# BIOGEOORGANICS IN THE SEDIMENTARY ENVIRONMENTS OF COCHIN ESTUARY

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# CERTIFICATE

This is to certify that this thesis is a bonafide record of research carried out by Sri.Vasudevan Nayar, T. under my guidance, in partial fulfilment of the requirements for the degree of **Philosophiae Doctor** of the Cochin University of Science and Technology.

Cochin-682 016,
July 1992.

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The corrections suggested by the examiners have been incorporated.

Certified that the corrections suggested by the examiners are incorporated wherever necessary.

# PREFACE

In the present global circumstances, no individual or country can remain immune to the environmental impact of economic development or to the man made consequence of a lack of it. As a sequel to the interaction between population growth, technological advancement and scientific discovery, the world of the historical past cannot persist into the changing conditions of the future. The overall conditions of earths environment have, therefore deteriorated and global risks have become more acute. This beckons the necessity for a change in perspective from the concept of growth at all costs to the idea of a sustainable development.

An assessment of the prevailing condition of the environment is essential for effective management and execution of programmes for a sustainable development of the ecosystem. The hydrosphere, no doubt, tops the list which requires immediate attention. The role of biogeoorganics of the hydrosphere in the evolution of the biosphere has been universally recognized. An insight into the processes governing the biogeoorganics can be gleaned from the distribution pattern and existing forms of organic matter, which, in turn are important factors controlling the microbiological activity, the trophic value of organic matter as well as degradation, redistribution and migration of organic and mineral component in the course of diagenesis.

The present work is a modest attempt at assessing the distribution and variation of biogeoorganics in the sedimentary environments around the industrial metropolis of Greater Cochin.

The work embodied in the thesis is under publication /under preparation as indicated below.

1.Geochemistry of C.N.P. in the surficial sediments of Cochin estuary. Vasudevan Nair, T. and Chandramohanakumar, N., *Indian J. Mar.Sci.*

2.Distribution of chlorophyll and pheopigments in the sedimentary environment of a tropical estuary. Vasudevan Nair, T. and Chandramohanakumar, N., *Chem. Geol.*

3. Biogeochemical studies of the pigments in the surficial sediments of Cochin estuary. Vasudevan Nair, T. and Chandramohanakumar, N., *Hydrobiologia.*

4. Flux and seasonality of biochemical compounds in the sedimentary environment of Cochin estuary. Vasudevan Nair, T. and Chandramohanakumar, N., *Estuar. Coast. Shelf. Sci.*

5. Distribution profile of humic substances and hydroxylated aromatic compounds in the surficial sediments of Cochin estuary. (Under preparation)

6. An overview of the biogeoorganics in the Cochin estuarine system. (Under preparation)

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CHAPTER 1

# INTRODUCTION

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## 1.1 Biogeoorganics

A remarkable feature of the current scientific activities is the mounting interest on investigations about the hydrosphere and the recognition of the importance of reclamation and rational use of its nutritive, mineral and power resources. The hydrosphere represents a colossal system of dynamic equilibrium between the saline solution, the liquid and solid inputs from land, the atmosphere, the aquatic organisms, dissolved and suspended matter and bottom sediments. Because of the exceptional complexity and the multifaceted nature, the study on hydrosphere essentially requires a fusion of different disciplines of science like chemistry, physics geology, biology and geography. One such integrational science is biogeochemistry which encompasses those area of biology, geology and chemistry that contribute to the investigations of the various functions of the biosphere, particularly the hydrosphere. Organisms and organic matter assume the principal role in the biogeochemical processes occurring in the hydrosphere. Biogeochemistry is essentially aimed at assessing the transformations, cycling and fate of the various forms of organic matter in the hydrosphere. It is therefore essential tool in alleviating the pressing problems that haunt the human race, *viz.*, depleting oil and gas reserves, alarming proportions of industrial pollution, irrational utilization of biological and mineral resources, etc.

Biogeoorganics is a term coined to represent the entire array of organic compounds in the aquatic realm, which includes compounds with known structures (such as lipids, sugars, hydrocarbons, etc.), humic acid and other hydrophobic acids of biological origin as well as compounds which have been subjected to geochemical processes like sorption/partition, precipitation, volatilization, oxidation/reduction etc.. The study of biogeoorganics include investigations on the source of organic substances, the pathways along which they enter the aquatic environment, the pattern of accumulation in the biotic and abiotic components of the ecosystems, the mechanisms and rates of migration of bioorganics and pollutants and their transformations and other processes which determine the fate of toxicants in the environment. The principles and methods developed for biogeochemistry involving the study of the behaviour, transformations and cycles of chemical elements in relation to dynamics and functions of living matter are particularly important. However, biogeochemical evaluation is also useful for the understanding of the behaviour of the other substances in the sea/estuaries, such as protein, sugars, lipids, toxic organochlorine compounds and surfactants and of the accumulation of micro-impurities in living matter, the migration of nutrients, production cycles and diagenesis of these organics in the aquatic environment.

The growth of population and the rapid advances in technological development have had significant detrimental effects on the natural environment. Anthropogenic inputs of industrial, municipal and agricultural nature containing enormous quantities of organic and inorganic toxic substances--- both dissolved and suspended--- into the water bodies cause serious water and sediment pollution problems. These substances have deleterious effects on the flora and fauna; photosynthesis, primary production and high trophic levels may be adversely affected. The pollutants may be lethal to one or more of the various estuarine communities. Toxic elements may get accumulated in the plant and animal tissues and through successive integration along the food web, they may finally reach man. To effectively combat such serious pollution problems, we require to ascertain the chemical species (both inorganic and organic) and their respective concentrations in the effluent and the receiving waters/ sediment and their interactions and transformations.

Estuaries are recognized as areas of commercial, industrial and recreational activities and play a pivotal role in the natural life cycle of aquatic organisms. Though, a few estuaries have been able to assimilate the waste loads depending on factors like mixing, flushing and nature of the waste, many of the more remote and unspoiled estuaries of the world are in danger due to the man's ruthless exploitation.

Estuaries are the transition zone between rivers and oceans. Rivers link the major carbon reservoirs of the continents and the oceans and thus play an important role in the global carbon cycles (Likens *et al.,* 1981). In recent years there has been a rapidly growing interest in research on aquatic environments/ estuaries and their organic contents in an effort to probe into the nature and cause of pollution and the pathways and means to control it. To study the past history of the lake, it is highly essential to study the sediment of the estuaries, as the sediment acts as a sink and a source of materials. Sediments adsorb organic and bioorganics and also release compounds to the overlying water column as the system needs. Quantitative studies of biogeoorganics from various estuaries have been reported. The studies on chemical characteristics of the sediments of estuaries are useful in assessing the water quality and management of ecosystems. Organic constituents of Visakhapatnam harbour and biochemical compounds from Bay of Bengal have been reported by Sarma and Rao (1988) and Bhosle *et al.*, (1979) respectively. Accumulation and transformations of organics have been reported by (Bordovskiy, 1965). Thus the study on biogeoorganics in the sedimentary environment will provide a deeper insight into the complexities that govern the organic load, source, fate and transformations of organics in the estuaries.

**Estuarine processes of Organics**

Estuaries are an important stage in the transport of the weathering products, besides being the meeting point of fresh water and sea water. Weathering products are brought by a variety of mechanisms which include river, wind and ice transport. Goldberg (1971) has estimated that $1.8x10^{16}$ $g\text{-}Yr^{-1}$ of suspended solids from river discharge are transported through estuaries to the oceans, while the contribution of solids by atmospheric transport directly into the oceans is between $1\text{-}5x10^{14} g\text{-}yr^{-1}$. Since the rivers are responsible for transporting solids to the oceans, estuaries assume an important role in the global sedimentary cycle.

Estuaries represent a transient zone since they are constantly being altered by the deposition and erosion of sediments and suffer extreme modification during small changes in the mean sea level. Estuaries are very complex environments in terms of sedimentation since the sediment themselves can originate from a number of areas which include both upstream and marine sources . Although, there are various intermediate sources such as river mouth and lower estuarine slopes, these two extreme sources impose severe limitations on the geochemical interpretation of estuarine sedimentary processes. Sedimentary processes are important in the evaluation of the effects of pollution on estuarine sediments, which are increasingly important as many of the world's major rivers are centers of industrial and urban development. Because of this, rivers are used as dumping grounds for waste products, often with the initial assumption that the dumped material will be carried out to the sea.

The flocculation of clay mineral particles have been studied by Whitehouse *et al.* (1960) and Postma (1967) who suggested that, in general, river water contained unflocculated clay particles, and that since flocculation occurred in saline waters due to an increase in the total ionic concentration, the flocculated particles settled out with bottom sediment.

The circulation and stratification of the estuarine waters tend to make the transport of the suspended and bed load material, complex. Estuarine environments are not simply areas in which there are direct transport of material between the continents and the oceans. The initial transfer takes place in estuaries and it is here that the first reaction occur between fresh water and sea water and their associated solids.

The production and destruction of organic matter in any ecosystem are primarily biologically mediated processes. Biological processes are probably more important in magnitude than purely chemical processes in the aerobic organic carbon cycle in aquatic environments. The processes of primary production, respiration and mineralization cause significant changes to the oxygen and carbon dioxide concentrations of the aquatic environments and are capable of altering the Eh and pH of the system and thereby, the speciation of many chemical constituents. Biological processes are particularly important in estuaries because the natural input of inorganic and organic matter is large and it usually results in high turnover rates.

The processes occurring within the estuary are dependent on flocculations in magnitude of marine limnetic and terrestrial influences (Burton and Liss, 1976).

Estuarine organic matter consists of an autochthonous contribution resulting from primary production within the estuary and an allochthonous content emanating from adjacent ecosystems. In estuaries the amount of organic matter, living and dead, is usually greater than in the open sea. The decomposition of organic matter in estuaries can lead to anoxic condition if the water exchange is poor or if large amounts of organic pollutants are introduced.

Since sediment is a substrate for biological and chemical reaction, it plays a pivotal role in biochemical and geochemical processes. The sediment serves as a surface for adsorption processes and a surface for bacterial activity. Sediments are considered as a major sink and a source of chemical components to the overlying water column.

Estuarine sediment acts as a short or long term reservoir for many hydrophobic organic compounds (Lee *et al*., 1979, Hit es *et al*., 1980; Prahl and Carpenter, 1984). Sorption reactions of sediment particles control the rates and mechanism of transport of organic compound into and out of sediment and also affect the bioavailability of these compounds. Diffusion, advection and mixing and resuspension of the sediment will also affect the distribution of hydrophobic organic compounds in the sediment and pore water. The relative importance of each of these processes depend on the molecular structure, biological activity and physico-chemical properties of the individual organic compounds as well as the properties of environment. Organisms in the sediment exist in a continuum.

The organic matter in the sediment is a complex mixture of dead and living material which originate from both water column transport of particulate organic carbon and insitu syntheses. Organic matter thus include both labile compounds such as aminoacids and sugars as well as more `refractory' compounds such as humic acid, lipids etc.

## The Cochin estuarine environment

Cochin estuary is subjected to increasing human interferences like any other estuary located in the vicinity of metropolis cities and industrial conglomerates (Gopalan *et al.*, 1983; Balchand, 1984; Joy *et al.*, 1990). Nearly 70% of the chemical industries of the Kerala State is situated on the banks of the river Periyar and the effluents from these industries (fertilizer, pesticides, fungicides, metallurgical, rare-earth, catalysts, food industries, oil mills etc.) form an important source of pollutants to the estuary. The point source of pollutants identified on the Muvattupuzha river is a newsprint factory. In addition to this, the estuary receives organic wastes also, from domestic sewage, coconut-husk retting yards, fish- processing units etc. These discharges have caused irrepairable damage to the flora and fauna of this water body and sediment and the productivity of the region has been seriously affected (Jayapalan *et al.*, 1976; Unnithan *et al.*, 1977; Saraladevi *et al.*, 1991; Remani *et al.*, 1983, Ouseph,

1990) Several workers have studied the physico- chemical parameters and nutrient status of the Cochin estuary (Sankaranarayanan and Qasim ,1969; Manikoth and Salih 1974; Sankaranarayanan and Panampunnayil, 1979; Sankaranarayanan *et al.*, 1984; Lakshmanan *et al.*, 1987; Anirudhan, 1988; Anirudhan and Nambisan, 1990; Saraladevi *et al.*, 1991;) and the hydroxylated aromatic compounds and protein in water and sediment of Cochin estuary (Nair *et al.*, 1989; Balchand *et al.*, 1990). Most of these studies related to the aqueous phase and were confined to the northern arm of the estuary. Other studies on the Cochin estuary include those on the bioavailability of trace metals (Babukutty, 1991); on trace metal speciation in water (Shibu, 1992); chemical partitioning of trace metal in sediment (Nair, 1992). These studies have indicated that seasonal hydrographic changes, play a major role in regulating the metal levels as well as that of the organics in the sediments.

## Scope of the present study

The distribution of biogeoorganics in the Cochin estuary is influenced by the increasing human activities, waste discharge from major industrial establishments into the Periyar and Muvattupuzha rivers, river runoff and by the sewage through a network of large and small canals. The detrimental effect of pollutants not only affect the water quality but also the quality of the sediment. Lake-sediment often constitutes a rich substrate to different types of organisms: photosynthetic plants, herbivorous and carnivores animals etc. In certain aspects, lake-sediments are a much more suitable environment for biological life than the lake water.

Since lake-sediment is formed mainly from material supplied from the terrestrial surroundings of the lake and from material synthesized in the lake water, the chemical structure of a given lake-sediment is a function of the characteristic of the catchment area and the lake-water.

Although studies on hydrographical, trace metal speciation and geochemical aspects of the Cochin estuary have received considerable attention during recent years no attempts have so far been made to study the biogeoorganics in the sediments of the Cochin estuary. Hence the present study, which is the first of its kind in this region, is an attempt to fill up this lacuna so as to generate adequate information on the relative abundances, the seasonal and spatial variations as well as on the source and fate of these compounds found associated with the sedimentary environment of the Cochin estuary. Since sediment management has received much attention, this study is expected to go a long way in evolving new sediment-standards for keeping the environment free from contamination. Sediment-quality standards can be used to control sediment contamination from ongoing permitted sources.

Chemical analysis of the sediment gives a lot of useful information concerning the lakes as well as its surroundings. Chemical analysis of sediment cores can offer a valuable key to the events in the history of the lakes.

Transport of substances across the sediment - water interface occurs both upwards and downwards and not only reflect the quality of lake-water but also the composition and processes of the super-imposed water body.

The work incorporated in this thesis deals with the assessment of salinity, dissolved oxygen, and $P^H$ of the surface and bottom waters besides analysis of the sediment for its textural characteristics, geochemical nature of carbon, total nitrogen, total phosphorus, sedimentary pigments (chlorophyll a,b,c, carotenoids, pheopigments), protein, lipid, carbohydrates, humic acid and hydroxylated aromatic compounds (tannin and lignin). Monthly collections were made from 11 Stations over a period of one year (April 1990 - March 1991). The above results were analysed seasonally to find out their spatial and temporal distributions. The study is presented in six chapters.

Chapter I gives a general overview of the subject. The influence of sediment on the estuarine chemical processes has been described and the scope of the study has been outlined.

Chapter 2 describes the location of the study area and the sampling site in terms of its hydrographical features. The sampling procedures for water and sediment and the analytical techniques adopted for the determination of various parameters are dealt with in detail. Further, the general hydrography is also included in the Chapter.

Chapter 3 deals with the distribution profile of the nutrient elements, carbon, nitrogen and phosphorus, and their seasonal interrelationships.

Chapter 4 deals with the spatial and temporal distribution of biogeoorganics such as the sedimentary pigments (Chlorophyll a, b, c), carotenoids and pheopigment, (degradation product of chlorophyll a), carbohydrate, lipids, and protein as well as their interrelationship with other parameters.

Chapter 5 reports on the concentration levels of humic acids and hydroxylated aromatic compounds in the sediment and correlations between these compounds. The distribution profile is discussed in terms of textural characteristics also.

The salient features of the studies conducted are summarized in Chapter 6. The list of references is included at the end. The monthly values of various parameters, in view of their exhaustive nature are removed from the text and given in Tables, which are appended at the end, while the corresponding figures depicting the seasonal variations and the derived parameters are incorporated in the text itself.

## CHAPTER 2

# MATERIALS AND METHODS

2.1 Description of location

2.2 Analytical techniques

    2.2.1 Sampling procedure
    2.2.2 Analytical methods

2.3 General hydrography

    2.3.1 Salinity
    2.3.2 Dissolved oxygen
    2.3.3 pH

A brief description of the Cochin estuarine system and an out line of the methods employed are given in this chapter. The Chapter is concluded with general hydrography of the study area.

## 2.1 Description of location

The Cochin estuary includes a system of interconnected lagoons, bays and swamps penetrating the main land and enclosing many islands in between, whose total area amounts to approximately 500 square km. The backwater around Cochin is located between Lat. 9°40' - 10° 12' N and Long. 76°10' - 76° 30' E. The estuary is connected with the Arabian (Lakshadweep) sea by a permanent opening, 450m wide (Fig. 2.1) through which tides act within the estuary. The tides have a maximum range of 1m and the lower reaches of the estuary (barmouth region) are dredged to a depth of 10 -15 m. The upper reaches of the estuary are shallower (2-5 m) with little or no tidal influence and have a low salinity. Cochin is the major port on the South west coast of India.

The major sources of fresh water in the estuary are the two rivers, the Periyar in the northern part and Muvattupuzha in the southern part. In addition, several small tributaries, irrigation channels and innumerable drains contribute to the system. A large number of heavy industrial establishments are situated on both sides of the river Periyar and on the southern bank of the river Muvattupuzha. These industrial concerns discharge their wastes into the estuary.

The depth of the estuary varies moderately. Most of the area is about 3m, but the shipping channel in Cochin harbour area is periodically dredged to a depth of about 13m. The estuary provides access to all types of boats, country crafts, ferries etc. including ocean going vessels to the Cochin harbour. The tides in the Cochin estuary are mixed semi-diurnal type with an average range of $\approx$90cm. During the flood tide, sea water enters the estuary via Cochin barmouth and the

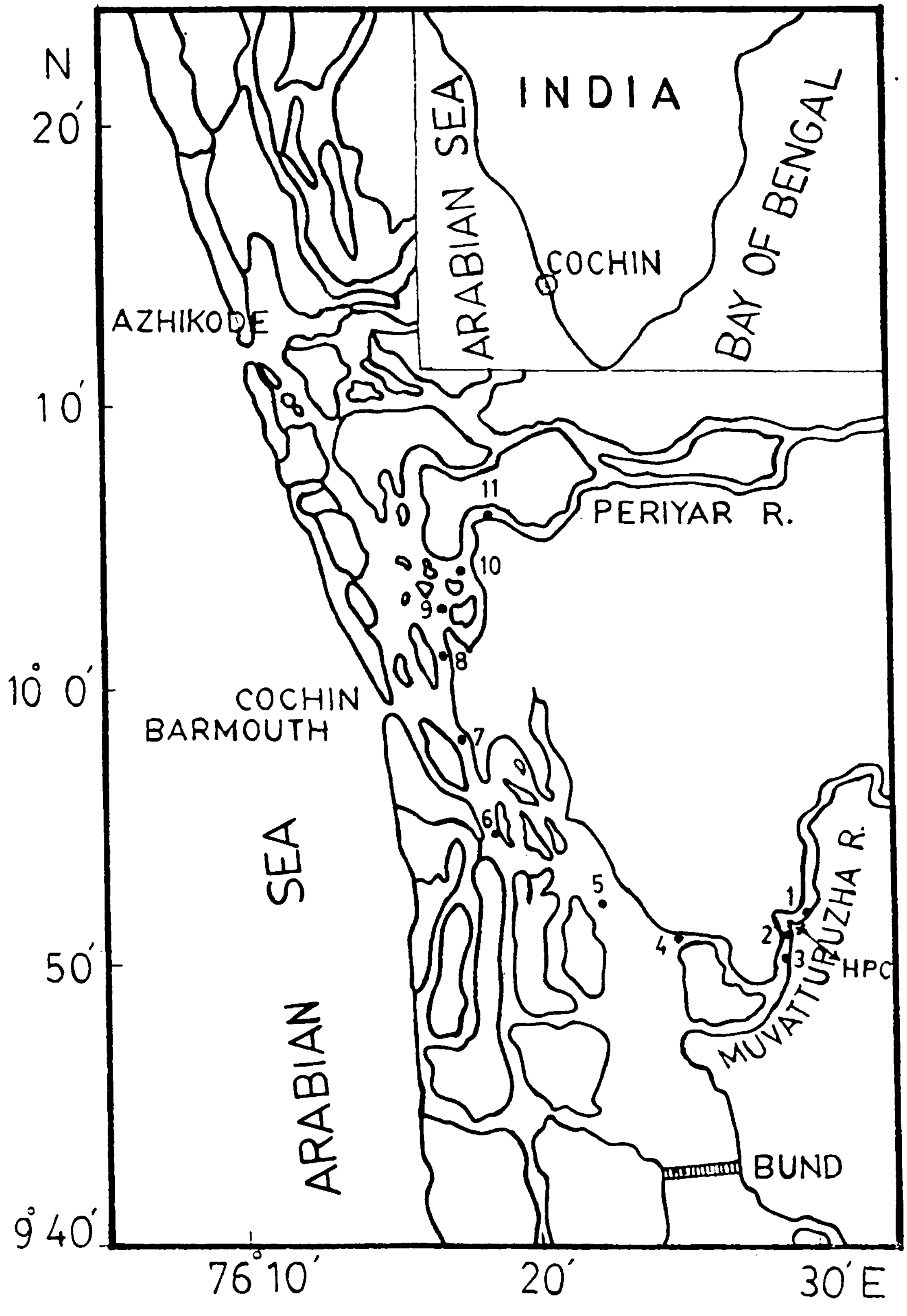

Fig. 2.1 Map of Cochin estuary showing location of stations

flow reverses during the ebb tide. The magnitude of influence of the tide progressively decreases with increasing distance from the barmouth.

The Cochin harbour has attained strategic importance because of its commercial prominence as well as defence potential. It houses a large oil tanker berth, a conveyor belt system for fertilizer transfer and a major ship building yard. Because of the significant influence of land, industries and harbour, the estuary is considerably polluted.

## Station locations

The area of investigation and the station locations are depicted in Fig. 2.1. The stations were fixed so as to obtain a fairly good coverage of the prevailing complex environmental conditions. The following is a brief description of the characteristics of the stations where the present study was carried out.

Station 1 is situated in the river Muvattupuzha which drains into the Cochin estuary through the southern side. It is about 20km away from the barmouth. The station represents a purely fresh water riverine system.

Station 2 is the discharge site of a paper pulp mill in the river Muvattupuzha and is always riverine.

Station 3 is 1 km down the discharge site. The characteristics of the station indicate that settling of most of the waste from the paper mill takes place at this region and has considerable vegetation.

Station 4 is located at the mouth of the river where the Muvattupuzha joins the estuary. During monsoon months, the Station behaves as a fresh water zone.

Station 5 is the mixing zone at the southern part of the estuary. The sediment in the region is always fine and sandy. During monsoon months the station exhibits riverine characteristics and as the season advances to post- and premonsoon, estuarine conditions prevail.

Stations 6 and 7 are located in the same arm of the estuary. These regions are always estuarine and the sediments are characterized by sand, silt, clay or silty clay. Numerous irrigation channels, carrying discharges from various industrial and sewage outfalls drain into these locations. Considerable navigational activities are also present in this region.

Station 8 is located in the northern arm of the estuary where the river Periyar empties its flux into the sea. This station is always typically estuarine. Sewage and waste from oil-mills, food industries etc. are discharged into this area.

Station 9 also represents an estuarine station in the northern arm of the estuary. The retting of coconut-husks is the major activity in this area and huge amounts of plant pith get accumulated in this region. The sediments of this region contain large quantities of pith and yarns of coconut husk.

Station 10 is a riverine region in the Periyar river. Salinity intrusion occurs during post- and premonsoon seasons. The sediment is always sandy in nature. The station is located about 2 km down the Station 11.

Station 11 is located in the Periyar river near the industrial complex FACT, and it is here that the effluents from the industrial concerns (the fertilizer and the insecticide manufacturing units, the Travancore Cochin Chemicals etc.) are discharged. The sediment of this region always contain oil and grease and when dried has a grey colour.

The stations were broadly grouped into riverine and estuarine ones, based on salinities. Thus, the Stations 1,2,3,4 and 5 in the southern arm and Stations 10 and 11 on the northern arm were classified as riverine. The other four, *viz.* Stations 6 and 7 in the southern arm and 8 and 9 in the northern arm represented estuarine locations.

The monthly data were pooled and divided into three seasons for getting reliable trends for explaining the features. The monsoon season comprised of the months May, June, July and August. September, October and November were considered as Postmonsoon and December, January, February, March and April as Premonsoon period. The classification was based on rainfall data (Table 2.1).

Table 2:1
Rainfall Data (April '90- March '91)

| Months | Rain in mm |
|---|---|
| Apr'90 | 54 |
| May'90 | 555 |
| Jun'90 | 437 |
| Jul'90 | 688 |
| Aug'90 | 190 |
| Sep'90 | 80 |
| Oct'90 | 291 |
| Nov'90 | 212 |
| Dec'90 | 2 |
| Jan'91 | - |
| Feb'91 | - |
| Mar'91 | - |

## 2.2 Analytical techniques

### 2.2.1 Sampling procedure

Surface and bottom water and surficial sediment samples from the Stations (Fig. 2.1) were collected at monthly intervals from April 1990 to March 1991. Surface water samples were collected using a clean plastic bucket and bottom water was taken by using a modified Hytech water sampler. The surficial sediment samples were collected using a van Veen grab (area $0.032m^2$). The samples were taken in polythene bags and stored deep frozen until analyses.

### 2.2.2 Analytical methods

pH measurements were made using a portable Elico pH meter. Salinity was estimated argentometrically by the modified Mohr's method developed by Knudsen. (Grasshoff *et al.*, 1983). The method described by Strickland and Parsons (1977) was adopted for the determination of dissolved oxygen.

Sediment organic carbon content was determined by the chromic acid oxidation method suggested by El Wakeel and Riley (1957). Total phosphorus in the sediments was measured by the modified method of Murphy and Riley (1962) and the total nitrogen by micro-Kjeldahl procedure given by Barnes (1959).

Textural analysis of the sediment was carried out by drying the sample in a hot air oven ($90^o$ C) for 6 hours, and subsequent mechanical sieving and pipette analysis as described by Krumbein and Pettijohn (1938). Shepard's nomenclature (Shepard, 1954) was used to describe the texture. Strickland and Parsons (1977) method was employed for the determination of pigments. Chlorophyll pigments, carotenoids and pheopigments of the sediments were determined spectrophotometrically in 90% acetone extract using the equation SCOR/UNESCO, 1966. Samples of the sediment which were dried within the folds of filter paper were ground in a mortar for 10 minutes and extracted with 10ml of 90% acetone. 0.1mg $MgCO_3$ having been added immediately before extraction. The samples were kept overnight at $4^0C$, centrifuged and the absorbance was measured for the total amount of pigments. Pheopigment was measured spectrophotometrically after acidifying the extract with 0.1N HCl.

The protein content was analysed by the method suggested by Herbert *et al.*, (1971). A weighed amount of sample was homogenized in 1N NaOH. The samples were maintained at $80^oC$ for 30 minutes to dissolve the proteins. After cooling, aliquots were transferred to clean test tubes and 5 ml of the copper reagent were added followed by 0.5ml of Folin-Ciocalteu reagent after 10 minutes. Appropriate blank and standards (bovine albumin) were similarly treated.

Lipids were extracted according to the method of Bligh and Dyer (1959). A known amount of the sample was extracted with chloroform- methanol mixture (1:2). Repeated the extraction four times. The extracts were pooled together and extracted with chloroform - water (1:1). The chloroform layer was separated and dried over anhydrous sodium sulphate. The lipid was weighed after removing chloroform.

Carbohydrates were estimated by the phenol-sulphuric acid method (Dubois *et al.*, 1956). Total carbohydrate from the sediment samples were leached by the hydrolysis of the sample with 1N $H_2SO_4$ at $100^oC$ for 1 hour. Cooled and filtered sample aliquots were taken in clean test tubes. Added 1 ml of 5% phenol and 5 ml of concentrated sulphuric acid. Cooled the test tube at room temperature and measured the optical density. Blank and standards of D-glucose were also treated similarly.

Humic acid in the sediment was analysed by the fluorimetric method. A known quantity of the dried sediment was extracted with 1N NaOH for 24 hrs., filtered and acidified. The precipitated humic acid was redissolved in NaOH and the absorbance measured in a fluorescence spectrophotometer (Hitachi F 3010). Humic acid standard was prepared by dissolving purified humic acid isolated from the aquatic sediments.

Hydroxylated aromatic compounds (tannin and lignin) were estimated by the method detailed in APHA (1981) and modified by Nair *et al.*, (1989). Sediment samples were subjected to 0.05M NaOH leaching for 90 minutes and filtered. 5ml aliquots of the filtrate were pipetted out and 1 ml of citrate solution followed by the tannin-lignin reagent and the carbonate tartarate reagent were added. The optical density was measured at 765nm.

All the chemicals used were of analytical reagent grade.

Milli - Q water was used for the estimations. A Hitachi (150-20) U.V. Visible spectrophotometer was used for the photometric measurements.

## 2.3 General Hydrography

The study of the hydrographical parameters has great importance in characterising the general features of an estuarine system. They are equally significant for pollution control, harbour design, marine traffic routing etc. The hydrographical conditions in an estuary mainly depend on the intrusion of sea water associated with tides and influx of fresh water from rivers. Precipitation and evaporation processes also contribute to hydrographical changes. In addition, the bottom topography and geographical condition in the estuary exert a profound influence on the hydrographical condition of the estuary. The sedimentary characteristic is more or less governed by the hydrography of the overlying water.

The hydrography of the Cochin estuary has been well documented (Ramamritham and Jayaraman, 1963; George and Kartha, 1963; Qasim and Reddy, 1967; Qasim *et al.*, 1968; Sankaranarayanan and Qasim, 1969; Josanto, 1971; Wellershaus, 1971; Haridas *et al.*, 1973; Shynamma and Balakrishnan, 1973; Joseph, 1974; Lakshmanan *et al.*, 1982; Sankaranarayanan *et al.*, 1986). Although the information available pertains to seasonal variation of temperature, salinity, dissolved oxygen, pH, alkalinity and nutrients of the region as a whole, the present study on hydrography (spatial and seasonal variation of salinity, dissolved oxygen and pH) was conducted as concurrent data are essential for interpretation of the sedimentary behaviour.

## 2.3.1 Salinity

Salinity has been recognised as an index of the estuarine mixing processes and the tidal effects. The salinity distribution pattern is largely influenced by the mixing and diffusion phenomena occurring in the estuaries. Wide fluctuations in salinity are generally observed in an estuarine system. Except for regions with high evaporation and little rainfall, where the salinity level may exceed $35 \times 10^{-3}$, the values would be normally lower than the salinity of sea water.

The monthly data on salinity of surface and bottom waters at Stations 1-11 are given in appendix and the seasonal distribution of salinity is presented in Fig. 2.2.

The Cochin estuary is highly influenced by the influx of fresh water from rivers and by the intrusion of sea water *via.* the bar mouth. In the southern region, except at Stations 1 and 2 during monsoon, low salinity values ranging from 0.00 to $3.42 \times 10^{-3}$ at the surace and 0.00 to $8.85 \times 10^{-3}$ at the bottom were observed. A gradual increase in salinity was encountered as the season progressed to postmonsoon and premonsoon. However Stations 1,2 and 3 exhibited fresh water characteristics throughout the period of study. Salinity intrusion occurred at Station 4 during premonsoon only. The highest

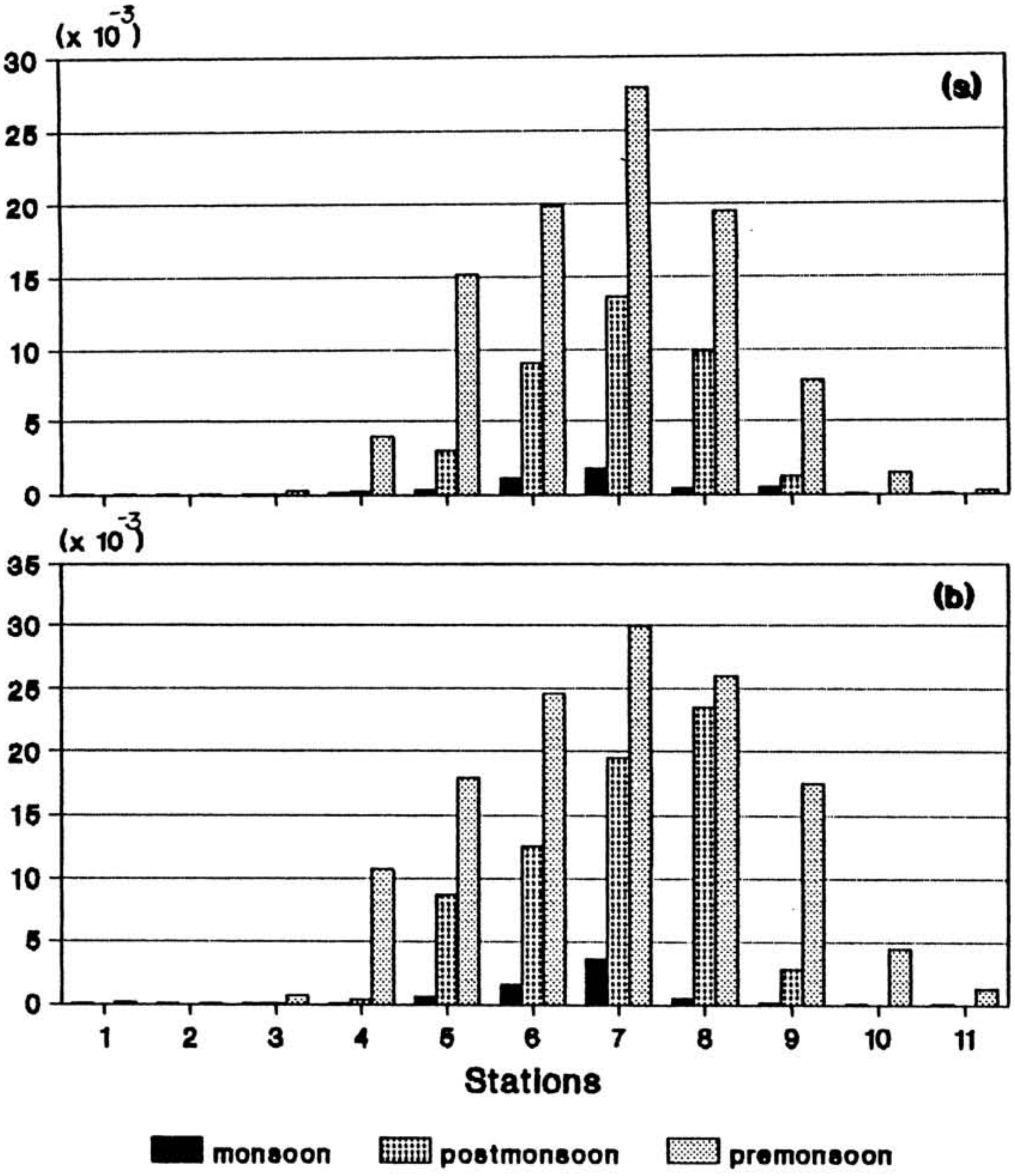

Fig. 2.2 Seasonal distribution of salinity
(s) surface (b) bottom

value ($35 \times 10^{-3}$) was recorded for surface and bottom waters at Station 7.

In the northern region, at Stations 8 and 9, salinity values ranging between 0.00 to 0.83 x $10^{-3}$ at surface and 0.00 to 0.83 $\times 10^{-3}$ at bottom were noticed during the monsoon months. This was brought about by the heavy monsoonal rain causing high fresh water discharge. As the season advanced to post and premonsoon, higher values ranging from 30.10 to 35.86 x $10^{-3}$ and 4.13 to 25.62 x $10^{-3}$ at the bottom and 12.03 to 23.7 x $10^{-3}$ and 2.37 to 15.39 $\times 10^{-3}$ at surface waters of Station 8 and 9 were observed respectively. This may be the result of the penetration of salt water and low discharge of fresh water into the estuary. A vertical salinity gradient also was observed at these regions during all the seasons. Fresh water conditions were observed at Stations 10 and 11. At Station 10 the salinity increased during the premonsoon period indicating an intrusion of sea water.

### 2.3.2 Dissolved oxygen

Dissolved oxygen is the most valuable water quality parameter in assessing water pollution. It is also important since the existence of aquatic life is intimately linked with the availability of oxygen for their survival. Though atmospheric oxygen is abundant its solubility in water is low, 9.94 ml $l^{-1}$ at $1^{o}$C and 5.28 ml $l^{-1}$ at $30^{o}$C in fresh water and 7.97 ml $l^{-1}$ and at $1^{o}$C and 4.41 ml $l^{-1}$ at $30^{o}$C in sea water of salinity $33 \times 10^{-3}$ (Riley and Chester, 1971). The depletion of oxygen content leads to undesirable obnoxious odours under extreme anaerobic conditions. ( Doudoroff Shumway and Peter, 1970; Nelson, 1978).

The concentration and distribution of oxygen in natural waters depend on various factors such as temperature, partial pressure and salinity . Studies on salinity dependent oxygen solubility may help to elucidate the various physical, chemical and biological processes taking place in the estuarine system (Desousa & Sen Gupta, 1986).

Results of dissolved oxygen at surface and bottom waters of all stations are given in appendix and the seasonal distribution in Fig. 2.3. Higher dissolved oxygen content was observed at surface and bottom waters all along the stations during the monsoon period. Dissolved oxygen values ranged from 2.54 to 5.85 ml $l^{-1}$ at surface and 2.82 to 5.89 ml $l^{-1}$ at the bottom during monsoon. The values decreased as the season advanced to post- and premonsoon. The lowest value was observed along Stations 4 to 9. This may be explained as the combined effect of low solubility of oxygen due to high salinity and temperature and due to the utilization of oxygen for the biodegradation of organic matter. In general, a spatial and seasonal variation of dissolved oxygen was observed. High dissolved oxygen contents were observed during monsoon due to the greater solubility of oxygen in fresh water and high turbulence.

