods for restoring contaminated sites include soil washing, excavation and reburial of soil and pump-and-treat systems for water. Remediation is a developing technology that reduces the concentration and/or toxicity of various chemical substances such as petroleum products, aliphatic and aromatic hydrocarbons including poly aromatic hydrocarbons and polychlorinated biphenyls, industrial solvents, phenols, benzene, acetone etc., batter liquids, pesticides and metals. This part of the chapter is an attempt to evaluate the most popular and effective methods for remediating contaminated sites-bioremediation, phytoremediation and chemoremediation, especially phytoremediation

5.1.1 Bioremediation

It can be defined as any process that uses microorganisms, fungi, or their enzymes to return the environment altered by contaminants to its original condition. There are two main avenues of bioremediation operation. One is *In-situ* process, which can simultaneously

treat soil and ground water in one step, without the generation of hazardous waste products. *Ex-situ* process involves an engineered treatment set up where contamination is placed for bioremediation. This treatment technology comprises of bio augmentation (the addition of microorganisms isolated from the contaminated site or cultured and enhanced in the laboratory suiting the contaminant and site conditions) and biostimulation (accelerating microbial reproduction and their metabolic activity by providing the necessary conditions like oxygen, water, nutrient media and making appropriate pH adjustments). *Indigenous* microorganisms are those microorganisms that are found already living at a given site. To stimulate the growth of these indigenous microorganisms, the proper soil temperature, oxygen, and nutrient content may need to be provided.

Bioremediation technology using microorganisms was reportedly invented by George M. Robinson. He was the assistant county petroleum engineer for Santa Maria, California. During the 1960's, he spent his spare time experimenting with dirty jars and various mixes of microbes. Bioremediation of polluted land and water has been extensively studied and much work is currently going on in the area of developing biologically active reagents that can work under chemically controlled environment.

The potential of microorganisms for bioremediation process depends on the existence of a microbial population capable of degrading the pollutants, the availability of contaminants to the microbial population and the environmental factors. The hydrocarbon utilizing bacteria population consists of Pseudomonas, bacillus, Proteus, Serratia, Aeromonas, Klebsiella and micrococcus. The growth and activity of the micro organisms must be estimated by adequate maintenance and supply of nutrients. These nutrients are the basic building blocks of life and allow microbes to create the necessary enzymes to break down the contaminants. In certain anaerobic systems, the availability of trace metals can be of concern. Presence of oxygen is the most crucial factor. Oxygen can become a limiting factor in all types of petroleum degradation, so aeration is required in most applications. Ramsay et al (2000) studied the response of hydrocarbon degrading bacteria in oiled mangroves and evaluated bioremediation as an oil response strategy in mangrove forests of tropical coastal environments contaminated by oil.

Mangrove sediments are predominantly anaerobic, comprising of sulphidic muds. In mangrove sediments, the rate of hydrocarbon biodegradation by the bacterial community is likely to be limited by oxygen concentration and nutrient levels. Bioremediation based on aeration and nutrient addition substantially promotes the growth of alkane degrading bacteria in tropical mangrove sediments and may therefore be useful strategy to accelerate degradation of oil contamination in this environment. Moisture is of greater concern in bioremediation. Moisture levels in the range of 20% to 80% of saturation generally allow suitable biodegradation in soils. Short-wavelength solar radiation is also a factor likely to affect microbial activity during bioremediation. The growth and survival of bacteria responsible for biodegradation are affected by UV radiation. Santas et al (1999) studied the effect of UV radiation on bioremediation and found that increase in the amount of UV radiation decreases and even inhibits the bioremediation activities.

Considering all these factors and providing the appropriate pH conditions, bioremediation can be successfully applied to contamined sites at a lower cost and at lower human risk. It does not produce toxic by-products. It is non-disruptive and non- invasive. It can be employed in areas which cannot be reached easily without excavation. For example, hydrocarbon spills may contaminate ground water well below the surface of the ground. Injecting the right organisms in conjunction with oxygen forming compounds may significantly reduce concentrations after a period of time. This is much less expensive than excavation followed by burial elsewhere, incineration or other ex-situ treatment and reduces or eliminates the need for pumping and treatment, which is a common practice at sites where hydrocarbon contamination has taken place. Bioremediation of contaminated soil samples enhance seed germination, seedling growth and survival thus increasing productivity.

5.1.2 Chemo remediation:

Chemo remediation refers to the reduction of contaminants in the environment using chemical methods. Chemical treatment of contaminated land and water involves the addition of an oxidizer to enhance the rate of degradation of the pollutants. Hydrogen peroxide can be used as an oxygen source in a bioremediation process of a crude oil polluted site (Adeyinka and Urum 2004). Oxygen is also provided by aerating the water and sediments.

Lovely et al (1994) have shown that contamination of ground water often produces anoxic conditions under which microbial degradation is slow. Addition of oxygen to contaminated ground waters is technically difficult and expensive. Insoluble Fe (III) oxides, which are abundant in shallow aquifers, can be used as alternative potential oxidants. Their bioavailability can be increased by adding organic ligands like NTA, EDTA etc. which bind to Fe (III). In the presence of these ligands, rates of degradation of aromatic hydrocarbons in anoxic sediments are comparable to those in oxic sediments. Under anaerobic conditions, NO_3^- , SO_4^{2-} and CO_2 may also serve as terminal electron acceptors. Machado et al (2005) used magnetic adsorbents based on vermiculite iron for the remediation of contaminated sites. These magnetic materials show two important features for the remediation: a) they float on water and can be used to absorb/adsorb spilled oils and, b) after adsorption they can be easily removed from the medium by a simple magnetic separation procedure. Min Jang et al (2005) conducted laboratory experiments to evaluate the extraction efficiency of arsenic using alkaline or acid washing. Alkaline washing using sodium hydroxide was found to be favourable in removing arsenic from tailings or soils having a higher portion of arsenic. This is due to the ligand displacement reaction of hydroxyl ions with arsenic species. Kioussis and Kofinas (2005) have shown that ion exchange systems containing polymer hydro gels can be used for the removal of nutrient pollutants, even at extremely low concentrations from wastewater effluents. This work reports on the features of batch sorption processes for the ultimate removal and recovery of reactive phosphorus, nitrogen and sulphur anions from aqua culture production wastewater effluents. Moore et al (1978) used polymer–based fibers for the efficient removal of petroleum-derived hydrocarbons from the oil-contaminated bioassay effluents. Three types of woven fiber filter catridges were selected, to test the effectiveness of the various filter materials.

5.1.3 Phytoremediation:

Phytoremediation is a method, which uses green plants to remove pollutants from the environment or render them harmless. Certain plant species have the ability to extract elements from the soil and concentrate them in the easily harvested plant stems, shoots and leaves. Phytoremediation takes advantage of the natural abilities of plants to take up, accumulate, store or degrade organic and inorganic substances. Although not a new concept, phytoremediation is currently being re-examined as an environmentally friendly, cost-effective means of reducing metal contaminated soil and other substrates. Processes include using plants that tolerate and accumulate metals at high levels and using plants that can grow under conditions that are toxic to other plants, also prevent soil erosion. Governments worldwide are establishing research and demonstration programs to use this potential. Phytoremediation can be made useful by selecting plants of nutritional value like young shoots of wheat grass, tomatoes and leafy vegetables like amaranthus. Wheat grass can be used to remediate sites polluted with petroleum hydrocarbons. Tomatoes are effective in removing toxic metals like zinc, copper and lead.

Phytoremediation works best at sites with low to medium amounts of pollution. Plants remove harmful chemicals from the ground when their roots take in water and nutrients from polluted soil, streams, and groundwater. Plants can clean up chemicals as deep as their roots can grow. Tree roots grow deeper than smaller plants, so they are used to reach pollution deeper in the ground. Plants grown for phytoremediation also can help keep harmful chemicals from moving from a polluted site to other areas. The plants limit the amount of chemicals that can be carried away by the wind or by rain that soaks into the soil or flows off the site.

There are five common types of phytoremediation which are summarized below.

Rhizofiltration refers to the adsorption or removal of contaminants surrounding a plants root zone. It is done by growing plants in the laboratory with their roots in water. Samples of contaminated soil are brought to the laboratory and the water is replaced with this soil.

Phytoextraction involves the accumulation and relocation of metal contaminants from soil. The metal contaminants are transferred from the soil to the plants roots, and then to other portions of the plant. This method removes the metals from soil, not ground water. This is done by growing plants at the site, not in a laboratory. After a couple growing seasons, the plants are harvested and incinerated.

Phytotransformation is the breakdown of contaminants through a plant's metabolic processes, or through the release of enzymes. Phytotransformation targets organic compounds which are reduced and accumulated into the plant tissues. These reduced or degraded compounds actually help the plants grow faster.

Phytostimulation is "plant assisted" bioremediation. The microbial processes, that occurs in plants, breakdown contaminants in the root zone. Microorganisms present in plants use organic compounds for food and energy. Examples of organic compounds degraded by this method are petroleum and PAHs.

Phytostabilization is the use of plants to immobilize, or reduce mobility of contaminants in soil. The large network of plant roots trap or accumulate pollutants. Once the contaminants are present in the above ground portion of the plant, they can be volatilized.

There are two factors that determine which type of phytoremediation is being used: 1) where the contaminants are being removed from and 2) how they are removed /immobilized from the contaminated area.

Phytoremediation was trailed and found to be fruitful at various sites in International level (**Table 5.1**). In India, phytoremediation was applied to sodic soil at Sultanpur District of Uttar Pradesh using three tree species *Prosopis juliflora, Dalbergia sissoo and Eucalyptus tereticornis* (Mishra et al., 2004). The three tree species were effective in reducing sodicity but *P.juliflora* proved more efficient in reducing pH, Na^+ concentration and increasing Ca^{2+}, Mg^{2+}, and K^+ concentration in comparison to *D. sissoo* and *E. tereticornis* plantations.

