SEASONAL RAMIFICATION IN THE BIOCHEMICAL COMPOSITION OF ORGANIC MATTER IN CHALAKUDY RIVER-ESTUARY

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Certificate

This is to certify that the thesis entitled "Seasonal ramification in the biochemical composition of organic matter in Chalakudy river-estuary" is an authentic record of the research work carried out by Smt. Suryakumari S under my supervision and guidance in the Department of Chemical Oceanography in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Cochin University of Science and Technology, and no part thereof has been presented for the award of any other degree, diploma or associateship in any University.

Muraleedharan Nair

DECLARATION

I hereby declare that the thesis entitled "Seasonal ramification in the biochemical composition of organic matter in Chalakudy river-estuary" is a genuine record of research work done by me under the supervision and guidance of Dr S Muraleedharan Nair, Department of Chemical Oceanography, School of Marine Sciences, Cochin University of Science and Technology. The work presented in this thesis has not been submitted for any other degree, diploma, associateship, fellowship or any other similar title or recognition.

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Preface

In rivers and estuaries, huge amounts of organic matter originating from in situ primary production, and anthropogenic inputs can alter the biochemical structure of the ecosystem. The study of organic biochemicals included 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 and other processes affecting a river- estuarine system.The study area, Chalakudy river is a natural ecosystem. It is the 5th longest river in Kerala and its basin is between 10° 05' to 10° 35' North latitude and 76° 15'to 76° 55' East longitude. Surface and bottom waters and surficial sediments were collected from the study area over a period of one year (May, 2005 to March, 2006) at bimonthly intervals.

The major objective of this study is to picturise the spatial and temporal distributional characteristics of labile organic constituents such as proteins and carbohydrates as well as refractory organic constituent, tannin and lignin in the dissolved, particulate and sedimentary compartments of Chalakudy riverine system. For the temporal variations, the seasons were divided as monsoon and nonmonsoon.

The thesis is divided into six chapters. Chapter I is *Introduction* where a general introduction about proteins, carbohydrates, tannin and lignin in the aquatic environment is attempted. Chapter II is *Materials and Methods,* containing a description of the study area, sampling techniques and analytical methodology. Chapter III is *Hydrographical parameters and sediment characteristics*, where spatial as well as temporal variations of hydrographical parameters and sedimentary characteristics are discussed. Chapter IV is *Proteins: phases-coupled spatio temporal variability*, dealing with the distribution profile of proteins in the dissolved, particulate and sediment phases. Chapter V is *Carbohydrates: phases-coupled spatio temporal variability.* Here, the inter compartmental variations of monosaccharides, polysaccharides and total carbohydrates are discussed on a spatial and temporal basis. Chapter VI, *Tannin and lignin: phases-coupled spatio temporal variability*, focusses on the distribution of dissolved, particulate and sedimental forms of tannin and lignin. In the present study, geostatistical analysis was a tool for discussion. Differences in parameters with station and season were tested using 3 way ANOVA. Pair wise comparison was carried out using students 't' test. The significance was put in the form of a Trellis diagram.

CONTENTS

SPATIOTEMPORAL VARIABILITY

CHAPTER I

INTRODUCTION

THE CARBON CYCLE

The carbon cycle is the biogeochemical cycle by which carbon is exchanged among the biosphere, pedosphere, geosphere, hydrosphere, and atmosphere of the earth. The carbon cycle (Figure1.1) is usually thought of as four major reservoirs of carbon interconnected by pathways of exchange. These reservoirs are:

- The plants
- The terrestrial biosphere, which is usually defined to include fresh water systems and non-living organic material, such as soil carbon.
- The oceans, including dissolved inorganic carbon and living and non-living marine biota,
- The sediments including fossil fuels.

The annual movements of carbon i.e., the carbon exchanges between reservoirs, occur because of various chemical, physical, geological, and biological processes. The ocean contains the largest active pool of carbon near the surface of the earth, but the deep ocean part of this pool does not rapidly exchange with the atmosphere.