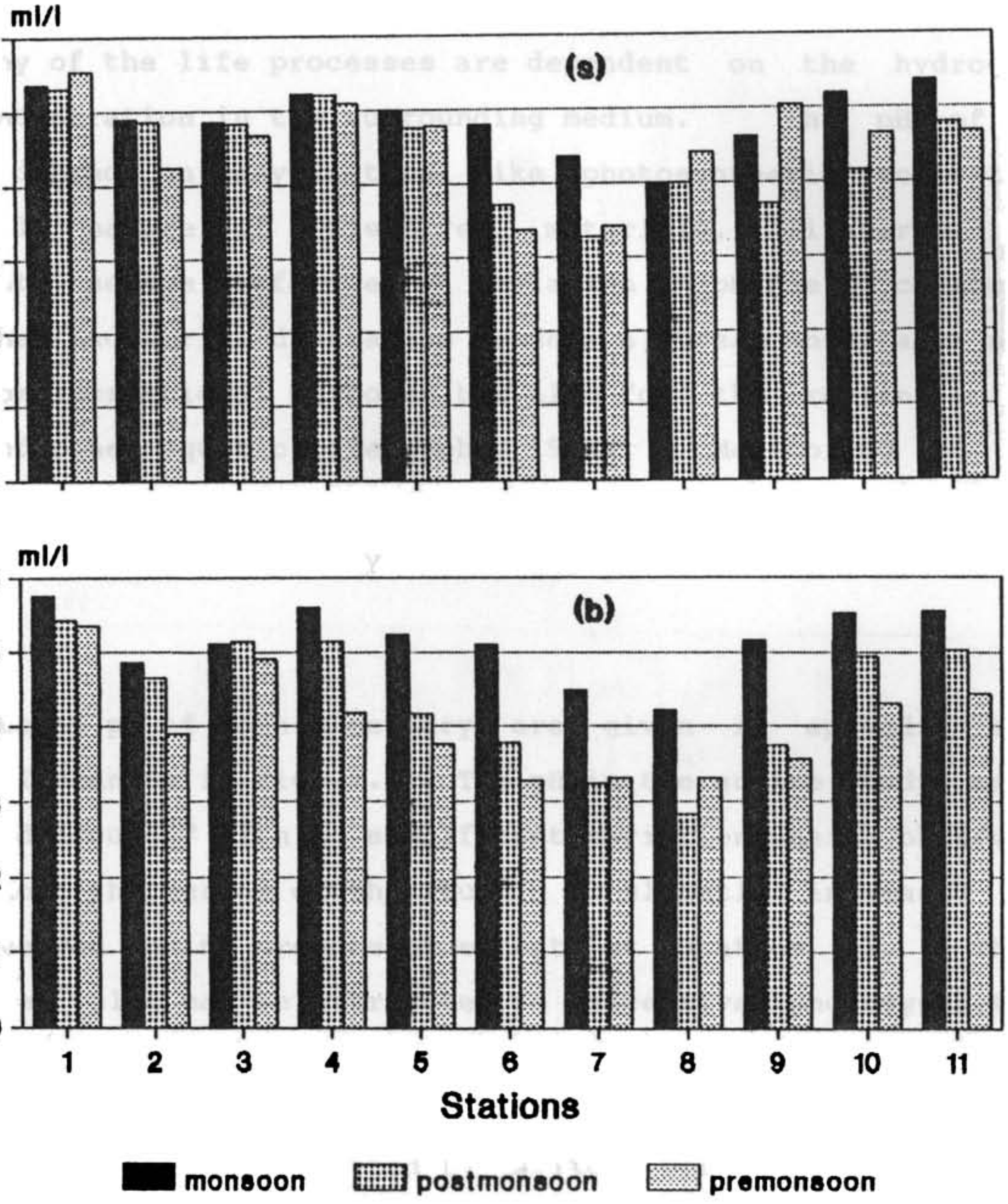

Fig. 2.3 Seasonal distribution of dissolved oxygen
(s) surface (b) bottom

### 2.3.3 pH

Many of the life processes are dependent on the hydrogen ion concentration in the surrounding medium. The pH of a medium depends on many factors like photosynthetic activity, rainfall, nature of dissolved materials, discharge of effluents, sewage outfall etc. Variation in pH due to chemical and other industrial discharges renders a stream unsuitable not only for recreational purposes but also for the rearing of fish and other aquatic life (Webb, 1982). Monitoring of pH values is therefore essential for identifying zones of pollution and other quality conditions of water (Clark *et al.*, 1977).

Data on pH of Cochin estuary are given in appendix and seasonal changes in Fig. 2.4. The pH in the entire study area remained around 7 with no significant variations being observed throughout the period of the study. A slightly increased pH was observed during premonsoon except at Station 11. This increased value may be attributed to excessive photosynthetic activity of algae and the near marine condition. The high photosynthetic production during post- and premonsoon in the Cochin backwater was reported by earlier workers also (Silas and Pillai, 1975; Nair *et al.*, 1975). The difference in pH between surface and bottom waters of the estuarine system during post- and premonsoon is not well defined. The discharge of acidic industrial waste and the decrease in flow lead to a successive decrease in pH from monsoon to premonsoon.

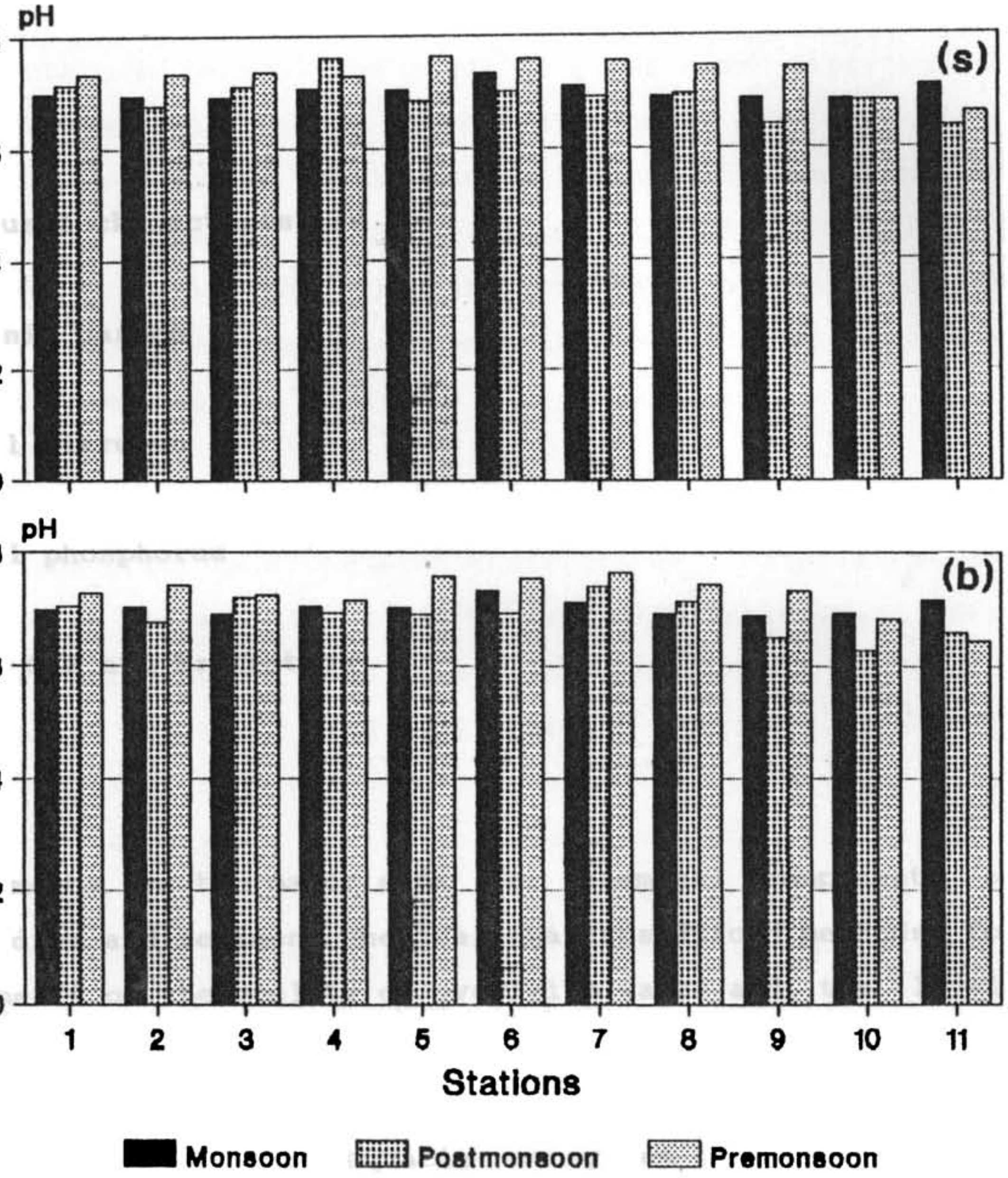

Fig. 2.4 Seasonal distribution of pH
(s) surface (b) bottom

CHAPTER 3

# SEDIMENTARY CHARACTERISTICS

**3.1 Textural characteristics**

**3.2 Organic carbon**

**3.3 Total nitrogen**

**3.4 Total phosphorus**

**3.5 C:N, C:P and N:P ratios**

Sediments are the major sink for chemical components of water bodies and sediment chemical analyses afford methods for measurements of the quality of overlying water and the levels of potential pollutants. Biological availability of the sedimentary components has a vital role in regulating the characteristics of the aquatic ecosystem and the natural processes that control the spatial and temporal variation in the sediment characteristics of the estuarine system. A comprehensive idea of the bottom sediment is thus a pre-requisite to water quality management procedures.

## 3.1 Textural characteristics

Grain size is one of the basic attributes of sediments and its determination is essential to delineate the sedimentary environments. In general the study of grain size distribution reveals the physical effects of the environment on deposition and the hydrodynamic conditions existing at the time of deposition. Textural characteristics of sediments play a significant role in the distribution and concentration of carbon, nitrogen and phosphorus both in the sediment and in the overlying water column.

The seasonal averages of sand, silt and clay fractions at each of the stations along with their textural classifications (according to Shepard, 1954) are presented in Table 3.1. Sand represents particles of size greater than $63\mu$, silt indicates sizes between $63\mu$ and $4\ \mu$and clay includes particles less than $4\mu$. The composition of the sediment varied markedly from place to place. The seasonal variation at each station was minimal.

At the southern part of the estuary and in the Muvattupuzha river (Stations 1 - 5), the main constiutent fraction in the sediment was sand (>80% sand) with negligible amount of silt and clay. The riverine regime was composed of sandy sediments through out the period of study. In contrast to this distribution, sand- silt- clay occupied a greater area in the estuarine regions of Station 6 and 7. At Station 7, clayey-silt was observed during the premonsoon months. This may be due to the settling of fine particles from the overlying waters as a result of the variations in salinity and in

Table 3.1 Size composition of Sediments

| Station No: | Season | Nature of Sediment | Sand % (>63µ) | Silt % (4-63µ) | Clay % (<4µ) |
|---|---|---|---|---|---|
| 1 | A | Sand | 84.77 | 9.59 | 5.64 |
| | B | Sand | 98.65 | 1.08 | 0.27 |
| | C | Sand | 96.86 | 1.82 | 1.32 |
| 2 | A | Sand | 94.4 | 1.02 | 4.58 |
| | B | Sand | 88.51 | 10.32 | 1.16 |
| | C | Sand | 95.91 | 2.11 | 1.98 |
| 3 | A | Sand | 92.91 | 1.8 | 5.29 |
| | B | Sand | 97.06 | 2.52 | 0.42 |
| | C | Silty Sand | 77.19 | 17.04 | 5.77 |
| 4 | A | Sand | 92.24 | 2.21 | 5.45 |
| | B | Sand | 98.19 | 1.25 | 0.56 |
| | C | Sand | 95.75 | 3.6 | 0.65 |
| 5 | A | Sand | 78.59 | 10.77 | 10.64 |
| | B | Sand | 96.01 | 2.25 | 1.74 |
| | C | Sand | 93.31 | 5.36 | 1.33 |
| 6 | A | Sand Silt Clay | 65.86 | 18.91 | 15.23 |
| | B | Sand Silt Clay | 18.07 | 55.99 | 25.94 |
| | C | Sand Silt Clay | 61.03 | 25.32 | 13.65 |
| 7 | A | Clayey Silt | 6.79 | 51.79 | 41.42 |
| | B | Sand Silt Clay | 22.45 | 51.63 | 25.92 |
| | C | Clayey Silt | 23.55 | 45.77 | 30.68 |
| 8 | A | Silty clay | 4.05 | 37.15 | 58.8 |
| | B | Clayey Silt | 19.38 | 44.57 | 36.05 |
| | C | Silty Clay | 1.86 | 45.65 | 52.49 |
| 9 | A | Sand Silt clay | 50.62 | 26.31 | 23.07 |
| | B | Sand Silt clay | 20.25 | 51.82 | 27.93 |
| | C | Sand Silt clay | 34.91 | 39.04 | 26.05 |
| 10 | A | Sand | 94.52 | 1.21 | 4.27 |
| | B | Sand | 98.41 | 1.27 | 0.32 |
| | C | Sand | 93.85 | 4.77 | 1.38 |
| 11 | A | Sand Silt Clay | 24.99 | 25.11 | 49.9 |
| | B | Sand Silt Clay | 30.85 | 10.39 | 58.75 |
| | C | Sandy Silt | 40.73 | 47.32 | 11.95 |

A-Monsoon, B-Postmonsoon, C-Pre monsoon

biogeochemical processes.

In the northern part, where the Periyar river joins the estuary (Station 8), the main constituent was silty-clay during monsoon and premonsoon and clayey-silt during postmonsoon. While at Stations 9 and 11, it was sand-silt-clay, Station 10 was sandy throughout the period of the study. The variation in grain size at Station 8 may be a result of the formation of a sheltered sedimentary environment (Pillai, 1989).

Grain size analyses indicated that the sediments of the estuarine region were composed of fine grained sediments whereas those of riverine region were made up of sand ($>63\mu$). Spatial variation in texture was noticed. Sediments at Stations 6,8,9 and 11 which received industrial and domestic sewage, were of sand-silt-clay in nature. However, the size analysis of bed sediments showed a decrease in size from upper reaches to lower reaches. Coarse sand dominated the upper reaches followed by fine sand silt and clay in the lower reaches. The decreasing trend of grain size indicated the transport of sediments from riverine to estuarine region. Pettijohn (1975) observed that, in general, the size of the clastic sediment carried in a current progressively decreased in the direction of the transport.

## 3.2 Organic carbon

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. The preservation of organic matter is almost exclusively restricted to aquatic sediments. The wide spectra of organic compounds which are present in varying proportion in the sediments are classified as allochthonous and autochthonous. The autochthonous materials resemble more closely the primary biological products whereas the allochthonous fraction is mainly composed of diagenetically formed secondary reaction products. Thus the allochthonous matter is expected to be stable, less susceptible to biodegradation or chemical degradation and therefore ecologically more persistent.

The production and destruction of organic matter in natural bodies of water are governed by a number of environmental factors-- availability of sunlight and dissolved nutrients, water temperature and mixing, composition of aquatic biological communities etc. Most of the organic matter present in the upper waters of lakes and oceans originate from aquatic biota. Yet only a small percentage of this material escapes remineralization during sinking and gets incorporated to the sediment. Organic material transported to lakes and oceans from anthropogenic and biological sources on land may behave differently from those of aquatic origin (Prahl *et al.,* 1980). Selective alteration and destruction of the organic components within the water column influence the ultimate character of sedimentary organics and effect the cycling of organic carbon in aquatic systems.

Important factors enhancing preservation of sinking organic matter are its incorporation into the fecal pellets of grazing zooplankton (Prahl and Carpenter, 1979; Suess, 1980) and its sorption by clay minerals (Suess and Muller, 1980). Such factors enhance the rate of transport of degradable compounds from surface water to the bottom.

The physical and chemical properties of sediment such as water retention capacity, porosity and compressibility are to a great extent controlled by the amount of organic material within the sediments. Organic matter supports microbial metabolism. This, in turn, influences the organic chemical reactions by regulating pH and Eh conditions. Apart from this, organic matter forms complexes/chelates with inorganic metals. Unlike the inorganic components, even small amounts of (≈ 1-2%) organic matter strongly influence the post-depositional behaviour of a sediment.

A knowledge of the nature , origin and transformations of organic matter in marine sediments may provide valuable information on the sedimentary environment of a basin sediment, formation of petroleum, cycling of nutrients in the aquatic system and chemical activities of marine organisms (Orr and Emery, 1956).

Organic carbon content in the ocean is estimated to be about 1 - 5 mg C $l^{-1}$ of which 85% is DOC. In closed seas and in highly productive coastal waters, the mean amount of organic carbon increases three or four times and even more (Menzel and Vaccaro, 1964). The organic matter in sea water is chemically complex, physically heterogenous and variable with time and space (Azam and Cho, 1987). In estuarine mixing zones, additional complexity is encountered because of transformation of chemical and biological species under extreme salinity gradient (Morris *et al.*, 1978; Mantoura, 1987).

Organic matter makes up about 0.7% of many sediments largely in the form of insoluble polymeric material. Organic matter includes labile compounds such as aminoacids, proteins and sugars as well as more refractory compounds such as humic acids and lipids. It is in general, the more insoluble hydrophobic components including lipids and membrane components of organisms living in the euphotic zone, which survive degradtion in the water column, that get incorporated into the sediments.

The surface sediments of the estuary are quantitatively the main reservior of organic matter. Bottom sediments regulate the fresh water ecosystem (Odum, 1971). Metabolism of detrital and particulate organic carbon which occurs largely in the sediments provides stability to the ecosystem (Wetzel,1975). Banin *et al.*(1974) suggested that the upper layer of lake sediments affects the cycles and balance nutritional elements in the lake water. Sediments can play a critical role in determining the trophic status of lakes (Golterman, 1966). Hargrave (1973) found that the bottom sediments yield valuable information about production and mineralization in the water column. McLachlan (1969) stated that the nature and distribution of the bottom fauna are strongly influenced by substrate characteristics.

The biogeochemical cycle of organic carbon and its distribution and seasonal variations have been studied extensively by several authors (Happ *et al.*, 1977; Pocklington and Tan, 1987; Meyers *et al.*, 1984; Rashid and Reinson, 1979; Aston and Hewitt, 1977; Stevenson and Cheng, 1972; Adams and Van Euk, 1988; Lara *et al.*, 1985; Cauwet, 1991; Yang and Hong, 1988; Jones and Jordan, 1979; Wafar *et al.*, 1989). However, only few investigations were made in Indian waters and sediments. They include the studies on the distribution of organic carbon in sediments of north-western continental shelf of India (Paropkari, 1979), seasonal variation of C, N and P in the sediments of Vellar estuary (Sivakumar *et al.*, 1983), nutrient status of the sediments of Hoogly estuary (Ghosh and Choudhury, 1987), organic matter and C, N and P in the sediments of Porto Novo (Shanmukhappa, 1987), organic constituents of harbour and coastal Visakhapatnam (Sarma and Rao, 1988), nature and composition of sediments of the harbour and coastal environment (Satyanarayana and Reddy, 1985) and organic carbon in the sediments of the Mandovi estuary, Goa (Alagarsamy, 1991).

The distribution of organic matter in the sedimentary environment of Cochin estuary with respect to texture and pollution has been documented by Murty and Veerayya (1972) and Sankaranarayanan and Panampunnayil (1979). It was however observed that most of the studies were either fragmentary or confined to the northern arm of the estuary. A systematic assessment of the organic carbon content in the sedimentary environment has therefore been carried out to characterise the abundance, fate and origin of carbon in the entire estuarine system.

Throughout the duration of this study a higher carbon content was noticed at the estuarine stations than at the riverine stations. The longitudinal gradation of organic carbon showed a well defined pattern: low concentrations were recorded at the riverine region with an abrupt increase at the estuarine stations. The results of monthly collections are given in appendix. The monthly organic carbon content in the sediment at Stations 1,2,3 and 4 in the fresh water regime of southern part of the estuary varied from 0.56 to 60.38 mg C $g^{-1}$. The Stations 2 and 3, which receive paper mill effluent discharges, though being fresh water zones recorded sediment organic carbon values of 26.61 and 60.38 mg C $g^{-1}$ respectively. The sediment organic carbon concentration at Station 5 ranged between 0.62 to 9.76 mg C $g^{-1}$. This station represented a mid-way mixing region of fresh and saline water during postmonsoon and premonsoon periods.

Stations 6 and 7 were in the estuarine region where the sediment organic carbon varied from 9.88 to 36.80mg C $g^{-1}$ while at Stations 8 and 9 on the northern arm of the estuary, the sediment organic carbon values ranged from 19.08 to 125.06mg C $g^{-1}$. Station 10 was again a fresh water zone on the northern arm of the estuary and the values ranged from 0.27 to 4.71mg C $g^{-1}$, Station 11 which was also riverine received effluent discharges from the industrial belt of Eloor, and the sediment organic carbon values varied from 30.68 to 46.64mg C $g^{-1}$.

Seasonal variation of sediment organic carbon was observed at all the Stations (Fig. 3.1). In the riverine zone (Stations 1, 2, 3, 4, 5, 10 and 11), the sediment organic

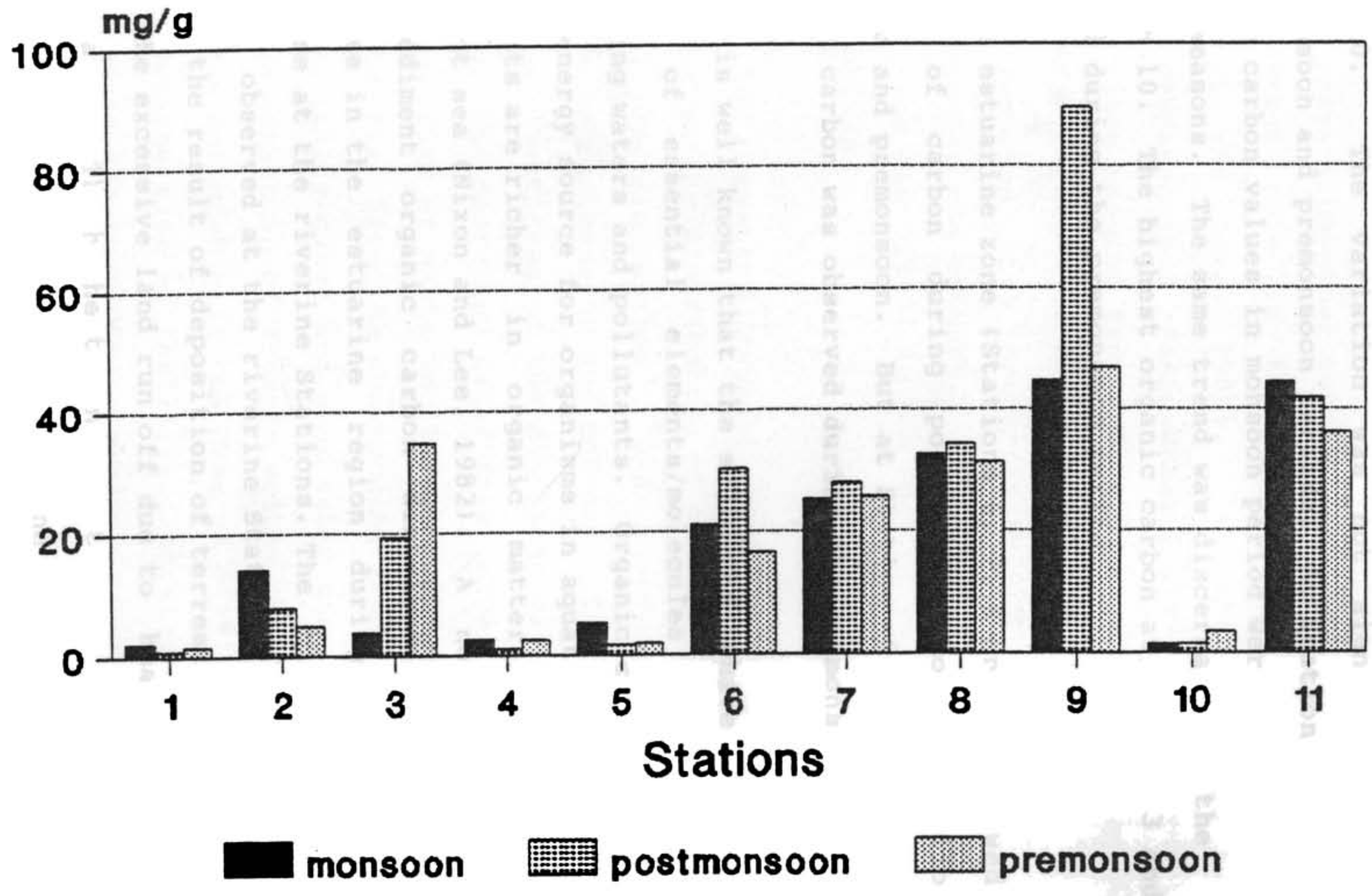

Fig. 3.1 Seasonal distribution of sedimentary organic carbon

carbon showed highest values during monsoon except at Stations 3 and 10. The variation was not significant during the postmonsoon and premonsoon periods. At Station 3, the sediment organic carbon values in monsoon period were low compared to other seasons. The same trend was discernable in the case of Station 10. The highest organic carbon at Station 3 and 10 was noticed during the premonsoon period.

The estuarine zone (Stations 6, 7, 8 and 9) showed higher values of carbon during postmonsoon months, followed by monsoon and premonsoon. But at Station 9, a high value of organic carbon was observed during the premonsoon period.

It is well known that the sediments behave as the "store house" of essential elements/molecules of productivity of overlying waters and pollutants. Organic carbon is important as an energy source for organisms in aquatic systems. Estuarine sediments are richer in organic matter than those of the adjacent sea (Nixon and Lee, 1982). A noteworthy feature of the sediment organic carbon distribution was a seasonal increase in the estuarine region during postmonsoon and a decrease at the riverine Stations. The high sediment organic carbon observed at the riverine Stations during monsoon months may be the result of deposition of terrestrial organic matter from the excessive land run off due to heavy rainfall during the season. The highest concentration of organic carbon in the postmonsoon season at the estuarine zone may be the combined effect of high productivity, settling of detritus matter, decay of vegetation and sewage effluent containing large amount of organic particles. In the ecosystem, organic production is favoured by vegetation , texture of the sediments and degree of oxidation. In addition to this, rain water run off through rivers, prevailing water current and depth of occurrence play an important role in the accumulation of organic matter (Purandara and Dora, 1987). In the Cochin backwaters, Sankaranarayanan and Panampunnayil (1979) observed organic carbon values ranging from 7.4 to 38.4 mg C $g^{-1}$ while, Qasim *et al.* (1968) reported to be about 195 mg C $m^{-2}$ $yr^{-1}$. Shibu (1992) reported high productivity, DOC and POC during postmonsoon in the estuary. A similar trend was also reported by Sarma and Rao (1988) in the case of coastal environment of Visakhapatnam.

In the riverine region, Station 3 showed a peculiar behaviour in the distribution of organic carbon. The highest sediment organic carbon was observed during premonsoon followed by postmonsoon and monsoon. This Station was located about 1km downstream of the discharge site of the paper mill effluent. The decreased water flow after monsoon led to an increased load of waste in the water column. Decomposition of plant material from the surrounding area, the grain size of the sediment (silty clay) and poor water flow contributed to the high concentration of organic matter in this region. The same trend was noticeable in the case of Station 10 which was below the discharge site of fertilizer industry. The highest value recorded in the postmonsoon period in the case of Station 9 may be due to the texture of the sediment as well as to additions from the retting husks.

The effluent discharge site (Station 11), a fresh water regime showed increased carbon content during the monsoon months. This may be due to the influence of effluents discharged from the factory (industrial unit located at Eloor), terrigenous material brought out by land run off and the texture of the sediment. The colour of the sediment was grey and contained sulphur and oil. Stations 9 and 11 were highly polluted due to the anthropogenic activity.

In the riverine region except Stations 3,10 and 11 no significant variation during monsoon and postmonsoon period was observed. Particle size had an inverse relationship with organic carbon content. The lack of seasonal fluctuations in the sediment organic carbon could be due to the particle size of the sediment at the riverine stations which reflected to the proximity of the terrestrial environment and its greater susceptibility to natural and man made turbulence.

The lower organic carbon concentrations observed in estuarine sediments during premonsoon might be a consequence of the regeneration/ resuspension of organic carbon to the water column, oxidation of carbon by high content of dissolved oxygen and physicochemical characteristics of the estuary.

A comparative study of organic carbon load in the two arms of estuary revealed that the northern arm of the estuary where the Periyar river drains, showed highest organic carbon at all the seasons throughout the year of the study, with a maximum during the postmonsoon period. The postmonsoon maximum was shown by the estuarine station in the southern arm of the estuary also. This study indicated that considerable contamination by organic compounds existed in the upper estuary. Land run off, effluent discharge from the factories, effect of retting yards at Vaduthala and grain size of the sediment all contributed to this. A similar observation was reported by Unnithan (1975) and Remani *et al.*, (1980). A longitudinal gradation resulted in sediments from riverine to estuarine stations in the southern arm of the estuary. The texture of the sediment also played a major role in the preservation of sedimentary organic matter. As the particle size increased, the organic carbon content decreased. Sediments of riverine stations which were always sandy (>75% sand) had low sediment organic carbon contents.

Organic carbon did not vary significantly among Stations in estuarine conditions except during postmonsoon. Kemp (1971) found that the quantity of organic matter in the surficial sediments was directly proportional to the clay-size fraction of the sediment and independant of depth, rate of sedimentation and degree of eutrophication. A linear relationship between organic matter and sediment particle size was reported by many workers (Trask, 1932; Bordovskiy, 1965; Thomas, 1969; Longbottom, 1970). Clay particles were higher in estuarine sediments, where preservation of organic matter occurred through sedimentation and incorporation into bottom sediment. Thus the sediment composition (sand, silt, clay, clayey-silt, silty-clay), productivity rate, land run-off and discharge from industries and sewage, markedly influence the organic carbon content in the estuarine region.

## 3.3 Total nitrogen

Nitrogen is one of the important nutrients for phytoplankton growth in the marine environment (Ryther and Dunsten , 1971; Thayer, 1974). Hunter (1970) suggested that food resources with a C :N (by weights)ratio greater than 17:1 were nitrogen deficient and would inhibit heterotrophic growth. Several investigators (Eppley *et al.,* 1973; McCarthy *et al.*, 1977; Solorzano and Elrich, 1977; Desousa *et al.,* 1981; Qasim and Sen Gupta, 1981; Sharp, 1983) studied the seasonal changes in the concentration of nitrogen species in relation to phytoplankton biomass and or production because of the influence of nitrogen in regulating primary production.

The hydrosphere contains about $23x10^{12}$ tons of dissolved nitrogen (an amount which represents only 0.5% of the global nitrogen budget). Of the soluble combined nitrogen, 65% is present as nitrate and nitrite (Martin, 1970). Van Bennekom and Salomons (1981) reported the data of nitrogen budget on a dozen major rivers including some highly polluted ones.

Nitrogen exists in nine oxidation states (-3 to +5), all of which have significant roles in the marine environment (Martin, 1970). The processes controlling the distribution of various forms of nitrogen between coastal waters, estuarine waters and near-shore shelf waters are not well known. The concentration of various forms of nitrogen in an estuarine system is the result of input rates, the interconversion reactions occurring within the water column and the rate of loss by way of out flow, denitrification and sediment associated deposition.

Studies on the temporal and spatial variations in the concentration of nitrogen provide an insight into the processes controlling the distribution of nitrogen in the estuarine ecosystem. Such studies on the distribution of nitrogen in the estuarine ecosystem were carried out at Pamlico river estuary (Hobbie *et al.,* 1975), Clyde estuary (Mackay and Leatherland, 1976), Mississipi river estuary (Ho and Barrett, 1977), Tamar estuary (Morris *et al.,* 1981) and Delaware estuary (Sharp *et al.,* 1982).

Though nitrogen cycling is of a complex nature, characterisation of its cycling in the riverine, estuarine and oceanic waters enable identification of the potential source, major pathways of losses as well as the internal processes. C:N ratio of the sediment provides information about the fertility of the sediment/soil as well as on the source and nature of the nitrogen in the aquatic environment. It is inferred that if the C:N ratio is high, the sediment/soil is deficient in nitrogen.

The role of nitrogen as well as of organic matter in the sediments of the Cochin estuary has been investigated by Sankaranarayanan and Panampunnayil (1979) and Remani *et al.,* (1980). Sivakumar *et al.,*(1983), Shanmughappa (1987) and Phani Ghosh and Choudhury (1987) reported on carbon, nitrogen, and phosphorous concentrations in the sediments of Vellar, Porto Novo and Hoogly estuaries respectively.

The month-wise data and seasonal distribution of the total sediment nitrogen are given in appendix and Fig. 3.2. A unique feature of the data was the irregularity in the levels of total nitrogen distribution with month, season and Stations. The total sediment nitrogen in the riverine Stations ranged from 0.14 to 0.65mg N $g^{-1}$ at Station 1, from 0.02 to 1.54mg N $g^{-1}$ at Station 2, from 0.25 to 2.38mg N $g^{-1}$ at Station 3, from 0.14 to 0.49mg N $g^{-1}$at Station 4 and from 0.21 to 0.46mg N $g^{-1}$ at Station 5. The concentration of nitrogen varied from 0.63 to 2.73 and 0.24 to 2.31mg N $g^{-1}$ respectively at Stations 6 and 7. The total nitrogen content in the sediment varied from 0.49 to 3.57mg N $g^{-1}$ at Station 8, from 1.05 to 4.2 mg N $g^{-1}$ at Station 9 and 0.21 to 0.58mg N $g^{-1}$ at Station 10, while at the disharge site (Station 11), higher values of nitrogen which were observed varied between 0.65 to 2.52mg N $g^{-1}$ through out the period of study.

No clear seasonal variation could be observed for nitrogen in the sediment. In the monsoon period, the riverine Stations 1, 2 and 5 showed a higher value for total nitrogen, whereas at Stations 3 and 4, a decrease was observed. In the riverine region, the sediment total nitrogen in the other two seasons (pre and post monsoon) showed a more or less similar trend except at Stations 3 and 4. The decrease in concentration of total nitrogen at these Stations might be due to the leaching of sediment nitrogen to the overlying water column. In contrast to this an increase in value was observed at Stations 3 and 4. During pre and post monsoon periods, the water flow was poor and the tidal effect of the estuary was more and hence nitrogeneous material discharged from the paper mill at the

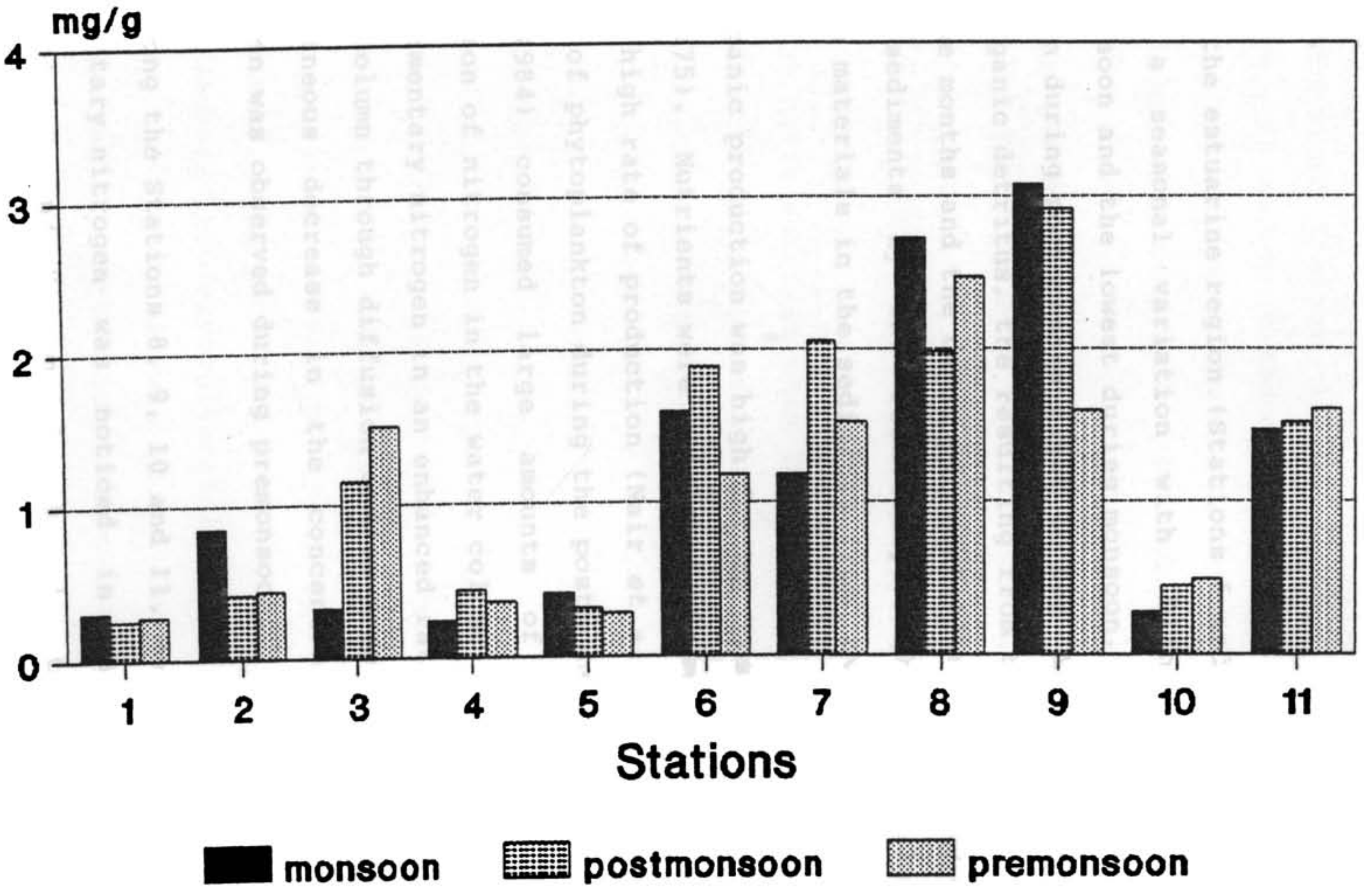

Fig. 3.2 Seasonal distribution of sedimentary nitrogen

upstream (Station 2) would settle at the Stations 3 and 4. This might be the reason for the increase of nitrogen in these regions.