Table 5.1: Some of the remedial measures taken and their results

Treatment adopted	Result
Application of chemical fertilizers and animal manure for enhancing biodegradation of crude oil-contaminated sites (Tehrani and Herfatmanesh, 2007).	54% reduction of crude oil in soil enriched with chemical fertilizers and wood chips and 46% reduction in soil enriched with animal manure.
Use of chitosan and Osmocote fertilizer as additives for increasing biodegradation of pyrene in marine sediments over a 63 day period (Li et al., 2007)	Without additives, loss of pyrene was 66.6% whereas application of additives resulted in a 98.2% loss of pyrene in a period of 63 days.
Biosorption of mercury by three fungi i.e,*Aspergillus niger, Trichoderma viride* and *Humicola insolens* was investigated (Javed et al., 2007).	The consortium of 24-h-old *H. insolens* and 48-h-old of *A. niger* and *T. viride* in equal ratio decreased the residual mercury from 2.02 to 0.001 µg/L after 7 days of incubation and caused 92.6% reduction in COD.
Biodegradation of phenanthrene in Antartic soils using i) biostimulation with fishmeal fertilizer(source of nutrients) ii) bioaugmentation with a PAH-degrading bacterial consortium (Ruberto et al., 2006)	Combination of biostimulation and bioaugmentation caused a significant removal (46.6%) of phenanthrene after 56 days under Antarctic environmental conditions.
Remediation of sodic soil in Sultanpur district of Uttar Pradesh using three tree species *Prosopis juliflora, Dalbergia sissoo and Eucalyptus tereticornis.* (Mishra et al;2004)	The three tree species were effective in reducing sodicity but *P.juliflora* proved more efficient in reducing pH, Na^- concentration and increasing Ca^{2+}, Mg^{2+}, and K^- concentration in comparison to *D.sissoo* and *E. tereticornis* plantations.
Remediation of copper polluted soil by Indian mustard (Wu et al., 2004).	A combined supply of nutrients (low N and high P) produced a yield increase in Indian mustard that was more than adequate to compensate for a slight decrease in Cu concentration resulting in the highest Cu removal from the contaminated soil.

Use of enzyme peroxidase found in Horseradish (*Armoracia rusticana*) for the detoxification of soils contaminated with phenolic compounds(Coyle et al.,1999).	Very rapid reaction with 74% removal of 2,4-dichlorophenol (initial concentration 5 mM) during the first 30 minutes.
Use of the fungus *Aspergillus niger* for bioremediation of heavy metals on three contaminated soils -a clay loam, a loam and a sandy clay loam (Syed et al., 1998).	After 15 days, for the clay loam, 37% Cr, 41% Mn, 84%Pb, 91% Hg; for the loam, 83% Pb, 99.7% Cd; for the clay sandy loam, 58%Pb, 99% Cd, 94% Cu and 99%Zn were leached out.
Degradation of xenobiotic glyceryl trinitrate using plant cells (Akshay et al., 1997).	Degradative activities of plant cells are only ten fold less than that of bacterial degradation of glyceryl trinitrate.
Transformation of trichloroethane in an aqueous medium using elemental iron as electron source (Lampron et al., 1998).	In samples with iron and no culture, 11µmols of TCE disappeared over a period of 39 days. In samples with culture and Iron, same amount was transformed in less than two weeks.
Use of sodium carbonate as a leachant in desulphurization of Mengen lignite (Bozdemir and Durusoy, 1999).	Use of 100ml of 0.2 M sodium carbonate solution at 40°C for three hours caused 96% removal of pyritic Sulphur.
Dechlorination of chloroethene-contaminated groundwater site at the Naval Air Station Pensacola using Fenton's treatment (Bradley et al., 2007).	Greater than 75 percent decrease in trichloroethene (TCE) concentrations was observed along a 30-m groundwater flow path.
Phytoremediation of malathion, demeton-s-methyl, and ruelene using three different types of plants (Gao et al., 1999).	After 8 days, malathion had >83% reduction, dementon-s-methyl had >78% reduction and ruelene had no reduction upto 58%.

Phytoremediation has several disadvantages but there are alternatives for it. Phytoremediation is time consuming. It may take several growing seasons for the plants to grow to a size that will be effective in removing pollutants. Therefore selection of plants with high nutritional values and less growing time is being considered. Volatilization can release contaminants into the air, creating air pollution; therefore the beginning of the initial experiments should be conducted in simulated field conditions. There are certain depth limitations with phytoremediation. Soils can be remediated by plants up to a depth of 3 feet. Trees can successfully remediate soils up to a depth of 15 feet. Standing water and groundwater can be successfully treated at depths up to 10 feet. So it is better to plant in a minimum depth which can effectively fulfill the remediation. There is possibility of contaminant entrance into the food chain, therefore the edible parts of the plant is being tested for the toxicants before use.

All the above-mentioned remedial measures are found to be effective, if applied at the correct site and appropriate conditions. The success of bioremediation lies in the application of the right types and quantities of fertilizers and also providing optimum moisture content, pH, aeration level and other environmental conditions for microbial growth. It was also found that aeration and nutrient addition significantly stimulated the growth of hydrocarbon degraders in oiled-mangrove sediment in the field. The results of chemoremediation show that it is also an effective method for restoring water and aqueous solutions. Because of the conditions that vary between each contaminated site, bioremediation and phytoremediation are not feasible in every case. Before a remediation project can begin, all of the site-specific factors must be taken into account, and a decision must be made upon the most suitable technology available. Though the above three methods are found to be fruitful to some extent, a combination of the three may be trialled depending on the contaminants present, for ensuring complete restoration of a polluted site.

Advantages of phytoremediation have made it more applicable than other remediation technologies. Phytoremediation generates little to no secondary wastes. There is minimal environmental disturbance. Phytoremediation is a form of in-situ treatment. In-situ treatment is the treatment of soil of water in its natural environment, which is less expensive and more

convenient to those working at the site. Most mechanical methods of remediation are an eye sore whereas phytoremediation is aesthetically pleasing. Plants reduce erosion of soil. As opposed to other mechanical methods, phytoremediation is solar-energy driven. The only source of power needed is the sun. The process of phytoremediation is much cheaper than most other remediation techniques.

5.2 Application of Phytoremediation:

Phytoremediation is a new technology for the restoration of contaminated sites. It involves the use of plants to decrease the concentration of toxicants in soils and sediments. Phytoremediation research began in the early 1980's and one of the first times phytoremediation was used was in Chernobyl, Ukraine, in 1986 to decontaminate water and soil. Plants used for phytoremediation vary widely and some plants work better than others for different contaminants. An important factor in determining the effectiveness of a plant is the root structure and rooting patterns. Another important factor that determines the success of phytoremediation is soil dynamics, which is based on the soil texture. The best soils for phytoremediation are soils that have a predominance of silt. Silt holds water well, yet it also allows plants to take up the water from the soil particles. Plants used for phytoremediation must be able to bring up water from soil particles and draw in carbon dioxide from the atmosphere to create glucose and oxygen.

The selection of wheat grass for phytoremediation was based on the following reasons:

- Studies have also shown that wheat is effective in removing pollutants, especially metals from soils and sediments. Unlike organic contaminants, metals cannot be degraded. Instead, phytoremediation strategies for metals are based on stabilization, accumulation, and in some cases volatilization (EPA, 1998).
- Wheat (*sort Umanka*) is capable to produce large biomass in the field and accumulate high concentrations of different metals. (Shtangeeva et al., 2004) metal concentration decreased by using wheat. After remediation, it was found that physiological parameters of the wheat plant (biomass, chlorophyll content) were improved. This resulted in more active metal uptake by the plants and decrease in concentrations of the metals in the soils.
- Rodrigues et al (2007) found that high-biomass crops can be considered as an alternative to hyperaccumulator plants to phytoremediate soils contaminated by heavy metals. The study proposes utilization of high-biomass crops, *e.g.*, maize, peas, oats, barley, wheat, Indian mustard, and cabbage, in conjunction with the appropriate chemical treatment to enhance the solubility of metals in soils.

- Plant physiologist Leon V. Kochian found that some plant species including wheat, corn, and sorghum can tolerate high levels of the metal in acid soils.
- Wheat grass juice is a wonderful cleanser and rejuvenator rich in vitamins, enzymes and nutrients which help our body to throw out toxins that have built up over the years and helps it replace old dead cells with new cells. Wheatgrass is one of the best sources of living chlorophyll available.

The present study was organized in two sections. **Section I** aims at evaluating the potential of wheat grass to decrease the concentration of Sulphur in the sediments of Cochin estuarine system. Since earlier studies have shown that wheat grass is effective in remediating pollutants particularly trace metals, reduction in the concentration of selected trace metals was also focussed. In **section II**, the nutritional value and trace metal concentration of wheat grass grown in different sediment conditions was noted for using it as a nutritional supplement

5.2.1 Materials and methods:

5.2.1.1 Growth of wheat grass:

Wheat seeds were grown in plastics trays containing 100g of each of the sediments. There were no sediment samples in Station 2 and 7. Sediment of station 1 was selected as control. Wheat grass was grown in the above different sediments in plastic trays. The details of growth are given in the table:

Table 5.2: Details of growth of wheat grass

	Stations								
Season	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**Control**
PRM	Y	NS	X	X	X	X	Y	X	Y
MON	Y	NS	Y	Y	X	Y	Y	Y	Y
PSM	Y	NS	X	X	X	Y	NS	X	Y

Y- Wheat grew X – Wheat not growing NS – no sediment sample

The grown wheat grass was cut after two weeks and dried. Various parameters (ash content, phosphorus, iron, sodium, potassium, calcium, magnesium, proteins, and carbohydrates) in the wheat grass were analyzed by standard methods to know the nutritional value.

Organic carbon, total nitrogen, total sulphur and concentration of metals in the different sediments were analyzed before and after growing wheat for assessing the efficiency of phytoremediation.

5.2.1.2 Analysis of sediments after phytoremediation:

After the desired period of time (2 weeks), the plants were harvested and dried in sunlight. The sediments were air dried and ground to fine powder in agate mortar. 2 grams of each sample were digested with a mixture of concentrated nitric acid and perchloric acid in 5:1 ratio until the sediment becomes clear, centrifuged and made upto 25 ml using milli-Q water. The metal content was analysed using atomic absorption spectrophotometer (AAS).

Organic carbon, total nitrogen and total sulphur in the sediments were also analyzed as per the procedure described in chapter 2.