The global carbon budget is the balance of the exchanges (incomes and losses) of carbon between the carbon reservoirs or between one specific loop (e.g., atmosphere ↔ biosphere) of the carbon cycle. An examination of the carbon budget of a pool or reservoir can provide information about whether the pool or reservoir is functioning as a source or sink for carbon dioxide.

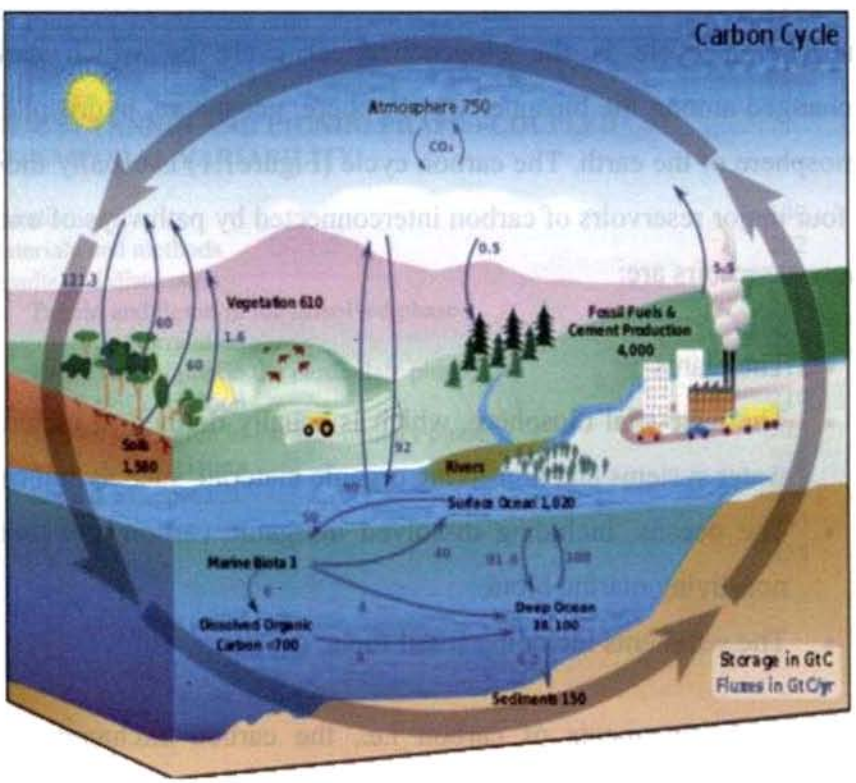

Figure 1.1 The carbon cycle (http://en.wikipedia.org/wiki/Carbon_cycle)

ORGANIC COMPOUNDS IN AQUATIC SYSTEMS

An organic compound is any member of a large class of chemical compounds whose molecules contain carbon. Organic matter plays a significant role in the biological, chemical and geological aquatic processes affecting water quality. As a result, the study of organic matter in aquatic environments has received increased attention. Among the natural ecosystems, the rivers are most intensively used by humans. Human activities in aquatic zones and contributing water sheds have dramatically changed the fluxes and biogeochemical composition of river inputs into the estuaries. At the present time, more than half of the large river systems of the world are affected by dams or other hydrological alterations (Nilsson et al., 2005).

The organic matter originates from two main autochthonous sources such as algal exudates and detritus, as well as from allochthonous sources like decayed dissolved and particulate materials from terrestrial organisms (Thorp and Delong, 2002). River systems are aquatic zones capable of trapping large quantities of pollutants, nutrients, organics etc. Sediment present in the river can provide sink for these materials that are derived from marine and terrestrial sources. Direct adsorption, complexation with organic matter and the formation of insoluble sulphides all contribute to the trapping mechanism. A major part of organic matter in natural waters and sediments is composed of proteins, carbohydrates, phenolic compounds, amino acids etc.