In the estuarine region (Stations 6 and 7), total nitrogen showed a seasonal variation with highest value during postmonsoon and the lowest during monsoon. The highest value of nitrogen during postmonsoon might be due to the contribution from organic detritus, the resulting from the planktonic bloom in these months and the decay of vegetation which reaches the bottom sediments by the relatively higher accumulation of organic materials in the sediments from overlying waters.

Organic production was high during postmonsoon (Joseph *et al.*, 1975). Nutrients were depleted from the water column during high rate of production (Nair *et al.*, 1984). The intense growth of phytoplankton during the postmonsoon period (Nair *et al.*, 1984) consumed large amounts of nitrogen causing depletion of nitrogen in the water column. This led to release of sedimentary nitrogen in an enhanced rate to the overlying water column through diffusion and/or desorption. As a result, simultaneous decrease in the concentration of sedimentary nitrogen was observed during premonsoon.

Among the Stations 8, 9, 10 and 11, monsoonal increase in sedimentary nitrogen was noticed in the estuarine regions (Stations 8 and 9), mainly due to the precipitation of nitrogenous materials from the watershed, while a decrease was observed in the riverine region (Stations 10 and 11) which would be attributed to the flushing of sediments during the monsoon and to the coarse sandy texture. A decrease in nitrogen values was observed in the estuarine region during pre and postmonsoon. Station 11 did not show any appreciable variation with season in the nitrogen concentration. This was only to be expected as it was the discharge site of ntrogen waste from FACT complex. Station 10, located further downstream, however, recorded an increased value of nitrogen during pre and postmonsoon period. This might be due to a salinity gradient induced accumulation and settling of the nitrogen wastes.

The distribution of nitrogen in the southern region was evidently different from that in the northern region suggesting significant variaton in the physicochemical characteristics and bio-geochemical processes of these regions.

### 3.4 Total phosphorus

Phosphorus is one of the most studied elements in lake sediments, primarily due to the fact that phosphorus has a regulatory role in primary production in most of the aquatic environments. The increased load of phosphorus in lakes during recent decades from agricultural land, sewage and industrial effluents has a crucial role in the eutrophication processes. (Vollenweider, 1968; Rohlich, 1969; Golterman, 1975; Wetzel, 1975). Phosphorus entering the lake participates in the biological cycle in the lake water and then gets deposited in the sediments. In the sediment, phosphorus stimulates biological processes and may return back to the water body.

Phosphate from land runoff, from agricultural areas, sewage and industries have been estimated at present to represent an addition of $6.5x10^{6}$ metric tons of phosphorus per annum to the world ocean, compared to $1.8x10^{4}$ metric tons added from natural weathering processes (Bowen, 1966; United Nations, 1968). The greatest impact of nutrient additions to coastal environment is seen in the excessive growth of non-endemic plants, frequently resulting in the reduction of species diversity, which inturn, modifies the food chain components for indigenous organisms, often increasing the biological oxygen demand, lowering water transparency and generally lowering aesthetic and commercial values of the area (Ketchum, 1972)

Phosphorus is deposited in the sediments as a) allogenic apatite minerals b) organic associates and c) precipitates with inorganic complexes. The relative importance of these different fractions depends on the external supply of apatite minerals, organic matter, complex forming agents and to a large extent on the productivity of the system.

The behaviour of dissolved inorganic phosphate during estuarine mixing of river and sea waters showed that phosphate levels were practically invarient over the whole salinity range (0 to 32%.) at a concentration of $\simeq 37 \mu g \ P \ l^{-1}$.

The biogeochemical cycle of phosphorus in the estuarine environment and its distribution and seasonal variations have been reported by many authors (Correll *et al.*, 1975; Aston, 1980). Biogeochemistry of phosphorus in an estuary is controlled by a combination of physical, chemical and biological processes. These processes generally fall into three categories: 1) addition of phosphorus to the active pool by various processes like input, decomposition of particulate matter and regeneration, ii) removal of phosphorus from the active pool by precipitation and other physical processes and iii) uptake or concentration of phosphorus by living organisms, consumers and destroyers (Martin, 1970).

The exchange of phosphorus between sediment and overlying water is a major component of the phosphorus cycle in the estuarine environment. Laboratory and field observations showed that adsorption was reversible and sediments acted as a phosphate buffer for keeping the phosphate concentration in the overlying water constant (Pomeroy *et al.,* 1965 and Harter, 1968). Hence the phosphate buffering mechanism has considerable importance in controlling the fertility of overlying waters.

Golterman (1973) suggested that when phosphorus was adsorbed onto sediment materials, one fraction was adsorbed into anionic site and another into the crystalline lattice structure by substitution of the hydroxyl ion. The principal factors controlling the exchange processes were redox potential (Mortimer, 1971), pH (Burns and Salomon 1969) and concentration of calcium and magnesium of overlying water (Upchurch *et al.,* 1974). When the dissolved oxygen was less than 2 mg $l^{-1}$ the phosphorus adsorbed onto ferric hydroxide was released on redissolution (Kramer *et al.,* 1972). The rate of release of phosphorus from sediments increased with increasing turbulence and infact doubled when the sediments were resuspended (Zicker *et al.*, 1956). Phosphate exchange capacity between sediment and overlying waters appeared to be related to the texture of the sediment also (Venkataswamy Reddy and Hariharan, 1986).

Phosphate distribution in the Cochin estuary showed a marked seasonal variation influenced by local precipitation and land runoff. The distribution of sediment phosphate in the Cochin estuary was studied by various authors (Ansari and Rajagopal, 1974; Remani *et al.*, 1981; Reddy and Sankaranarayanan, 1972). These studies were confined to certain areas only, namely the northern arm of the estuary. The present study has been carried out to elucidate the distribution, cycling and flux of phosphorus as well as the phosphorus pollution in the Cochin estuarine system, in the background of an acknowledged variation of phosphorus concentration in sediments with respect to time, space and texture.

In shallow water systems, where the mud acts as a reservoir of phosphorus in various forms and as a generator into overlying water under suitable conditions, a knowledge of the phosphorus content in the sediment is important. Phosphorus is considered to be present in sediment as interstitial, adsorbed and as phosphate bound to some soluble inorganic or organic compounds. The distribution of total phosphorus, which includes all these forms is governed largely by hydrobiological features of the overlying water, the texture and mineralogical composition of the sediment.

The concentration level of total P in the sediments is given in appendix. The seasonal distribution pattern of total P is presented Fig. 3.3. The monthly values of total P in the riverine region of the southern part of the estuary, varied from 0.16 to 2.6 mg P g$^{-1}$ at Station 1, from 0.21 to 0.78 mg P g$^{-1}$ at Station 2, from 0.22 to 1.29 mg P g$^{-1}$ at Station 3, from 0.10 to 0.3 mg P g$^{-1}$ at Station 4 and 0.03 to 0.36 mg P g.$^{-1}$ at Station 5, while in the estuarine zone, the values of total P ranged from 0.62 to 1.94 mg P g$^{-1}$ and from 1.45 to 2.06 mg P g$^{-1}$ at Stations 6 and 7 respectively.

In the northern region of the estuary the total phosphorus content varied from 0.77 to 2.81 mg P g$^{-1}$ at Station 8 and from 0.94 to 4.48 mg P g$^{-1}$ at Station 9. In the riverine region of the northern part, Station 10 showed a minimum of .08 mg P g$^{-1}$ and a maximum of 0.98 mg P g -$^{-1}$ The effluent receiving site (Station 11) had the highest value of 8.39 mg P g$^{-1}$ and a lowest of 5.05 mg P g.$^{-1}$

In the riverine region of the southern part of the estuary (Stations 1 to 5), the total P content in the sediment varied from 0.03 to 1.29 mg P g$^{-1}$ dry mud. No seasonal variation was observed in this region except at Station 3. The sediment composition in the zone was found to be mainly composed of sands (>80% sand) with negligible amount of silt and clay, throughout the period of study. Station 5 recorded a maximum value of phosphate during premonsoon period followed by post monsoon. During the premonsoon period the sediments contained more clay and silt than during the other seasons. Stations 6 and 7 (estuarine stations) showed a clear seasonal variation and the highest value was noticed during postmonsoon (1.94 mg P

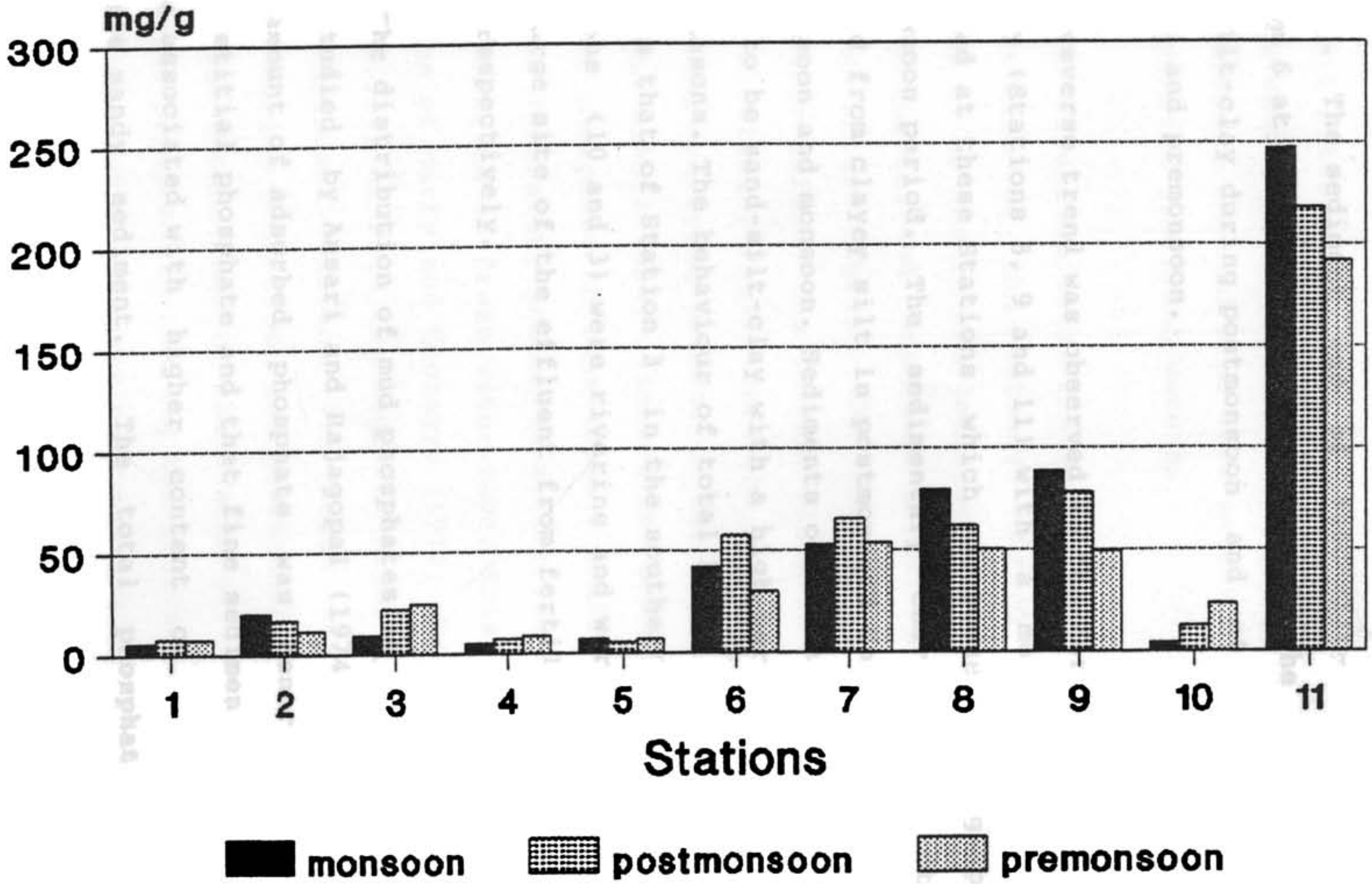

Fig. 3.3 Seasonal distribution of sedimentary phosphorus

$g^{-1}$ at Station 6 and 2.51 mg P $g^{-1}$ at Station 7) followed by monsoon (1.93 and 1.97 mg P $g^{-1}$) and premonsoon (1.34 and 1.67 mg P g). The sediment was of sand-silt-clay in nature at Station 6 at all seasons. At Station 7 the sediment was of sand-silt-clay during postmonsoon and of clayey-silt during monsoon and premonsoon.

A reverse trend was observed in the northern part of the estuary (Stations 8, 9 and 11) with a monsoon maximum being obtained at these Stations which decreased during post and premonsoon period. The sedimentary character of Station 8 changed from clayey silt in postmonsoon to silty clay during premonsoon and monsoon. Sediments of Stations 9 and 11 were found to be sand-silt-clay with a high percentage of silt at all seasons. The behaviour of total P at Station 10 was the same as that of Station 3 in the southern region . These two stations (10 and 3) were riverine and were situated below the discharge site of the effluent from fertilizer plant and paper mill respectively.

The distribution of mud phosphates in the Cochin estuary was studied by Ansari and Rajagopal (1974); they observed that the amount of adsorbed phosphate was generally higher than interstitial phosphate and that fine sediments of silt and clay were associated with higher content of phosphate than the coarse sandy sediment. The total phosphate concentration revealed a decreasing trend from marine to estuarine zone. Since the Cochin estuary was shallow, (2 m- 5 m) that one of the major factors governing the distribution and variation of phosphorus would be the difference in the regenerative property of the bottom sediment (Reddy and Sankaranarayanan, 1972). Their experiments on phosphate regenerative activity of muds of the Cochin estuary revealed that sediment from high saline brackish water released phosphate continuously to overlying waters whereas the mud from less saline brackish area adsorbed phosphate from overlying waters.

Lower values of total P observed in the sediment of the southern part of the estuary, during monsoon months, was believed to be due to the leaching of the phosphorus (both in the interstitial and adsorbed forms) from the mud to the overlying waters. During the monsoon months, the increased fresh water inflow, the intense circulation of water and the very low salinity facilitated the release of phosphate from the mud to the overlying waters. The texture of the sediment which was always sandy limited the seasonal variation of the sediment phosphate to considerably small levels in the riverine region. This study indicated a decrease in phosphorus content from estuarine to fresh water zone. This is consistent with the findings of Murty and Veerayya (1972) who suggested that the variablility of P in the sediment might be due to the texture of the sediment. Station 3, though riverine, showed higher values during premonsoon and postmonsoon. This station was about 1km downstream of the discharge site of the effluent from the paper mill. During the premonsoon and the postmonsoon period the water flow was poor and the settling of particles occurred within a few hundred meters of the discharge site and hence the increase in the concentration of phosphorous at the Station. This was in full agreement with the finding of McIntyre and Johnston (1975). The higher value of phosphorus observed during postmonsoon could be due to the incorporation of detrital matter, decay of vegetation, and adsorption of phosphate from the water column. Moreover, the biological activity and hydrological conditions like low salinity, high dissolved oxygen and nature of the sediments may also influence the accumulation of phosphate in the sediment. The desorption of both interstitial and adsorbed phosphate from the sediment to the water column might be responsible for lower concentration of phosphate in the mud. Cochin estuary was observed to be highly productive (Joseph *et al.*, 1975) and phosphate was a limiting nutrient in the euphotic zone. High organic production in the estuarine zone causes depletion of phosphate from the water column. The estuary exhibited marine characteristics during premonsoon showing a pH >7.5 which also enhanced the desorption of phosphorus from the mud to the overlying water, to compensate the depletion. Reddy and Sankaranarayanan (1972) reported that sediment from high saline brackish water released phosphate continuously to overlying waters.

The phosphate distribution in the northern region, showed a different nature from that of the other counterpart. The highest phosphate concentration observed at Stations 8, 9 and 11 during monsoon months, steadily decreased during post and premonsoon periods. Pomeroy *et al.*, (1965) reported that low salinity and high dissolved oxygen favoured adsorption of P from overlying waters to the sediment. Reddy and Sankaranarayanan (1972), observed that the adsorptive tendency was high with higher silt percentage. Stations 8 and 9 were mostly dominated by silt (42.4 and 36% respectively.). The salinity during monsoon was $0.37 \times 10^{-3}$ and $0.45 \times 10^{-3}$ at Stations 8 and 9 respectively and dissolved oxygen was 3.97 and 4.6 ml $l^{-1}$. The particle size exerted a control on the phosphorus distribution in sediments, silty and smaller sized grains showing an adsorption effect of increasing phosphorus content with decreasing grain size (Aston and Hewitt, 1977). High land runoff due to monsoon and sewage discharge at the estuarine region from the Cochin Corporation area and discharge from the FACT complex influenced the higher concentration of phosphorous in the sediments. Besides this, the high value observed during the monsoon period may also be due to the behaviour of the zone as a "protected sedimentary environment" (Pillai, 1989). Earlier studies (Murty and Veerayya, 1972; Ansari and Rajagopal, 1974) in the Cochin backwaters also have reported high phosphate concentration in areas with higher proportion of silt and clay content in the sediment.

At the northern region, the phosphate content decreased through postmonsoon and attained a minimum value during premonsoon. This was attributed to the release of phosphorus from the sediment to the overlying water. Reddy and Sankaranarayanan (1972) have shown that the bacterial activity and the physicochemical composition of the sediments at different sites were related to the difference in the release phosphorus. Further, it has been shown that increased salinity and low dissolved oxygen of overlying water enhanced the release of phosphorus from the sediment to overlying water (Burns and Salmon, 1969; Mortimer, 1971). The present study revealed that increase of salinity from 9.8 to $34.5 \times 10^{-3}$ and reduction of dissolved oxygen from 3.36 to 2.80 ml $l^{-1}$ favoured the desorption of phosphorous from sediments.

Station 10 which was a fresh water region down to Station 11, recorded an increase in values of phosphate with the progress of the period from monsoon to premonsoon. The area was composed of coarse sand. This increase in value might be due to the adsorption of phosphorus from the overlying water which contained large quantities of phosphate due to the leaching of phosphate from the discharge site.

However, the total P in the sediment behaved in a different way in the two arms of the estuary. The phosphorus load was high in the northern region compared with the southern region. Sediments from the northern region have high phosphorus content indicating that the environment is substantially polluted by local sources of sewage, fertilizer plant effluent etc.

## 3.5 C:N, C:P and N:P ratios

### Carbon:Nitrogen ratio (C:N)

Carbon : Nitrogen ratio is generally used to identify the source of organic matter in the sediment. Trask (1932) has attributed C:N ratio 8 for the surface samples of southern California.

Values of C:N ratio at Stations 1-11 in the estuary are given in appendix. Seasonal variation of C:N ratio at these stations is given in Table 3.2. In the riverine regions on the

Table 3.2 Seasonal C:N, C:P, and N:P ratios

|  | Month | Stations |  |  |  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
| C/N | mon | 6.08 | 57.32 | 11.64 | 13.00 | 12.45 | 16.88 | 41.60 | 12.26 | 15.37 | 6.02 | 36.54 |
|  | post | 3.71 | 18.27 | 12.98 | 2.60 | 5.39 | 17.70 | 13.80 | 17.44 | 36.01 | 3.17 | 32.18 |
|  | pre | 5.92 | 14.57 | 21.45 | 7.28 | 7.24 | 14.36 | 17.76 | 22.65 | 26.81 | 7.15 | 28.08 |
| C/P | mon | 10.04 | 20.89 | 14.14 | 14.57 | 33.77 | 16.51 | 15.69 | 13.39 | 17.52 | 9.41 | 5.84 |
|  | post | 4.17 | 14.70 | 22.11 | 4.93 | 10.48 | 16.83 | 14.44 | 18.28 | 38.27 | 3.43 | 6.19 |
|  | pre | 6.73 | 13.40 | 41.31 | 9.74 | 8.59 | 17.45 | 15.53 | 22.91 | 27.27 | 4.66 | 6.16 |
| N/P | mon | 1.49 | 1.21 | 1.25 | 1.72 | 3.39 | 1.13 | 0.75 | 1.11 | 1.15 | 2.35 | 0.20 |
|  | post | 1.08 | 0.80 | 1.75 | 1.94 | 1.94 | 1.07 | 1.03 | 1.04 | 1.29 | 1.38 | 0.23 |
|  | pre | 1.24 | 1.30 | 2.31 | 1.40 | 1.48 | 1.25 | 0.92 | 1.91 | 1.09 | 0.72 | 0.28 |

southern part of the estuary, the C:N ratio values varied between 2.67 - 10.10, 3.55 - 103.58, 3.66 - 45.39, 1.45 - 27.50 and 2.48 - 21.21 for Stations 1, 2, 3, 4 and 5 respectively. In the estuarine region, the C:N ratio values ranged from 10.72 to 29.17 at Station 6, 11.43 to 113.75 at Station 7, 8.94 to 71.37 at Station 8, and from 10.44 to 56.47 at Station 9. The values at Station 10 varied from 0.64 to 15.52 and at Station 11 it was between 15.71 and 61.42. Monthly data indicated that higher values were observed at the estuarine stations. A higher value was also observed at Station 11 which was a discharge-receiving site housed on the bank of the river Periyar.

Seasonal and spatial variation of C:N was noticed at all stations along the estuarine system. A low value of C:N was observed at all riverine stations ranging from 2.60 to 13 except for Stations 2, 3 and 11, where a higher ratio was obtained. A higher value was observed at the estuarine zone, varying from 12.26 to 41.60. The highest value was obtained during post monsoon (13.80 - 36.01) followed by premonsoon (12.87 - 31.95).

Trask (1932) compared values of organic carbon and nitrogen in the sediments of estuaries, lagoons and oceans throughout the world and reported a C:N ratio between 8 and 12. Carbon and nitrogen values obtained from sediment samples collected from west coast of India during cruise R.V. Meteor showed a variation between 1 and 8. Bhosle *et al.* (1978) observed a high C:N ratio (2.48 - 37.50) for the shelf sediments of the Arabian sea and attributed it to degradation of complex protein. Qasim and Sankaranarayanan (1972) reported C:N ratios between 5 and 10.5 (average 7.6) for the detritus of the Cochin backwaters. Ghosh *et al.* (1987) reported the C:N ratio ranging from 3.2 to 34 for the sediments of the Hoogly estuary. Sarma and Rao (1988) estimated the C:N ratio of the coastal sediments of Visakhapatnam and the values which ranged from 4.56 to 8.88 were related to the significant contribution of *in situ* planktonic matter to the sediment. Shanmukhappa (1987) reported higher values (3.91 to 30.5) of C:N ratio in Porto Novo which was attributed to the high concentration of humic acid and high production. Sankaranarayanan and Panampunnayil (1979) have reported C:N ratio between 2.5 and 16.9 (average 6.4) in the sediments of the Cochin estuary. Sivakumar *et al.*, (1983) reported higher values for C:N ratio for the sediments of Vellar estuary (2 to 137.5) which was considered to be due to the fresh water discharge, terrestrial runoff bringing high organic matter and also to the nature of the sub-stratum. In this study, the observed high seasonal variation of C:N ratio in the sediments of the estuary could be attributed to the changes in the physicochemical characteristics of the sediments caused by the discharge of fresh water containing high terrestrial organic matter during monsoon months and also to the more stable condition favourable for high planktonic production prevalent during post and premonsoon seasons.

As compared with the estuarine region, the riverine C:N ratios were lower and could be attributed to the substratum/ texture of the sediments (sandy). The higher values of C:N ratio at the riverine stations during monsoon months could be due to the high organic matter in the sediments resulting from the N-poor land run-off during monsoon months. Stations 2, 3 and 11 also behaved in a similar manner. It may be noted that Stations 2 and 11 were the effluent -receiving sites of a paper mill and a fertilizer factory respectively whereas at the Station 3, the organic material settled and hence the organic carbon was high.

### Carbon : Phosphorus ratio (C:P)

C:P ratio can be used as an index of pollution by domestic sewage in any aquatic environmental system. Monthly variation of C:P ratio is presented in appendix and the seasonal vaiation is shown in Table 3.2. In general, higher values were observed at estuarine region as compared with riverine stations. The C:P ratio of the sediments varied between 2.36 and 70.28 in the riverine station of the southern part of the estuary, whereas in the estuarine region, the values ranged from 15.12 to 21.29 at Station 6 and 10.08to 18.3 at Station 7. In the northern part, the C:P values varied between 11.34 to 44.37 at Station 8 and 9.79 to 51.36 at Station 9. In the same zone, the riverine C:P ratio ranged from 1.98 to 18.22 at Station 10 and from 4.7 to 7.77 at Station 11.

Seasonally, the C:P ratio varied from 13.39 to 38.27 at the estuarine region (Stations 6, 7, 8, and 9) while at the riverine stations, the ratio varied from 3.43 to 41.5. These results were consistent with the findings of Sankaranarayanan and Panampunnayil (1979), their values being 2.78 to 27.41. Qasim and Sankaranarayanan (1979) reported C:P ratio of

22.61-60.40 (average 41.1) for the detritus collected from the Cochin estuary. Shanmukhappa (1987) attributed the higher C:P ratio of the sediments of Porto Novo (21.1 - 105.4) to the unpolluted nature of the biotopes by domestic sewage.

The lower C:P ratio observed at the estuarine region could be considered as the result of the increased load of phosphates reaching the estuary through domestic sewage. The lowest value observed at Station 11 could be due to the high phosphate content in the sediment resulting from the accumulation of phosphate from the discharge of effluents from the fertilizer factory. In the riverine region, the sediment was always poor in carbon and phosphorus due to the substratum. The lower C:P ratio observed in this estuarine system indicated that the major portion of the phosphorus in the sediment was of abiogenic origin, from domestic sewage and from other anthropogenic sources.

### Nitrogen : Phosphorus ratio (N:P)

The monthly variation of N:P ratio is given in appendix and Table 3.2 shows the seasonal variation of N:P ratio. The monthly N:P ratio varied between 0.10 to 8.21 at the riverine stations (Stations 1, 2, 3, 4, 5, 10 and 11) whereas the N:P ranged from 0.15 to 4.63 at the estuarine region (Stations 6, 7, 8 and 9). The lowest value was observed at Station 11 and the value ranged from 0.10 to 0.49.

Seasonally the N:P ratio at the riverine region varied from 0.20 to 3.39, while in the estuarine region the N:P ratio ranged from 0.75 to 1.91. Again, seasonally the lowest value (0.20 to 0.28) noticed at Station 11 could be due to the higher amount of phosphate accumulated/ adsorbed in the sediments as a result of the discharge of the effluent from the fertilizer factory, which was rich in phosphate.

In general, low N:P ratio values were obtained in this study as compared with the values of Sivakumar *et al.,* (1983). Shanmukhappa (1987) reporterd a N:P ratio between 2.3 and 13.2 for the sediments of Porto Novo. The results of N:P ratios of this investigation was in full agreement with the values (1.2 - 4.0) of Sankaranarayanan and Panampunnayil (1979). This value was lower than that of plankton. Grasshoff (1975) reported N:P in plankton as 13.3 :1. Sen Gupta *et al.,* (1976) have reported a value of 13.8 :1 for natural plankton and 18.2:1 for culture plankton. Rettenberg *et al.,*(1955) reported relatively low N:P values (5.8 :1, 3.3 :1 and 1.4 :1 respectively) for the sediments of Catalina, Santa Barbara and Santa Monica basins. The low N:P observed in the Cochin estuary in the present study indicated that the major portion of the phosphorus in the sediment was of abiogenic origin.

Interrelationships: The regression analysis of the values found for the sediments of the Cochin estuary yields linear correlation lines. (Fig. 3.4) The correlation equations are given below

1. Organic carbon vs total nitrogen.

Riverine

$Y = 0.2863 + 0.02326x$ (n=72) $r=0.68$ $P < 0.001$

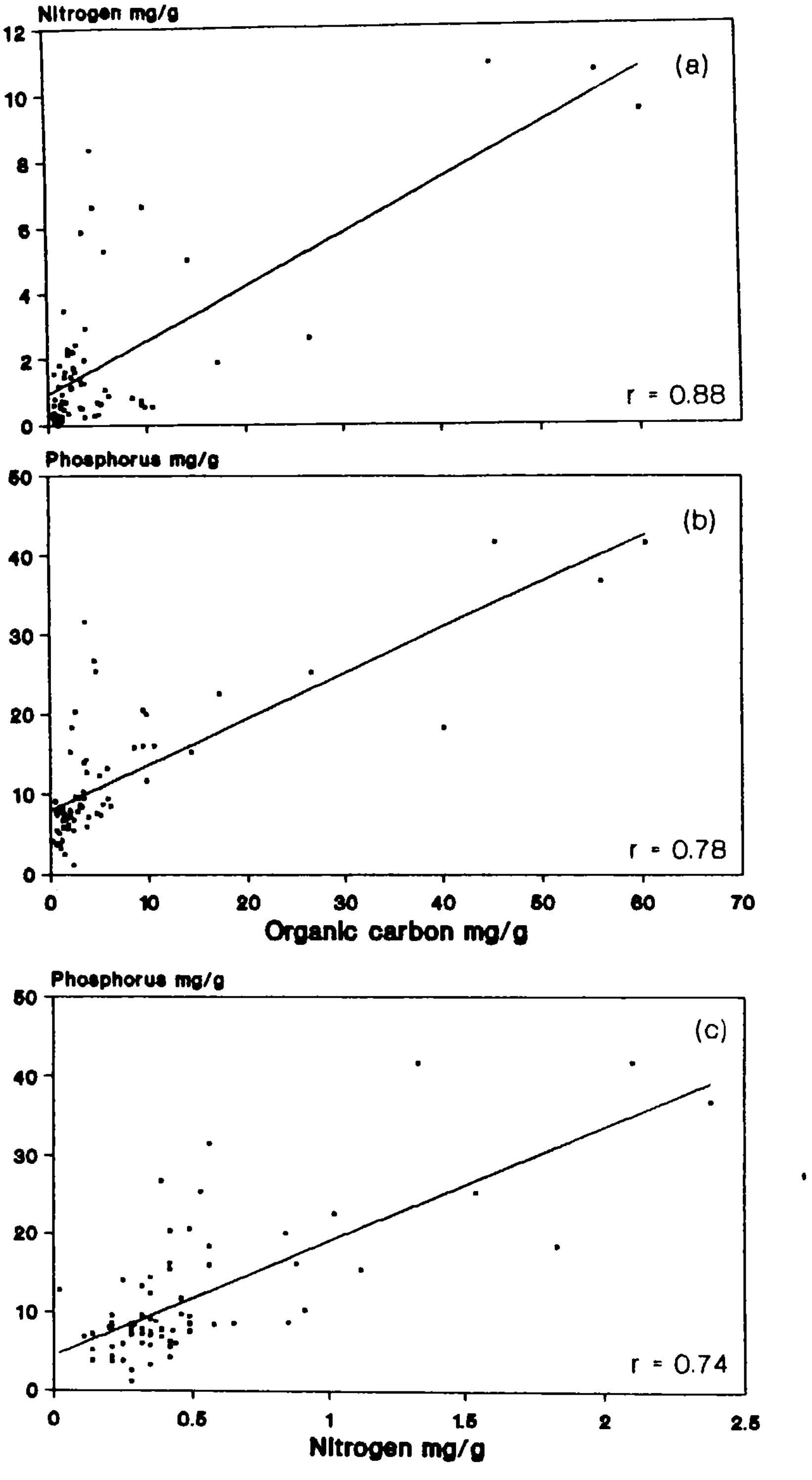

Fig. 3.4 Relationship between organic carbon (riverine) and
(a) nitrogen (b) phosphorus (c) nitrogen and phosphorus

(contd.)

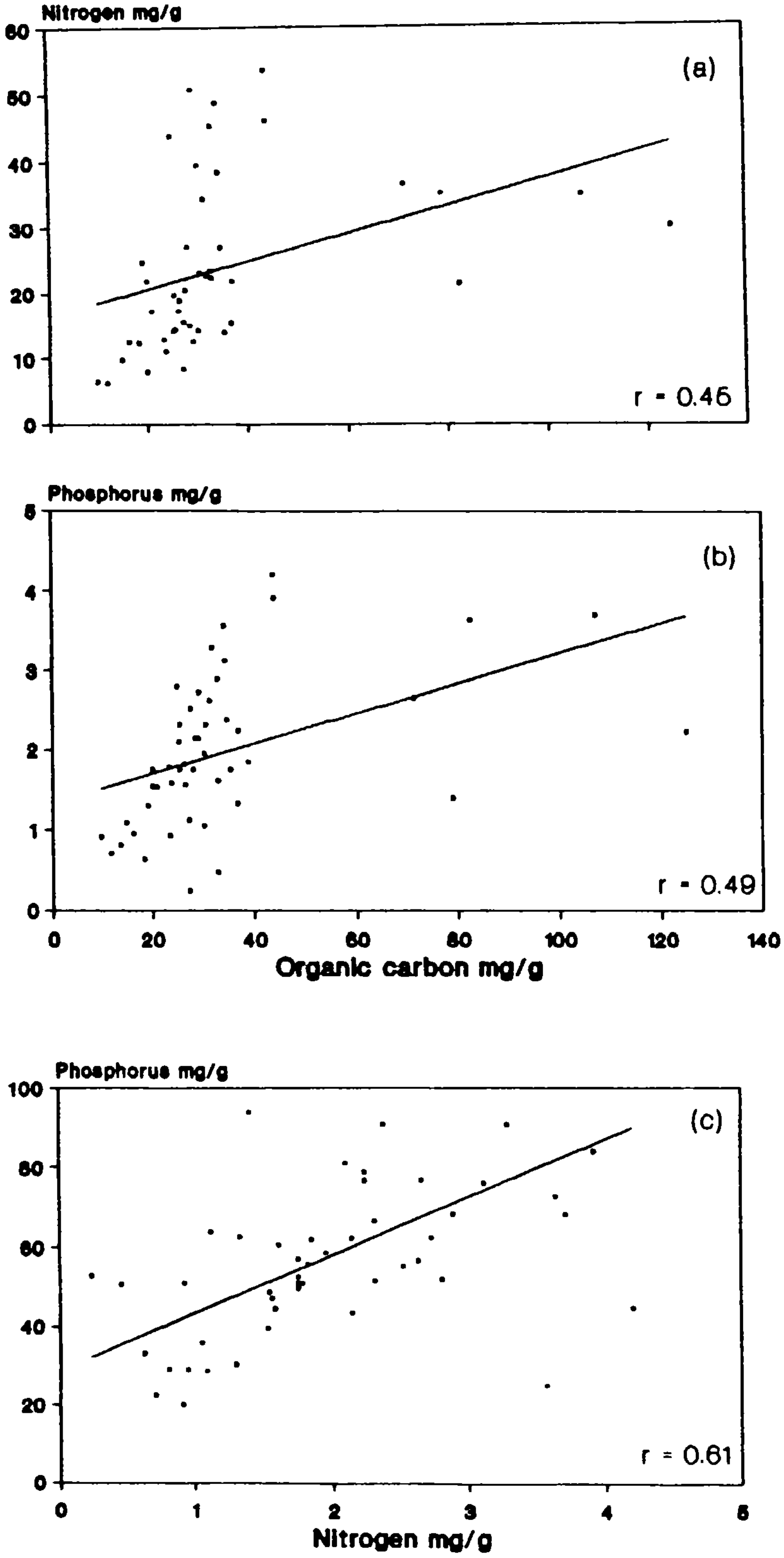

Fig. 3. 4 Relationship between organic carbon (estuarine) and (a) nitrogen (b) phosphorus (c) nitrogen and phosphorus

Estuarine

$Y = 1.3245 + 0.0189x$ (n=48) r=0.45 $P < 0.01$

2. Organic carbon vs total phosphorus

Riverine

$Y = 7.9257 + 0.5773x$ (n=72) r=0.78 $P < 0.001$

Estuarine

$Y = 40.420 + 0.4968x$ (n=48) r=0.49 $P < 0.001$

3. Total Nitrogen vs total phosphorus

Riverine

$Y = 4.397 + 14.599x$(n=72) r=0.74 $P < 0.001$

Estuarine

$Y = 28.709 + 14.569x$(n=48) r=0.61 $P < 0.001$

Comparing the correlation equations, relationships between riverine and estuarine it was noticed that the composition of the estuarine sediments were influenced by allochthonous input and high biological activity of the estuary.

## CHAPTER. 4

# BIOGEOORGANICS

4.1 Sedimentary pigments

4.2 Carbohydrates

4.3 Lipids and Proteins

4.3.1 Lipids

4.3.2 Proteins

4.4 Interrelationships

The organic matter in sediments is derived from terrestrial and estuarine/marine sources. Aquatic organisms like algae are more abundant in the marine/estuarine environment, and primary productivity is an important factor controlling the distribution of organic molecules in sediments. Moreover, rivers can bring about the distribution of large quantities of terrestrially derived organic matter to the sediments. Atmospheric transport of land derived natural compounds to the estuarine sediments can also take place. Organic matter exists in particulate and dissolved forms within the water column. Initial input of the organic matter consists of all major classes of naturally occurring organic compounds such as carbohydrates, proteins, aminoacids, pigments, phenolic substances, lipids and other constituents of living organisms (Premuzic *et al.*, 1982). During sedimentation only a small portion of this initial input in the form of large particles reaches the bottom (Wakeham and Canuel, 1986; Asper, 1987). Studies on lipids (Wakeham and Canuel, 1986) amino acids and sugars (Ittekkot *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 more dominant in relatively shallow depths (Suess, 1980). The survival of individual organic constituents during sedimentation depends on a number of factors including their chemical stability, biochemical usefulness, oxygen concentration and their interaction with clay minerals. Thus vertical transport of organic matter in the water column or in particulate material is an important source of carbon to surface sediments. After reaching the sediments, significant modification of organic matter takes places due to the activities of benthic organisms.