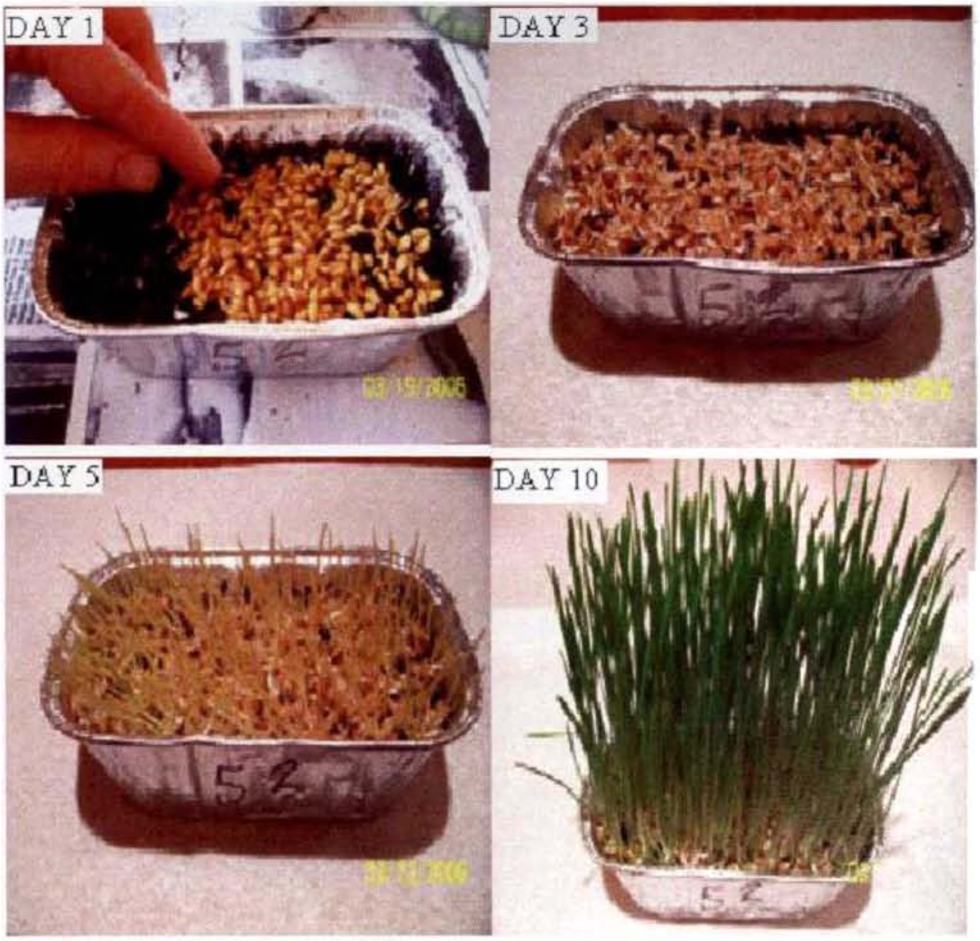


Figure 5.1: Different stages of growth of wheat grass

5.2.1.3 Analysis of wheat grass:

The wheat grass was dried in sunlight and the parameters analysed by the following methods:

Ash content by calcination in muffle furnace at 550^{0}C, Proteins using Folin-Ciocalteu phenol reagent (Lowry et al 1951) , Carbohydrates by phenol-sulphuric acid method, Calcium and Magnesium by Complexometry, Iron and Phosphurus by colorimetry (APHA), Sodium and Potassium by Flame emission spectrophotometry.

Metals in wheat grass was analysed as follows:

The harvested wheat grass was air dried and powdered. 1g of each sample was digested with diacid mixture (con. HNO_3 and conc.$HClO_4$ in 5:1 ratio) and the extract was made upto 25 ml using milli-Q water and metal content was analysed using AAS.

The calorific value of wheat grass is calculated using the formula

Calorific value (kcal/g) = (5.65 * P + 9.45 * L + 4.2 * C) / 100 where P is the concentration of proteins, L is the concentration of Lipids and C is the concentration of total carbohydrates in the corresponding wheat grass samples.

5.2.2 Results:

Section I: Analysis of sediments after phytoremediation:

After phytoremediation, the sediment samples were analysed for Sulphur, TOC, TN, and metals to know if there is any decrease in their concentration.

5.2.2.1 Sulphur:

Plant species have a high biodiversity in uptake, metabolization and accumulation of sulfur so that there are potentials to use plants for phytoremediation of sulfur-enriched sites (Ernst, 1998). According to Marschner (1995), the effectiveness of phyto-extraction for remediation of sulfur enriched soils is highly dependent on the availability of sulfur for the plant. Roots can take up sulfate which is the most important source of sulfur for higher plants. On the contrary, reduced sulfur in the rhizosphere is phytotoxic. As far as sulfur is bound to organic compounds in the soil, it has to be mineralized by microorganisms to become available as sulfate to higher plants. To a lesser degree volatile sulfur compounds such as carbondisulphide, hydrogen sulphide, methyl mercaptan and sulfur dioxide can be taken up by leaves (Goldan etal. 1988, Bosma et al. 1990, Van der Kooij et al. 1997).

Total sulphur in the sediments was analysed before and after remediation. In the monsoon season, growth of wheat grass in the sediments was found to decrease 61 % of Total Sulphur in the sediments. The highest % decrease was shown in the monsoon season. In pre monsoon and post monsoon, the percentage decrease in sulphur was 58 and 47 % respectively. According to Ebbs et al. (1997), the potential of sulfur extraction from the soil by plants is quite high in comparison to that of the accompanying elements like aluminum and heavy metals due to the role of sulfur as major nutrient. In the present study, decrease was found more effective in the monsoon season due to the scanty growth of wheat grass in the pre monsoon and post monsoon season.

5.2.2.2 Sulphate:

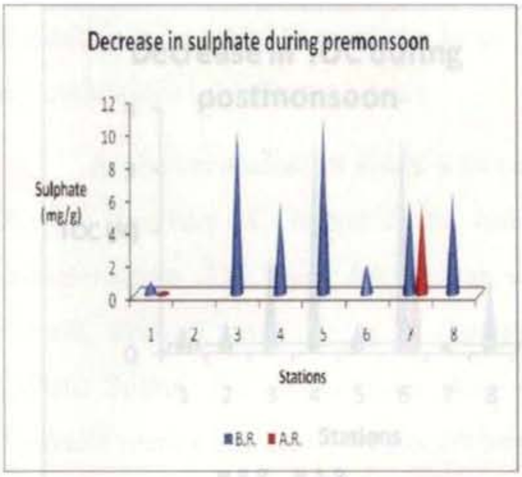
Sulphate showed the highest percentage reduction among the parameters studied **(Figure 5.2, 5.3 and 5.4).** Station1 sediments showed reduction of about 88% during monsoon, 86% during premonsoon and 55% during post monsoon.

5.2.2.3 TOC

As a result of phytoremediation, TOC was found to decrease about 18- 67 % **(Figure 5.5 – 5.7)**. Highest percentage reduction was found to be 67% in the sediments of station 3 and & where excellent wheat grass growth was reported. During pre monsoon, station 1 sediments showed 44% reduction in TOC and Station 7 Sediments showed 65% reduction. Post monsoon season recorded wheat grass growth only in the sediments of station 1 and station 6 which showed a decrease of 50 and 43% respectively.

5.2.2.4 TN:

TN was found to have maximum decrease among the analysed parameters, especially during monsoon **(Figure 5.8 - 5.10).** Percentage decrease in TN ranged from 8-92% during monsoon with the highest at the reference station. During pre monsoon station 1 and station 7 showed 84 and 53% reduction respectively. But post monsoon showed 80 and 46% reduction in TN for Stations 1 and 6 respectively.



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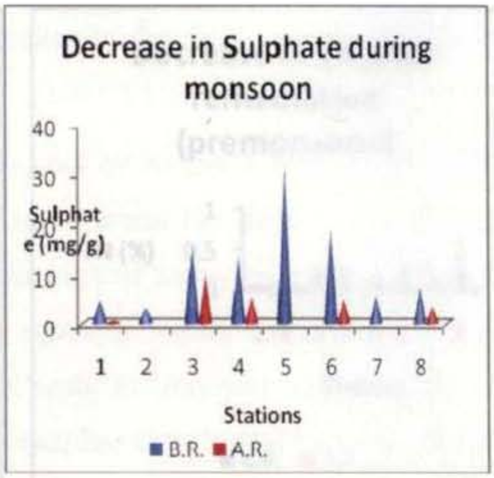

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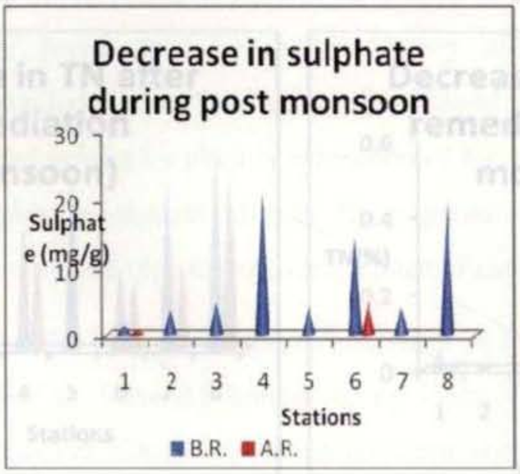

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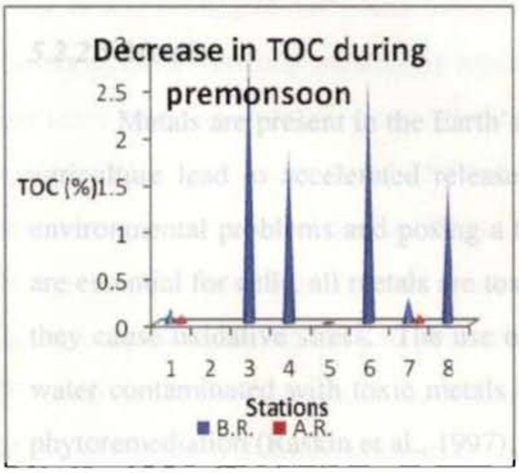

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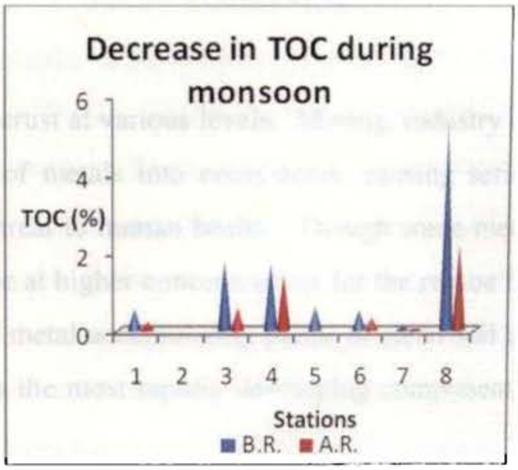

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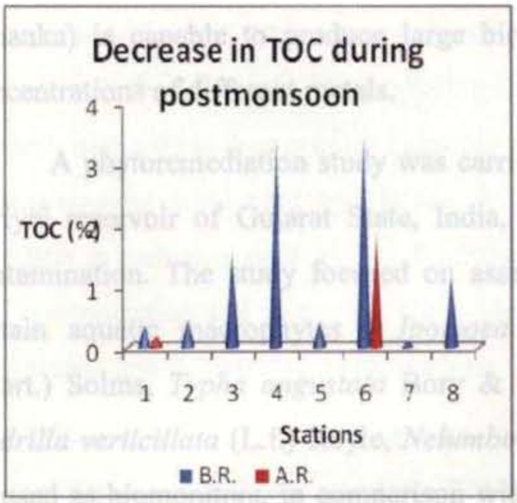