Phenolic materials are found to be the main components of soil and riverine humic substances. The synthesis of humus is based on plant residues, most important compounds in this respect being lignin, carbohydrate and proteins (Gjessing, 1976). According to Flaig (1963), 50-60% carbohydrates, 1-3% proteins, 10-30% lignin and some phenolic compounds participate in the humification process. Among these groups of organics, lignins are considered to be the most important, because carbohydrates and proteins have a higher rate of decomposition as compared to lignin. Most of these substances are derived from decaying vegetation and play a significant role in productivity and biological cycle in the aquatic environment.

ORGANICS IN RIVERS / ESTUARIES

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 an essential tool in alleviating the pressing problems that haunt the human race, viz, depleting the oil and gas reserves, alarming proportions of industrial pollution, irrational utilization of biological and mineral reserves, etc.

Biogeoorganics is the word 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 acids and other

hydrophobic acids of biological origin as well as compounds which have been subjected to geochemical processes like sorption/partition, precipitation, volatalisation, oxidation/reduction etc. The study of biogeo organics includes investigations on the sources of organic substances, the pathways along which they enter the aquatic environment, the pattern of accumulation in the biotic and abiotic components of the aquatic ecosystem, the mechanisms and rates of migration of bioorganic and pollutant and their transformations and other processes which determine the fate of toxicants in the environment. Biochemical evaluation is also useful for the understanding of the behaviour of the substances such as proteins, sugars, lipids, toxic organochlorine compounds and surfactants and of the accumulation of microimpurities in living matter, the migration of nutrients, production cycles and diagenysis 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. Such serious pollution problems can be dealt with

knowing the concentrations of inorganic and organic chemical species in the receiving waters/sediments, their interactions and transformations.

Estuaries are complex dynamic systems that serve as a transition zone between terrestrial and marine environments. Estuarine processes control the distribution and transportation of suspended sediments. These processes vary in a systematic manner with in the tidal cycles and weather conditions. 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 rapidly growing interest in research on aquatic environment/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. Sediments adsorb organic and bioorganics and also release compounds to the overlying water column as the system needs. The studies in chemical characteristics of the sediments of the estuaries are useful in assessing the water quality and management of the ecosystems. 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.

Estuaries are an important stage in the transport of the weathering products, besides being the meeting point of freshwater and seawater. Weathering products are brought by a variety of mechanisms which include river wind and ice transport. Goldberg (1971) has estimated that 1.8×10^{16} g y^{-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 1-5 $\times 10^{14}$ g y^{-1}. Since the rivers are

responsible for transporting solids to the oceans, estuaries assume an important role in global sedimentary cycle.

Organic matter present in estuaries consists of autochthonous contribution resulting from primary production with in the estuary and an allochthonous content emanating from adjacent ecosystems. The decomposition of organic matter in estuaries can lead to anoxic conditions if the water exchange is poor or if large amounts of organic pollutants are introduced.

Estuarine sediments acts as a short or long term reservoir for many hydrophobic organic compounds (Prahl and Carpenter, 1984). The organic matter in the sediment is a complex mixture of dead and living material which originate from both water column transport of organic carbon and in-situ synthesis. Organic matter thus include both labile compounds such as aminoacids and sugars as well as more refractory compounds such as humic acids, tannin and lignin etc.

TYPES OF ORGANIC COMPOUNDS

Carbohydrates

Carbohydrates or saccharides are the most abundant of the major classes of biomolecules. They fill numerous roles in living things, such as the storage and transport of energy (e.g., starch, glycogen) and structural components (e.g., cellulose in plants and chitin in animals). In addition, carbohydrates

and their derivatives play major roles in the working process of biocommunities. Carbohydrates make up most of the organic matter on earth because of their extensive roles in all forms of life. These are simple organic compounds that are aldehydes or ketones with many hydroxyl groups added, usually one on each carbon atom that is not part of the aldehyde or ketone functional group. The basic carbohydrate units are called monosaccharides. Monosaccharides can be linked together into what are called polysaccharides (or oligosaccharides) in a large variety of ways. Many carbohydrates contain one or more modified monosaccharide units that have had one or more groups replaced or removed.