## 4.1 Sedimentary pigments

Chlorophyll(a,b,c), Carotenoids and pheopigments.

Three kinds of pigments are usually found in aquatic plants, animals and sediments.

(1) Chlorinoid pigments including chlorophylls and porphyrins

(2) Carotenoids including the orange pigments-carotene and xanthophylls and

(3) Flavoproteins, the yellow pigments and related N-heterocyclic substances.

The chlorophyll of living plant material is principally chlorophyll(a) ($C_{55}H_{72}MgN_4O_5 \cdot H_2O$), the fundamental structure of which has four pyrrole ($C_4H_5N$) nuclei joined in a complex called a porphyrin nucleus. Chlorophyll is a magnesium chelate complex of the porphyrins in which a double bond of the pyrrole group is saturated with two hydrogen atoms (a dehydroporphyrin)

Degradation of chlorophyll in the aquatic environment involves a two step process in which magnesium is released and a free chlorin pigment, pheophytin(a) is formed; this in turn gets complexed with another metal atom to form porphyrin. The transformation of chlorophyll(a) to pheophytin(a) involves replacement of Mg by two hydrogen atoms, a change which is thought to be brought about either by the acidic digestive fluids of herbivores (feeding on the phytoplankton and other aquatic vegetation) or by the action of bacteria.

Chlorophyll(b) differs from chlorophyll(a) in the presence of an aldehyde (CHO) group in place of (3 position) the methyl group of chlorophyll(a). Chlorophyll(a) is about 2.5 times more abundant in leaves of green plants than chlorophyll(b). Chlorophyll(c), chlorophyll(d) and bacterio chlorophyll are relatively scarce.

Chlrophyll(a) predominates over the other chlorinoid pigments in all the plants. Chlorophyll(a) constitutes approximately 1 to 2% of the dry weight of organic material in all planktonic algae and is the preferred indicator for algal biomass estimation. Chlorophyll content of cells varies with species or taxonomic groups and is affected by age, growth rate, light and nutrient condition.

Carotenoids are defined as yellowish red pigments of aliphatic or alicyclic structure, composed of isoprene units (Karrer and Jucker, 1950). Carotenoids are ubiquitous in nature, occur in all green plant tissues and are an integral element of the photosynthetic process. They can be found in some non-photosynthetic bacteria and fungi as well. The occurrence of carotenoids in lake sediments was first reported by Lyubimebko (1923) and in marine sediments by Trask and Wu (1930). Carotenoids were shown, both theoretically and experimentally, to be the probable precursors of such aromatics as toluene and xylene. About twenty different carotenoids have been indentified in sediments. Vallentyne (1957) identified $\beta$-carotenoid from the Searless Lake sediments.

Organic pigments, chlorophyll(a), carotenoids and pheopigments are considered as organic markers which provide information on the chemotaxonomic and the physiological state of phytoplankton population and more generally on the extent of degradation of algal derived organic matter (Jeffrey, 1974; Johansen *et al.*, 1974; Goodwin, 1976; Liaaen-Jensen, 1977; Mantoura and Llewellyn, 1983; Klein and Sournia 1987; Vernet and

Lorenzen, 1987). Documented evidence on the distribution of chlorophyll(a) and its pheopigments showed that most of the studies were related to water bodies.

Studies on the organic pigments in marine or estuarine sediments are very few (Orr and Grady, 1957; Glasby and Hodgson, 1971; Tietjen, 1968; Engstrom *et al.*, 1985; Swain, 1985; Heffernan and Gibson, 1983; Yang and Hong, 1988). Jacob and Qasim (1974) reported on chlorophyll(a) and pheopigment present in the mud- bank area of Alleppey. No report is available on organic pigments (chlorophyll a, b, c), carotenoids and pheopigments of the sediments of this area. The present study was undertaken to fill up this void by estimating the concentration levels of chlorophyll (a, b, c) carotenoids and pheopigments to assess the water quality as well as the nutritive value of the sediments.

The sedimentary pigments probably originated from a variety of sources such as offshore transport of sediments, degradation of phytoplankton from the overlying water column, fecal pellet transport and other surface to bottom linkages.

Materials and methods used for these studies are presented in Chapter 2.

Monthly variations of chlorophyll (a, b, c), carotenoids and pheopigments in the sediments of the Cochin estuary at Stations 1 - 11 are given in appendix. Seasonal variations of chlorophyll (a,b,c), carotenoids and pheopigments at these stations are given in Figs. 4.1 - 4.5.

Monthly values of chlorophyll(a) at the riverine Stations (1-4) in the southern arm of the estuary were lower than that at the estuarine Stations (5,6 and 7). The values of chlorophyll(a) ranged from 0.00 to 3.09 μg g$^{-1}$ at Station 1, from 0.39 to 2.75 μg g$^{-1}$ at Station 2, from 0.14 to 17.23 μg g$^{-1}$ at Station 3 and from 0.28 to 6.90 μg g$^{-1}$ at Station 4. The estuarine stations showed a minimum of 0.78 μg g$^{-1}$, 3.57 μg g$^{-1}$ and 13.95 μg g$^{-1}$ and a maximum of 22.82, 25.73 and 37.77 μg g$^{-1}$ at Stations 5, 6 and 7 respectively. In general, the minimum chlorophyll(a) content was observed during monsoon and maximum during post- and premonsoon periods. In the northern arm of the estuary, the monthly values varied from 19.29 to 93.47μg g$^{-1}$ at Station 8, from 28.8 to 119.54 μg g$^{-1}$ at Station 9, from 0.42 to 11.62 μg g$^{-1}$ at Station 10 and from 5.35 to 15.09 μg g$^{-1}$ at Station 11. In contrast to the southern arm, increased concentrations of chlorophyll(a) were noticed in the northern arm. It was also observed that, in general, chlorophyll(a) concentration was low at all riverine stations. Monthly data indicated that the pigments were widely distributed in the sediment column and variations were noticed with respect to time and space.

Chlorophyll(a) is an ubiquitous pigment and can be used as global algal biomass indicator. At all stations except 8 and 9, chlorophyll(a) showed clear seasonal and spatial variations in its concentration exhibiting a primary peak during post monsoon and another during premonsoon. All through the

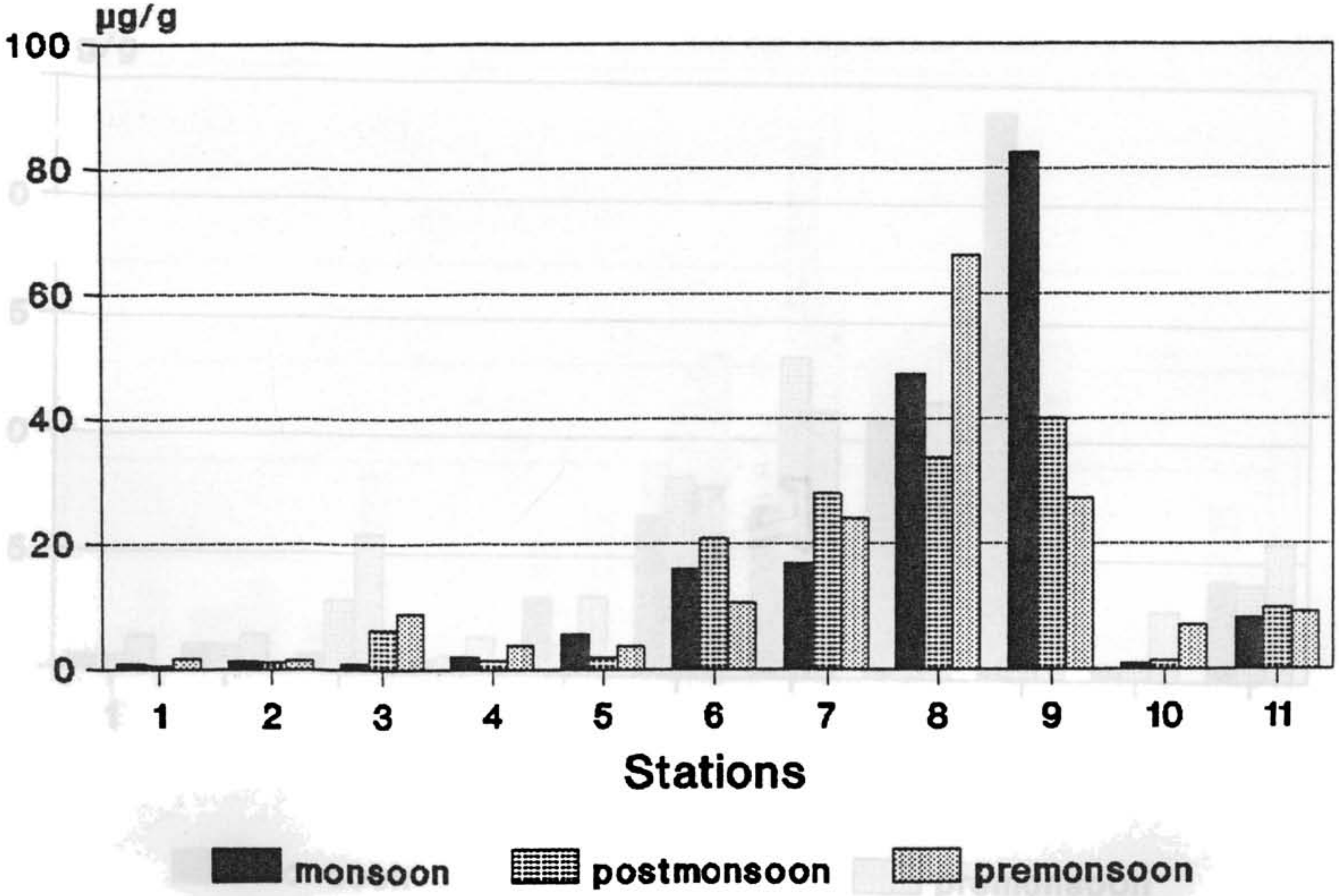

Fig. 4.1 Seasonal distribution of sedimentary chlorophyll a

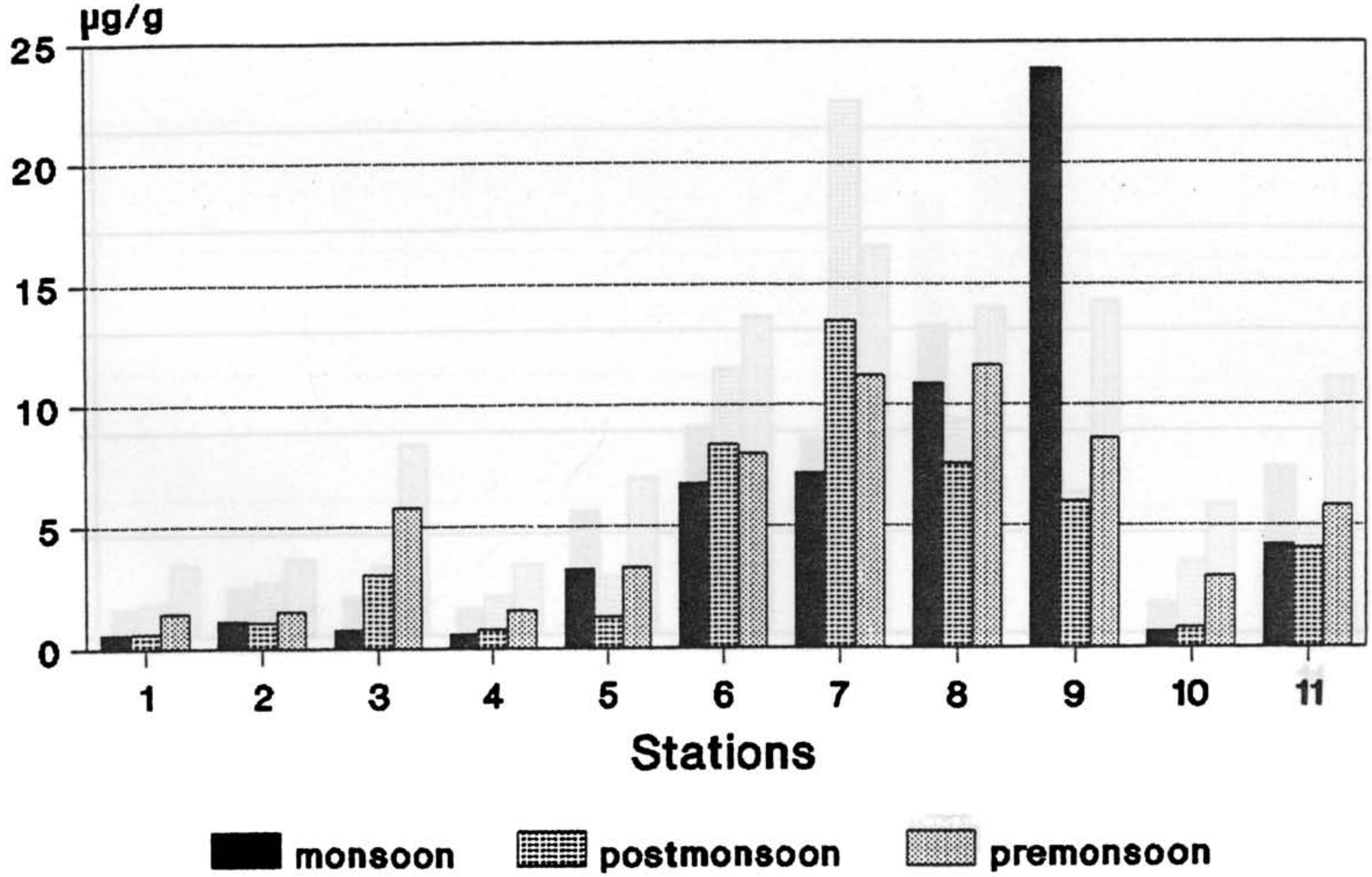

Fig. 4.2 Seasonal distribution of sedimentary chlorophyll b

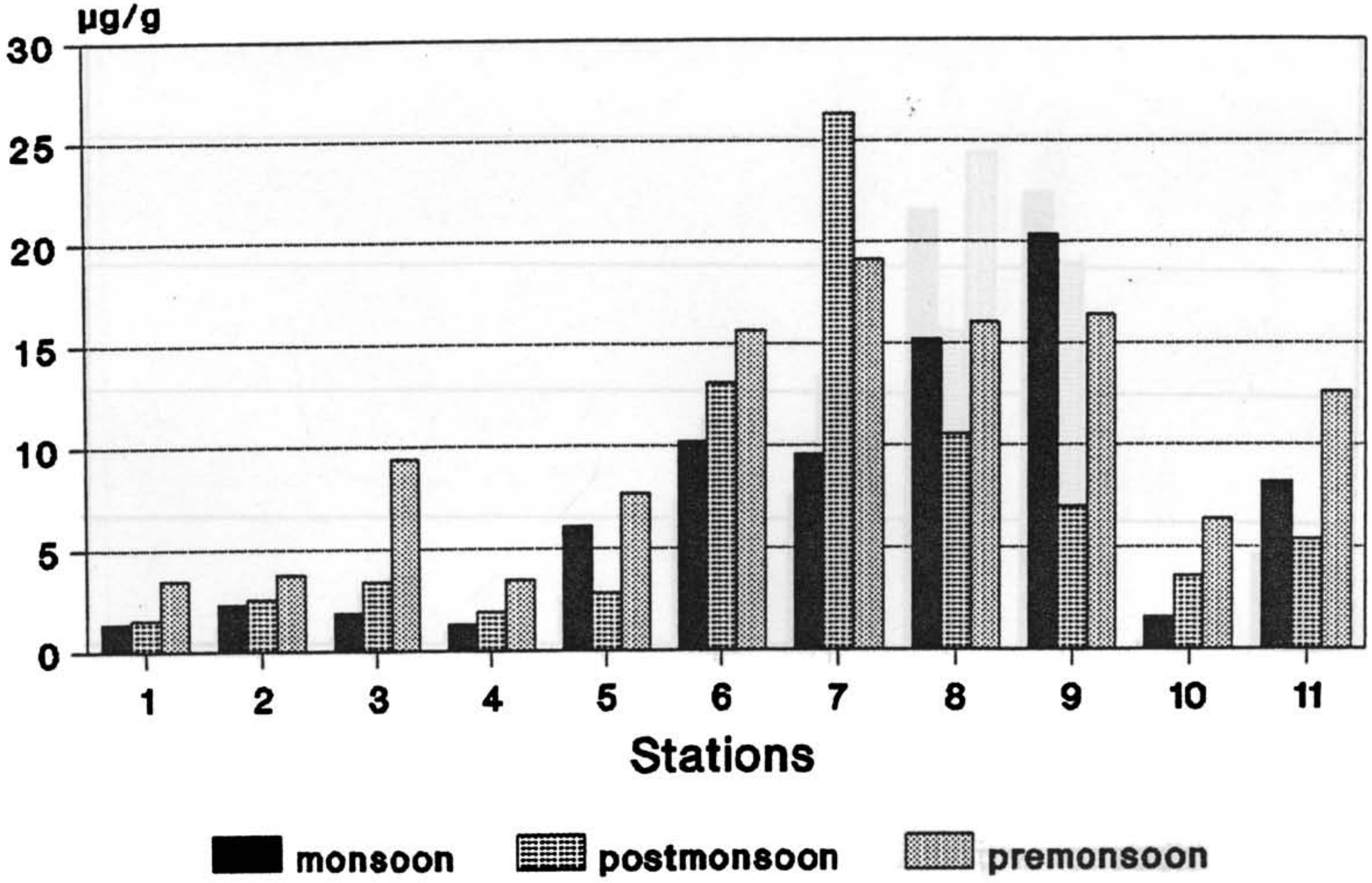

Fig. 4.3 Seasonal distribution of sedimentary chlorophyll c

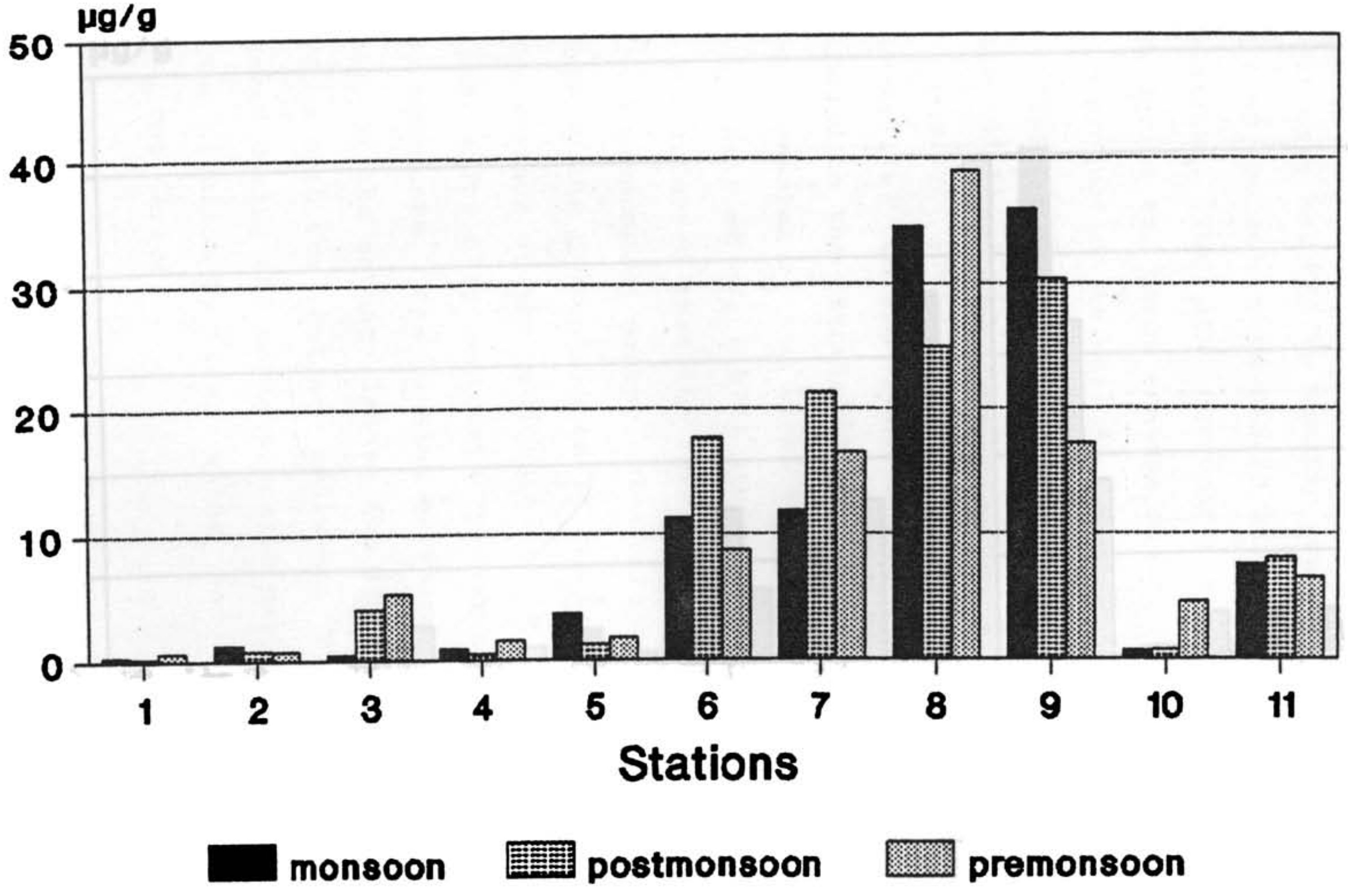

Fig. 4.4 Seasonal distribution of sedimentary carotenoids

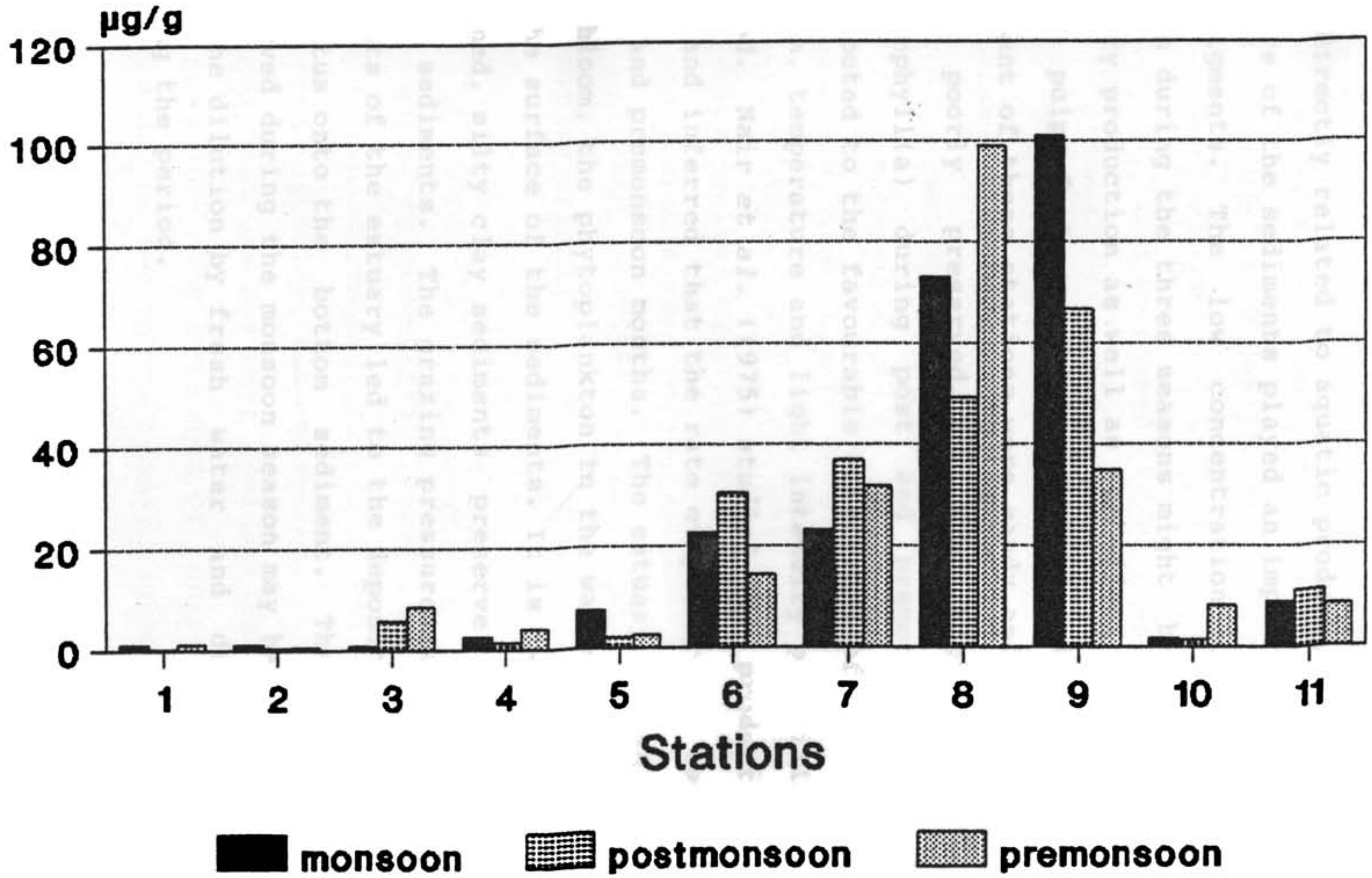

Fig. 4.5 Seasonal distribution of sedimentary pheopigments

seasons, the levels were lower at the riverine stations than at the estuarine ones. The pigment concentrations in the sediment were directly related to aquatic productivity. In addition, the texture of the sediments played an important role in preserving the pigments. The low concentration of pigments in these region during the three seasons might be the result of low primary production as well as the effect of effluent from the paper pulp factory which inhibits plankton growth. The sediment of these stations were sandy and hence the pigments were poorly preserved. The high concentration of chlorophyll(a) during post and premonsoon period may be attributed to the favourable conditions of salinity, dissolved oxygen, temperature and light intensity prevailing during this period. Nair *et al.* (1975) studied the productivity of this lake and inferred that the rate of production was high during post and premonsoon months. The estuary was shallow and after the bloom, the phytoplankton in the water column got deposited on the surface of the sediments. It is well known that fine grained, silty clay sediments preserve pigments better than sandy sediments. The grazing pressure as well as the tidal effects of the estuary led to the deposition of more and more detritus onto the bottom sediment. The lower concentration observed during the monsoon season may be due to the turbulence and the dilution by fresh water and decrease in insolation during the period.

The northern arm of the estuary (Stations 8 and 9) showed a higher concentration of chlorophyll(a) during the monsoon period. Pillai (1989) studied the siltation in this region and reported that these Stations formed a "sheltered sedimentary environment". The high values of chlorophyll(a) observed in this region during monsoon months may be associated with the accumulation of sedimentary pigments carried by the river runoff and deposited in this "sheltered sedimentary environment". The increased value also reflected the high primary productivity that occurred during the premonsoon period. A decrease in the concentration of chlorophyll(a) in the sediment was observed during the other seasons, as compared with the monsoon season. This can be explained either as the result of the termination of algal bloom in this locality accompanied by high organic load or the decomposition of algae when it reached the bottom sediment. Stations 10 and 11 were fresh water regions (Station 11 being an effluent receiving site) and showed higher concentration of pigments compared with other riverine stations. This may be due to the high productivity stimulated by a higher nutrient (phosphate) content.

Although chlorophyll(a) generally occurred in greater quantity than chlorophyll(b) and chlorophyll(c), a similar behavioural profile was observed for all the fractions. Chlorophyll(a) was the most dominant while chlorophyll(b) was least dominant. The dominance of chlorophyll(c) at riverine stations may be due to the clear succession of diatoms and dinoflagellates in the environments.

The sediment concentrations of carotenoids were much lower than those of the chlorinoid pigment chlorophyll(a). Both chlorophyll(a) and carotenoids are well known as biogeochemical fossils and appear to be universally present in organic fresh, marine and estuarine sediments. Investigations in the past decade have shown that plant pigments preserved in the sediments may indicate lake productivity. Belcher and Fogg (1964) suggested that the ratio of chlorophyll derivatives to carotenoids in the sedimentary column might reflect changes in lake fertility. The great diversity of sedimentary pigment is partly a consequence of decomposition. Among the factors affecting diversity, source material has the most pronounced influence, particularly on carotenoids. Decaying aquatic organisms yeild a large array of carotenoids while terrestrial detritus is low in diversity. Decomposing algae sinking to the bottom exhibit a sharp increase in pigments over fresh undecomposed algae.

## Pheopigments

The distribution pattern of pheopigments in the surficial sediments generally followed that of organic carbon and chlorophylls. Pheopigments, being mostly Mg-free decomposition products of chlorophylls, are an index of the physiological state of phytoplankton and the concentrations are governed by the intensity of light and grazing pressure (Nakajima, 1973). The riverine region of the southern arm of the estuary, exhibited a lower seasonal concentration of pheopigments. A general increase was observed in the pheophytin content from riverine to estuarine stations. Sediments with a higher content of silt and clay contained larger amounts of the pigments than the sandy sediments. In the southern arm of the estuary, the pheopigment concentration was highest during post and premonsoon periods while low values were observed during monsoon period.

In the northern arm, the pheopigment behaved in a different manner. In the riverine zone, at Station 10, a low concentration of pheopigment was observed during the monsoon period but it increased during the post- and premonsoon seasons. At Station 11 also the lowest concentration was observed during the monsoon period (8.98 $\mu g\ g^{-1}$), whereas the highest concentration of 11.19 $\mu g\ g^{-1}$ was observed during postmonsoon, the premonsoon values being intermediate (10.41 $\mu g\ g^{-1}$). The highest concentration of pheopigment at Stations 8 and 9 was observed during post monsoon and monsoon periods respectively. The lowest value was observed during postmonsoon at Station 8. During premonsoon, pheopigment values recorded a higher concentration at the northern part of the estuary, as compared with southern part. The values reported in this study were slightly higher than those of the Chinhae Bay measured by Cho *et al.*, (1982) (7.6 to 48.2 $\mu g\ g^{-1}$). The observed values of pheopigment in the Cochin estuary were much higher than Deulkryang Bay and Kasmayyang Bay where the values ranged between 2.3 and 5.0 $\mu g\ g^{-1}$, from 2.5 to 5.8 $\mu g\ g^{-1}$ respectively (Cho *et al.*, 1982 b).

Previous studies on pheopigment in aquatic ecosystems were primarily concerned with their depth distribution. Gorham (1960) found from sediment traps that chlorophyll is decomposed before dead algal materials got deposited on sediment surfaces. Brown *et al.*, (1964) found an increase in chlorophyll degradation products with depth in the euphotic zone. In marine waters, Patterson and Parsons (1963) found appreciable amounts of pheopigments in net-tows with slightly higher pheophorbide than pheophytin; the latter was found in sea water samples. Yentsch (1965) found that pheopigments increased with depth in the photic zone. The temporal distribution of pheopigments was studied by Leach (1970) who found that the percentage in intertidal mudflat sediments was higher in winter than the other seasons.

Processes affecting the concentration of chlorophyll and pheopigment in the sedimentary environment include phytoplankton growth, zooplankton grazing, cell sinking, physical mixing and advective transport. It is well known that grazing on microbial population by herbivores result in the production of chlorophyll degradation products (pheopigments) as a residue. Pheopigments may be produced by herbivores of wide size range (Levi and Wyatt, 1971; Daley, 1973) whose fecal material might not remain confined to the water column. Pheopigments that are packaged into fecal pellets by large crustacean grazers exhibit short residence times in the water column due to their rapid sinking rates. (Lorenzen and Welschmeyer, 1983). Pheopigment may also be produced by bivalves (Moreth and Yentch, 1970; Gelder and Robinson ,1980). The above processes fully justified the occurrence of high concentrations of pheopigments in the estuarine environment.

High productivity and high grazing pressure established an equilibrium maximum, resulting in an effective production of organic material. In this condition effective uptake of phytoplankton by organisms would produce large amounts of pheophytin in the fecal pellets, which would easily sink to the bottom because of their larger size. Moreover, ambient tidal effects and hydrological conditions facilitate the settling of phytoplankton onto the sediment. The results of the present study indicated that pheopigment constituted more than 50% of chlorophyll. This significantly high amount of pheopigment in these sediments were not unexpected, since these areas offerred conditions favourable to the formation of detrital chlorophyll. Qasim and Sankaranarayanan (1972) reported settling of high amount of detritus during post and premonsoon periods. The relatively weak currents favoured the deposition of allochthonous materials. The dead plant materials were retained and under the influence of biological activity, the conversion of chlorophyll to pheopigment would have taken place. Kemp and Lewis (1968) found that values of chlorophyll degradation products in the east basin sediment was twice that in the other basins, with little undegraded chlorophyll.

The lower values of pheopigments observed at the southern part of the estuary during the monsoon months might be the result of the low primary productivity of the overlying water and dilution of the sediment by high runoff. Contrary to this, in the northern arm, Stations 8 and 9 showed a peculiar nature. The highest concentration of pheopigment during monsoon months would have been a consequence of the formation of the "sheltered sedimentary enviromnet" (Pillai, 1989), where the sediments containing pheopigment were deposited and preserved due to the silty clay or clayey silt nature of the sediment. It is well known that the organics are best adsorbed and preserved in finer grained sediments. Although production was high in these regions (Nair *et al.*, 1975), the lower values of pheopigment at Station 9 could be due to the decomposition of organic material or to the biotransformation of these compounds to other organic compounds or the result of low productivity due to pollution caused by retting of husks.

Ratios of chlorophyll(a) to chlorophyll(c) and that of chlorophyll(a) to carotenoids indicated the physiological state of phytoplankton. For a healthy crop they usually had values greater than unity (Ketchum *et al.*, 1958; Bhargava, 1973; Desai *et al.*, 1984; Jiyalal Ram *et al.*, 1984). The ratios of chlorophyll(a) to chlorophyll(b), chlorophyll(a) to chlorophyll(c), chlorophyll(a) to carotenoids and chlorophyll(a) to pheopigments are given in Table 4.1. Ketchum *et al.* (1958) have reported chlorophyll(a)/ chlorophyll(b) ratio (ranging between 2.8 to 3.0) for various cultures of phytoplankton. The variation in the ratio, 0.97 to 5.72, observed in the present study might be due to the presence of a composite group of phytoplankton in the sediment instead of a pure culture.

Because of the faster degradation of carotenoids than chlorophyll, the ratio of chlorophyll to carotenoids has been

Table 4.1. Seasonal variation of chl a : chl b, chl a : chl c, chl a : ctd, chl a : pheo pigments.

| Stations No: | Season | Chla/Chlb | Chla/Chlc | Chla/Ctd | Chla/Pheo |
|---|---|---|---|---|---|
| 1 | A | 1.64 | 0.73 | 2.83 | 0.98 |
|  | B | 0.97 | 0.39 | 2.54 | 2.14 |
|  | C | 1.19 | 0.50 | 2.73 | 1.55 |
| 2 | A | 1.25 | 0.63 | 1.12 | 1.21 |
|  | B | 1.06 | 0.44 | 1.42 | 2.73 |
|  | C | 0.94 | 0.39 | 1.98 | 2.60 |
| 3 | A | 1.23 | 0.50 | 2.20 | 1.07 |
|  | B | 2.08 | 1.85 | 1.56 | 1.09 |
|  | C | 1.54 | 0.95 | 1.69 | 1.05 |
| 4 | A | 3.33 | 1.65 | 2.33 | 0.79 |
|  | B | 1.89 | 0.78 | 2.83 | 1.02 |
|  | C | 2.46 | 1.10 | 2.50 | 0.97 |
| 5 | A | 1.74 | 0.94 | 1.52 | 0.76 |
|  | B | 1.54 | 0.70 | 1.58 | 0.91 |
|  | C | 1.13 | 0.49 | 2.09 | 1.47 |
| 6 | A | 2.38 | 1.57 | 1.41 | 0.71 |
|  | B | 2.50 | 1.60 | 1.18 | 0.69 |
|  | C | 1.34 | 0.68 | 1.23 | 0.75 |
| 7 | A | 2.36 | 1.78 | 1.43 | 0.73 |
|  | B | 2.08 | 1.07 | 1.31 | 0.76 |
|  | C | 2.15 | 1.26 | 1.46 | 0.76 |
| 8 | A | 4.34 | 3.10 | 1.36 | 0.64 |
|  | B | 4.48 | 3.20 | 1.35 | 0.68 |
|  | C | 5.69 | 4.12 | 1.70 | 0.67 |
| 9 | A | 3.46 | 4.05 | 2.30 | 0.82 |
|  | B | 6.69 | 5.73 | 1.32 | 0.60 |
|  | C | 3.17 | 1.66 | 1.58 | 0.78 |
| 10 | A | 1.49 | 0.65 | 1.40 | 0.60 |
|  | B | 1.77 | 0.40 | 1.95 | 1.01 |
|  | C | 2.44 | 1.11 | 1.54 | 0.87 |
| 11 | A | 1.97 | 1.03 | 1.11 | 0.93 |
|  | B | 2.42 | 1.83 | 1.22 | 0.88 |
|  | C | 1.57 | 0.73 | 1.41 | 1.10 |

A-Monsoon, B-Postmonsoon, C-Premonsoon

used both as an index of the quality of preservation in sediments and as an index of the relative input of the allochthonous organics, in which, pigments are poorly preserved (Sanger and Graham, 1972). High chlorophyll to carotenoid ratios are expected in oligotrophic lakes, because poor preservation and relatively high allochthonous inputs tend to be correlated with oligotrophy. Indeed, oligotrophic lakes exhibited high ratio while eutrophic lakes showed low values (Gorham *et al.*, 1974; Santelmann, 1981; Swain, 1985).