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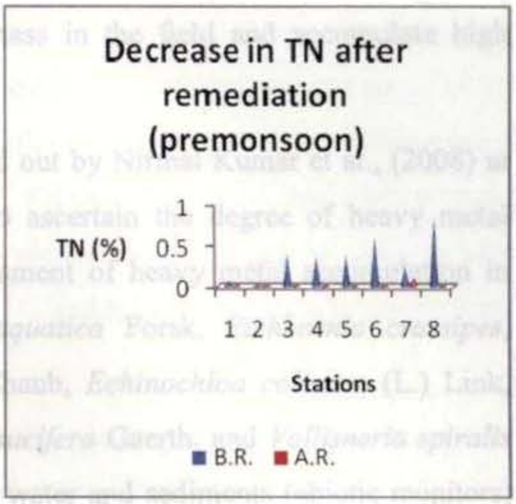

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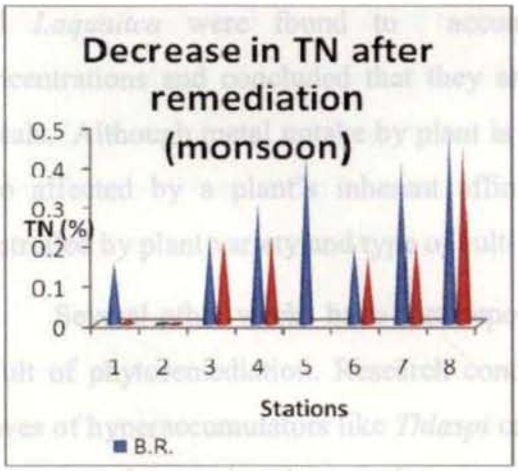

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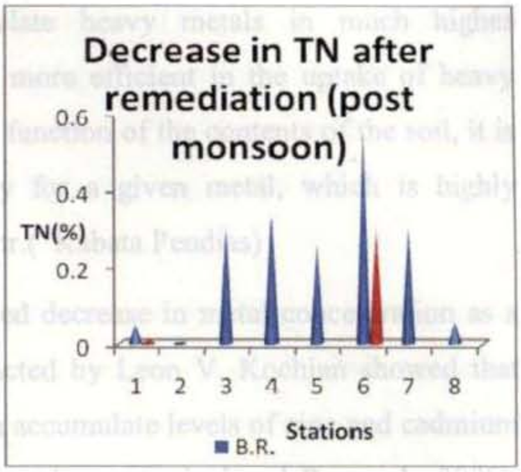


Figure 5.10

5.2.2.5 Metals:

Metals are present in the Earth's crust at various levels. Mining, industry and agriculture lead to accelerated release of metals into ecosystems, causing serious environmental problems and posing a threat to human health. Though some metals are essential for cells, all metals are toxic at higher concentrations for the reason that they cause oxidative stress. The use of metal-accumulating plants to clean soil and water contaminated with toxic metals is the most rapidly developing component of phytoremediation (Raskin et al., 1997).

Study conducted by Shtangeeva et al., (2004) has shown that wheat (sort Umanka) is capable to produce large biomass in the field and accumulate high concentrations of different metals.

A phytoremediation study was carried out by Nirmal Kumar et al., (2008) at Pariyej reservoir of Gujarat State, India, to ascertain the degree of heavy metal contamination. The study focused on assessment of heavy metal accumulation in certain aquatic macrophytes – *Ipomoea aquatica* Forsk, *Eichhornia crassipes*, (Mart.) Solms, *Typha angustata* Bory & Chaub, *Echinochloa colonum* (L.) Link, *Hydrilla verticillata* (L.f.) Royle, *Nelumbo nucifera* Gaerth. and *Vallisneria spiralis* L. used as biomonitors, in comparison with water and sediments (abiotic monitors) for phytoremediation. Three native aquatic plant species *T. angrustata*, *E. crassipes* and *I.aquaitca* were found to accumulate heavy metals in much higher concentrations and concluded that they are more efficient in the uptake of heavy metals. Although metal uptake by plant is a function of the contents of the soil, it is also affected by a plant's inherent affinity for a given metal, which is highly controlled by plant variety and type of cultivar.(Kabata Pendias)

Several other works have also reported decrease in metal concentration as a result of phytoremediation. Research conducted by Leon V. Kochian showed that leaves of hyperaccumulators like *Thlaspi* can accumulate levels of zinc and cadmium many times higher than leaves of many other plants (Agricultural Research, 2000). Pilar et al., (2001) investigated the tolerance, uptake and accumulation of several metals of environmental interest by lupin plants. After 4 weeks of growth, the results indicated that lupins were quite tolerant to Cd(II), Pb(II), Cr(III) and Hg(II) since contamination with those metals did not cause significant weight differences between metal-treated and control plants. Wu et al., (2003) showed that a combination of low N and high P produced a yield increase in Indian mustard that was more than adequate to compensate for a slight A combined supply of nutrients (low N and high P) produced a yield increase in Indian mustard that was more than adequate to compensate for a slight decrease in Cu concentration resulting in the highest Cu removal from the contaminated soil. Decrease in Cu concentration, resulting in the highest Cu removal from the contaminated soil. Inorder to assess their practical capability for the absorption and accumulation of Hg in shoots, Rodriguez et al., (2004) tested barley, white lupine, lentil and chickenpea in pot experiments using several growth substrates. Remediation of sodic soil in Sultanpur district of Uttar Pradesh using three tree species Prosopis juliflora, Dalbergia sissoo and Eucalyptus tereticorniswas conducted by Mishra et al., (2004). The three tree species were effective in reducing sodicity but P.juliflora proved more efficient in reducing pH, Na^+ concentration and increasing Ca^{2+}, Mg^{2+}, and K^+ concentration in comparison to D.sissoo and E. tereticornis plantations.

Peciulyte et al., (2006) searched for the plants possible to grow in metal-contaminated soil and accumulate metals in their biomass. Maize (*Zea mays* L.) and vetch (*Vicia sativa* L.) were chosen for that and found that maize plants growing in contaminated soils had accumulated higher a Cu content (338 mg kg–1), while vetch plants accumulated a higher Zn content (365 mg kg–1 dry wt). The content of metals accumulated in plants growing in the soil from the 10–20 cm layer containing organic matter did not differ from that in the plants growing on the soil from the 25–56 cm layer with a low nutrient concentration.

Heavy metals such as Cu and Zn are essential for normal plant growth, although elevated concentratins of both essential and non-essential metals can result in growth inhibition and toxicity symptoms. Plants possess a range of potential cellular mechanisms that may be involved in the detoxification of heavy metals and thus tolerance to metal stress. These include :' for mycorrhiza and binding to cell wall and extracellular exudates; for reduced uptake or efflux pumping of metals at the plasma membrane; for chelation of metals in the cytosol by peptides such as phytochelatins; for the repair of stress-damaged proteins; and for the compartmentation of metals in the vacuole by tonoplast-located transporters. A review by Hall (2002) provides a broad overview f the evidence for an involvement of each mechanism in heavy metal detoxification and tolerance. Moore et al., (2007) examined the use of rice (*Oryza sativa*) for luxury uptake of nitrogen and phosphorus components associated with agricultural storm runoff.

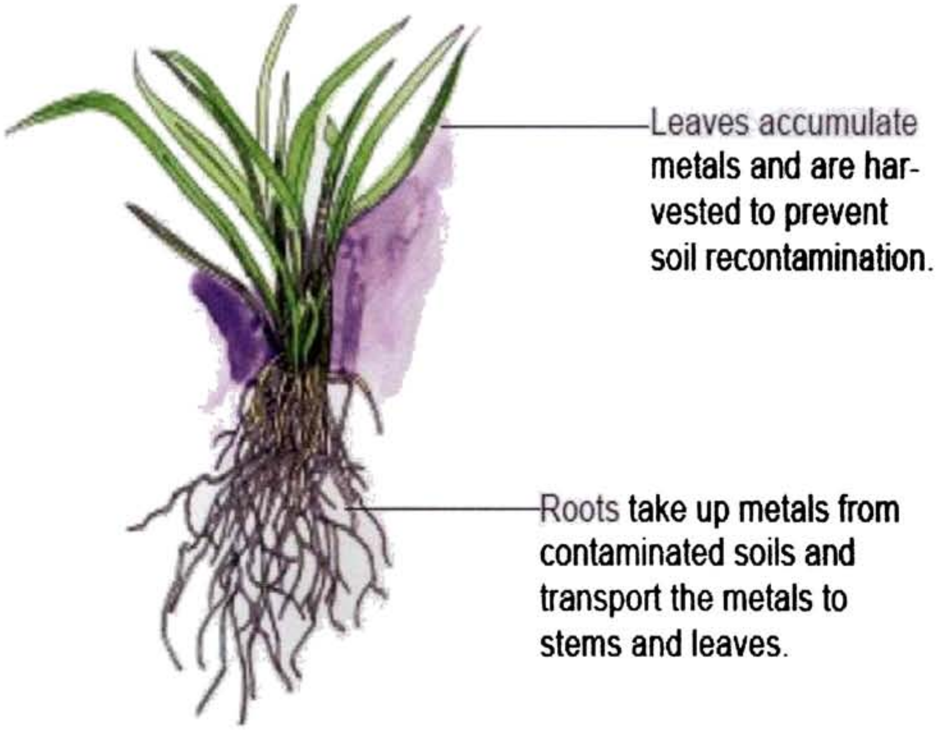


Figure 5.11: Metal Uptake by Plants

As measure of using wheat grass for remediating pollutants, the decrease in the selected trace metal concentration (Cu, Cr and Pb) was also noted and the results are given in **Table 5.3**

Table 5.3 Concentration of trace metals before and after remediation

Station	Premonsoon			Monsoon			Postmonsoon		
	B.R.	A.R.	% reduction	B.R.	A.R.	% reduction	B.R.	A.R.	% reduction
				COPPER(mg/kg)					
1(C)	14.24	13.84	2.81	4.87	4.79	1.67	116.44	114.23	1.90
2	NA			NA			NA		
3				15.33	12.58	17.94			
4				50.70	46.28	8.72			
5									
6				25.64	24.40	4.84	43.06	40.53	5.88
7	20.12	18.32	8.95	25.73	24.79	3.65			
8				122.00	100.98	17.23			
				CHROMIUM (mg/kg)					
1(C)	36.15	35.48	1.85	23.62	20.64	12.62	13.77	11.69	15.11
2	NA			NA			NA		
3				6.67	4.56	31.63			
4				15.03	12.03	19.96			
5									
6				40.37	35.94	10.97	19.48	17.52	10.06
7	89.01	80.54	9.52	12.91	10.25	20.60			
8				15.69	11.93	23.96			
				LEAD (mg/kg)					
1(C)	42.87	36.22	15.51	1.16	1.10	5.17	137.50	129.52	5.80
2				NA			NA		
3				6.70	4.54	32.24			
4				15.04	9.95	33.84			
5									
6				14.66	10.32	29.59	39.90	26.84	32.73
7	60.50	55.00	9.09	3.09	1.56	49.51			
8				14.90	11.05	25.84			

Though wheat plant was grown in all the sediments in all the three seasons, growth of the plant was well reported only in the monsoon season, in which wheat plant grew in almost all the sediments. Pre monsoon and post monsoon seasons recorded moderate growth. During pre monsoon, wheat grew only in the sediments of stations 1 and 7 but in monsoon, growth was reported only in the sediments of stations 1 and 6.