Seasonally, the ratio of chlorophyll(a)/carotenoid varied between 1.11 to 2.83. The estuarine regions had a maximum of 2.30, while the riverine zone recorded high ratios ranging from 1.12 to 2.83. Higher ratios could be the result of the higher proportion of allochthonous organics (which possessed high chlorophyll/carotenoid values) than the oligotropic sediment (Sanger and Gorham, 1972; Gorham and Sanger, 1976). Gorham and Sanger (1976) also pointed out that changes in kinds of phytoplankton or macrophytes could cause chlorophyll/carotenoid values to vary to an unknown extent. Such chlorophyll/carotenoid changes might correlate with trophic state, yet not be caused by changes in preservation conditions. Sanger and Crowl (1979) interpreted low ratios as an indication of enhanced preservation conditions concomitant with high primary production, but interpreted high ratios as indicating greater allochthonous inputs. The result of this study was in unison with the above finding and suggested that the high value reflected a greater proportional input of allochthonous detritus and possibly a greater degree of aerobic decomposition of the autochthonous sedimentary organic matter, both being compatible with shallowing and invasion of the lake by wetland vegetation. The result was also in agreement with the nature of organic carbon in the area. In general, the present study revealed a greater accumulation and preservation of sedimentary pigment in the estuarine region than the riverine region where primary production and allochthonous materials were low.

Vallentyne (1957) reported that extracts of sedimentary pigments contained chlorophyll degradation products as well as chlorophyll(a). Although most of the chlorophyll in healthy plant tissue was cholorophyll(a), its degradation products might be relatively more abundant in the sediment. In estuarine regions, a large portion of the plant detritus from both plankton and benthos was ultimately deposited on the bottom where it became a potential food source for bacteria and other benthic organisms whose feeding activities could possibly convert the chlorophyll to pheopigments (Currie, 1962).

The chlorophyll(a)/pheopigment ratios ranged from 0.60 to 0.91 at estuarine stations whereas in the riverine region it ranged from 0.60 to 2.73. The ratios in the estuarine region were significantly lower than that of the riverine stations. The data indicated that pheopigments constituted the major fraction of the pigments in estuarine sediments. This might suggest that the dead plant material was retained in the sediment and might come under the influence of biological activity which brought about the conversion of cholorophyll to pheopigments. Comparison of the chlorophyll/ pheopigment ratio and relative amount of chlorophyll and degradation products showed that sediments generally contained more pheopigments than chlorophyll. Patterson and Parsons (1963) observed that 93% of the pigment in a littoral mud sample from the Pacific Ocean was pheopigment and Moss (1967) noted that acetone extracts of fresh water muds of two English Ponds contanied 53 and 55% respectively of the degraded pigment. The pigment data, of this study indicated that sedimentary environments of estuarine region provided more favourable condition for deposition of detritus because of the higher quantities of organic matter, lower redox potential, smaller media grain size and silt-clay content in the sediment

## 4.2 Carbohydrates

Organic matter exists in particulate and dissolved forms within the water column. Initial input of the organic matter consists of all major classes of naturally occurring organic compounds such as carbohydrates, proteins, aminoacids, pigments, phenolic substances, lipids and other constituents of living organisms (Premuzic *et al.*, 1982). During sedimentation only a small portion of this initial input in the form of a large particles such as fecal pellets or "marine snow" reaches the sediment floor (Deuser and Ross,1980; Honjo,1982; Wakeham and Canuel,1986; Asper,1987). Biochemical and transformation processes acting on rapidly sinking particles in the water column are dominant in relatively shallow depths (Suess, 1980; Liebezeit, 1985). The survival of individual organic constituents during sedimentation depends on a number of factors including their chemical stability, biochemical usefulness, oxygen concentration and their interaction with clay minerals (Premuzic *et al.*, 1982; Stein *et al.*,1986; Degens and Ittekkot, 1984). Vertical transport of organic matter in the water column in particulate material is an important source of carbon to the surface sediment. After incorporation into the sediment, significant alteration of organic matter takes place due to the activities of benthic organisms. Carbohydrates are the main components of the sedimentary organic carbon. Many of them are labile and rapidly recycled and are also known to influence various biogeochemical processes occurring in the aquatic environment.

Carbohydrates are polyhydroxy aldehydes, polyhydroxy ketones, or compounds that can be hydrolysed to these compounds. Carbohydrates form an important reactive fraction of organic matter in sediment and water where they exist as several classes: monosaccharides, oligosaccharides, polysaccharides and saccharides bound to humic substances.

Carbohydrates are the most abundant class of compounds produced in the biosphere. Generally they are linked together into polymers, and there are several important polymeric sugars that decompose and enter into the aquatic system. The important plymers include amylose, and hyaluronic acid. Another important polysaccharide that may be present in the aquatic system is alginic acid which is a component of algae and kelp. All of these biopolymers are susceptible to degradation, both chemical and biochemical, and are important sources of monosaccharides and polysaccharides in aquatic environment.

The majority of the cabohydrates in fresh water orginate in terrestrial systems, i.e. from plants after death and dryout and may release 30% of the organic matter into water (Dahm 1981; Caine, 1982). Half of this material is simple carbohydrate, probably monosaccharides and polysaccharides, the remaining half being organic acids rich in cabohydrates. Thus water leachates of plant matter is an important source of carbohydrates in water.

On the other hand, soils contain cabohydrate-rich organic debris not readily soluble in water and Stevenson (1982) stated that as much as 5 to 25 percent of soil organic matter is cabohydrate, including amino sugars, uronic acids, hexoses, pentoses, cellulose and its derivatives. The enzymatic hydrolysis of polysaccharides by soil microbes releases simple monosaccharides and oligosaccharides into soil solutions, which are flushed from soil, during wet seasons, into streams and rivers. Because simple sugars are easily utilised by soil organisms such as bacteria, mould and fungi, they are a reactive fraction and are continually released and used. Thus plant and soil organic matter are important contributors to carbohydrates in water. In aquatic systems, such as large lakes and oceans, algae are the important source of carbohydrates. Carbohydrate concentration correlates closely to algal population and usually concentration of carbohydrate increases with depth as the algal population decreases. Spatial and temporal variation in the carbohydrates were reported in different water systems (Romankevich,1984; Thurman, 1985). The study of carbohydrate in lake sediments has been very meagre and hence this work was undertaken to gather information on the abundance and distribution of total carbohydrate in the sediments of the Cochin estuary.

Monthly data of total carbohydrate in the sediments at Stations 1-11 are given in appendix and the seasonal variation of carbohydrate is depicted in Fig. 4.6. Carbohydrate content in the sediment samples showed large variation between stations. The monthly value of carbohydrate of the riverine stations in the southern arm ranged from 0.53 to 3.23 mg $g^{-1}$ at Station 1, from0.79 to 6.08 mg $g^{-1}$at Station 2,from 0.75 to 20.26 mg $g^{-1}$ at Station 3, from 0.64 to 3.36 mg $g^{-1}$ at Station 4 and from 0.53 to 1.83 mg $g^{-1}$ at Station 5, while in the estuarine region an increased concentration of carbohydrate was noticed and the value varied between 2.1 to 13.64 mg $g^{-1}$ at Station 6 and between 4.48 to 13.52 mg $g^{-1}$ at Station 7. The northern part of the estuary showed higher contents of carbohydrate ranging from 5.35 to 15.98 mg $g^{-1}$ and from 4.15 to 22.86 mg $g^{-1}$ at Stations 8 and 9 respectively. Again in the riverine region a lower concentration ranging from 0.29 to 4.01 mg $g^{-1}$ at Station 10 was observed. However, Station 11 showed an abnormally higher concentration ranging from 0.33 to 15.5 mg $g^{-1}$.

Carbohydrate was widely distributed along the sedimentary environment and showed clear spatial and seasonal variations.

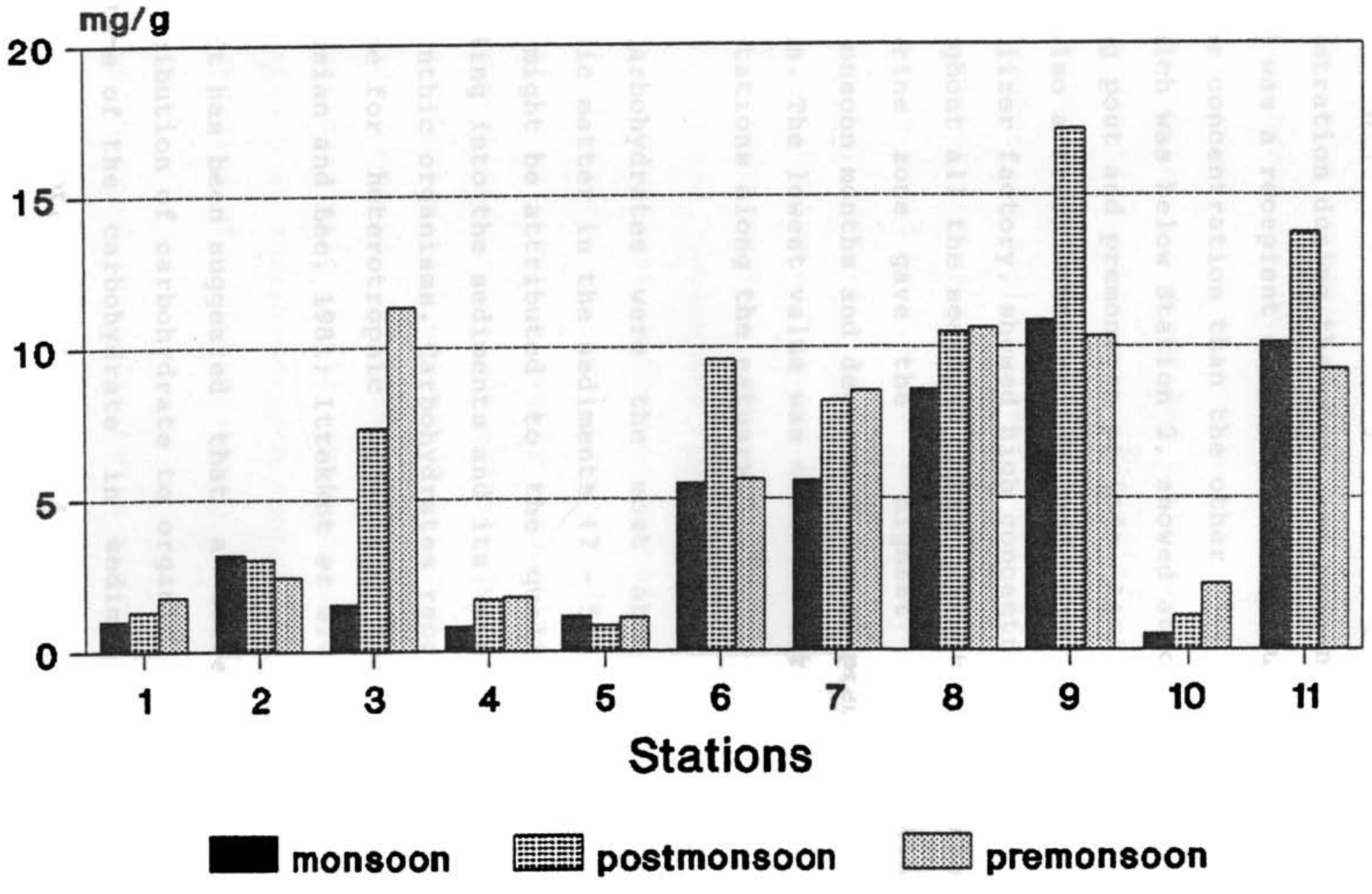

Fig. 4.6 Seasonal distribution of sedimentary carbohydrates

All the riverine stations showed seasonal variations exhibiting lower concentration during the monsoon months and higher concentration during the post- and premonsoon months. Station 2 which was a recepient of paper mill effluent showed relatively higher concentration than the other riverine stations. Station 3, which was below Station 2, showed abnormally higher values during post and premonsoon periods. Again, Station 11, which was also a fresh water region and the discharge site of a fertilizer factory, showed high concentration of carbohydrates throughout all the seasons. The carbohydrate level at the estuarine zone gave the highest concentration during postmonsoon months and decreased during premonsoon and monsoon months. The lowest value was observed during monsoon months at all Stations along the estuary.

Carbohydrates were the most abundant fraction of the organic matter in the sediments (7 - 58% of organic carbon). This might be attributed to the quality of organic matter settling into the sediments and its subsequent transformation by benthic organisms. Carbohydrates represent an important food source for heterotrophic organisms and is rapidly recyled (Gagosian and Lee, 1981; Ittekkot *et al.*, 1984).

It has been suggested that a decrease in the relative contribution of carbohydrate to organic carbon reflected the nature of the carbohydrate in sediments or the extent of selective biotransformation of the carbohydrate compared to the other organic compounds. (Klok *et al.*, 1984 a, b). The observed low values of carbohydrates (at Stations 1-11) during the monsoon months compared to other seasons suggested that it was related to the dilution of both allochthonous and autochthonous organic matter by minerals and clays from upstream areas due to increased rate of erosion. In addition to this, a reduction in autochthonous input was expected during monsoon months since reduced light penetration, turbulance and high sediment discharge would result in a decrease in primary production. The observation was in agreement with the findings of Ittekkot and Arain (1986). The highest concentration of total carbohydrates observed in the estuarine system in post or premonsoon could be due to the combined effect of several contributory factors: high productivity, transport of organic matter (estuarine and terrestrial), anthropogenic input, high rate of sedimentation and decomposition (both aerobic and anaerobic) and subsequent preservation due to the ambient condition prevalent in the ecosystem such as pH, salinity, dissolved oxygen, Eh etc. Nair *et al.* (1975) suggested that the Cochin estuary was highly productive and showed two peaks during post and premonsoon months. Qasim and Sankaranarayanan (1972) reported high amount of detritus during the post and premonsoon months. In addition to this, decay and decomposition of floating plants in the estuarine region (Stations 6,7,8 and 9) during post and premonsoon contributed to an increase in concentration of carbohydrates.

The observed irregularity in the levels of carbohydrates at the riverine Stations 2 and 3 might be the result of settling and decomposition of paper mill effluent. The high concentration of carbohydrates at Station 3 was perhaps, due to the decomposition of leafy material from mangrooves as well as the deposition of the remains of wood containing carbohydrate materials. Station 11 showed higher concentration during all the seasons with a marginal increase during postmonsoon months; this may be due to biogenic production caused by nutrient rich water. High organic production in the area was also recorded by Joy *et al.*(1990).

Grain size of the sediment plays a pivotal role in controlling the distribution of organic compounds. Concentration levels of carbohydrates at the riverine Stations (1, 2, 3, 4, 5 and 10), where the sediment was sandy, was low as compared with estuarine Stations 6, 7, 8, and 9, where the sediment was fine grained (sand silt clay, silty-clay or clayey silt). The association of organic matter with smaller grain size was a well known phenomenon (Erlenkeuser *et al.*, 1981; Joctear- Monrozier *et al.*, 1983; Liebezeit, 1986). The reason for this was the high surface area and the high adsorptive capacity of the fine grained sediments (Hunt, 1963; Suess 1973).

The ratio of carbohydrate/sediment organic carbon showed that the estuarine values were below 20 and in riverine region it was higher. It suggested that the carbohydrates in the estuarine sediments were mainly of autochthonous origin while in the riverine it was allochthonous. The data presented indicated that upto 32% of organic carbon existed as carbohydrate carbon and that microbial/planktonic communities of the systems were more important in controlling the carbohydrate in the sedimentary environment.

In the present study, all the sediments showed high concentration of carbohydrate. The carbohydrate concentration in the sediment could be used to identify the origin of organic carbon in the sediment. Although carbohydrate was widely present in organisms contributing to the organic matter of estuarine sediments and hence did not appear to be useful as markers for organic carbon origin, a number of studies have been undertaken to link sedimentary carbohydrates with possible sources. Ratios such as mannose/xylose, glucose/ribose and glucose/galactose have been used to distinguish between terrestrial and marine sources (Cowie and Hedges, 1984; Ittekkot and Arian, 1986; Liebezeit, 1986). Cowie and Hedges (1984) suggested a further possible means for distinguishing these geographic sources through total carbohydrate yields. He suggested that terrestrial vascular plant tissues yielded significantly more (> 20%) carbohydrate (normalized to organic carbon content) than either plankton or bacteria. This inference was quite reasonable because vascular land plants were the only important source to have carbon normalized total carbohydrate yields >20% and because diagenesis of this or any other organic material should result in less yields.

Carbon-normalized total carbohydrate yields for the surficial sediments of the Cochin estuary varied from 21.66 to 65.45 mg total carbohydrate per 100 mg organic carbon and hence indicated the presence of terrestrially derived vascular plant remains in the sediment

## 4.3 Lipids and proteins

### 4.3.1 Lipids

Lipids are heterogenous substances of biological origin, insoluble in water but soluble in fat solvents such as ether, benzene or chloroform. Lipids are classified into simple lipids, compound lipids and derived lipids. All the forms of lipids are widely distributed in the sediments. The obvious sources of lipids are plant and animal residues and the soil microbial population. Large amounts of plant litter are continually being deposited on the surface of the soil and are potential sources of a wide variety of lipids.

Although the composition of organic matter in estuarine/ marine sediment has been a subject of study for several decades, there are only few instances of detailed analyses (Degens *et al.*, 1984; Bordovskiy, 1965; Hatcher *et al.*, 1982; Klok *et al.*, 1984a). A survey on the distribution and abundance of some biochemical compounds in the sediments of the Bay of Bengal and shelf and slope regions of the west coast of India has been reported by Bhosle and Dhople (1988) and by Bhosle *et al.*, (1978) respectively. Studies on the lipid concentrations in the sediments of estuarine system are very scanty. With reference to the Cochin estuarine region no reports are available at all. Hence an attempt has been made to gather information on the abundance and temporal variation of lipids as well as protein in the aquatic environment around Cochin.

The monthly data of total lipid at the different stations are presented in appendix. The total lipid concentration at the riverine stations, varied from 0.04 to 0.42 mg $g^{-1}$ at Station 1, from 0.07 to 1.00 mg $g^{-1}$ at Station 2, from 0.07 to 3.18 mg $g^{-1}$ at Station 3, from 0.03 to 0.50 mg $g^{-1}$ at Station 4 and from 0.04 to 0.40mg $g^{-1}$ at Station 5. In the estuarine region of the southern arm, the lipid level ranged between 0.30 and 1.46 mg $g^{-1}$ at Station 6, and 0.15 to 2.12 mg $g^{-1}$ at Station 7. In the northern arm of the estuary, the estuarine stations showed a minimum concentration of 0.80 mg $g^{-1}$ and 0.36 mg $g^{-1}$ and a maximum concentration of 2.21 mg $g^{-1}$ and 5.22 mg $g^{-1}$ at Stations 8 and 9 respectively. Again at the riverine zone the lipid level varied from 0.05 to 0.30 mg $g^{-1}$at Station 10 and from 2.29 to 10.14 mg $g^{-1}$ at Station 11 which was a discharge receiving site. The high concentration of lipid level observed at Station 11 was perhaps due to the interference of grease and oil which got accumulated into sediment. Therefore in the present study, the lipid values obtained at Station 11 were discarded. In general, higher values of total lipids were registered at the estuarine region as compared with riverine region.

Lipid in the surficial sediments are probably part of a common pool of organic matter which in most cases, is cycled by microorganisms at a rapid rate relative to the rate of burial. Biochemical and chemical alteration of these lipids appears immediately. Lipid is widely distributed in the sediments and its abundance depends on the environmental conditions such as production, anthropogenic inputs etc.

The seasonal variation of lipids along Stations 1 to 11 is presented in Fig. 4.7. Although, lipid was present in all the sediment samples studied, low values were registered at the riverine zone compared to the estuarine region. No seasonal variation of lipid was observed at the riverine Stations (except at Stations 2 and 3) while the lipid varied seasonally in the estuarine regions. The highest concentration of lipid in the estuarine zone was observed during postmonsoon and the lowest during monsoon months. Among the bioorganics studied, the lipid percentage was low being only 0.63% to 4.23% of the organic matter. Bhosle *et al.* (1988) studied the biochemical compounds in the sediments of Bay of Bengal and reported that lipids constituted 1.91 to 4.28% of organic matter. The present data also was within this range but with a lower value of 0.63.

Lipids are derived from algal and terrestrial plants and are present in low concentrations. Although, literature on sedimentary lipids is limited, it appears that lipids follow the concentration of organic carbon in the sediments with eutrophic lakes having the largest concentration of lipids. The lipid concentration of sediment in lake varies with the trophic status of the lake and the concentration of organic carbon. This suggests that biological activity associated with production of organic carbon by phytoplankton is the major source of formation of lipids. The highest concentration of lipids noticed at the estuarine as well as riverine stations should be due to the biological activity associated with the primary production and the decay of vascular plants in the estuarine region due to high salinity intrusion and subsequent

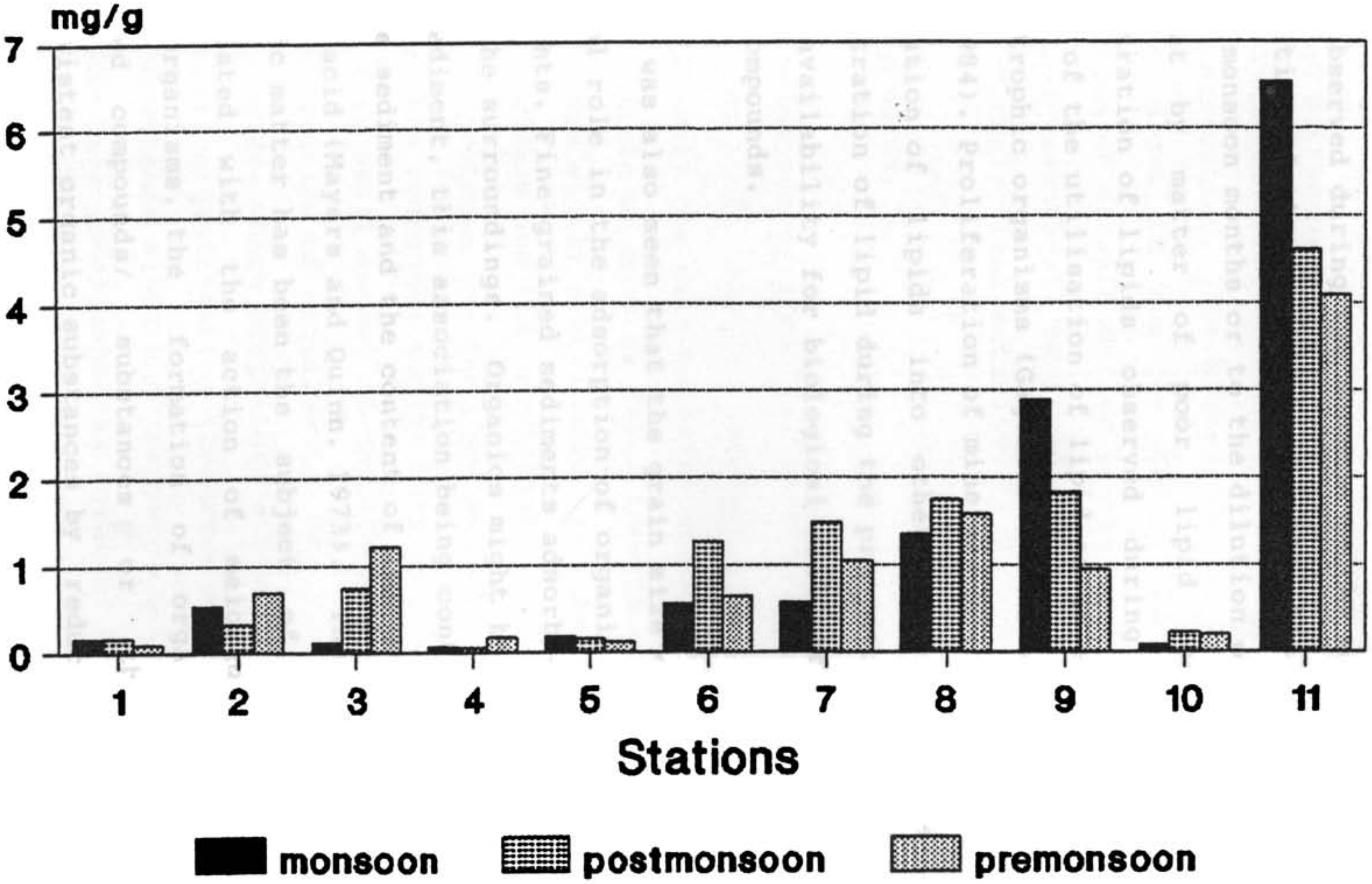

Fig. 4.7 Seasonal distribution of sedimentary lipids

transformation of organic matter by micro-organisms, the high rate of sedimentation and subsequent preservation. The lowest value observed during the monsoon months might be due to the devastation of the sediment by the heavy runoff occurring during monsoon months or to the dilution of organic matter of sediment by matter of poor lipid content. The lower concentration of lipids observed during premonsoon was the result of the utilisation of lipid as an energy source by the heterotrophic organisms (Gagosian and Lee, 1981; Ittekkot *et al.*, 1984). Proliferation of minerals might also influence the degradation of lipids into other compounds. The decreased concentration of lipid during the premonsoon period indicated their availability for biological utilization as high energy rich compounds.

It was also seen that the grain size of the sediment played a vital role in the adsorption of organics like lipids into the sediments. Fine-grained sediments adsorbed and preserved lipids from the surroundings. Organics might be adsorbed directly by the sediment, this association being controlled by the nature of the sediment and the content of indigenous matter such as humic acid (Mayers and Quinn, 1973). The early diagenesis of organic matter has been the subject of several discussions. Associated with the action of meiofauna, macrofauna and microorganisms, the formation of organics from the other related compounds/ substances or the modification of pre-existent organic substances by reduction, decarboxylation or aromatization is induced by adsorption phenomena and a complex series of interaction between the mineral fractions of the sediment. The changes observed in the relative distribution of lipids in the surficial sediment could be explained either by early diagenesis, by the bacterial activity (Johnson and Calder, 1973; Cranwell, 1976) or by changes in the lipid contribution. 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.

### 4.3.2 Proteins.

Proteins occupy a central position in the architecture and functioning of living organic matter. Proteins are quantitatively the main material of animal tissues; for they may constitute as much as three fourths of the dry substances. Proteins are widely distributed in the sediments. Plants, animal residues and the microbial population are the major source of proteins in the sediments. Proteins are easily hydrolyzable compounds and so they are preferentially utilized. Only a very small number of reports are available on the amount and distribution of proteins in the sediments. Proteins and carbohydrates, which constitute a substantial portion of the sedimentary organic matter (Dengenes and Mopper, 1976), assume vital importance since the organic matter of sediments and water has been established as forming a strong link between several known and unknown phenomena.

Monthly data on protein content in the sediments of

Stations are presented as appendix. Protein is abundant and widely distributed in the sedimentary environment. The abundance of protein was seen to be influenced by the substratum as well as the season and the anthropogenic inputs. The protein concentration at the riverine zone of the southern arm of the estuary varied from 0.24 to 5.59 mg $g^{-1}$ at Station 1, from 2.32 to 13.2 mg $g^{-1}$ at Station 2, from 0.99 to 46.07 mg $g^{-1}$ at Station 3, from 0.43 to 3.94 mg $g^{-1}$ at Station 4 and from 1.3 to 4.37 mg $g^{-1}$ at Station 5. The estuarine Stations of the same region showed higher values of proteins, ranging from 0.03 to 16.73mg $g^{-1}$ and 5.67 to 13.98mg $g^{-1}$at Stations 6 and 7 respectively. In the northern arm of the estuary, the protein concentrations ranged between 9.25 to 24.97mg $g^{-1}$, 9.13 to 45.66mg $g^{-1}$, 0.69 to 4.65 mg $g^{-1}$ and 18.94 to 32.27mg $g^{-1}$ at Stations 8,9,10 and 11 respectively. The result indicated that higher amounts of protein were always associated with the northern arm of the estuary than the southern arm.

The seasonal distribution profile of protein is presented in Fig. 4.8. A marginal variation with season was observed at all Stations. The low concentration of protein observed at the riverine stations (except Station 2) during the monsoon months gradually increased during post and premonsoon periods. An abnormal increase in protein content was noticed at Station 3 (24.61 mg $g^{-1}$). Station 2, which was a recepient site of effluent from paper mill recorded the highest concentration of protein during monsoon months, but subsequently decreased during post and premonsoon. The result indicated that the protein content at the estuarine stations in the southern part

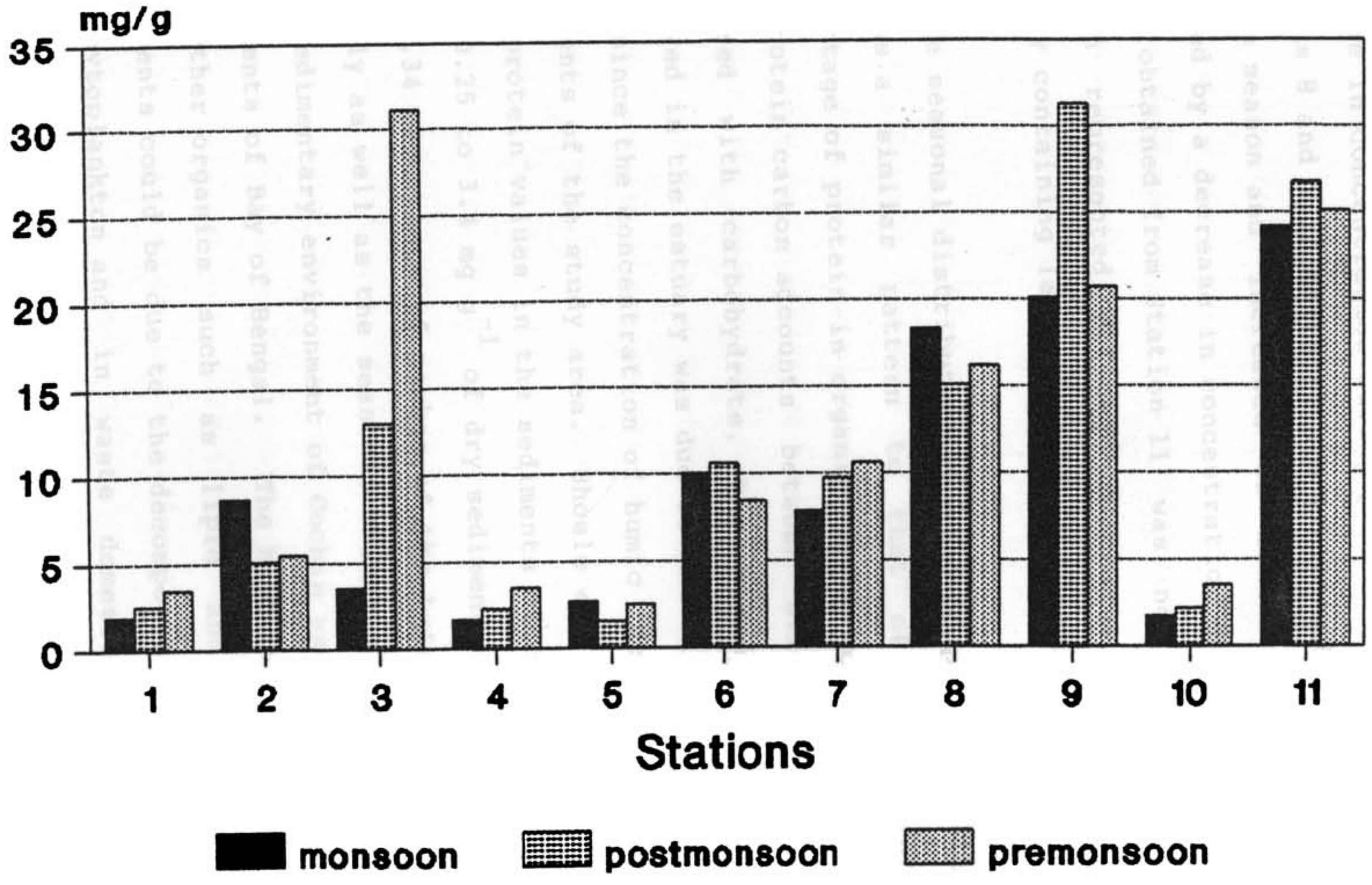

Fig. 4.8 Seasonal distribution of sedimentary protein

showed lower values during monsoon months followed by an increase in concentration during post and premonsoon seasons. Stations 8 and 9 in northern arm exhibited lower values during monsoon season and increased to maximum during postmonsoon followed by a decrease in concentration during premonsoon. The values obtained from Station 11 was not included since the Station represented effluent discharge site of fertilizer factory containing large amounts of inorganic nitrogen.

The seasonal distribution profile of protein followed more or less a similar pattern to that of carbohydrate. The percentage of protein in organic matter accounts to 17 to 49.76 and protein carbon accounts between 0.16 to 14.85 mg $g^{-1}$. Compared with carbohydrate, the higher amount of protein observed in the estuary was due to the interference of humic acid since the concentration of humic acid was high in the sediments of the study area. Bhosle *et al.,* (1988) reported that protein values in the sediments of Bay of Bengal varied from 0.25 to 3.4 mg $g^{-1}$ of dry sediment and accounted for 5.05 to 20.34 percentage of carbon of the total organic carbon. The monthly as well as the seasonal values of protein observed in the sedimentary environment of Cochin was higher than in the sediments of Bay of Bengal. The high turn-over of proteins and other organics such as lipid and carbohydrate in the sediments could be due to the decomposition of organic matter in phytoplankton and in waste domestic water. Skopintsev (1981) stated that both domestic waste waters and phytoplankton were rich in protein, carbohydrates and fats. The post- and premonsoon maxima at all Stations might be due to the enhanced biological activity, especially in the estuarine region. The decomposition of phytoplankton and other vegetation and the sewage which contains enormous amounts of proteinaceous materials contribute to the protein concentration. The higher concentration of protein found at Stations 3 and 9 during pre- and post monsoon seasons could be due to the settling of plant materials discharged from the paper pulp factory and the retting yards of coconut husk at these areas respectively.

In general, the high content of protein in the sediments of the Cochin estuary could be due to the accumulation of plant material into the clay minerals of sediments where they were particularly resistent to chemical and biological breakdown. A number of fish peeling and processing units are housed on the banks of the estuary. The wastes from these units are dumped into the estuary where animal tissues undergo decomposition and liberate proteins, which are adsorbed/settled into the sediments. Apart from this the wastes from the `Modern Food Industries' also drains into the estuary. This and other anthropogenic inputs may be the reason for the higher concentration of protein in the estuary. A decrease in the concentration at Stations 6,8 and 9 during premonsoon season may be due to the preferential utilisation of protein by the benthic organisms and biological activity or to the N-compounds are incorporated into humic matter through various humification pathways (Bhosle *et al.*, 1988).

The grain size of the sediment seems to play a significant role in controlling the distribution of organic compounds.

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 the riverine sediments were always sandy. This could be the reason for the lower concentration of protein in the riverine stations compared to the estuarine ones.

## 4.4 Interrelationships

Regression analyses of biogeoorganics in surficial sediments of the cochin estuary with sedimentary organic carbon and chlorophyll a indicated highly significant correlations (Figs.4.9 - 4.14). The regression equation obtained are presented below

Riverine

SOC vs Chl a

$Y = 1.9434 + 0.2339x$ $n=65$ $r=0.67$ $P < 0.001$

SOC vs Chl b

$Y = 1.235 + 0.1325x$ $n=65$ $r=0.62$ $P < 0.001$

SOC vs Chl c

$Y = 2.371 + 0.1627x$ $n=65$ $r=0.40$ $P < 0.01$

SOC vs Ctd

$Y = 0.9108 + 0.1626x$ $n=65$ $r=0.73$ $P < 0.001$

SOC vs Pheo

$Y = 1.9459 + 0.2257x$ $n=65$ $r=0.60$ $P < 0.001$

SOC vs Carbohydrate

$Y = 0.8247 + 0.2257x$ $n=72$ $r=0.90$ $P < 0.001$

SOC vs Protein

$Y = 1.0007 + 0.7290x$ $n=72$ $r=0.95$ $P < 0.001$

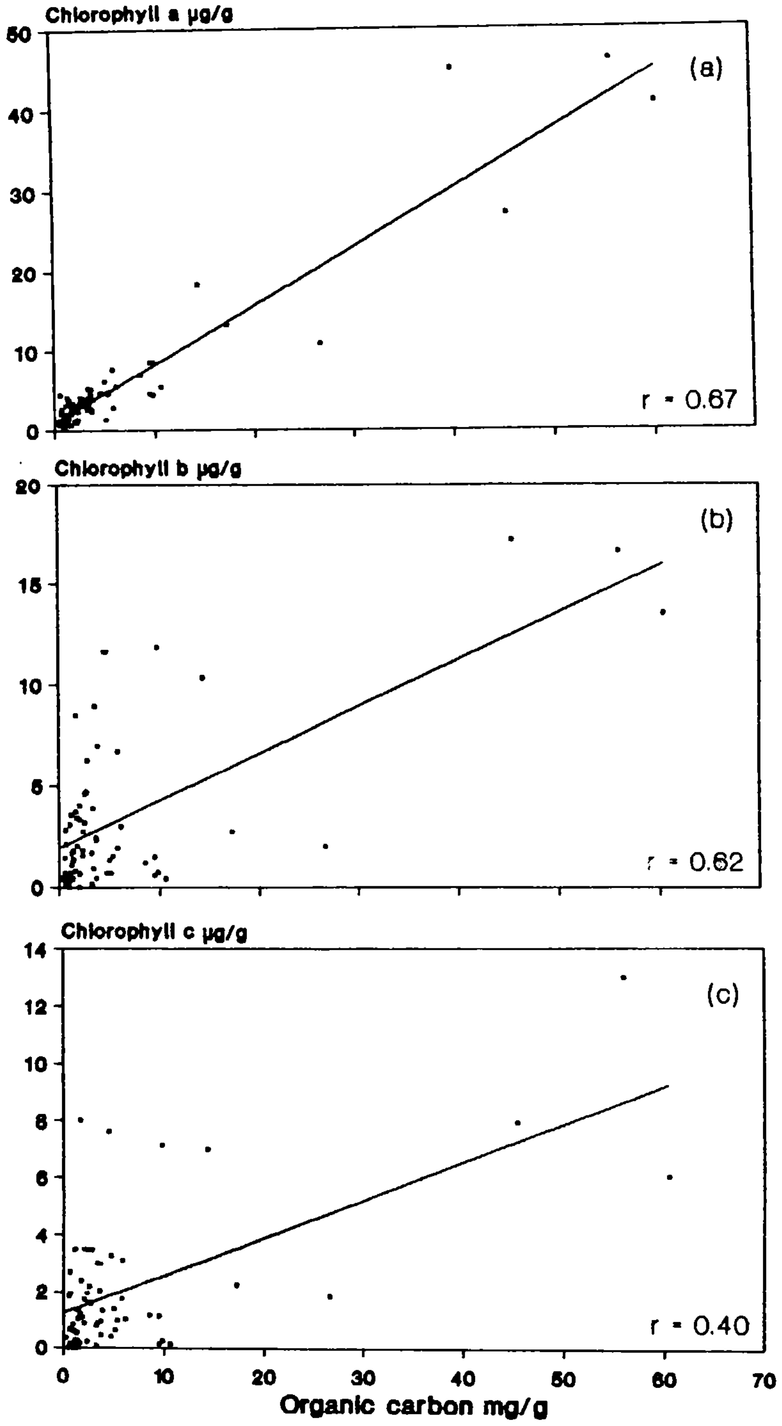

Fig. 4.9 Relationship between organic carbon (riverine) and (a) chlorophyll a (b) chlorophyll b (c) chlorophyll c

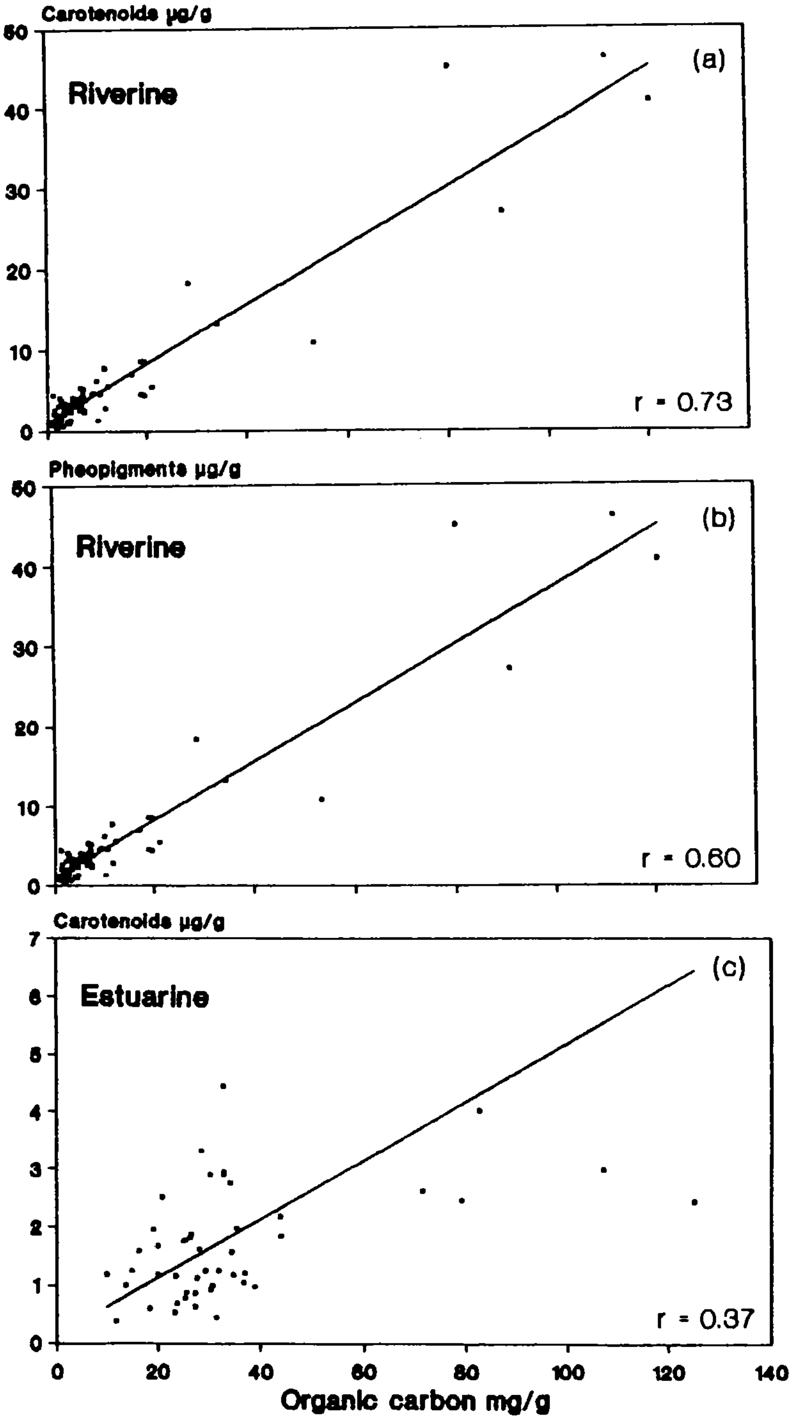

Fig. 4.10 Relationship between organic carbon and
(a) carotenoids (b) pheopigments (c) carotenoids

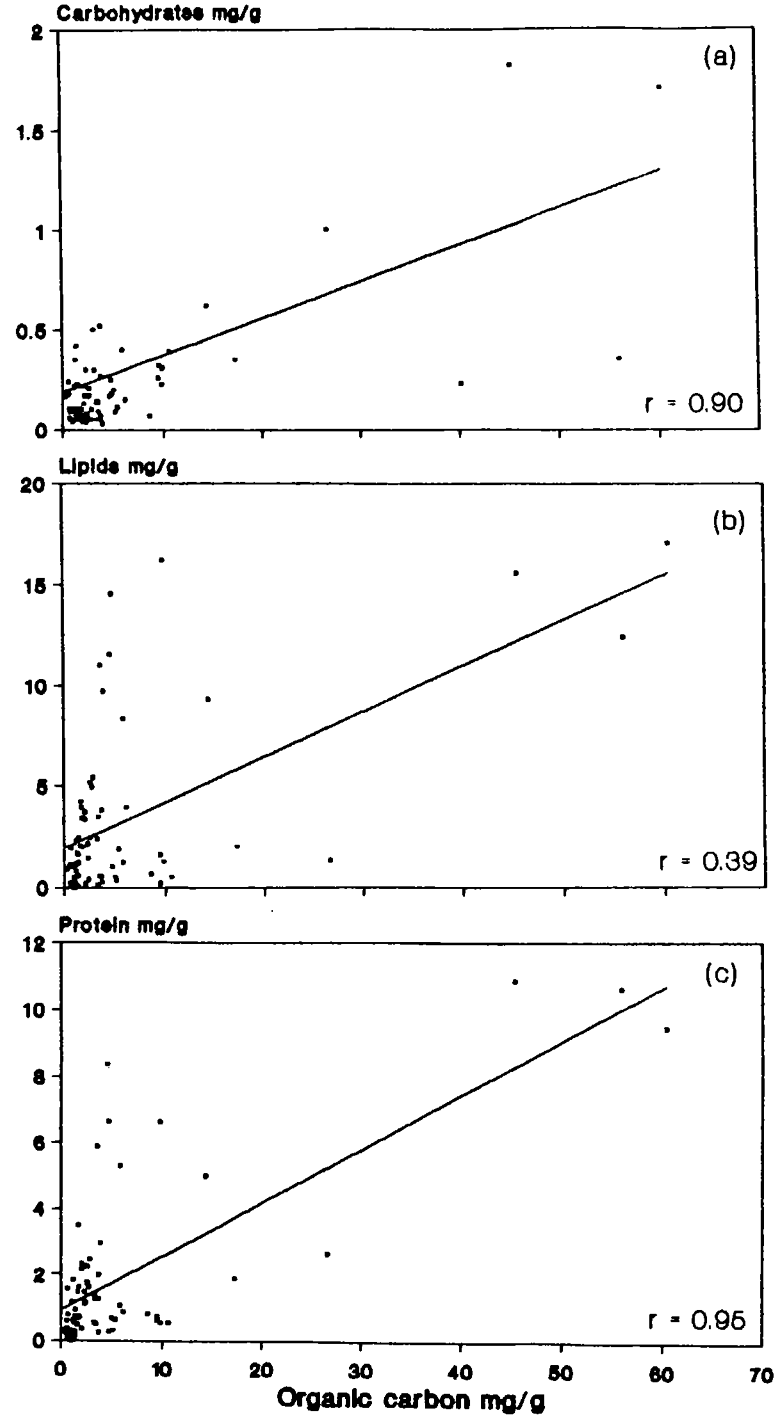

Fig. 4.11 Relationship between organic carbon (riverine) and (a) carbohydrates (b) lipids (c) protein

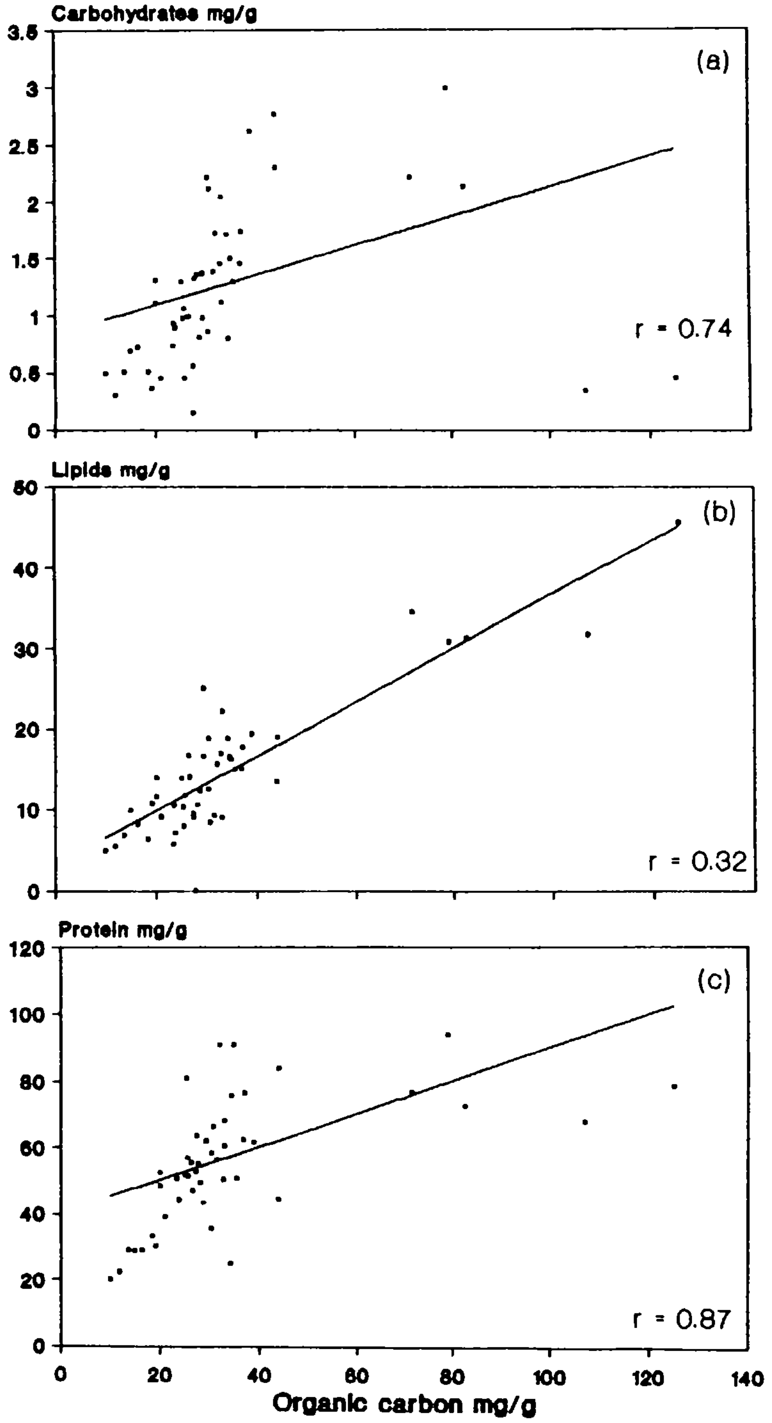

Fig. 4.12 Relationship between organic carbon (estuarine) and (a) carbohydrates (b) lipids (c) protein

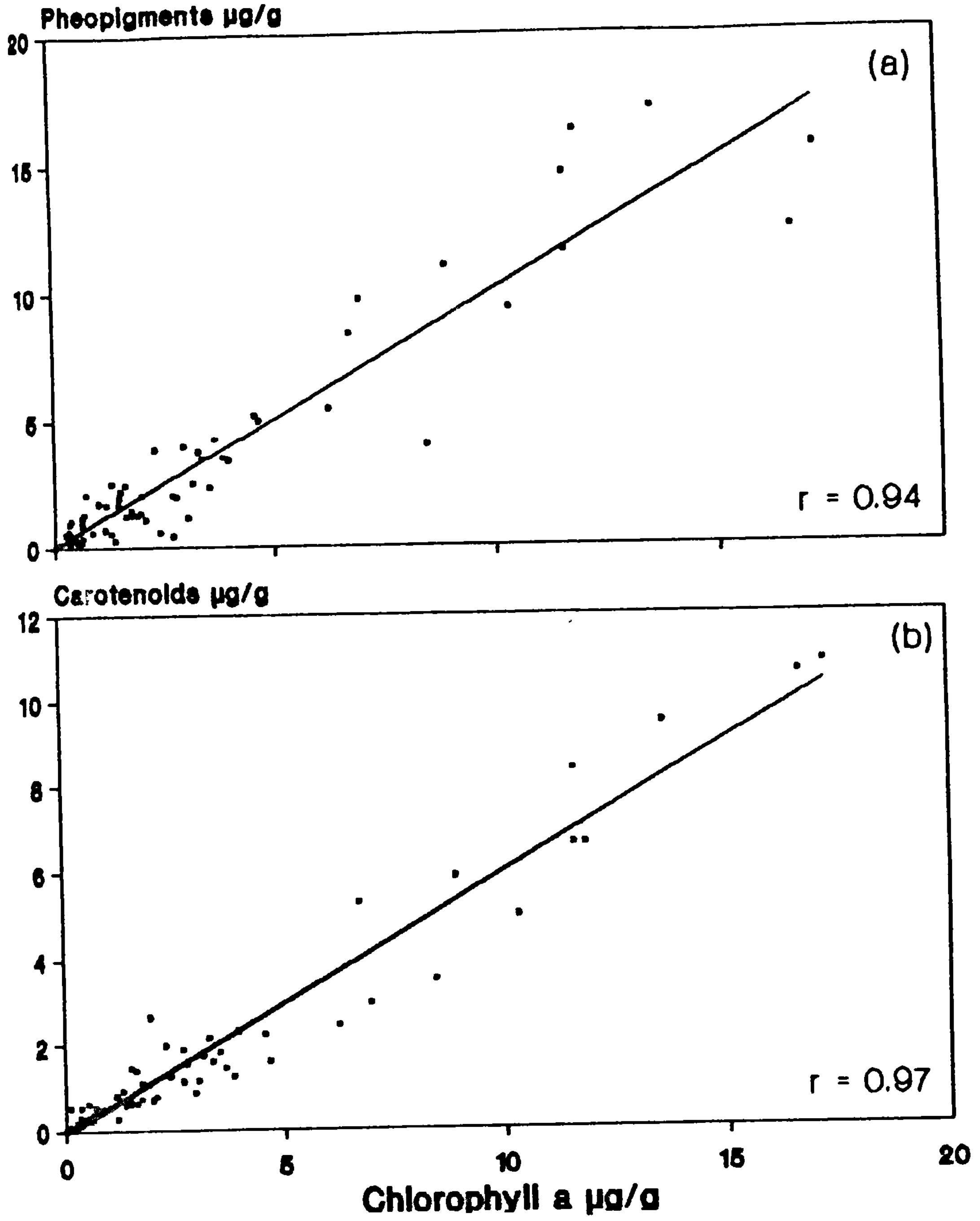

Fig. 4.13 Relationship between chlorophyll a (riverine) and (a) pheopigments (b) carotenoids

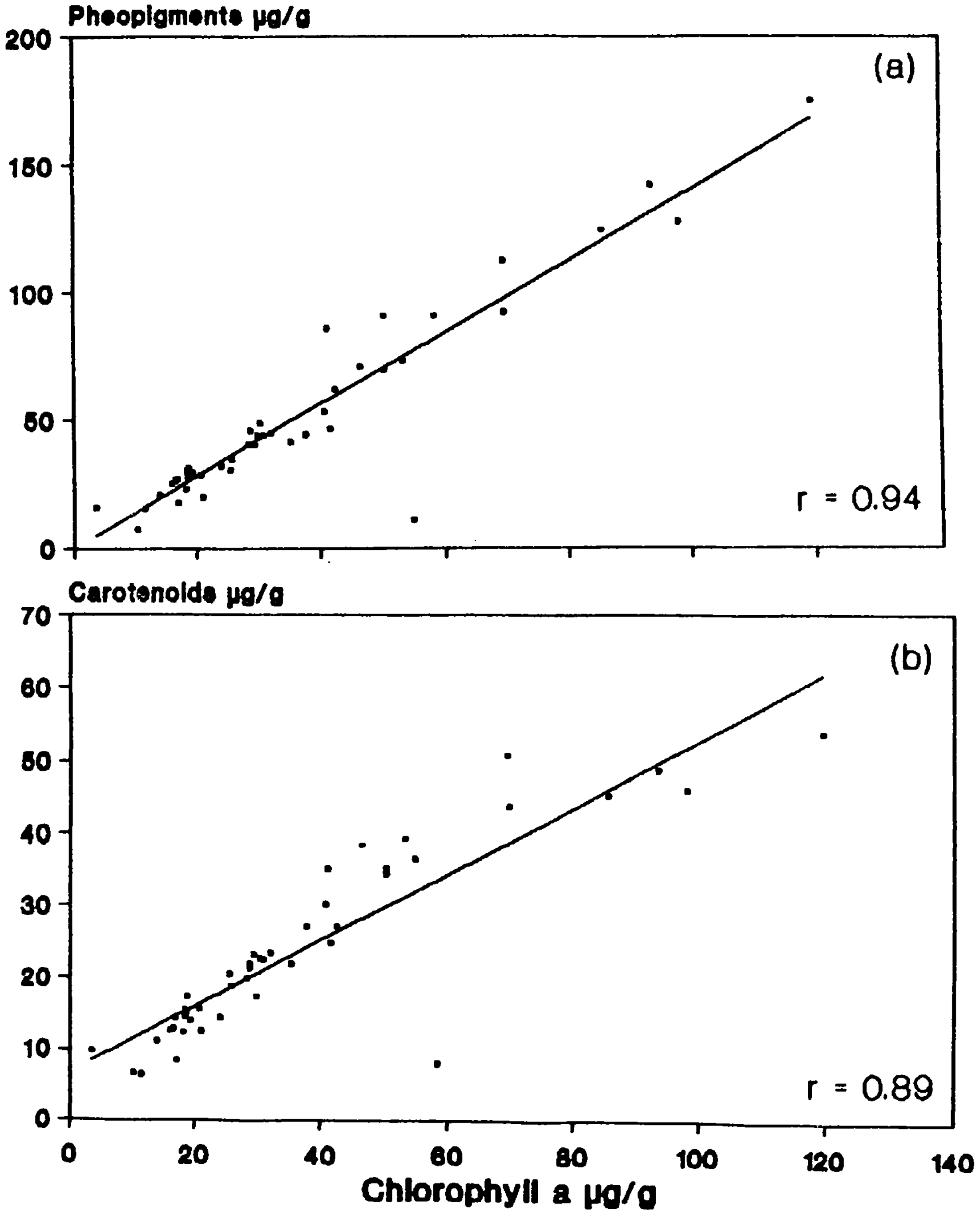

Fig. 4.14 Relationship between chlorophyll a (estuarine) and (a) pheopigments (b) carotenoids

SOC vs Lipid

$Y = 0.1905 + 0.0183x$ n=72 r=0.39 $P < 0.001$

Chl a vs Chl (b)

$Y = 0.2392 + 0.5356x$ n=65 r=0.88 $P < 0.001$

Chl a vs Chl (b)

$Y = 1.31640 + 0.8622x$ n=65 r=0.74 $P < 0.001$

Chl a vs Ctd

$Y = -0.161 + 0.6133x$ n=65 r=0.97 $P < 0.001$

Chl a vs Pheo

$Y = -0.093 + 1.0129x$ n=65 r=0.94 $P < 0.001$

Chl a vs CHS

$Y = 0.5743 + 0.5763x$ n=72 r=0.67 $P < 0.001$

Chl a vs Lipid

$Y = 0.1820 + 0.0391x$ n=72 r=0.27 $P < 0.1$

Chl a vs protein

$Y = 0.6808 + 1.3715x$ n=72 r=0.69 $P < 0.001$

Estuarine

SOC vs ctd

$Y = 16.334 + 0.211x$ n=45 r=0.37 $P < 0.02$

SOC vs Chs

$Y = 3.3146 + 0.1677x$ n=48 r=0.74 $P < 0.001$

Soc vs lipid

$Y = 0.8422 + 0.0139x$ n=48 r=0.32 $P < 0.05$

SOC vs protein

$Y = 3.1994 + 0.3358x$ n=48 r=0.87 $P < 0.001$

Chl a vs Chl b

$Y = 6.3354 + 0.1283x$ n=45 r=0.41 $P < 0.01$

Chl a vs Ctd

$Y = 6.7513 + 0.4588x \quad n=45 \quad r=0.89 \quad P < 0.001$

Chl a vs Pheo

$Y = -0.285 + 1.4104x \quad n=45 \quad r=0.94 \quad P < 0.001$

In the estuarine stations no significant correlation was observed between sedimentary organic carbon and pigments except carotenoid. At the same time, highly significant correlations were observed at the riverine stations between sedimentary carbon and pigments. This suggests that the organic matter which is brought in by high land run-off into the estuary is subjected to diagenetic changes. Further, the organic matter in the estuarine regions contain contributions from *insitu* biological prouction activities of the overlying waters. It also suggests that riverine sediments are not subjected to diagenetic processes. The correlation observed between Chl a and carotenoid is an indicative of pronounced activity of benthic organism. A highly significant correlation was observd between SOC and CHS, lipid and protein in both regions. Comparing the a and b values of the regression equation it suggest that the riverine SOC are depended completely of allochthonous input whereas the estuarine are combinations of autochthonous and allochthonous. This is in confirmation with the C : N : P ratios.

CHAPTER 5.

# HUMIC ACIDS AND HYDROXYLATED AROMATIC COMPOUNDS

5.1 Humic acids.

5.2 Hydroxylated aromatic compounds.

## 5.1 Humic acids.

Most of the organic matter in natural waters and sediments, as in soils, consists of the complex, heterogenous, brown or yellow acidic polymers collectively known as humic matter (Bordovskiy,1965). Humic acids represent an extremely heterogenous mixture of molecules which range in molecular weight from as low as several hundreds to perhaps several millions. Humic Acid may be defined as " polymeric bodies which in turn are composed of monomeric bodies".

Humic matter is a relatively stable byproduct of the microbial transformation of a great variety of biochemical compounds derived from the dead cells and extracellular products of various organisms -- chiefly land plants and aquatic algae. Humification occurs under a wide range of environmental conditions- anaerobic as well as aerobic, though the process may be especially intense under aerobic conditions (Bordovskiy, 1965). Being resistant to microbial and chemical decomposition, humic matter tends to accumulate even under aerobic conditions.

The humic matter of natural waters and sediments is partly allochthonous (leached or eroded from soil and transported to the lakes and oceans by streams and ground water) and partly autochthonous (formed from the cellular constituents and exudates of indigenous aquatic organisms) (Waksman, 1933; Kalle, 1966; Otsuki and Hanya, 1967; Bordovskiy,1965; Nissenbaum and Kaplan,1972).

Sedimentary humic substance generally has a high $^{13}C/^{12}C$ ratio than soil humic matter (Nissenbaum and Kaplan, 1972) and it tends to be more highly less aromatic, less highly condensed, poor in phenolic groups, poorer in carbon and richer in nitrogen, sulphur, hydrogen and carboxyl groups (Nissenbaum and Kaplan, 1972; Otsuki and Hanya,1967; Rashid and Prakash,1972; Ishiwatari,1969;1970; Bordovskiy, 1965). The autochthonous component of dissolved or dispersed marine "water humus" or Gelbstoff can be distinguished from its terrigenous counterpart by its greater flourescence in ultraviolet light, its lower degree of condensation (Kalle, 1966; Sieburth and Jenson,1968) and possibly by the prominence of its UV absorption band at approximately 260 or 265nm.

Most of the autochthonous humic matter is formed from algal protiens, carbohydrates and lipids (and phenols in the case of

Gelbstoff formed from extracellular products of seaweeds) (Sieburth and Jenson,1969; Craigie and McLachlan, 1964); whereas soil humic matter is largely composed of degraded lignin derived from vascular plants (Kalle, 1966).

In general, the character of humic matter varies with the biological source material (Rashid and Prakash, 1972; Christman and Ghassemi, 1966; Alexandrova *et al.*, 1968). Environmental factors —— in particular, those relating to redox potential and rate of sedimentation may result in additional diversification. The humic matter in deep water sediment is slightly more condensed than that in shallow water sediment (Bordovskiy, 1965; Nissenbaum and Kaplan,1972).

The abdundance and nature of humic substances in natural waters and sediment show marked geochemical variability. Water humus is most highly concentrated in certain inland waters (Christman and Minear,1971) and marine coastal waters (Bordovskiy, 1965). Sedimentary humic matter is concentrated more in the clay and silt-sized sediments of the nearshore marine enviroments than of the central region of lakes and inland seas (Waksman,1933; Bordovskiy,1965). The accumulation of humic matter and other organic substances in sediment has been correlated with the environmental variables which control the rate of sedimentation, redox conditon (Degens,1965; Bradley,1966), biological production and the mineralogy and grain size of the sediment (Waksman,1933; Drozdova and Gurskiy,1972; Bordovskiy, 1965).

The humic substances of lake muds may be predominantly allochthonous or autochthonous (Ishiwatari,1973; Otsuki and Hanya,1967) depending on local conditions such as character of land drainage into the lake. In some lakes, precipitated $CaCO_3$ may scavenge humic matter from the water and transport it to the bottom sediments (Otsuki and Wetzel, 1973). The most important source of autochthonous material in lakes is the algal flora (Ishiwatari,1973; Otsuki and Hanya,1967). In some tropical and subtropical lakes this organic detritus is mostly in the form of fecal pellets (Bradley,1966).

Deposition of allochthonous and autochthonous humic matter in the environment is controlled not only by flocculation but also by adsorption to clay particles, incorporation into fecal pellets of filter feeding invertebrates (Bordovskiy, 1965) aggregations on bubbles (Riley,1963) and of course by the hydraulic factors that regulate the mechanical deposition of sediments.

Aquatic and sedimentary humic substances have cation exchange properties (Rashid,1969; Szalay,1964) and form stable complexes with a wide range of divalent and trivalent metal ions (Rashid,1971; Rashid and Leonard,1973; Barsdate, 1970; Siegel, 1971; Shapiro,1964). Carboxyl and phenolic groups are probably the most important ligands involved (Rashid,1971, Schintzer,1969). The formation of these complexes makes possible extensive migration and segregation of metals. Humic matter forms complexes with a variety of non-humic organic compounds including amino acids, carbohydrates, fatty acids, phenols and porphyrins. Simple biochemical compounds "fixed" to humic colloids may thereby be protected from microbial decomposition (Degens *et al.*, 1964; Nissenbaum *et al.*, 1972).

One of the principal reasons for the geochemical and economic importance of humification is that the process causes the carbon and nitrogen of biochemical compounds to be partially shunted into relatively inert humic substances instead of being completely mineralized and recycled. More over humic matter plays a key role in the migration and concentration of various metallic elements on the surface of the earth and thus is responsible for the accumulation of a number of economically valuable elements, such as uranium, in peat, coal and black shale (Manskaya and Drozdova,1968; Szalay,1964).

The ecological significance of humic matter in natural waters and sediments is that it stimulates the growth of phytoplankton (Shapiro,1957; Prakash,1971). Another beneficial effects of humic acid are its metal binding and cation exchange properties. Detoxification of water by scavenging of heavy metals and other toxic dissolved substances, including man-made organics (Schnitzer and Khan,1972), may be another useful function of humic acid (Shapiro,1957; Siegel,1971). Szalay (1964) suggested that humic acid could be employed in the disposal of radio active wastes. In short although the sorbed pollutants may be highly concentrated in humic rich sediments, humic substances play an important role in combating water pollution (Rashid and Leonard,1973).

In spite of their great ecological, economic and geochemical relevance, humic substances of natural waters and sediments have not been thoroughly investigated. Relatively little information is available on their distribution in estuaries, particularly in sediments (Hair and Basett,1973; Visser,1984) and in Indian estuaries (Shanmukhappa and Kusuma Neelakantan 1989; Sardessai 1989; Poutanen and Morris 1985). No information is available on the distribution of humic substances in the sedimentary environment of the Cochin estuary and hence the present study has been undertaken.

Methods adopted for the estimation of humic acid are presented in Chapter 2.

The monthly data and seasonal average of the concentration of the humic acid in the sediments at Stations 1-11 are presented in appendix and Fig. 5.1 respectively. Humic acid was widely distributed in riverine as well as the estuarine regions. Humic acid concentration in the riverine region varied from 0.34 to 3.64 mg $g^{-1}$ at Station 1, from 1.43 to 9.36 mg $g^{-1}$ at Station 2, from 1.04 to 6.18 mg $g^{-1}$ at Station 3 and from 0.51 to 3.07 mg $g^{-1}$ at Station 4 and from 0.37 to 6.40 mg $g^{-1}$ at Station 5. While the level of humic acid in the estuarine zone ranged between 4.51 and 12.2 mg $g^{-1}$ at Station 6 and between 7.59 to 17.00 mg $g^{-1}$ at Station 7. In the northern arm of the estuary where the Periyar river drains, the humic acid value showed a minimum of 6.95, 1.32, 0.14, 4.47 mg $g^{-1}$ and a maximum of 16.08, 13.7, 2.82 and 16.5 mg $g^{-1}$ at Stations 8,9,10 and 11 respectively of which Station 10 was a freshwater region and Station 11 is the discharge receiving site. The estuarine zone showed the highest concentration of humic acid.

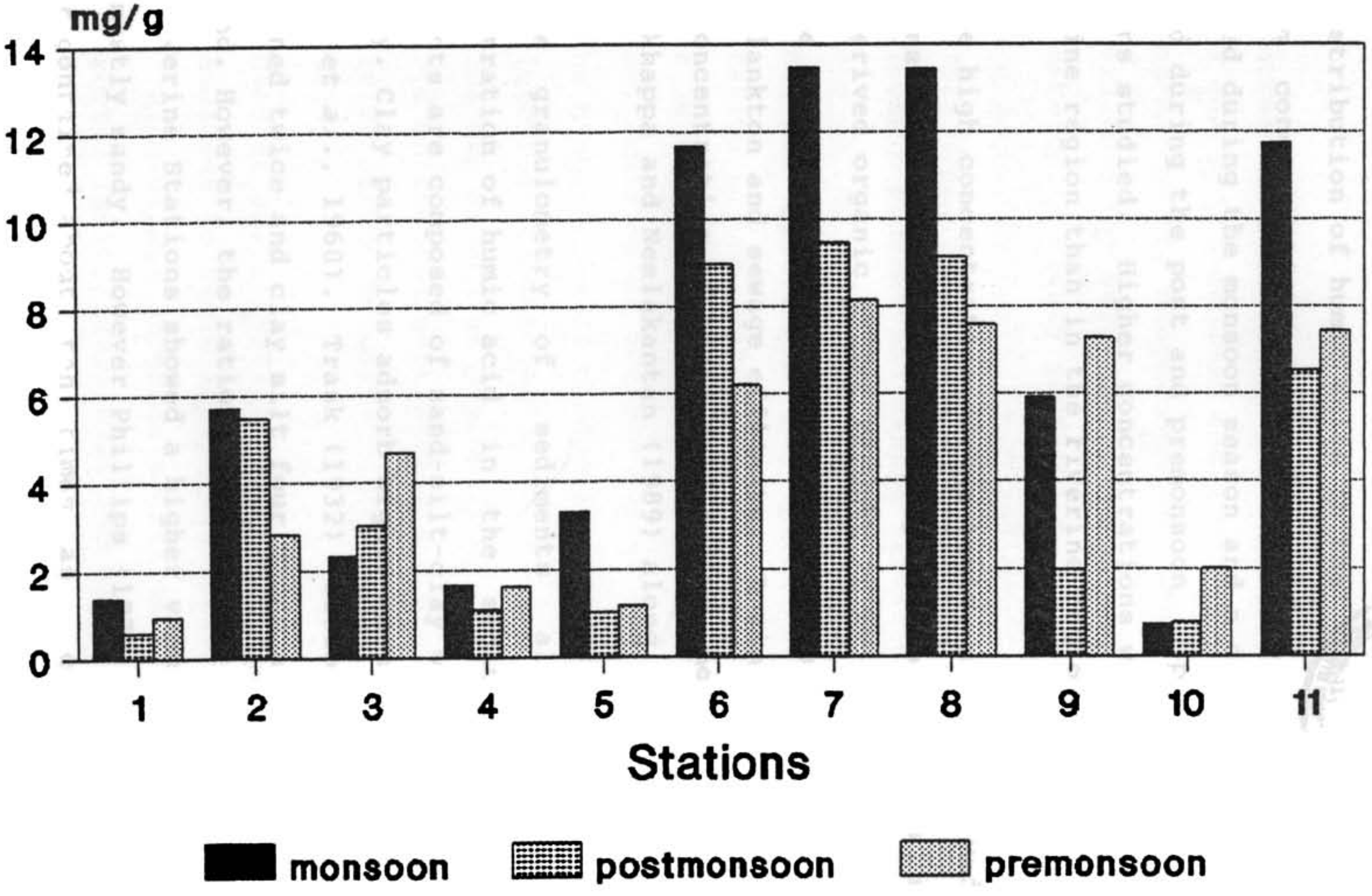

Fig. 5.1 Seasonal distribution of sedimentary humic acids

A distinct spatial and temporal variation was noticed in the distribution of humic acids in the estuarine system. The maximum concentration of humic acid in the sediment was observed during the monsoon season and a decreasing trend was noticed during the post and premonsoon periods at all the Stations studied. Higher concentrations were noticed in the estuarine region than in the riverine region.

The high concentration of the humic acid observed during the monsoon season could be largely due to the high input of land-derived organic matter brought in by land runoff and due to the addition of autochthonous materials derived from phytoplankton and sewage effluents. A similar observation of high concentration of humic acid during monsoon was made by Shanmukhappa and Neelakantan (1989) along the Karwar coast.

The granulometry of sediments also influenced the concentration of humic acid in the sediment. The estuarine sediments are composed of sand-silt-clay with high percentage of clay. Clay particles adsorb higher amount of organic matter (Bader *et al.*, 1960). Trask (1932) established that silts contained twice and clay silt four times as much organic matter as sand. However, the ratio of humic acid to organic matter, in the riverine Stations showed a higher value though the sediment was mostly sandy. However Phillips (1972) reported that fresh water contained about ten times as much dissolved organic matter as sea water. Precipitation of terrigenous humic material on contact with sea water was demonstrated by Sieburth and Jenson(1968). Clearly, further work needs to be carried out on polluted estuarine region where high levels of humic material are known to be present.

A decreasing trend of humic acid in the sediment was observed during postmonsoon and premonsoon. The reason for the reduction may be the biogeochemical resuspension or leaching of humic acid from the surficial sediments to the overlying water. Cochin estuary is highly productive and shows two peaks of intense prductivity during post and premonsoon periods (Nair *et al.*, 1975). This results in a depletion of nutrients from the water cloumn. Prakash and Rashid (1968) studied the effect of humic acid on the growth of diatoms and found that humic acid stimulated the growth of phytoplankton. As the nutrient concentration in the water column decreases, the sediments which is a source for nutrients, releases, under ambient condition, humic acid/ organic matter to the water colunmn. Thus, the higher rate of productivity in this region may be due to the leaching of humic acid to the overlying water which stimulates the growth of phytoplankton. Thus, in general the humic acid in the sediment exerts a profound influence on the productivity of the estuary.

Swanson *et al.*, (1966) attributed the enrichment of metals in the sediment to humus acting as scavenging or complexing agents. High values of trace metals in the Cochin estuary have been reported (Nair, 1992; Paul and Pillai, 1983). Enrichment of trace metals may be due to the complexation/ binding of the humic substances which in turn may reduce the availability of free humic acid. The complexation of humic acid with toxic metals reduces the toxicity of metals. Paul and Pillai (1983) indicated that the general trend of trace metal did not indicate any preferential accumulation in the biological tissues.

## 5.2 Hydroxylated aromatic compounds

Tannin and lignin (collectively referred to as hyroxylated aromatic compounds) are high molecular weight polycyclic aromatic compounds, widely distributed throughout the plant kingdom. Lignin is defined as the encrusting material of plants which is built-up of methoxy and hydroxy-phenyl propane units (Pearl, 1967). It is not hydrolysable with acids but is readily oxidised and soluble in hot alkali and bisulphite. The exact chemical composition of lignin-like compounds commonly found in the environment is not known. According to Geissman and Crout (1969), tannins are either polymers of gallic acid linked to carbohydrate residues (hydrolysable tannins) or polymeric flavanoid compounds (condensed tannins). Both tannins and lignins are highly resistant to chemical and biological degradation.