The percentage decrease of metal concentration was also high in the monsoon season. Decrease in the concentration of sodium and Potassium and three trace metals- Cu, Cr and Pb were noted.

Sodium:

Before remediation, the sediments showed sodium concentrations in the range 250-10970 mg/kg, 372-9290 mg/kg and156-13961 mg/kg during pre-monsoon, monsoon and post-monsoon respectively(**Figure 5.12 - 5.13**). During pre-monsoon wheat plant grew only in the sediments of stations 1 and 7. In Monsoon, wheat growth was reported in almost all stations except in stations 3 and 6 where high levels of pollutants was reported.

Potassium:

During premonsoon, decrease in potassium concentration was very low. For station 1 and 7 where the wheat plant grew, the reduction was only 11% and 1% respectively (**Figure 5.14 – 5.16**). Before remediation, potassium concentration in sediments varied from 39 to 113 mg/kg, 374 to 2443 mg/kg and 461 to 4098 mg/kg during premonsoon, monsoon and postmonsoon respectively.

Table 5.4: Percentage reduction in sodium and potassium

	SODIUM(mg/kg)			POTASSIUM(mg/kg)		
Sediments	**B. R.**	**A.R.**	**% reduction**	**B. R.**	**A.R.**	**% reduction**
PRM 1	249.6	186.8	25	96	85	11
PRM 2		-	-		-	-
PRM 3	5249	-	-	113	-	-
PRM 4	8033	-	-	111	-	-
PRM 5		-	-		-	-
PRM 6	1097	-	-	39	-	-
PRM 7	466	311	33	81	70	1
PRM 8	2154	-	-	71	-	-
Sediments	**B. R.**	**A.R.**	**% reduction**	**B. R.**	**A.R.**	**% reduction**
MON1	340	187	45	374	224	40
MON2		-	-	-	-	-
MON3	620	-	-	1347	-	-
MON4	2847	1120	61	1574	1220	22
MON5	372	289	22	1798	1444	20
MON6	3221	-	-	2092	-	-
MON7	745	187	75	823	299	64
MON8	5896	5014	15	2443	2016	17
Sediments	**B. R.**	**A.R.**	**% reduction**	**B. R.**	**A.R.**	**% reduction**
PSM 1	291	198	32	1148	773	33
PSM 2	156	-	-	200	-	-
PSM 3	499	-	-	-	-	-
PSM 4	2248	-	-	4098	-	-
PSM 5	1528	-	-	1012	-	-
PSM 6	3808	749	80	1419	491	65
PSM 7		-	-	-	-	-
PSM 8	6851	-	-	461	-	-

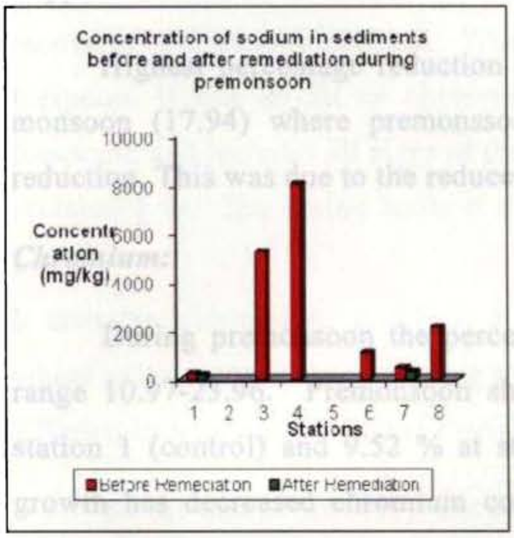


Figure 5.12

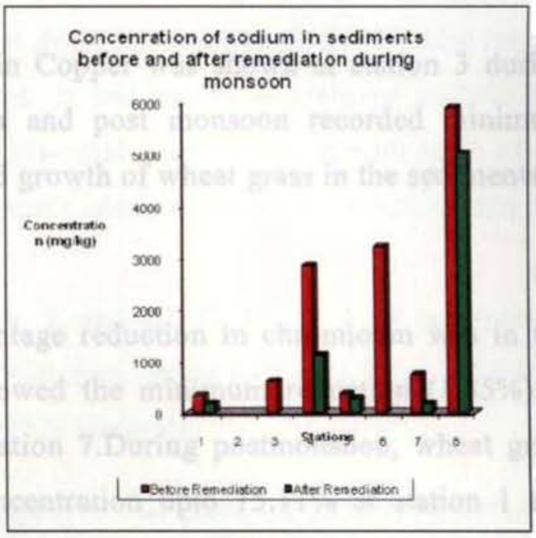


Figure 5.13

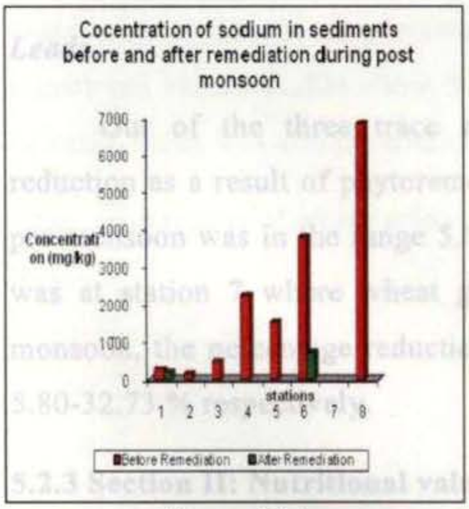
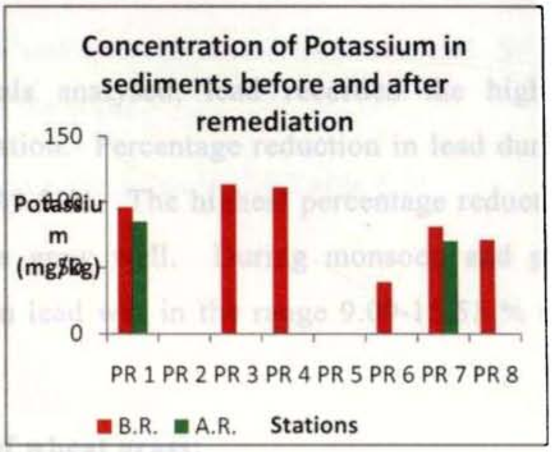


Figure 5.14



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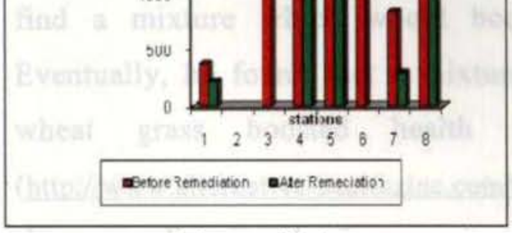

Figure 5.16

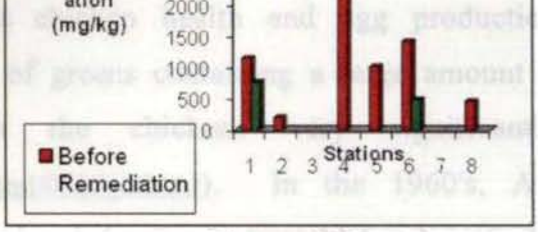

Figure 5.17

Copper:

Highest percentage reduction in Copper was shown at station 3 during monsoon (17.94) where premonsson and post monsoon recorded minimum reduction. This was due to the reduced growth of wheat grass in the sediments.

Chromium:

During premonsoon the percentage reduction in chromioum was in the range 10.97-23.96. Premonsoon showed the minimum reduction (1.85%) at station 1 (control) and 9.52 % at station 7.During postmonsoon, wheat grass growth has decreased chromium concentration upto 15.11% at station 1 and 10.06% at station 6.

Lead:

Out of the three trace metals analysed, lead recorded the highest reduction as a result of phytoremediation. Percentage reduction in lead during pre monsoon was in the range 5.17-49.51%. The highest percentage reduction was at station 7 where wheat grass grew well. During monsoon and post monsoon, the percentage reduction in lead was in the range 9.09-15.51 % and 5.80-32.73 % respectively.

5.2.3 Section II: Nutritional value of wheat grass:

Wheat grass is one of the best sources of living chlorophyll available. Wheatgrass contains a vast amount of nutrients such as vitamins, minerals, enzymes, and amino acids. But the nutritional value of wheatgrass is largely due to its high content of chlorophyll – 70% high in fact.

In 1931, a food scientist called Charles Schnabel was experimenting to find a mixture which would boost chicken health and egg production. Eventually, he found that a mixture of greens containing a large amount of wheat grass boosted health in the chickens very significantly. (http://www.alternative-healthzine.com/html/0500_2.html). In the 1960's, Ann Wigmore discovered wheat grass, curing her own 'untreatable' colitis in the process. She gave wheat grass to several sick neighbours - all of whom recovered and were revitalized. Wheat grass has only about 10-15 calories per teaspoon. It has no fat or cholesterol. It has nearly a gram of protein per teaspoon, and includes all eight of the essential amino acids, as well as 13 of the remaining 16. The amino acids it doesn't contain are easily made within the body.

It contains Vitamins A, B1, 2, 3, 5, 6, 8, and 12; C, E and K. A teaspoon of wheat grass contains around 15mg of Calcium, 8mcg Iodine, 3.5mcg Selenium, 870mcg Iron, 62mcg Zinc, and many other minerals.

So the aim of the study was to apply wheat grass for phytoremediation of metals by growing it for a period of two weeks and to utilize the grown wheat grass as a nutritional supplement. The grown wheat grass was tested for its nutritional value. Studies show that wheat grass produces large biomass. So the calorific value was also determined in the study.

The results of wheat grass analysis are given in the **Table 5.5:**

Table 5.5

Results of the analysis of Nutritional value of wheat grass in the three seasons

Sample	Ash (%)	Proteins mg/g	Carbohydrate mg/g	P mg/g	Fe mg/g	Na mg/g	K mg/g	Ca mg/g	Mg mg/g
Pre monsoon:									
1(C)	14.24	389.25	245.65	7.58	5.11	55	78	369.12	1026.36
7	12.89	406.38	305.52	11.65	9.77	75	70	408.36	763.42
Monsoon:									
1(C)	16.38	439.17	200.10	13.16	85.74	114.31	382.70	497.02	2425.45
3	12.07	349.62	303.66	14.13	6.93	64.95	314.75	1498.80	2133.29
4	20.38	455.05	278.20	14.75	1.281	219.26	154.48	498.31	3951.57
6	24.25	277.98	239.58	14.18	31.24	209.46	129.66	997.41	9126.27
7	13.03	391.95	380.42	11.53	40.25	99.40	178.93	497.02	303.181
8	21.2	389.92	304.99	12.45	8.443	218.86	139.47	996.21	3951.57
Post monsoon:									
1(C)	12.63	355.4	186.79	11.25	53.47	30	56	862.54	2149.35
6	19.58	211.35	298.06	16.01	28.41	35	48	1158.61	7694.25

Ash content of the wheat grass ranged from 12.89 – 15.25 %, 13.03 – 24.25 % and 10.54 – 19.58 % during pre monsoon, monsoon and post monsoon respectively. This was found to be completely divergent from the values reported for wheat (6-7)% by Bakker and Elberson (2005). Protein concentrations of the wheat grass varied from 341.12-406.38mg/g, 277.98-455.05mg/g and 211.35-386.12 mg/g and carbohydrates varied from 245.65-305.52 mg/g, 200.10-380.42mg/g and from 186.79-298.06 mg/g during pre monsoon, monsoon and post monsoon respectively. Studies by Hamilton (1989) and Laboratory Analyses (1989) have shown protein concentrations of about 320mg/g in wheat grass which is in agreement with the present study. Carbohydrate concentration was found to be around 2.77 mg/g. The ranges for phosphorus and iron during pre monsoon were 7.28-11.65 mg/g and 5.11-9.77 mg/g respectively. During monsoon, these values ranged from 11.53-17.16 mg/g and 1.28-219.26mg/g respectively. Post monsoon season showed phosphorus and iron concentrations in the range 11.25- 15.85mg/g and 28.41-53.47 mg/g respectively. Iron concentrations in wheat grass was found to be about 34 mg/g in a study conducted by Hamilton (1989) and Laboratory Analyses (1989). Sodium, potassium, calcium and magnesium concentrations showed seasonal variations. Sodium concentration varied from 55-75 mg/g, 65-219 mg/g and 25-35 mg/g during pre monsoon, monsoon and post monsoon respectively. The ranges for Potassium were 62-78 mg/g, 129-382 mg/g and 48-56 mg/g during pre monsoon, monsoon and post monsoon respectively. Calcium ranged from 369-580 mg/g, 497-1498 mg/g and 690-1159 mg/g during pre monsoon, monsoon and post monsoon respectively. Magnesium was found to vary from 763-874 mg/g, 303-3952 mg/g and 1057-7694 mg/g during pre monsoon, monsoon and post monsoon respectively. As per the report by Hamilton (1989) and Laboratory Analyses (1989), Calcium concentrations in wheat grass 277mg/g.

5.2.3.1 Calorific value of wheat grass:

The seasonal variation in the calorific value of wheat grass is depicted in table

Table 5.6: Calorific value of wheat grass

SAMPLE	PRE MONSOON	MONSOON	POST MONSOON
1(Control)	433.35	359.89	332.88
2	-	-	-
3	-	116.51	-
4	-	74.12	-
5	-	-	-
6	-	46.36	50.08
7	35.79	38.12	-
8	-	187.11	-

5.2.3.2 Trace metals in wheat grass:

The concentration levels (mg/kg) of selected toxic trace metals (Cr, Cu and Pb) and were estimated in the grown wheat grass. Cu, Cr and Pb concentrations in the grown wheat grass ranged from 1.10 – 61.45 mg/kg, ND – 124.94 mg/kg and 15.71- 110.81 mg/kg respectively. The trace metals values in both the control and the samples were found to be within the toxicity levels as reported by Awofolu et al. (2007) and Francis (2005). Out of the three metals, zinc recorded the highest concentration but within the normal limit (1-400 mg/kg) and toxicity limit (100-400 mg/kg) as per **Table 5.8**

5.2.3.3 Bioconcentration Factor (BCF)

The Bioconcentration Factor (BCF) of metals was used to determine the quantity of heavy metals that is absorbed by the plant from the soil. This is an index of the ability of the plant to accumulate a particular metal with respect to its concentration in the soil (Ghosh and Singh, 2005a) and is calculated using the formula:

$$\text{BCF} = \frac{\text{Metal concentration in plant tissue (whole plant)}}{\text{Initial concentration of metal in substrate (soil)}}$$

The higher the BCF value the more suitable is the plant for phytoextraction (Blaylock et al., 1997). BCF Values > 2 were regarded as high values.

BCF values of zero indicate limited movement from the soil to the plant. The BCF index **(Table 5.7)** in premonsoon was all less than 2 showing the inability to extract the metals from soil. During monsoon, highest BCF was shown by Cr followed by Cu. The BCF index of the metals during postmonsoon was all less than 2 except for Chromium in station 1. From the above observations, it can be concluded that seasons have a prominent influence on the extraction of metals from the sediments by plants. Growth of wheat grass and extraction of metals both are found to be appreciable during monsoon season where the salinity values are found to be the minimum.

Table 5.7 : Bioconcentration factor for Cu, Cr and Pb

Metal	Stations	BIOCONCENRATION FACTOR (BCF)		
		PRM	MON	PSM
Cu (mg/kg)	1 (Control)	0.5	1.7	0
	2			
	3		**4.0**	
	4		0.3	
	5			
	6		0.1	
	7	0.4	0	
	8		0	
Cr (mg/kg)	1 (Control)	0.2	1.0	**9.1**
	2			
	3		1.9	
	4		1.4	
	5			
	6			1.2
	7	0	1.2	
	8		**12.4**	
Pb (mg/kg)	1 (Control)	0	0.4	0.6
	2			
	3		0.1	
	4		0	
	5			
	6			0.5
	7	ND		
	8		0	

® Higher values are shown in bold

Table 5.8:

Trace metal concentration in the grown wheat grass (Compared with toxicity range in plants and for man)

Metal	Stations	PRM	MON	PSM	Normal* range	Toxicity* range	Toxic doses to plants * (mg/kg)	Toxic doses for Man * (mg/kg)
Cu (mg/kg)	1 (Control)	7.15	8.40	4.99	5 - 20	20-100	-	-
	2	-	-	-				
	3	-	61.45	-				
	4	-	16.84	-				
	5	-	-	5.98				
	6	-	3.13	-				
	7	8.69	1.10	-				
	8	-	3.69	4.60				
Cr (mg/kg)	1 (Control)	6.12	22.71	124.94	-	-	0.5 - 10	200
	2	-	-	-				
	3	-	12.74	-				
	4	-	21.63	-				
	5	-	-	-				
	6	-	ND	24.28				
	7	4.35	15.06	-				
	8	-	194.51	-				
Pb (mg/kg)	1 (Control)	0.26	0.44	ND	5-10	30-300	3-20	1
	2	-	-	-				
	3	-	0.36	-				
	4	-	0.19	-				
	5	-	-	-				
	6	-	ND	0.28				
	7	ND	ND	-				
	8	-	0.16	-				

* Source: Awofolu *et al.*, (2007) and Francis (2005)

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Chapter 6

SUMMARY

The thesis deals with a benchmark study of dissolved and sedimentary sulphur compounds which play prominent roles in the prevailing redox conditions in the selected sites of Cochin estuarine system. Sulphur and its analogues play prominent roles in estuarine biochemical processes. A complete knowledge on the sulphur involvement in these processes is restricted due to the lacking of data on the organic sulphur compounds. Sulphate and sulphide in surface and bottom water and Sulphate, acid volatile sulphide and total sulphur in sediments were studied and correlated to know their interrelations in determining the redox condition of the environment. It also characterises the sediments of the sites on the basis of total organic carbon: total sulphur ratio. The study had attempted to decrease the concentration levels of sulphur in the sedimentary environment by the application of a remedial measure. Knowledge of sulphur uptake by plants from prior literatures has prompted to use phytoremediation for decreasing the sulphur concentration. Phytoremediation is an emerging technology that uses plants to clean up or remediate contaminated soil, sludges, sediments, and ground water through contaminant removal, degradation or containment. The plant selected was wheat grass since earlier studies have shown that wheat grass is effective in remediating pollutants particularly trace metals. So reduction in the concentration of selected trace metals was also focussed.

Cochin estuarine system, one of the largest tropical estuaries of India (256 km2), are facing gross pollution problems following the release of untreated effluents from industries (0.104 x 106 m3d−1) and domestic sectors (0.26 x 103m3d−1). Reclamations over the past several decades have resulted in considerable shrinkage of the Cochin backwaters. The hydraulic barriers constructed to prevent saline incursion into the upstream agricultural fields imposed flow-restrictions and increased sedimentation in the estuary.

The tropical estuarine environment shows multitudinal features which characterize freshwater and seawater mixing, and provide breeding ground for marine organisms Cochin backwaters face serious environmental threats by intertidal land reclamation, pollution discharges, expansion for harbour development, dredging activities and urbanisation. The construction of Thannirmukham bund near

Vaikom also created severe environmental consequences within and out of adjacent Kuttanad agricultural fields. Extensive studies have been carried out in Cochin estuary especially on the physical, chemical and biological aspects as cited above and impacts due to dredging are discussed earlier.

The present study was concentrated in the Cochin estuarine system (CES) involving the riverine zones of Periyar and Muvattupuzha. The physico-chemical characteristics summarized in the above study points to a serious exploitation of the aquatic system. Other than hydrographic changes, humic material brought down by the river sediment plays an important role in the cycling of organic matter in these backwaters. Low DO content is an indication of high organic pollution in the water body. The chief sources of pollution are land run-off, agricultural drainage and urban sewage disposal. Municipal effluents drained into the system create siltation and eutrophication and deteriorates the water quality. The chemo-dynamic estuarine system makes its characteristics complex in nature along with the alarming development like commissioning LNG terminal, container terminal, international transshipment base, a well-known tourists attractive centre etc. Besides, Kochi-the metropolitan city is witnessed tremendous population growth, which envisages proper environmental management plans to minimize the excessive pollution menace and to conserve this pristine ecosystem.

Analysis of Sulphur compounds in the water and sediments of selected sites of Cochin estuary reveals higher amounts of sulphur compounds in the estuarine sites than the riverine sites. Sulphate concentration showed deviation from conservative behavior in certain stations and this could be due to the biogeochemical activities of sulphate in the estuary. The higher sulphate concentrations in stations 5 and 6 might be due to the influx of saline water from the barmouth. Seasonal variation of the concentrations of sulphates and sulphide in the dissolved and sedimentary forms are also depicted. Significant positive correlation of sulphate with finer fractions of sediments shows that fine textured sediments of estuarine stations retain more sulphate than sandy sediments of riverine stations. The variation in the distribution of AVS in sediments is due to the variation in the amount of organic matter. Absence of significant correlation of AVS with sedimentary sulphate reveals that it is formed from the inorganic sulphate reaching the sediments from the overlying saline waters or by the direct conversion of organic S compounds by the action of microorganisms in an oxygen deficient condition. TOC: TS ratio was used as an indicator of the redox condition of the sediments of the sites. The ratio shows that domestic and urban wastes have made the estuarine sediments rich in organic matter and poor in oxygen. But the conditions vary seasonally. It reflect the importance of sulfide reduction in the decomposition of organic matter, and thus give a qualitative indication of the redox status of the environment of deposition Based on the ratio obtained in the present study, the sediments of the sites were characterized into three types. Correlation analysis of the Sulphur compounds with the hydrographical parameters and sediment characteristics were also carried out.