Lignins are polyphenolic biochemicals unique to vascular plants and thus produced only in terrestrial environments. Oxidation of lignin (nitrobenzene (Leo and Barghoorm,1970; Gardner & Menzel,1974) or alkaline cupric oxide,(Pearl, 1967; Hedges,1975; Hedges and Ertel, 1982)), in plant material or sedimentary mixtures yield a series of simple phenols whose characteristic substitution patterns indicate an unambiguous lignin source and whose relative distributions can indicate vascular plant and tissue types (Hedges and Parker, 1976;

Hedges amd Mann 1979a). Due to their specific plant sources and general refractory nature, lignins have been used as molecular level tracers for land-derived organic matter in a variety of marine, lacustrine and riverine environments (Hedges *et al.,* 1982).

Lignin have also been implicated as a major source material for terrestrial humic substances (Flaig *et al.,* 1975). Humic substances also represent a major fraction of the organic matter in lacustrine, coastal and deep sea sediments. Chemical oxidation of sedimentrary humic substances have produced lignin-derived phenols, in samples collected from coastal environments (Hedges and Parker, 1976; Pempkowiak and Pocklington, 1983).

The use of organic markers in the differentiation of organic inputs into sediments has proved to be a valuable tool in the examination of a number of major problems facing environmental chemists such as the reconstruction of the depositional and diagenetic histories of the organic fraction of these sediments. Molecular tracers have been used to establish terrestrial input to marine waters and to trace pollution in water ways (Readman *et al.,* 1986). Almost all molecular tracers used to distinguish between geographical and/or biological source organic matter in natural environments are derived from photosynthetic plants.

The lignin components of vascular plant tissue represent a source-specific tracer that can characterize terrestrial organic matter. The breakdown of terrestrial plant tissue gives rise to a considerable variety of lignin compounds. These generally take the form of small particulates which are readily spread about within the environment by processes such as runoff. It would, therefore, seem reasonable to expect a proportion of the organic material in estuarine particles to consist of lignin.

The discharge of paper mill effluent containing large quantities of organic compounds (tannin and lignin) into the river water/ coastal water have resulted in the adverse environmental conditions such as high BOD, undesirable aesthetic effects, fish fainting or toxicity to fish and other aquatic life. Investigations on the isolation and characterization of lignin and its oxidation compounds from sediments, waters and particulates have been well documented (Requejo *et al.*, 1986; Sandilands,1977; Brownlee and Strachan, 1977; Lawrence, 1980; Ertel and Hedges, 1984; Burges *et al.*, 1964; Reeves and Preston, 1989). Nair *et al.*, (1989) reported on the distribution of hyroxylated aromatic compounds in the Cochin estuary sampled in a random survey.

Hydrocarbons and other organic material are readily adsorbed by fine grained sediments and particulates and therefore studies on depositional and transport characteristics of such organic materials would yield significant information on pollutant dynamics of the estuarine system.

The analytical methods are described in Chapter 2.

The concentration levels of hydroxylated aromatic compounds are presented in appendix. The seasonal variation of hydroxylated aromatic compounds is shown in Fig. 5.2. The hydroxylated aromatic compounds in the sediments of riverine region varied from 0.09 to 6.4 mg $g^{-1}$ at Station 1, from 0.18 to 2.46 mg $g^{-1}$ at Station 2, from 0.13 to 19.79 mg $g^{-1}$ at Station 3, from 0.07 to 0.61 mg $g^{-1}$ at Station 4 and from 0.05 to 0.59 mg $g^{-1}$ at Station 5. In the estuarine zone its concentration ranged from 0.38 to 3.32mg $g^{-1}$ at Station 6, from 0.53 to 2.94mg $g^{-1}$ at Station 7, from 0.44 to 4.43mg $g^{-1}$ at Station 8, from 0.96 to 10.56 mg $g^{-1}$ at Station 9, from 0.03 to 0.98 mg $g^{-1}$ at Station 10 and from 1.29 to 5.92 mg $g^{-1}$ at Station 11. From the monthly data, it can be seen that they are widely distributed spatially as well as temporally.

Hydroxylated aromatic compounds registered a low concentrations during the monsoon months and increased concentrations during the post and premonsoon seasons. Higher values were observed in the estuarine region as compared with the riverine zone except Stations 2 and 3. Station 2 was close to and Station 3 was a kilometer down the discharge site of the pulp-mill effluent. The increased hydroxylated aromatic compounds concentrations observed at these Stations could therefore be attributed to the influence of the effluents and to the gravitational settling of the organics occurring in this region. The lower levels of tannin and lignin noticed in the riverine region was the consequence of the increased particle size which decreased the adsorption/ incorporation of organics.

Station 11 showed a high value of hydroxylated aromatic compounds because the site was the recipient of high amount of

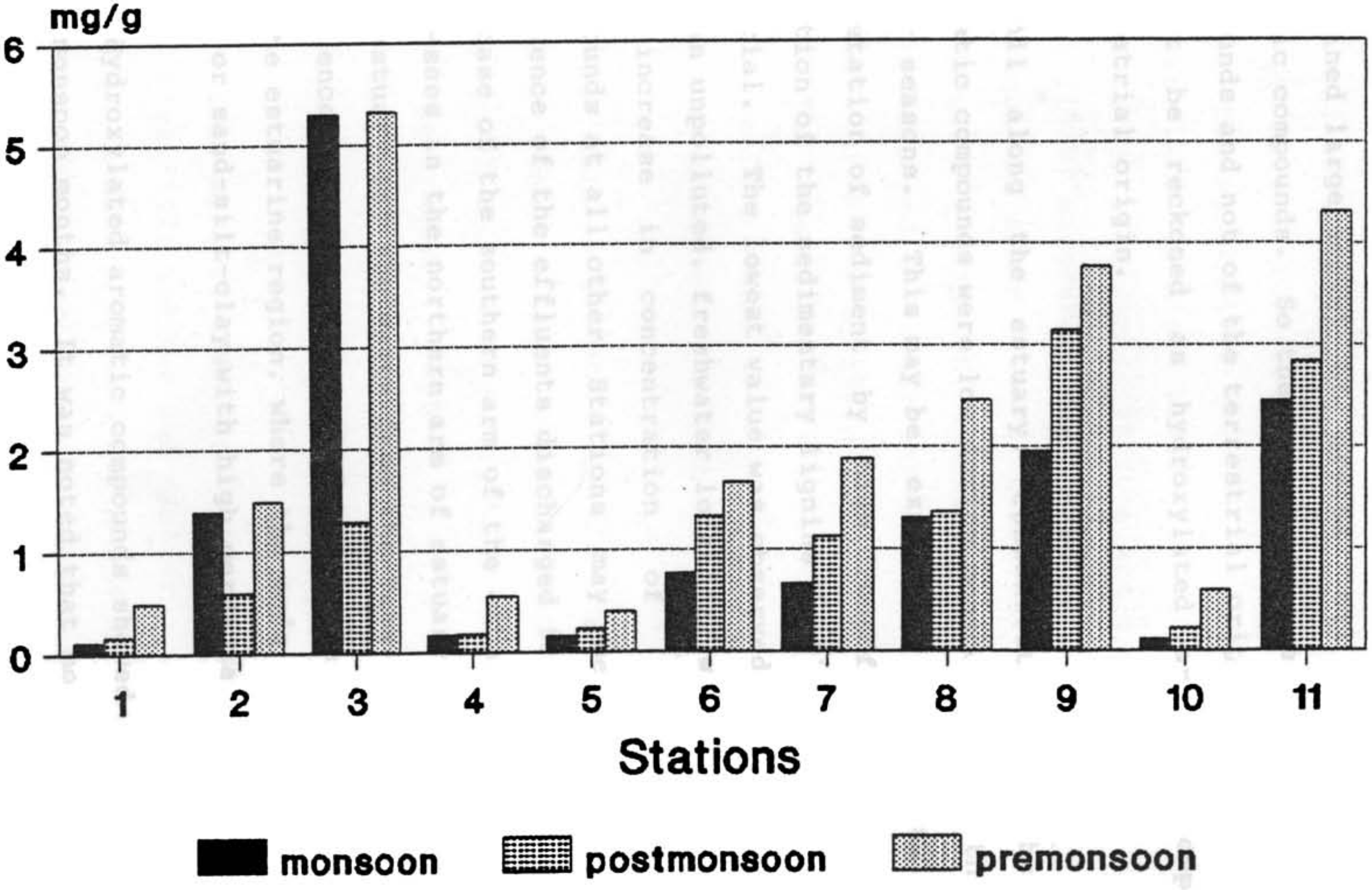

Fig. 5.2 Seasonal distribution of sedimentary hydroxy. aromatic compounds

discharge from industrial concerns like FACT, HIL and TCC which contained large amount of grease, oil and other synthetic organic compounds. So the values observed may be of synthetic compounds and not of the terrestrial origin and hence the value cannot be reckoned as hydroxylated aromatic compounds of terrestrial origin.

All along the estuary, concentrations of hydroxylated aromatic compounds were low during monsoon months than during other seasons. This may be explained as a result of the devastation of sediment by high runoff or as due to the dilution of the sedimentary lignins by lignin-deficient organic material. The lowest value was observed at Station 1 which was an unpolluted, freshwater location, with a sandy sediment. The increase in concentration of hydroxylated aromatic compounds at all other Stations may be the result of the influence of the effluents discharged from the paper mill in the case of the southern arm of the estuary and of the retting processes in the northern arm of estuary. The sewage outfall in the estuary and the waste from the Tata Oil Mill Company also influenced the distribution of hydroxylated aromatic compounds in the estuarine region, where the muds were composed of silty clay or sand-silt-clay with high percentages of clay particles.

Hydroxylated aromatic compounds showed an increase during postmonsoon months. It was noted that most of the parts of the estuary became covered with water plants and *Salvinia molesta* towards the end of the monsoon season. After the monsoon flow, sea water intrusion increased the salinity and the water plants underwent death and decay, settled to the bottom and got incorporated into the sediments. Apart from this, the organics in the effluents discharged from the pulp factory into the river and carried downstream got precipitated in the estuarine region. Mixing of river water of low ionic strength and of estuarine water of high ionic strength known to result in precipitation of organics (Burton and Liss,1976). Sieburth and Jensen (1970) suggested that dissolved organic matter exuded from fucus and other littoral brown algae could condense to form organic aggregates consisting of polyphenol, tannins, carbohydrate and proteinaceous material. The POM produced by such mechanisms was quickly colonized by bacteria and protozoa; some of the organic matter was converted to microbial biomass, whilst some was broken down to simpler organic and inorganic substances which sank to the bottom sediment.

Paper mill effluents usually contain organic compounds (ranging from simple carbohydrates to complex lignin derivatives) which have a very high potential to damage the aquatic environment. Michael Fox (1977) identified several such compounds which, being slowly degradable substances, inhibited the growth of microflora.

Several workers (Ferm and Nilson, 1969; Korner and Moore, 1953; Kirk, 1971 and Lee and Mueller, 1976) reported on the coagulative nature of mill effluents in fresh water /seawater and discussed the presence of lignosulphonates which are very resistant to biologicl degradation processes. Day *et al.* (1953) and Woodward *et al.* (1963) have noticed the disappearance of lignin like compounds from water media and have attributed this to the adsorption of lignosulphonates as well as of craft mill lignin onto the microbial cell wall. The decrease of tannin-lignin compounds during monsoon may be attributed to the dilution of receiving waters. The low content noticed in the riverine region may be a result of the frequent dredging of the river sand and of the influence of the grain size (sand). The high concentration of hydroxylated aromatic compounds observed at the Station 9 might be a consequence of the increased retting of husks.

Comparing the two arms of the estuary the concentration of hydroxylated aromatic compounds was more in the nothern part of the estuary. Besides the influence of the retting zone at Station 9 that this region behaved as a `sheltered sedimentary environment'. Concentrations were relatively lower in the riverine region probably due to the flushing process. Distribution of hydroxylated aromatic compounds in this study showed a correlation with organic carbon. It was noticed that the particle-size also influenced the concentration of hydroxylated aromatic componds in the sediments, it being less in sandy sediments and higher in silty clay or clayey silts. As the grain size of the sediment decreased the concentration of hydroxylated aromatic compounds increased.

It was interesting to compare the lignin concentration in the surficial sediments with previously reported values (Readman *et al.*, 1986). Although they observed a mean concentration of 394 μg g$^{-1}$ (range 121-846 g gμ$^{-1}$, n = 8), a high concentration ranging from 0.014 to 10.56 mg g$^{-1}$ was found in the Cochin estuarine system. The higher values of sedimentry hydroxylated aromatic compounds could be explained in terms of either the preferential adsorption of lignin-rich material under low flow conditions or differences in inputs to sediments and suspended particulates arising from decay of vegetation or the influence of small streams.

Interrelationships:

The significant correlations of humic acid and hydroxylated aromatic compounds related to SOC, and salinity are given below.

Riverine

SOC vs HA

$Y = 1.7899 + 0.0743x$ n=72 r=0.44 $P < 0.001$

SOc vs HAR

$Y = 0.3543 + 0.1201x$ n=72 r=0.051 $P < 0.001$

Estuarine

SOC vs HA

$Y = 10.848 - 0.0653x$ n=48 r=0.042 $P < 0.01$

SOC vs HAR

$Y = 0.1091 + 0.0506x$ n=48 r=0.71 $P < 0.001$

Sal vs HA

$Y = 9.4978 - 0.0867x$ n=48 r=0.25 $P < 0.1$

The negetive correlation observed in the case of humic acid and salinity indicates the dissolution/desorption of humic acid from the sediment to the overlying water column, the prevailing pH in the estuarine region (>7) may be the facilitation factor for the dissolution.

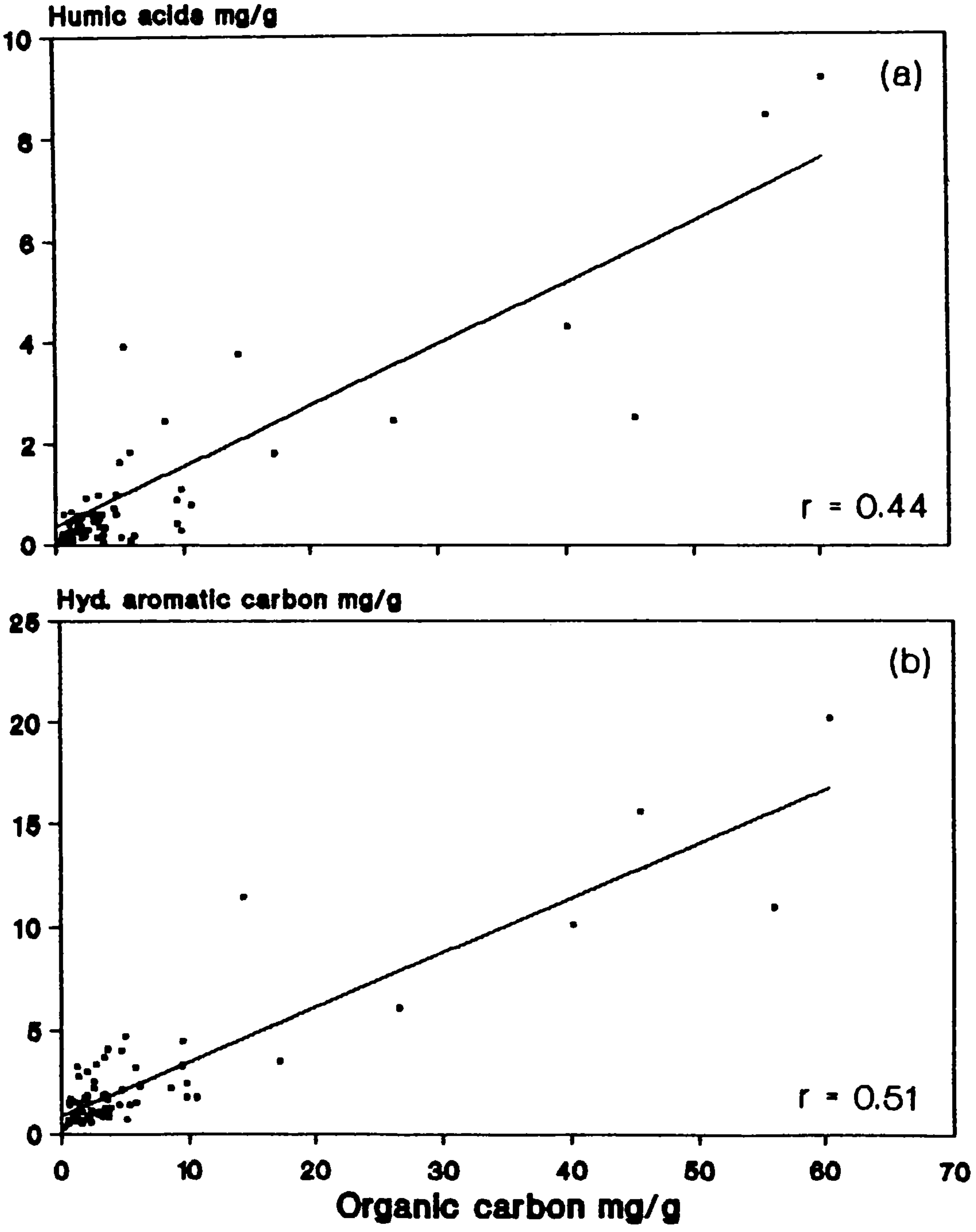

**Fig. 5.3 Relationship between organic carbon (riverine) and (a) humic acids (b) hydroxylated aromatic compounds**

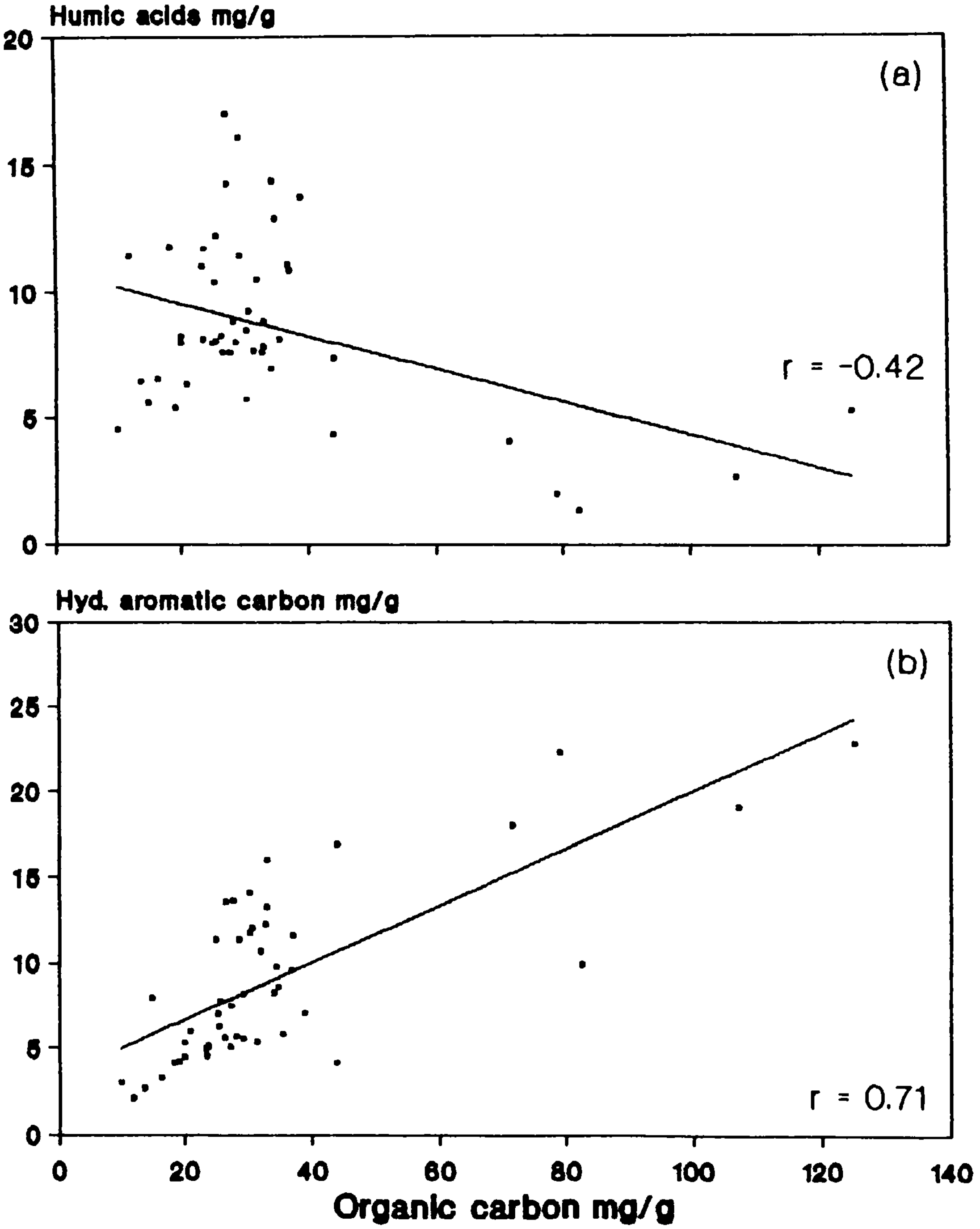

Fig. 5.4 Relationship between organic carbon (estuarine) and (a) humic acids (b) hydroxylated aromatic compounds

## CHAPTER 6

# SUMMARY

Biogeochemistry is an emerging discipline which encompases the entire gamut of interative effects involving the biosphere, atmosphere, hydrosphere and lithosphere. Environmental biogeochemistry is a dynamic subject because it is greately concerneed with chemical transformations especially those that are catalyzed by living organisms. The exceedingly slow rates of chemical reactions may be enhanced by a million or more times by the presence and function of living catalysts.

Cochin is often referred to as the industrial capital of the State of Kerala and most of the manufacturing concerns are located along the shore of the Cochin estuarine system. The Cochin estuary, thus receives a large variety of inputs - allochthonous and autochthonous, industrial effluents, urban and domestic wastes etc.

This thesis focuses attention on the role of biogeoorganics in modifying the ecological and environmental condition as well as the nutrient status of the sediments with their minute variability subjected to various physical, chemical and biogeochemical processes. The investigations reported herein pertain to the studies conducted on the sedimentary environments of the Cochin estuarine system between April 1990 and March 1991. Besides characterising the sediment for their texture, carbon and nitrogen and phosphorus contents, analyses of chlorophyll a,b,c, carotenoids, pheopigment, carbohydrate, lipids, protein, humic acid and hydroxylated aromatic compounds have been carried out.

The hydrographical features of the Cochin estuary were subjected to considerable seasonal changes influenced by influx of river water and tidal intrusion of seawater. Salinity showed distinct seasonal variations in the estuarine region of the Cochin estuary. High values of salinity were registered during premonsoon period and low values during the monsoon months. The northern arm of the estuary registered high salinity as compared with southern arm. However, the salinity distribution showed conspecuous seasonalvariability with the onset and withdrawal of south west monsoon.

High monsoonal values of dissolved oxygen were observed all along the estuary; the values decreased as the season advanced to post- and premonsoons. However, no anoxic condition was observed although a lowering in the dissolved oxygen content was noticed at the locations which were badly polluted. The pH of the entire area of study, remained almost neutral with no significant variations. The slightly increased value of pH observed during premonsoon period might be due to the excessive photosynthetic productivity in this region and the influence of industrial wastes.

Textural studies based on sand, silt and clay ratios of sediments indicated that sand was predominant in the riverine region, and sand, silt, clay or sitly clay or clayey silt in the estuarine region. The decreasing trend observed in grain size suggested the transport of sediment from riverine to estuarine region.

The concentration levels of sediment organic carbon showed marked seasonal variations. In the riverine stations, the sediment organic carbon registered highest values during monsoon months, while the estuarine zone showed higher values during the postmonsoon months. The results of organic carbon indicated that the northern arm was considerably polluted with high organic load. The lower concentrations of organic carbon noticed at all riverine stations could be due to the sandy character of the sediment. An inverse relationship existed between particle size and sediment organic carbon. No significant variation was observed among estuarine stations

No seasonal variation of nitrogen was observed at the riverine stations. In the estuarine region, however, (except Station 8 and 9) a postmonsoonal maxima was observed which was the result of contributions from detritus plankton and decay of vegetation.. The premonsoonal decrease in the nitrogen at estuarine region of the northern part could be due to the replenishment of nitrogen to the water column from sediment. The nitrogen distribution profile of the southern arm was different from that of northern part due to the physicochemical charactristics and biogeochemical procesess.

Distribution of phosphorus was almost similar to that obtained for nitrogen. The variation observed in the riverine stations were attributed to the sandy nature of the sediment. The study indicated a decrease in phosphorus content from the estuarine to riverine region. The northern part of the estuary showed higher concentrations of phosphorus during monsoon months as a result of adsorption behaviour of mud.

Studies of carbon, nitrogen and phosphorus in the sediment thus suggested that the estuary was polluted with high organics and phosphorus content and that these inputs were mostly of allochthonous in nature

The biochemical compounds such as carbohydrates, proteins and lipids were studied and it was observed that all of them were abundant and widely distributed in the sediment and varied spatially and temporally. Carbohydrates were lowest during monsoon months and increased during post- and premonsoon months . The carbohydrate in the sediment composed of > 58% of the organic carbon. The high concentrations of carbohydrate in the estuarine region could be attributed to the anthropogenic input, high rate of sedimentation, productivity and the death and decay of aquatic organisms and floating plants. In the present study, the carbon normalised value was suggestive of its terrestrial origin.

The high concentration of lipid observed during the post-monsoon period was indicative of the biolgical activity associated with productivity and the death and decay of organisms and plants. The decrease in concentration of lipids during premonsoon period indicated their availability for biological utilization as high energy rich compounds.

Higher amount of protein was always found to be associated with the northern arm of the estuary than the southern arm during both post and premonsoon periods. This could be due to the accumulation of plant material into the clay minerals of the sediment where they remained resistant to chemical and biological breakdown. The premonsoonal decrease observed at the estuarine stations may be due to the preferential utilization of protein by benthic organisms or the condensation of protein into humic acids.

Humic acids were bountiful in the surficial sediments and varied significantly with soil and ecosystem strata, type of vegetation and season. Humic acid in the surficial sediment exerted a profound influence on the productivity of the ecosystem, trace metal toxicity and nutrient availability. The negative correlation obtained between organic carbon and humic acid in the estuarine region was suggestive of the leaching of humic acids to the overlying water column.

Hydroxylated aromatic compounds were high in the estuarine zone and it could be used as biomarker of the transport and pathways of pulp- paper mill effluents and vascular plant material.

In general, the present study indicated that the estuary, especially, the northern part where the Periyar river drains, was polluted with high organic matter and phosphorus. The studies of biogeoorganics revealed that the organic matter is mostly of terrestrial origin and make profound influene in the biogeochemical processes

This study has been the first comprehensive attempt ever made to characterise the biogeoorganics in an estuarine sedimentary environment. It has served to emphasis the prominent role of biogeoorganics in regulating the complex interactive forces that operate within the estuarine system. Characterisation of organic matter has made it possible to trace the source and predict the fate of allochthonous and autochthonous inputs that find thier way into this transition zone. Most of the parameters analysed herein could individually be used as biomarkers of the health of the estuary. It was not the intention in this study to seperate the parameters into their respective constituents: such an approach would warrant more rigorous and comprehensive investigations and would open up new vistas in estuarine biogeoorganic chemistry.

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# APPENDIX

Table 1. Distribution of salinity ($x10^{-3}$) in the Cochin estuary.

| Month | | Stations | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
| Apr'90 | s | 0.00 | 0.00 | 0.25 | 2.54 | 13.53 | 22.24 | 24.82 | 17.54 | 6.88 | 0.33 | 0.00 |
| | b | 0.00 | 0.00 | 0.52 | 10.76 | 16.78 | 24.45 | 25.96 | 25.13 | 16.02 | 0.17 | 0.00 |
| May'90 | s | 0.00 | 0.00 | 0.00 | 0.08 | 0.88 | 2.47 | 3.42 | 0.56 | 0.83 | 0.00 | 0.00 |
| | b | 0.00 | 0.00 | 0.00 | 0.11 | 1.84 | 3.75 | 8.85 | 0.83 | 0.17 | 0.08 | 0.00 |
| Jun'90 | s | 0.06 | 0.08 | 0.06 | 0.06 | 0.16 | 0.24 | 0.43 | 0.23 | 0.83 | 0.03 | 0.03 |
| | b | 0.06 | 0.08 | 0.06 | 0.06 | 0.16 | 0.24 | 0.51 | 0.32 | 0.08 | 0.03 | 0.03 |
| Jul'90 | s | 0.00 | 0.00 | 0.00 | 0.00 | 0.08 | 0.30 | 0.67 | 0.08 | 0.00 | 0.00 | 0.00 |
| | b | 0.00 | 0.00 | 0.00 | 0.00 | 0.14 | 0.40 | 0.67 | 0.03 | 0.00 | 0.00 | 0.00 |
| Aug'90 | s | 0.04 | 0.04 | 0.04 | 0.40 | 0.16 | 1.46 | 2.45 | 0.61 | 0.14 | 0.14 | 0.11 |
| | b | 0.04 | 0.04 | 0.04 | 0.04 | 0.19 | 1.73 | 4.07 | 0.51 | 0.08 | 0.08 | 0.08 |
| Sep'90 | s | 0.00 | 0.00 | 0.14 | 0.14 | 1.50 | 9.80 | 9.91 | 7.25 | 0.35 | 0.00 | 0.00 |
| | b | 0.00 | 0.00 | 0.14 | 0.24 | 4.28 | 10.86 | 10.97 | 16.39 | 1.20 | 0.00 | 0.00 |
| Oct'90 | s | 0.00 | 0.00 | 0.00 | 0.35 | 3.90 | 6.62 | 15.96 | 12.03 | 2.37 | 0.00 | 0.00 |
| | b | 0.00 | 0.00 | 0.00 | 0.03 | 7.04 | 9.70 | 22.33 | 24.03 | 2.90 | 0.00 | 0.00 |
| Nov'90 | s | 0.00 | 0.00 | 0.00 | 0.16 | 3.57 | 10.65 | 15.13 | 10.27 | 1.05 | 0.00 | 0.00 |
| | b | 0.00 | 0.00 | 0.00 | 0.80 | 15.00 | 17.18 | 25.11 | 30.10 | 4.13 | 0.00 | 0.00 |
| Dec'90 | s | 0.00 | 0.00 | 0.00 | 10.54 | 12.83 | 2.51 | 35.86 | 23.70 | 15.39 | 4.64 | 0.93 |
| | b | 0.00 | 0.00 | 0.54 | 11.93 | 20.51 | 23.06 | 35.00 | 35.86 | 25.62 | 13.98 | 5.41 |
| Jan'91 | s | 0.16 | 0.26 | 0.80 | 1.95 | 21.78 | 23.70 | 26.90 | 20.47 | 6.68 | 0.80 | 0.00 |
| | b | 0.41 | 0.26 | 1.18 | 14.23 | 11.02 | 24.34 | 28.18 | 26.90 | 15.62 | 0.00 | 0.00 |
| Feb'91 | s | 0.00 | 0.00 | 0.16 | 4.38 | 16.66 | 28.45 | 30.10 | 19.87 | 7.07 | 0.93 | 0.00 |
| | b | 0.00 | 0.00 | 0.29 | 4.64 | 21.14 | 29.46 | 31.00 | 21.14 | 10.90 | 1.31 | 0.00 |
| Mar'91 | s | 0.00 | 0.00 | 0.19 | 0.54 | 11.04 | 22.42 | 21.78 | 16.00 | 3.23 | 0.67 | 0.19 |
| | b | 0.00 | 0.00 | 0.67 | 11.68 | 19.99 | 21.79 | 25.62 | 21.79 | 19.20 | 6.68 | 0.93 |

s: surface b: bottom

Table 2. Distribution of dissolved oxygen (ml/l) in the Cochin estuary.

| Month | | Stations | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
| Apr'90 | s | 5.63 | 4.45 | 4.60 | 5.20 | 4.28 | 3.17 | 3.55 | 6.99 | 5.56 | 5.12 | 4.76 |
| | b | 5.43 | 4.19 | 4.91 | 3.93 | 4.54 | 3.00 | 3.01 | 3.11 | 2.29 | 4.78 | 4.76 |
| May'90 | s | 4.93 | 4.56 | 4.43 | 4.48 | 4.43 | 4.09 | 3.65 | 2.54 | 4.09 | 4.43 | 4.81 |
| | b | 5.34 | 4.43 | 3.70 | 5.04 | 4.37 | 3.98 | 3.32 | 2.82 | 4.21 | 4.65 | 4.98 |
| Jun'90 | s | 4.98 | 4.42 | 4.53 | 5.10 | 4.87 | 4.76 | 4.76 | 4.08 | 4.76 | 5.33 | 5.21 |
| | b | 5.89 | 4.31 | 5.10 | 5.55 | 5.33 | 5.78 | 5.10 | 4.31 | 5.21 | 5.44 | 5.33 |
| Jul'90 | s | 5.66 | 5.33 | 5.55 | 5.44 | 5.21 | 5.33 | 4.76 | 4.53 | 5.66 | 5.67 | 5.55 |
| | b | 5.89 | 5.67 | 5.89 | 5.78 | 5.44 | 5.33 | 4.87 | 4.65 | 5.67 | 5.89 | 5.89 |
| Aug'90 | s | 5.85 | 5.28 | 4.83 | 5.85 | 5.40 | 4.95 | 4.27 | 4.72 | 3.94 | 5.28 | 5.85 |
| | b | 5.85 | 4.95 | 5.73 | 5.96 | 5.73 | 5.28 | 4.61 | 5.06 | 5.51 | 6.07 | 5.96 |
| Sep'90 | s | 5.21 | 4.99 | 4.08 | 5.55 | 4.76 | 3.74 | 3.74 | 4.98 | 4.87 | 4.76 | 4.76 |
| | b | 5.33 | 4.20 | 4.65 | 5.10 | 4.19 | 3.63 | 3.85 | 2.95 | 4.42 | 5.10 | 4.99 |
| Oct'90 | s | 5.27 | 4.70 | 5.21 | 4.87 | 4.53 | 3.74 | 2.38 | 2.83 | 3.29 | 4.42 | 4.53 |
| | b | 5.44 | 4.99 | 5.33 | 4.99 | 3.51 | 4.53 | 2.72 | 1.93 | 3.29 | 4.97 | 4.87 |
| Nov'90 | s | 5.44 | 4.87 | 5.21 | 5.21 | 4.99 | 3.63 | 3.74 | 4.19 | 2.95 | 3.29 | 5.10 |
| | b | 5.44 | 4.76 | 5.44 | 5.33 | 4.76 | 3.17 | 3.17 | 3.63 | 3.51 | 4.76 | 5.21 |
| Dec'90 | s | 5.44 | 4.87 | 4.87 | 5.10 | 5.84 | 4.08 | 3.63 | 3.85 | 6.91 | 4.19 | 4.53 |
| | b | 5.33 | 5.10 | 4.76 | 4.76 | 3.83 | 2.89 | 3.97 | 3.40 | 3.23 | 5.56 | 3.40 |
| Jan'91 | s | 5.13 | 3.32 | 5.14 | 5.00 | 4.91 | 3.32 | 3.59 | 4.16 | 3.19 | 5.05 | 4.62 |
| | b | 4.60 | 2.43 | 5.14 | 3.94 | 3.72 | 3.50 | 3.72 | 4.74 | 4.96 | 5.69 | 4.21 |
| Feb'91 | s | 5.95 | 4.19 | 4.42 | 4.99 | 3.74 | 3.06 | 2.88 | 2.49 | 4.76 | 4.30 | 4.65 |
| | b | 5.95 | 3.63 | 5.21 | 4.65 | 3.51 | 3.06 | 3.17 | 2.61 | 4.30 | 2.15 | 4.99 |
| Mar'91 | s | 5.56 | 4.42 | 4.31 | 5.10 | 5.10 | 3.17 | 3.40 | 4.53 | 4.76 | 4.65 | 4.76 |
| | b | 5.32 | 4.19 | 4.53 | 3.62 | 3.17 | 3.97 | 2.72 | 2.72 | 3.06 | 3.29 | 4.76 |

s: surface  b: bottom

Table 3. Distribution of pH in the Cochin estuary

| Month |  | Stations |  |  |  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
| Apr'90 | s | 7.18 | 7.34 | 6.92 | 7.28 | 7.53 | 7.39 | 7.42 | 7.08 | 7.12 | 6.86 | 6.98 |
|  | b | 7.27 | 7.49 | 7.34 | 7.48 | 7.64 | 7.44 | 7.49 | 7.10 | 7.10 | 6.77 | 6.79 |
| May'90 | s | 7.04 | 6.89 | 6.97 | 7.00 | 7.01 | 7.00 | 7.02 | 7.01 | 6.94 | 7.01 | 7.05 |
|  | b | 7.05 | 6.97 | 6.97 | 7.00 | 7.00 | 7.01 | 7.01 | 7.09 | 7.04 | 7.02 | 7.02 |
| Jun'90 | s | 6.96 | 6.88 | 6.65 | 7.02 | 6.96 | 6.88 | 7.00 | 6.95 | 6.95 | 7.00 | 6.92 |
|  | b | 6.91 | 6.89 | 6.53 | 7.01 | 6.89 | 7.06 | 6.94 | 6.83 | 6.98 | 6.97 | 7.02 |
| Jul'90 | s | 6.99 | 6.99 | 6.99 | 6.95 | 7.00 | 7.55 | 6.90 | 6.95 | 7.00 | 6.93 | 6.68 |
|  | b | 7.00 | 6.99 | 7.00 | 6.85 | 7.00 | 7.59 | 6.97 | 6.95 | 6.98 | 6.95 | 6.61 |
| Aug'90 | s | 7.00 | 7.05 | 7.10 | 7.35 | 7.20 | 8.00 | 7.50 | 6.80 | 6.70 | 6.53 | 7.80 |
|  | b | 7.00 | 7.25 | 7.15 | 7.30 | 7.25 | 7.60 | 7.60 | 6.80 | 6.60 | 6.85 | 8.00 |
| Sep'90 | s | 7.36 | 7.20 | 7.36 | 7.59 | 7.45 | 7.79 | 7.63 | 7.67 | 6.73 | 6.93 | 6.53 |
|  | b | 7.23 | 7.23 | 7.29 | 7.29 | 7.51 | 7.63 | 7.59 | 7.47 | 6.74 | 6.77 | 6.49 |
| Oct'90 | s | 6.70 | 6.30 | 6.90 | 7.60 | 6.75 | 7.00 | 6.40 | 7.30 | 6.85 | 6.76 | 6.86 |
|  | b | 6.53 | 6.40 | 6.80 | 6.92 | 6.80 | 6.80 | 7.10 | 7.46 | 6.80 | 6.57 | 6.83 |
| Nov'90 | s | 7.40 | 6.80 | 7.10 | 7.70 | 6.40 | 6.30 | 6.80 | 6.00 | 5.70 | 6.80 | 5.80 |
|  | b | 7.40 | 6.70 | 7.50 | 6.60 | 6.40 | 6.40 | 7.50 | 6.50 | 6.00 | 5.50 | 6.50 |
| Dec'90 | s | 7.34 | 7.31 | 7.37 | 7.18 | 8.15 | 7.91 | 7.92 | 7.74 | 8.17 | 6.52 | 6.46 |
|  | b | 7.24 | 7.37 | 7.14 | 7.42 | 7.81 | 7.73 | 7.95 | 7.85 | 7.67 | 7.25 | 6.24 |
| Jan'91 | s | 7.68 | 7.39 | 7.56 | 7.52 | 7.35 | 7.53 | 7.56 | 7.37 | 7.36 | 6.92 | 6.45 |
|  | b | 7.42 | 7.43 | 7.17 | 7.04 | 7.45 | 7.52 | 7.71 | 7.31 | 7.15 | 6.75 | 6.58 |
| Feb'91 | s | 7.18 | 7.38 | 7.58 | 7.09 | 7.34 | 7.53 | 7.48 | 7.03 | 7.09 | 6.81 | 6.40 |
|  | b | 7.13 | 7.39 | 7.27 | 6.95 | 7.43 | 7.55 | 7.59 | 7.09 | 7.18 | 6.58 | 5.99 |
| Mar'91 | s | 7.41 | 7.37 | 7.43 | 7.46 | 7.87 | 7.61 | 7.37 | 8.09 | 7.47 | 7.02 | 6.89 |
|  | b | 7.28 | 7.41 | 7.27 | 6.84 | 7.53 | 7.44 | 7.48 | 7.75 | 7.50 | 6.86 | 6.64 |

s: surface  b: bottom

Table 4. Monthly data of total sedimentary organic carbon (mg/g) in the Cochin estuary

| Month | Stations | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
| Apr'90 | 2.02 | 3.02 | 40.13 | 2.97 | 3.40 | 13.61 | 23.51 | 31.44 | 38.88 | 2.23 | 39.92 |
| May'90 | 6.13 | 3.67 | 5.31 | 3.85 | 9.76 | 11.73 | 27.30 | 29.24 | 20.00 | 3.26 | 39.48 |
| Jun'90 | 1.31 | 26.61 | 3.42 | 5.11 | 5.84 | 18.38 | 27.38 | 34.42 | 43.91 | 1.44 | 46.56 |
| Jul'90 | 0.93 | 17.18 | 2.06 | 1.06 | 2.32 | 25.61 | 23.76 | 34.80 | 43.83 | 0.58 | 45.57 |
| Aug'90 | 0.63 | 9.79 | 4.72 | 0.96 | 3.69 | 29.28 | 23.40 | 31.93 | 71.44 | 0.27 | 46.64 |
| Sep'90 | 1.38 | 9.45 | 9.42 | 1.25 | 1.58 | 36.80 | 25.30 | 37.03 | 107.09 | 0.53 | 41.28 |
| Oct'90 | 0.99 | 10.55 | 3.24 | 1.35 | 2.32 | 26.30 | 28.12 | 35.43 | 82.59 | 1.13 | 40.15 |
| Nov'90 | 0.56 | 3.64 | 45.39 | 0.71 | 1.20 | 27.67 | 30.66 | 30.32 | 79.06 | 2.54 | 44.11 |
| Dec'90 | 1.41 | 5.79 | 60.38 | 2.74 | 0.62 | 28.59 | 33.03 | 32.83 | 125.06 | 2.04 | 32.00 |
| Jan'91 | 1.85 | 8.55 | 3.33 | 1.63 | 1.77 | 9.88 | 25.48 | 34.18 | 20.90 | 3.59 | 30.68 |
| Feb'91 | 1.28 | 4.97 | 14.30 | 2.56 | 2.06 | 14.86 | 26.54 | 33.03 | 30.29 | 4.71 | 38.47 |
| Mar'91 | 1.11 | 2.39 | 55.95 | 2.85 | 1.69 | 16.31 | 20.00 | 25.03 | 19.08 | 4.53 | 39.28 |

Table 5. Monthly data of total sedimentary nitrogen (mg/g) in the Cochin estuary

| Month | Stations | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
| Apr'90 | 0.20 | 0.85 | 1.83 | 0.29 | 0.21 | 0.81 | 0.93 | 2.63 | 1.85 | 0.56 | 0.65 |
| May'90 | 0.65 | 0.02 | 0.37 | 0.14 | 0.46 | 0.71 | 0.24 | 2.14 | 1.54 | 0.21 | 0.85 |
| Jun'90 | 0.25 | 1.54 | 0.25 | 0.35 | 0.49 | 0.63 | 1.12 | 3.12 | 3.92 | 0.28 | 1.65 |
| Jul'90 | 0.14 | 1.02 | 0.32 | 0.35 | 0.28 | 2.31 | 1.58 | 2.38 | 4.20 | 0.21 | 0.86 |
| Aug'90 | 0.21 | 0.84 | 0.39 | 0.14 | 0.44 | 2.73 | 1.78 | 3.29 | 2.66 | 0.42 | 2.52 |
| Sep'90 | 0.28 | 0.49 | 0.88 | 0.39 | 0.32 | 1.33 | 2.10 | 2.24 | 3.71 | 0.35 | 2.31 |
| Oct'90 | 0.28 | 0.42 | 0.49 | 0.43 | 0.42 | 1.82 | 1.75 | 1.75 | 3.64 | 0.58 | 1.33 |
| Nov'90 | 0.21 | 0.35 | 2.10 | 0.49 | 0.21 | 2.52 | 2.31 | 1.95 | 1.40 | 0.42 | 0.91 |
| Dec'90 | 0.28 | 0.32 | 1.33 | 0.39 | 0.25 | 2.14 | 1.61 | 0.46 | 2.24 | 0.42 | 1.68 |
| Jan'91 | 0.42 | 0.56 | 0.91 | 0.35 | 0.35 | 0.91 | 1.75 | 3.57 | 1.53 | 0.56 | 1.75 |
| Feb'91 | 0.21 | 0.35 | 1.12 | 0.46 | 0.32 | 1.09 | 1.56 | 2.89 | 1.05 | 0.53 | 1.44 |
| Mar'91 | 0.28 | 0.11 | 2.38 | 0.32 | 0.28 | 0.95 | 1.75 | 2.80 | 1.30 | 0.39 | 2.50 |

Table 6. Monthly data of total sedimentary phosphorus (mg/g) in the Cochin estuary.

| Month | Stations | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
| Apr'90 | 0.25 | 0.27 | 0.57 | 0.26 | 0.29 | 0.90 | 1.57 | 1.75 | 1.91 | 0.57 | 6.24 |
| May'90 | 0.26 | 0.40 | 0.27 | 0.22 | 0.36 | 0.69 | 1.64 | 1.92 | 1.50 | 0.26 | 8.39 |
| Jun'90 | 0.18 | 0.78 | 0.43 | 0.23 | 0.29 | 1.03 | 1.97 | 2.35 | 2.60 | 0.08 | 7.29 |
| Jul'90 | 0.16 | 0.70 | 0.22 | 0.10 | 0.03 | 1.59 | 1.37 | 2.81 | 4.48 | 0.12 | 7.73 |
| Aug'90 | 0.17 | 0.62 | 0.24 | 0.12 | 0.18 | 1.93 | 1.57 | 2.81 | 2.37 | 0.13 | 7.31 |
| Sep'90 | 0.22 | 0.64 | 0.50 | 0.21 | 0.19 | 1.94 | 2.51 | 2.37 | 2.10 | 0.28 | 6.38 |
| Oct'90 | 0.26 | 0.50 | 0.26 | 0.23 | 0.17 | 1.72 | 1.53 | 1.58 | 2.25 | 0.26 | 6.75 |
| Nov'90 | 0.24 | 0.44 | 1.29 | 0.23 | 0.13 | 1.71 | 2.06 | 1.81 | 2.91 | 0.63 | 7.17 |
| Dec'90 | 0.23 | 0.41 | 1.29 | 0.24 | 0.12 | 1.34 | 1.87 | 1.56 | 2.44 | 0.48 | 6.58 |
| Jan'91 | 0.19 | 0.49 | 0.32 | 0.21 | 0.18 | 0.62 | 1.76 | 0.77 | 1.22 | 0.98 | 6.39 |
| Feb'91 | 0.26 | 0.38 | 0.48 | 0.30 | 0.24 | 0.89 | 1.45 | 2.11 | 1.11 | 0.79 | 5.54 |
| Mar'91 | 0.25 | 0.21 | 1.14 | 0.30 | 0.22 | 0.90 | 1.63 | 1.61 | 0.94 | 0.83 | 5.05 |

Table 7. Monthly C:N ratio in the Cochin estuary.

| Month | Stations | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
| Apr'90 | 10.10 | 3.55 | 21.93 | 10.24 | 16.19 | 16.80 | 25.28 | 11.95 | 21.02 | 3.98 | 61.42 |
| May'90 | 9.43 | 183.50 | 14.35 | 27.50 | 21.22 | 16.52 | 113.75 | 13.66 | 12.99 | 15.52 | 46.45 |
| Jun'90 | 5.24 | 17.28 | 13.68 | 14.60 | 11.92 | 29.17 | 24.45 | 11.03 | 11.20 | 5.14 | 28.22 |
| Jul'90 | 6.64 | 16.84 | 6.44 | 3.03 | 8.29 | 11.09 | 15.04 | 14.62 | 10.44 | 2.76 | 52.99 |
| Aug'90 | 3.00 | 11.65 | 12.10 | 6.86 | 8.39 | 10.73 | 13.15 | 9.71 | 26.86 | 0.64 | 18.51 |
| Sep'90 | 4.93 | 19.29 | 10.70 | 3.21 | 4.94 | 27.67 | 12.05 | 16.53 | 28.87 | 1.51 | 17.87 |
| Oct'90 | 3.54 | 25.12 | 6.61 | 3.14 | 5.52 | 14.45 | 16.07 | 20.25 | 22.69 | 1.95 | 30.19 |
| Nov'90 | 2.67 | 10.40 | 21.61 | 1.45 | 5.71 | 10.98 | 13.27 | 15.55 | 56.47 | 6.05 | 48.47 |
| Dec'90 | 5.04 | 18.09 | 45.40 | 7.03 | 2.48 | 13.36 | 20.52 | 71.37 | 55.83 | 4.86 | 19.05 |
| Jan'91 | 4.40 | 15.27 | 3.66 | 4.66 | 5.06 | 10.86 | 14.56 | 9.57 | 13.66 | 6.41 | 17.53 |
| Feb'91 | 6.10 | 14.20 | 12.77 | 5.57 | 6.44 | 13.63 | 17.01 | 11.43 | 28.85 | 8.89 | 26.72 |
| Mar'91 | 3.96 | 21.73 | 23.51 | 8.91 | 6.04 | 17.17 | 11.43 | 8.94 | 14.68 | 11.62 | 15.71 |

Table 8. Monthly N:P ratio in the Cochin estuary.

| Month | Stations | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
| May'90 | 2.47 | 0.05 | 1.36 | 0.63 | 1.27 | 1.02 | 0.15 | 1.11 | 1.03 | 0.80 | 0.10 |
| Jun'90 | 1.38 | 1.96 | 0.58 | 1.52 | 1.67 | 0.61 | 0.57 | 1.33 | 1.51 | 3.54 | 0.23 |
| Jul'90 | 0.89 | 1.46 | 1.44 | 3.53 | 8.21 | 1.45 | 1.15 | 0.85 | 0.94 | 1.82 | 0.11 |
| Aug'90 | 1.24 | 1.35 | 1.64 | 1.19 | 2.40 | 1.42 | 1.13 | 1.17 | 1.12 | 3.24 | 0.34 |
| Sep'90 | 1.28 | 0.77 | 1.76 | 1.87 | 1.73 | 0.69 | 0.84 | 0.95 | 1.76 | 1.24 | 0.36 |
| Oct'90 | 1.09 | 0.84 | 1.88 | 1.83 | 2.49 | 1.06 | 1.14 | 1.11 | 1.62 | 2.25 | 0.20 |
| Nov'90 | 0.89 | 0.79 | 1.62 | 2.10 | 1.61 | 1.48 | 1.12 | 1.08 | 0.48 | 0.67 | 0.13 |
| Dec'90 | 1.24 | 0.78 | 1.03 | 1.61 | 2.13 | 1.59 | 0.86 | 0.29 | 0.92 | 0.88 | 0.26 |
| Jan'91 | 2.20 | 1.14 | 2.88 | 1.64 | 1.98 | 1.47 | 0.99 | 4.63 | 1.26 | 0.57 | 0.27 |
| Feb'91 | 0.82 | 0.92 | 2.35 | 1.54 | 1.32 | 1.22 | 1.08 | 1.37 | 0.95 | 0.67 | 0.26 |
| Mar'91 | 1.14 | 0.52 | 2.08 | 1.08 | 1.25 | 1.06 | 1.08 | 1.74 | 1.38 | 0.47 | 0.49 |

Table 9. Monthly C:P ratio in the Cochin estuary.

| Month | Stations | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
| Apr'90 | 8.19 | 11.22 | 70.28 | 11.52 | 11.56 | 15.12 | 14.97 | 17.98 | 20.33 | 3.92 | 6.39 |
| May'90 | 23.32 | 9.29 | 19.53 | 17.32 | 26.98 | 16.90 | 16.69 | 15.20 | 13.32 | 12.34 | 4.71 |
| Jun'90 | 7.24 | 33.91 | 7.93 | 22.13 | 19.94 | 17.85 | 13.87 | 14.65 | 16.89 | 18.22 | 6.38 |
| Jul'90 | 5.91 | 24.55 | 9.26 | 10.69 | 68.04 | 16.10 | 17.31 | 12.37 | 9.79 | 5.02 | 5.89 |
| Aug'90 | 3.71 | 15.79 | 19.83 | 8.15 | 20.14 | 15.18 | 14.89 | 11.35 | 30.09 | 2.08 | 6.38 |
| Sep'90 | 6.31 | 14.82 | 18.85 | 6.00 | 8.52 | 18.98 | 10.08 | 15.62 | 50.88 | 1.88 | 6.48 |
| Oct'90 | 3.84 | 21.11 | 12.43 | 5.75 | 13.76 | 15.30 | 18.33 | 22.49 | 36.76 | 4.38 | 5.94 |
| Nov'90 | 2.36 | 8.18 | 35.05 | 3.05 | 9.17 | 16.21 | 14.90 | 16.74 | 27.18 | 4.04 | 6.15 |
| Dec'90 | 6.22 | 14.14 | 46.69 | 11.32 | 5.29 | 21.29 | 17.63 | 20.99 | 51.32 | 4.29 | 4.87 |
| Jan'91 | 9.70 | 17.37 | 10.53 | 7.65 | 10.03 | 15.97 | 14.45 | 44.37 | 17.16 | 3.67 | 4.80 |
| Feb'91 | 5.00 | 13.00 | 30.05 | 8.56 | 8.48 | 16.70 | 18.29 | 15.64 | 27.32 | 5.97 | 6.95 |
| Mar'91 | 4.52 | 11.29 | 49.00 | 9.66 | 7.57 | 18.17 | 12.30 | 15.59 | 20.23 | 5.47 | 7.77 |

Table 10. Monthly data of sedimentary chlorophyll a (µg/g) in the Cochin estuary.

| Month | Station | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
| May'90 | 3.01 | 0.42 | 1.54 | 6.98 | 11.88 | 11.49 | 17.06 | 69.37 | 58.31 | 1.69 | 9.06 |
| Jun'90 | 0.38 | 2.02 | 0.93 | 0.70 | 6.73 | 18.25 | 20.65 | 46.44 | 97.99 | 1.37 | 7.39 |
| Jul'90 | 0.59 | 2.74 | 0.67 | 0.54 | 1.81 | 18.49 | 13.95 | 42.50 | 119.54 | 0.69 | 5.35 |
| Aug'90 | 0.13 | 0.73 | 0.69 | 0.28 | 2.36 | 16.03 | 16.61 | 30.38 | 54.82 | 0.38 | 11.75 |
| Sep'90 | 0.36 | 0.57 | 1.52 | 1.07 | 0.78 | 18.39 | 16.96 | 28.81 | 41.16 | 0.42 | 8.01 |
| Oct'90 | 0.00 | 0.39 | 0.14 | 1.25 | 1.57 | 18.76 | 37.77 | 19.29 | 28.80 | 0.69 | 7.45 |
| Nov'90 | 1.44 | 2.45 | 17.23 | 2.13 | 3.57 | 25.57 | 29.41 | 53.22 | 50.24 | 3.20 | 13.98 |
| Dec'90 | 1.79 | 1.95 | 13.61 | 4.68 | 2.82 | 18.68 | 30.92 | 32.13 | 40.77 | 3.33 | 6.87 |
| Jan'91 | 2.05 | 1.21 | 3.87 | 3.70 | 3.41 | 10.23 | 28.42 | 93.47 | 29.88 | 8.93 | 8.95 |
| Feb'91 | 1.70 | 1.36 | 10.36 | 4.58 | 3.99 | 3.57 | 25.80 | 85.48 | 24.03 | 11.62 | 14.94 |
| Mar'91 | 3.09 | 2.75 | 16.67 | 6.25 | 8.45 | 21.04 | 35.32 | 69.64 | 41.63 | 11.62 | 15.09 |

Table 11. Monthly data of sedimentary chlorophyll b (µg/g) in the Cochin estuary.

| Month | Station | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
| May'90 | 1.01 | 0.44 | 0.97 | 1.30 | 7.12 | 5.93 | 9.03 | 12.72 | 7.12 | 0.77 | 5.25 |
| Jun'90 | 0.54 | 1.82 | 0.89 | 0.63 | 3.10 | 10.54 | 9.58 | 6.89 | 28.87 | 1.03 | 4.87 |
| Jul'90 | 0.81 | 2.24 | 0.87 | 0.59 | 1.93 | 5.85 | 5.66 | 18.35 | 15.51 | 0.65 | 1.93 |
| Aug'90 | 0.14 | 0.22 | 0.38 | 0.03 | 0.93 | 4.71 | 4.62 | 5.53 | 44.09 | 0.33 | 4.98 |
| Sep'90 | 0.02 | 0.13 | 1.13 | 0.19 | 0.15 | 4.86 | 4.21 | 5.87 | 3.81 | 0.01 | 2.38 |
| Oct'90 | 0.00 | 0.13 | 0.05 | 0.24 | 0.21 | 5.53 | 22.82 | 5.45 | 3.85 | 0.26 | 2.54 |
| Nov'90 | 1.83 | 2.96 | 7.92 | 1.93 | 3.48 | 14.67 | 13.41 | 11.30 | 10.32 | 2.17 | 7.26 |
| Dec'90 | 1.34 | 1.72 | 6.03 | 1.57 | 2.68 | 8.30 | 10.78 | 8.67 | 10.97 | 1.70 | 5.21 |
| Jan'91 | 1.08 | 1.15 | 2.99 | 1.18 | 2.36 | 5.98 | 11.21 | 6.63 | 6.08 | 2.01 | 3.97 |
| Feb'91 | 1.35 | 1.37 | 6.96 | 1.59 | 3.48 | 8.63 | 12.93 | 10.07 | 7.03 | 3.26 | 6.75 |
| Mar'91 | 3.46 | 3.47 | 13.00 | 3.46 | 8.01 | 16.98 | 21.17 | 23.68 | 18.94 | 7.60 | 13.21 |

Table 12. Monthly data of sedimentary chlorophyll c (µg/g) in the Cochin estuary.

| Month | Station | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
| May'90 | 1.78 | 1.06 | 1.87 | 2.08 | 13.11 | 10.32 | 11.82 | 14.95 | 7.42 | 1.57 | 10.24 |
| Jun'90 | 1.54 | 4.03 | 2.01 | 1.59 | 5.18 | 20.20 | 15.46 | 5.96 | 59.99 | 2.39 | 11.57 |
| Jul'90 | 2.06 | 4.21 | 2.31 | 1.45 | 4.84 | 6.34 | 7.75 | 36.10 | 13.14 | 1.64 | 3.67 |
| Aug'90 | 0.27 | 0.12 | 1.50 | 0.02 | 1.17 | 3.96 | 3.28 | 3.88 | 1.06 | 0.80 | 7.23 |
| Sep'90 | 0.01 | 0.14 | 2.19 | 0.35 | 0.04 | 3.54 | 2.47 | 6.32 | 1.52 | 0.16 | 1.44 |
| Oct'90 | 0.00 | 0.18 | 0.07 | 0.74 | 0.22 | 6.11 | 51.56 | 8.54 | 2.84 | 5.67 | 2.54 |
| Nov'90 | 4.58 | 7.39 | 7.97 | 4.63 | 8.24 | 29.63 | 24.97 | 16.79 | 16.61 | 4.93 | 12.11 |
| Dec'90 | 3.33 | 4.01 | 5.38 | 3.01 | 6.31 | 12.82 | 13.37 | 12.65 | 17.64 | 3.56 | 10.71 |
| Jan'91 | 2.38 | 2.70 | 5.37 | 2.72 | 4.89 | 10.73 | 16.65 | 2.69 | 10.10 | 3.79 | 7.51 |
| Feb'91 | 3.22 | 3.43 | 11.36 | 3.51 | 7.90 | 17.94 | 24.35 | 10.13 | 12.75 | 6.74 | 13.75 |
| Mar'91 | 8.45 | 8.60 | 24.84 | 8.19 | 19.24 | 36.80 | 41.41 | 46.59 | 41.62 | 17.80 | 31.06 |

Table 13. Monthly data of sedimentary carotenoids (µg/g) in the Cochin estuary.

| Month | Stations | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
| May'90 | 0.87 | 0.23 | 0.62 | 2.94 | 6.64 | 6.21 | 8.33 | 50.68 | 7.86 | 1.38 | 6.92 |
| Jun'90 | 0.22 | 2.64 | 0.50 | 0.30 | 5.28 | 12.22 | 15.55 | 38.33 | 45.93 | 0.92 | 9.00 |
| Jul'90 | 0.29 | 1.88 | 0.34 | 0.25 | 1.10 | 14.44 | 11.08 | 26.85 | 53.67 | 0.36 | 5.22 |
| Aug'90 | 0.07 | 0.53 | 0.28 | 0.16 | 1.97 | 12.55 | 12.78 | 22.60 | 36.43 | 0.29 | 9.16 |
| Sep'90 | 0.13 | 0.61 | 0.71 | 0.53 | 0.48 | 15.41 | 14.15 | 21.78 | 34.80 | 0.22 | 6.68 |
| Oct'90 | 0.00 | 0.53 | 0.53 | 0.26 | 1.45 | 17.19 | 26.93 | 13.89 | 21.29 | 0.24 | 5.39 |
| Nov'90 | 0.58 | 1.26 | 10.87 | 0.78 | 1.82 | 20.45 | 23.08 | 39.33 | 35.04 | 1.75 | 12.14 |
| Dec'90 | 0.72 | 1.06 | 9.45 | 1.59 | 1.53 | 14.92 | 22.32 | 23.31 | 29.93 | 2.16 | 4.53 |
| Jan'91 | 0.69 | 0.82 | 1.25 | 1.45 | 1.59 | 6.49 | 19.69 | 48.67 | 17.19 | 5.88 | 6.15 |
| Feb'91 | 0.61 | 0.67 | 4.99 | 2.22 | 2.31 | 9.72 | 18.75 | 45.19 | 14.25 | 6.65 | 11.72 |
| Mar'91 | 1.14 | 1.12 | 10.62 | 2.43 | 3.49 | 12.40 | 21.76 | 43.72 | 24.66 | 8.35 | 10.13 |

Table 14. Monthly data of sedimentary pheopigments (µg/g) in the Cochin estuary.

| Month | Station | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
| May'90 | 3.96 | 0.28 | 1.87 | 9.72 | 16.22 | 15.32 | 17.56 | 112.42 | 90.80 | 2.42 | 9.05 |
| Jun'90 | 0.07 | 1.33 | 0.54 | 0.33 | 8.34 | 22.81 | 28.39 | 70.50 | 127.76 | 2.48 | 7.25 |
| Jul'90 | 0.09 | 1.99 | 0.17 | 0.27 | 1.44 | 27.40 | 20.76 | 61.81 | 174.59 | 1.12 | 6.53 |
| Aug'90 | 0.09 | 1.27 | 1.00 | 0.47 | 3.84 | 24.97 | 26.19 | 48.40 | 10.74 | 0.90 | 13.07 |
| Sep'90 | 0.59 | 0.19 | 1.59 | 1.70 | 2.02 | 29.84 | 27.03 | 45.48 | 85.97 | 1.00 | 10.09 |
| Oct'90 | 0.00 | 0.50 | 0.10 | 1.62 | 2.15 | 30.88 | 43.95 | 29.30 | 45.22 | 0.82 | 9.42 |
| Nov'90 | 0.25 | 0.56 | 15.58 | 1.04 | 2.33 | 30.43 | 39.94 | 73.15 | 69.45 | 2.46 | 14.08 |
| Dec'90 | 1.22 | 1.24 | 17.09 | 4.95 | 1.93 | 28.93 | 43.59 | 44.63 | 52.93 | 3.74 | 5.68 |
| Jan'91 | 2.01 | 0.68 | 3.51 | 4.24 | 3.42 | 7.19 | 40.07 | 142.25 | 43.52 | 11.01 | 9.87 |
| Feb'91 | 1.21 | 0.50 | 9.29 | 5.18 | 3.38 | 15.69 | 34.21 | 124.51 | 31.94 | 14.54 | 16.39 |
| Mar'91 | 1.12 | 0.38 | 12.39 | 5.42 | 3.96 | 19.85 | 40.84 | 92.46 | 46.08 | 11.52 | 9.70 |

Table 15. Monthly data of sedimentary carbohydrates (mg/g) in the Cochin estuary.

| Month | Stations | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
| Apr'90 | 1.59 | 0.93 | 10.18 | 1.04 | 1.19 | 2.69 | 4.48 | 5.35 | 7.08 | 0.86 | 3.28 |
| May'90 | 2.26 | 0.79 | 1.39 | 1.23 | 1.78 | 2.10 | 4.99 | 5.51 | 4.44 | 0.84 | 0.33 |
| Jun'90 | 0.58 | 6.08 | 1.89 | 0.69 | 1.48 | 4.11 | 7.47 | 9.78 | 16.92 | 0.59 | 12.93 |
| Jul'90 | 0.76 | 3.51 | 0.75 | 0.64 | 0.53 | 7.77 | 5.07 | 8.60 | 4.13 | 0.47 | 13.64 |
| Aug'90 | 0.53 | 2.42 | 2.12 | 0.66 | 0.90 | 8.18 | 4.92 | 10.64 | 18.05 | 0.29 | 13.74 |
| Sep'90 | 1.03 | 3.30 | 4.48 | 0.68 | 0.44 | 9.58 | 7.01 | 11.56 | 19.13 | 0.60 | 14.80 |
| Oct'90 | 1.52 | 1.75 | 1.86 | 2.77 | 1.08 | 5.59 | 5.66 | 5.80 | 9.96 | 0.62 | 10.98 |
| Nov'90 | 1.45 | 4.10 | 15.68 | 1.70 | 1.00 | 13.64 | 12.03 | 14.10 | 22.32 | 2.19 | 15.50 |
| Dec'90 | 1.46 | 3.20 | 20.26 | 3.36 | 1.33 | 11.34 | 13.25 | 12.29 | 22.86 | 3.01 | 17.14 |
| Jan'91 | 1.71 | 2.18 | 3.72 | 1.02 | 0.63 | 3.01 | 6.24 | 8.25 | 5.92 | 1.63 | 9.00 |
| Feb'91 | 3.23 | 4.73 | 11.47 | 2.55 | 1.83 | 7.96 | 13.52 | 15.98 | 11.70 | 4.01 | 11.21 |
| Mar'91 | 0.91 | 1.08 | 11.08 | 0.96 | 0.55 | 3.29 | 5.27 | 11.32 | 4.15 | 1.36 | 5.61 |

Table 16. Monthly data of sedimentary lipids (mg/g) in the Cochin estuary.

| Month | Stations | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
| Apr'90 | 0.13 | 0.30 | 0.23 | 0.50 | 0.14 | 0.51 | 0.94 | 1.39 | 2.62 | 0.30 | 4.66 |
| May'90 | 0.15 | 0.52 | 0.11 | 0.03 | 0.23 | 0.30 | 0.56 | 1.37 | 1.31 | 0.05 | 4.64 |
| Jun'90 | 0.42 | 1.00 | 0.09 | 0.09 | 0.40 | 0.51 | 0.15 | 0.80 | 2.30 | 0.06 | 6.11 |
| Jul'90 | 0.04 | 0.35 | 0.07 | 0.05 | 0.08 | 0.45 | 0.90 | 1.50 | 2.77 | 0.06 | 10.14 |
| Aug'90 | 0.09 | 0.31 | 0.18 | 0.10 | 0.07 | 0.98 | 0.73 | 1.73 | 5.22 | 0.17 | 5.24 |
| Sep'90 | 0.23 | 0.32 | 0.26 | 0.08 | 0.08 | 1.46 | 0.98 | 1.74 | 0.34 | 0.24 | 4.17 |
| Oct'90 | 0.10 | 0.39 | 0.14 | 0.05 | 0.04 | 1.00 | 1.36 | 1.30 | 2.14 | 0.22 | 2.67 |
| Nov'90 | 0.18 | 0.27 | 1.82 | 0.05 | 0.35 | 1.33 | 2.12 | 2.22 | 2.99 | 0.21 | 7.00 |
| Dec'90 | 0.10 | 2.80 | 1.71 | 0.10 | 0.10 | 0.81 | 1.12 | 1.46 | 0.45 | 0.22 | 2.29 |
| Jan'91 | 0.04 | 0.07 | 3.18 | 0.07 | 0.10 | 0.49 | 1.07 | 1.72 | 0.45 | 0.05 | 2.46 |
| Feb'91 | 0.10 | 0.20 | 0.62 | 0.17 | 0.17 | 0.69 | 1.00 | 2.05 | 0.86 | 0.25 | 4.47 |
| Mar'91 | 0.10 | 0.07 | 0.35 | 0.05 | 0.06 | 0.72 | 1.11 | 1.30 | 0.36 | 0.17 | 6.60 |

Table 17. Monthly data of sedimentary proteins (mg/g) in the Cochin estuary.

| Month | Stations | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
| Apr'90 | 3.12 | 3.06 | 45.02 | 3.88 | 3.23 | 6.83 | 10.56 | 9.25 | 19.37 | 0.99 | 24.18 |
| May'90 | 5.59 | 2.32 | 4.53 | 3.82 | 4.37 | 5.44 | 9.51 | 24.97 | 13.90 | 2.57 | 20.96 |
| Jun'90 | 0.95 | 10.82 | 4.08 | 1.27 | 2.78 | 6.30 | 9.04 | 16.57 | 18.98 | 3.17 | 18.94 |
| Jul'90 | 0.24 | 13.20 | 0.99 | 0.43 | 1.30 | 11.79 | 7.14 | 16.29 | 13.46 | 0.69 | 24.71 |
| Aug'90 | 1.09 | 8.58 | 4.60 | 1.17 | 2.56 | 16.64 | 5.67 | 15.62 | 34.45 | 0.81 | 32.27 |
| Sep'90 | 1.38 | 4.58 | 8.59 | 1.01 | 0.56 | 15.12 | 10.25 | 17.71 | 31.69 | 0.78 | 26.38 |
| Oct'90 | 1.79 | 5.50 | 3.47 | 3.46 | 2.33 | 16.73 | 10.59 | 15.04 | 31.32 | 1.87 | 30.73 |
| Nov'90 | 4.35 | 5.15 | 26.96 | 2.49 | 1.77 | 0.03 | 8.40 | 12.50 | 30.77 | 3.88 | 23.20 |
| Dec'90 | 3.79 | 7.70 | 40.73 | 3.12 | 2.06 | 12.31 | 9.02 | 16.96 | 45.66 | 2.97 | 25.30 |
| Jan'91 | 3.37 | 7.01 | 5.31 | 2.51 | 2.27 | 4.95 | 7.99 | 18.82 | 9.13 | 4.48 | 19.92 |
| Feb'91 | 4.05 | 6.19 | 18.33 | 4.08 | 2.90 | 9.92 | 13.98 | 22.14 | 18.80 | 4.65 | 30.68 |
| Mar'91 | 3.04 | 3.21 | 46.07 | 3.94 | 2.10 | 8.22 | 11.61 | 13.88 | 10.73 | 4.56 | 25.50 |

Table 18. Monthly data of sedimentary humic acids (mg/g) in the Cochin estuary.

| Month | Stations | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
| Apr'90 | 1.21 | 1.90 | 5.99 | 1.78 | 2.18 | 6.45 | 8.12 | 7.67 | 13.70 | 1.35 | 9.10 |
| May'90 | 3.64 | 2.21 | 3.24 | 2.31 | 6.40 | 11.40 | 17.00 | 16.08 | 7.97 | 1.65 | 11.50 |
| Jun'90 | 1.08 | 9.36 | 1.93 | 3.07 | 3.25 | 11.74 | 14.27 | 14.35 | 7.39 | 0.76 | 16.55 |
| Jul'90 | 0.54 | 5.81 | 1.34 | 0.63 | 1.40 | 12.20 | 11.70 | 12.87 | 4.33 | 0.30 | 12.35 |
| Aug'90 | 0.34 | 5.49 | 2.82 | 0.68 | 2.30 | 11.41 | 11.01 | 10.48 | 4.02 | 0.14 | 6.61 |
| Sep'90 | 0.81 | 5.74 | 5.85 | 0.75 | 0.96 | 11.08 | 10.39 | 10.82 | 2.63 | 0.16 | 6.92 |
| Oct'90 | 0.62 | 7.20 | 2.01 | 2.01 | 1.35 | 8.26 | 8.83 | 8.13 | 1.32 | 0.73 | 4.47 |
| Nov'90 | 0.34 | 3.51 | 1.20 | 0.51 | 0.76 | 7.60 | 9.23 | 8.47 | 1.97 | 1.49 | 8.21 |
| Dec'90 | 0.87 | 5.02 | 1.04 | 1.80 | 0.37 | 8.00 | 8.83 | 7.59 | 5.26 | 1.12 | 4.92 |
| Jan'91 | 1.09 | 2.92 | 5.27 | 1.34 | 1.05 | 4.51 | 8.03 | 6.95 | 6.33 | 2.06 | 6.05 |
| Feb'91 | 0.83 | 2.88 | 4.95 | 1.55 | 1.23 | 5.57 | 7.59 | 7.80 | 5.74 | 2.82 | 8.11 |
| Mar'91 | 0.72 | 1.43 | 6.18 | 1.67 | 1.05 | 6.55 | 8.22 | 7.98 | 5.39 | 2.70 | 9.01 |

Table 19. Monthly data of sedimentary hydroxylated aromatics (mg/g) in the Cochin estuary.

| Month | Stations | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
| Apr'90 | 0.37 | 0.61 | 4.27 | 0.46 | 0.35 | 0.98 | 1.15 | 0.44 | 0.96 | 0.15 | 1.29 |
| May'90 | 0.16 | 0.18 | 19.99 | 0.34 | 0.27 | 0.38 | 0.62 | 1.23 | 1.17 | 0.13 | 2.65 |
| Jun'90 | 0.09 | 2.46 | 0.50 | 0.13 | 0.07 | 0.59 | 0.85 | 1.57 | 1.84 | 0.26 | 2.21 |
| Jul'90 | 0.10 | 1.83 | 0.13 | 0.07 | 0.24 | 0.86 | 0.68 | 1.17 | 2.18 | 0.03 | 2.19 |
| Aug'90 | 0.09 | 1.10 | 0.59 | 0.14 | 0.05 | 1.26 | 0.53 | 1.24 | 2.63 | 0.06 | 2.74 |
| Sep'90 | 0.09 | 0.41 | 0.88 | 0.10 | 0.24 | 1.04 | 0.77 | 1.20 | 2.99 | 0.11 | 3.17 |
| Oct'90 | 0.21 | 0.78 | 0.45 | 0.23 | 0.17 | 1.82 | 1.61 | 1.97 | 4.00 | 0.26 | 3.34 |
| Nov'90 | 0.19 | 0.59 | 2.51 | 0.20 | 0.27 | 1.12 | 0.98 | 0.92 | 2.46 | 0.29 | 2.02 |
| Dec'90 | 0.49 | 1.84 | 9.15 | 0.61 | 0.59 | 3.32 | 2.94 | 4.43 | 10.56 | 0.52 | 5.92 |
| Jan'91 | 0.56 | 2.45 | 0.97 | 0.48 | 0.43 | 1.17 | 1.78 | 2.75 | 2.52 | 0.58 | 5.61 |
| Feb'91 | 0.64 | 1.62 | 3.76 | 0.61 | 0.29 | 1.23 | 1.88 | 2.91 | 2.90 | 0.98 | 4.12 |
| Mar'91 | 0.39 | 0.91 | 8.42 | 0.58 | 0.32 | 1.58 | 1.67 | 1.76 | 1.95 | 0.72 | 4.62 |