The seasonal variation of proteins, carbohydrates and lipids in the water and sediments were determined and expressed as total organic matter. Total organic carbon and total nitrogen were also determined. The chapter also discloses a correlation study of bio geoorganics with the Sulphur compounds. Total Sulphur is found to be in high positive correlation with TOC in pre monsoon, with clay in monsoon and in good correlation with proteins in post monsoon and with Total nitrogen and Silt in both pre monsoon and monsoon. There is no significant correlation of AVS with sedimentary sulphate or other Sulphur compounds. This shows that AVS was not formed by the reduction of sulphate in sediments. It can be formed from the inorganic sulphate reaching the sediments from the overlying saline waters or by the direct conversion of organic S compounds by the action of microorganisms in an oxygen deficient condition. Total Sulphur is in high positive correlation with TOC in pre monsoon, with clay in monsoon and in good correlation with proteins in post monsoon and with Total nitrogen and Silt in both pre monsoon and monsoon.

Three factor ANOVA was carried out for Proteins, Total Carbohydrates and Total Lipids expressing the variations in the parameters with spatial factor, station and season. The results show that protein, total carbohydrates and total lipid concentrations show significant variations ($p<0.05$) with station and spatial factor but no significant variations ($p>0.05$) with season.

Phytoremediation was carried out in the sediments of estuarine and riverine sites by growing wheat grass for a period of two weeks. Seasonal variations were observed in the growth of wheat grass. During monsoon, when the salinity was comparatively low, wheat grass grew in almost all the sediments. But during pre monsoon and post monsoon, growth of wheat grass was found only in the sediments of riverine stations. From this, it can be concluded that salinity has a profound influence on growth of wheat grass.

The concentration of TS, TN and TOC in sediments were noted before and after remediation and found that wheat grass has the potential for decreasing the amount of pollutants in the sediments. But there was seasonal variation. Analysis of sodium, potassium and selected trace metals in the sediments were done and observed that monsoon season which had maximum plant growth recorded maximum decrease in metal concentration. This is attributed to the influence of salinity on plant growth. The period of plant growth can also influence the percentage reduction in metal concentration. Wheat grass was grown for two weeks in the present study. This was intended to use the grown wheat grass for making wheat grass juice which is considered to be a nutritional supplement.

The use of wheat grass as a nutritional supplement requires the analysis of its nutritional value. The results show that the growth of wheat grass has decreased the concentration of Cr, Cu and Pb in the sediments. There was seasonal variation in the percentage decrease of the metals which further depends upon the sedimentary characteristics and status of metal pollution. The period of growth of wheat grass have a profound influence in the percentage decrease of metal concentration. Further advance field studies are required to get a complete picture of phytoremediative potential of wheat grass. Analysis of metal concentrations in the wheat grass shows that all the three metal concentrations are below the toxicity limits. This shows the possibility of using whaet grass as a nutritional supplement.

Phytoremediation can be made further useful by selecting plants which suits our climatic conditions and are of nutritional value. Amaranthus, commonly used leafy vegetable in Kerala was found to have high fibre content and nutrients. Amaranthus (Marog) is a popular nutritious leafy vegetable crop, rich in proteins, vitamins and minerals and is consumed virtually in the whole continent of Africa, Asia and South America. Their quick growth and great biomass makes them some of the highest yielding leafy crops which would be beneficial as a primary food source, thus preventing starvation and malnutrition in the third world countries. Their high yield, ability to grow in hot weather conditions, high nutritive value and their pleasant taste and the fact that they grow all year; makes the Amaranth a popular vegetable. Phytoremediation can be trialed with this plant and edible parts have to be tested for its toxicity. Marigold, an ornamental plant, is of great value in Kerala during the Onam festival season for making floral carpet. The plant is found to suit our environment as it is growing well in our premises. Potential of marigold plant to take up metals from the soils can be tested by growing it in metal contaminated sites of our city. Advanced research is required for the better understanding and application of Phytoremediation for environment management.

APPENDIX

Appendix I (Hydrographical Parameters)

		SURFACE mg/l				BOTTOM mg/l		
	SAMPLES	**PREMON**	**MONSOON**	**POSTMON**	**SAMPLES**	**PREMON**	**MONSOON**	**POSTMON**
pH	1S	6.72	6.33	6.37	1B	6.67	6.31	6.2
	2S	7.02	6.39	5.77	2B	NA	NA	NA
	3S	6.7	6.93	6.02	3B	6.93	6.77	6.03
	4S	7.49	7.62	6.61	4B	NA	NA	NA
	5S	7.51	7.8	7.04	5B	7.52	7.84	7.07
	6S	7.42	7.92	6.99	6B	7.42	7.94	7.07
	7S	8.41	7.25	6.44	7B	NA	NA	NA
	8S	6.82	7.05	6.33	8B	6.65	6.79	6.52
Temperature	1S	30	29	30	1B	28	28	28
	2S	30	28	29	2B	NA	NA	NA
	3S	31	30	31	3B	30	29.5	30
	4S	30	30	30	4B	NA	NA	NA
	5S	31	30	31	5B	31	29	30.5
	6S	31	29	31	6B	30.5	28	30.5
	7S	31	30	30	7B	NA	NA	NA
	8S	31.5	29	31.5	8B	31	28	31
EC	1S	28	43	4	1B	183	43	4
	2S	48	70	1212	2B	NA	NA	NA
	3S	8430	849	4035	3B	8385	884	3025
	4S	18440	7002	3510	4B	NA	NA	NA
	5S	16655	18501	3700	5B	16580	22502	3500
	6S	151275	18550	4100	6B	17300	24500	4300
	7S	171	115	5465	7B	NA	NA	NA
	8S	818	110	7170	8B	3425	168	2080

	SAMPLES	PREMON	MONSOON	POSTMON	SAMPLES	PREMON	MONSOON	POSTMON
TDS	1S	13.44	20.4	1.92	1B	87.84	20.64	1.92
	2S	23.04	33.6	581.76	2B	NA	NA	NA
	3S	4046.4	407.52	1936.8	3B	4024.8	424.08	1452
	4S	8851.2	3360.68	1684.8	4B	NA	NA	NA
	5S	7994.4	8880.65	1776	5B	7958.4	10801.32	1680
	6S	72612	8904.1	1968	6B	8304	11760.09	2064
	7S	82.08	55.2	2623.2	7B	NA	NA	NA
	8S	392.64	52.8	3441.6	8B	1644	80.4	998.4
	SAMPLES	**PREMON**	**MONSOON**	**POSTMON**	**SAMPLES**	**PREMON**	**MONSOON**	**POSTMON**
DO (mL/L)	1S	5.77	1.96	4.37	1B	4.27	2	5.49
	2S	4.33	2.08	3.87	2B			
	3S	2.99	3.99	4.99	3B	2.35	0.9	2.8
	4S	3.21	1.5	4.44	4B			
	5S	4.7	1.85	5.1	5B	2.99	1.55	4.73
	6S	1.92	1.5	2.9	6B	2.14	1.35	3.86
	7S	3.36	2.89	3.56	7B			
	8S	2.99	1.3	3.64	8B	1.28	1.25	3
	SAMPLES	**PREMON**	**MONSOON**	**POSTMON**	**SAMPLES**	**PREMON**	**MONSOON**	**POSTMON**
SALINITY (psu)	1S	0.06	0.04	0.062	1B	0.17	0.03	0.068
	2S	2.16	1.97	2.34	2B			
	3S	8	0.5	1.19	3B	7.83	0.5	1.84
	4S	20.9	12.43	34.36	4B			
	5S	15.67	11.79	31.67	5B	16.55	14.19	33.62
	6S	17.89	11.61	27.47	6B	18.55	16	21.92
	7S	0.34	0.16	0.48	7B			
	8S	0.08	0.05	0.09	8B	2.75	0.07	1.16

	SURFACE				BOTTOM				SEDIMENT			
	SAMPLE	PRM	MON	PSM	SAMPLE	PRM	MON	PSM	SAMPLE	PRM	MON	PSM
PHOSPATE (mg/L)	1S	0.041	0.072	0.062	1B	0.086	0.039	0.049	1 (mg/kg)	0.171	0.16	0.079
	2S	0.029	0.582	0.003	2B	0	0		2	0	0.021	0.111
	3S	2.132	1.528	3.7	3B	2.005	1.147	4.412	3	0.677	0.697	0.38
	4S	0.364	0.214	0.123	4B	0	0		4	0.639	0.781	0.35
	5S	0.346	0.283	0.066	5B	0.358	0.194	0.016	5	0.633	1.168	0.238
	6S	0.356	0.263	0.021	6B	0.364	0.23	0.222	6	0.574	1.164	0.483
	7S	0.136	0.393	1.127	7B	0	0		7	0.321	0.82	0.424
	8S	0.118	0.346	1.283	8B	0.227	0.424	1.139	8	0.543	0.96	0.515
	SAMPLE	PRM	MON	PSM	SAMPLE	PRM	MON	PSM	SAMPLE	PRM	MON	PSM
NITRITE (mg/L)	1S	0.083	0.253	0.022	1B	0.06	0.243	0.026	1 (mg/kg)	0.53	0.48	0.67
	2S	0.436	0.028	0.014	2B				2	0	0.05	0.22
	3S	0.319	0.021	0.036	3B	0.301	0.028	0.02	3	0.44	0.08	0.48
	4S	0.091	0.028	0.002	4B				4	0.36	0.2	0.33
	5S	0.098	0.204	0.016	5B	0.12	0.047	0.005	5	0.24	0.04	0.2
	6S	0.116	0.057	0.009	6B	0.053	0.029	0.014	6	0.34	0.16	0.25
	7S	0.015	0.014	0.019	7B				7	0.51	0.12	0.18
	8S	0.11	0.103	0.043	8B	0.016	0.001	0.042	8	0.46	0.12	0.41

Appendix II (Sulphur Compounds)

	SURFACE				BOTTOM				SEDIMENT			
	SAMPLES	PREMON	MONSOON	POSTMON	SAMPLES	PREMON	MONSOON	POSTMON	SAMPLES	PREMON	MONSOON	POSTMON
SULPHIDE (mg/L)	1S	0.068	0.064	0.346	1B	0.166	0.11	0.421	1 (mg/g)	0.073	0.265	0.177
	2S	0.036	0.388	0.388	2B	0.166	0.317	0.352	2	0.065	0.214	0.23
	3S	0.163	0.134	0.442	3B	0.193	0.221	0.38	3	0.097	0.199	0.265
	4S	0.131	0.178	0.443	4B	0.166	0.117	0.393	4	0.003	0.271	0.566
	5S	0.163	0.019	0.223	5B	0.221	0.097	0.338	5	0.061	0.277	0.577
	6S	0.036	0.227	0.222	6B	0.11	0.097	0.325	6	0.052	0.228	0.282
	7S	0.534	0.497	0.319	7B	0.221	0.317	0.366	7	0.055	0.215	0.222
	8S	0.249	0.186	0.36	8B	0.11	0.11	0.421	8	0.03	0.249	0.267
	SAMPLES	PRM	MON	PSM	SAMPLE	PRM	MON	PSM	SAMPLE	PRM	MON	PSM
SULPHATE (mmols/l)	1S	0	0.42	3.1	1B	0.04	0.01	0.05	1 (mg/g)	0.83	0.57	1.45
	2S	2.65	0.43	2.45	2B				2	3.47	3.19	4.01
	3S	74.05	6.56	47.33	3B	0.98	0.22	1.42	3	9.99	15.8	4.85
	4S	44.38	26.59	61.97	4B				4	5.61	13.6	20.98
	5S	109.5	32.77	79.66	5B	3.35	0.99	2.43	5	10.88	31.85	4.18
	6S	107	15.28	98.16	6B	1.39	0.75	2.13	6	1.86	19.42	14.59
	7S	14.27	1.65	7.58	7B				7	5.82	5.68	4.09
	8S	18.21	1.28	16.93	8B	2.02	0.09	1.34	8	6.32	7.38	19.72

Appendix III (Sediment Parameters)

	TS (mg/g)			TN (%)			TP (%)			TOC (%)		
SAMPLES	PREMON	MONSOON	POSTMON	PREMON	MONSOON	POSTMON	PREMON	MONSOON	POSTMON	PREMON	MONSOON	POSTMON
1	1.98	0.88	1.99	0.068	0.0254	0.05	1.68	2.84	11.18	0.16	0.73	0.36
2	5.1	4.03	6.02	0.204	0.156	0.287	1.75	2.06	4.05	0.15	0.54	0.45
3	32.37	46.82	28.19	0.406	0.234	0.308	1.92	2.52	8.59	2.91	0.46	1.54
4	29.09	35.97	36.69	0.376	0.224	0.334	1.64	2.14	21.79	1.87	1.8	3.43
5	42.09	47.37	40.66	0.389	0.306	0.259	2.42	5.61	30.38	NA	1.76	0.42
6	39.81	43.05	39.46	0.615	0.428	0.563	1.16	4.26	7.99	2.61	0.61	3.45
7	8.13	12.08	16.75	0.254	0.198	0.307	2.51	1.54	5.04	0.28	0.54	0.098
8	30.31	31.91	37.79	0.863	0.412	0.0559	2.22	5.08	13.99	1.54	0.09	1.16

TEXTURE ANALYSIS									
	PREMON			MONSOON			POSTMON		
Stations	Sand (%)	Silt (%)	Clay (%)	Sand (%)	Silt (%)	Clay (%)	Sand (%)	Silt (%)	Clay (%)
1	93.7	2.31	3.99	97.75	0.39	2.16	97.03	0.8	2.17
2	87.55	3.89	8.56	92.56	1.89	5.55	89.45	2.78	7.77
3	69.22	8.24	22.54	71.23	7.56	21.21	87.55	3.89	8.56
4	20.52	5.66	73.82	42.29	38.72	18.99	22.54	5.01	72.45
5	20.52	73.82	5.66	34.63	43.39	21.98	35.93	42.52	21.55
6	5.45	78.54	16.01	19.1	53.59	27.31	94.35	0.08	5.57
7	89.25	5.75	5	84.85	8.76	6.39	53.02	23.04	23.94
8	85.91	6.77	7.32	15.58	57.39	27.03	38.12	36.38	25.5

Appendix IV (Biogeoorganics)

		SURFACE mg/l				BOTTOM mg/l		
	SAMPLES	PREMON	MONSOON	POSTMON	SAMPLES	PREMON	MONSOON	POSTMON
Proteins	1S	3.55	2.56	5.09	1B	7.32	1.45	2.44
	2S	7.76	4.45	8.76	2B	NA	NA	NA
	3S	4.88	10.78	1.21	3B	3.55	8.12	2.21
	4S	1.11	3.85	2.21	4B	NA	NA	NA
	5S	5.99	5.36	1.89	5B	4.44	12.66	4.21
	6S	4.44	4.96	0.99	6B	3.11	3.19	2.11
	7S	6.65	2.44	7.65	7B	NA	NA	NA
	8S	9.54	3.82	2.77	8B	5.99	5.7	3.8
Total Carbohydrates	1S	2.91	1.76	5.07	1B	3.32	2.12	6.39
	2S	4.59	4.3	NA	2B	NA	NA	NA
	3S	13.09	5.09	9.23	3B	12.55	2.14	16.33
	4S	7.64	7.92	15	4B	NA	NA	NA
	5S	3.64	8.91	8.89	5B	2.55	7.04	8.56
	6S	6.55	11.95	7.43	6B	7.64	7.88	12.16
	7S	2.96	4.41	0.45	7B	NA	NA	NA
	8S	3.73	32.53	7.91	8B	4.32	20.64	15.65
Total Lipids	1S	BDL	0.156	3.17	1B	BDL	0.546	2.67
	2S	0.198	0.24	3.56	2B	NA	NA	NA
	3S	1.58	2.31	2.67	3B	1.98	2.56	25.54
	4S	2.37	2.56	4.65	4B	NA	NA	NA
	5S	1.39	1.84	9.3	5B	3.96	1.55	4.15
	6S	3.56	4.25	5.64	6B	2.97	3.98	2.87
	7S	4.25	3.98	1.76	7B	NA	NA	NA
	8S	5.54	6.23	5.06	8B	3.56	5.84	3.28

	PROTEINS	mg/kg		CARBOHYDRATES	mg/kg		LIPIDS	mg/kg	
SAMPLES JUNE '06	PREMON	MONSOON	POSTMON	PREMON	MONSOON	POSTMON	PREMON	MONSOON	POSTMON
1	60	536	70	381	201	406	2047	1169	551
2	NA	1335	456	NA	662	354	NA	401	807
3	1285	797	387	2019	532	469	3661	1978	984
4	323	803	1179	577	617	648	925	1977	1007
5	267	873	543	NA	590	433	NA	3911	905
6	501	928	1291	558	541	499	1043	6300	1012
7	752	871	1223	602	519	364	767	1694	NA
8	1175	2452	1667	985	3368	1755	767	11263	6889

Appendix V (Reduction in Sediment parameters as a result of phytoremediation)

PREMONSOON								
Sample	Sulphate (mg/g)		TOC (%)		TN (%)		TS (mg/g)	
	B.R.	A.R.	B.R.	A.R.	B.R.	A.R.	B.R.	A.R.
1(Control)	0.83	0.12	0.16	0.09	0.068	0.011	1.98	0.83
2	3.47	-	0.15	-	0.204	-		
3	9.99	-	2.91	-	0.406	-	32.37	
4	5.61	-	1.87	-	0.376	-	29.09	
5	10.88	-	NA	-	0.389	-	42.09	
6	1.86	-	2.61	-	0.615	-	39.81	
7	5.82	5.5	0.28	0.098	0.254	0.119	8.13	3.98
8	6.32	-	1.54	-	0.863	-	30.31	
Sample	Sulphate (mg/g)		TOC (%)		TN (%)		TS (mg/g)	
	B.R.	A.R.	B.R.	A.R.	B.R.	A.R.	B.R.	A.R.
1(Control)	4.65	0.57	0.54	0.22	0.156	0.013	0.88	0.34
2	3.19		0.46	-	0.234			
3	15.8	9.86	1.8	0.587	0.224	0.206	46.82	31.54
4	13.6	5.44	1.76	1.436	0.306	0.224	35.97	29.21
5	31.85		0.61	-	0.428		47.37	
6	19.42	4.99	0.54	0.34	0.198	0.171	43.05	36.54
7	5.68		0.09	0.03	0.412	0.205	12.08	5.64
8	7.38	3.65	5.453	2.216	0.489	0.452	31.91	25.3

POST MONSOON

Sample	Sulphate (mg/g)		TOC (%)		TN (%)		TS (mg/g)	
	B.R.	A.R.	B.R.	A.R.	B.R.	A.R.	B.R.	A.R.
1(Control)	1.45	0.65	0.36	0.18	0.05	0.01	1.99	1.05
2	4.01	-	0.45	-	0.287	-		
3	4.85	-	1.54	-	0.308	-	28.19	
4	20.98	-	3.43	-	0.334	-	36.69	
5	4.18	-	0.42	-	0.259	-	40.66	
6	14.59	4.99	3.45	1.98	0.563	0.305	39.46	25.36
7	4.09	-	0.098	-	0.307	-	16.75	
8	19.72	-	1.16	-	0.056	-	37.79	

LIST OF ABBREVATIONS

A.R - After Remediation

AVS - Acid Volatile Sulphide

B - Bottom

B.R – Before Remediation

CARB - Carbohydrate

CES - Cochin Estuarine System

DMS - Dimethyl Sulphide

DO - Dissolved Oxygen

EC - Electrical Conductivity

MON - Monsoon

NA - Not analysed

ND - Not detected

PRM - Premonsoon

PRT - Pretain

PSM - Post Monsoon

S - Surface

TEMP - Temperature

TN - Total Nitrogen

TOC - Total Organic Carbon

TP - Total Phosphrus

TS - Total Sulphur

LIST OF PUBLICATIONS

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2. Sujatha C.H, Nify Benny, Ranjitha Raveendran, Fanimol C.L and Samantha N.K, "Nutrient Dynamics in the two Imperative lakes of Kerala, India, accepted in *Indian Journal of Marine Sciences.*
3. Sujatha C.H & Nify Benny. "Impact of December 2004 Tsunami on Indian coasts and Mitigation measures". Book chapter accepted for publication in the book "Natural and Anthropogenic Disasters-Vulnerability, preparedness and mitigation edited by Madan Kumar Jha.
4. Nify Benny and Sujatha C.H. Remedial Measures on Pollutants in the Ecosystems. Expecting acceptance in *Resonance.*

Paper Presented

1. "Nutrient Dynamics in the two Imperative Lakes of Kerala India"- Paper presented at the International workshop on Sustainability of Lake Remediation and Interventions (JICA-HUDA) held at Hyderabad.
2. "Application of a Remedial Measures to Metal Contaminated Sediments of Cochin Estury"-Paper presented at school cum workshop on trace Element specification (SEIS'08) held at Saha Institute of Nuclear Physics, Kolkata.