Carbohydrates are important structural and storage components of aquatic organisms. They exist as monosaccharides, disaccharides, trisaccharides, polysaccharides etc. They are important carbon and energy sources for microheterotrophs in both freshwater and marine ecosystems (Romankevich, 1984; Thurman, 1985) and contribute essentially to the bacterial production (Hanisch et al., 1996; Rich et al., 1996). Carbohydrates are some of the major biochemicals produced by living organisms, and constitute an important fraction of dissolved, particulate and sedimentary organic matter (Skoog and Benner, 1997; Borsheim et al, 1999; Burdige et al., 2000). The extra-cellular degradation of macromolecular particulate organic carbon to a range of organic carbon intermediates is an important part of sediment carbon remineralization (Henrichs, 1992; Burdige and Gardner, 1998), and carbohydrates are known to be produced and consumed as intermediates during remineralization (Boschker et al., 1995; Arnosti and Holmer, 1999).

Due to the high percentage of structural carbohydrates in vascular plant tissues, most carbon and energy flow results directly from the oxidation of carbohydrates. Storage carbohydrates such as starch and sucrose, which play critical roles in cellular metabolism also contribute to the total carbohydrate reserves in plants (Loewus and Tanner, 1981). Additionally certain carbohydrates are either peripheral or integral components of other major compounds such as lignins and tannins (Zucker, 1983).

Despite the well recognized importance of carbohydrates in the aquatic carbon food web, there is surprisingly little information about the in-situ composition, concentration and dynamics of the different fractions of carbohydrates such as monosaccharides and the polysaccharides in dissolved and particulate forms as well as in sediments.

Proteins

Proteins or polypeptides are organic compounds made of amino acids arranged in a linear chain. In chemistry, an amino acid is a molecule containing both amine and carboxyl functional groups. These molecules are particularly important in biochemistry. The amino acids in a polymer chain are joined together by the peptide bonds between the carboxyl and amino groups of adjacent amino acid residues. The sequence of amino acids in a protein is defined by the sequence of a gene, which is encoded in the genetic code. Proteins can also work together to achieve a particular function, and they often associate to form stable complexes like other biological macromolecules such as polysaccharides and nucleic acids.

Proteins are essential parts of organisms and participate in virtually every process within cells. Many proteins are enzymes that catalyze biochemical reactions and are vital to metabolism. Proteins also have structural or mechanical functions, such as actin and myosin in muscle and the proteins in the cytoskeleton, which form a system of scaffolding that maintains cell shape. Other proteins are important in cell signaling, immune responses, cell adhesion, and the cell cycle. Proteins are also necessary in animals' diets, since animals cannot synthesize all the amino acids they need and must obtain essential amino acids from food. Through the process of digestion, animals break down ingested protein into free amino acids that are then used in metabolism.

Most amino acids in living organisms are present as constituents of proteins (Billen, 1984) and proteins account for more than about 50% of the organic matter (Romankevich, 1984) and 85% of the organic nitrogen (Billen, 1984) of marine organisms. In nature, the breakdown of proteins is easily brought about by bacterial and fungal action.

Phenolic compounds (tannin and lignin)

Polyphenols are a group of chemical substances found in plants, characterized by the presence of more than one phenol unit or building block per molecule. Polyphenols are generally divided into hydrolyzable tannins (gallic acid esters of glucose and other sugars) and phenylpropanoids, such as lignins, flavonoids, and condensed tannins.The division of polyphenols into tannins, lignins, and flavonoids is derived from

the variety of simple polyphenolic units derived from secondary plant metabolism as well as classical divisions based upon the relative importance of each base component to different fields of study. Tannin chemistry originated in the importance of tannic acid to the tanning industry; lignins to the chemistry of soil and plant structure.

As vegetable matter decomposes in water, some lignin degrades as long as oxygen is present. As the materials settle to the bottom where anaerobic conditions prevail, the cellulose portion will be decomposed via hydrolytic and fermentative reactions but the lignin portion will accumulate. The process contributes to the build up of organics in sediments and to the formation of bogs. The lignin component of vascular plant tissue represents a source-specific tracer that can uniquely characterize terrestrial organic matter (Hedges and Mann 1979a, b). Hedges and co-workers (Hedges and Ertel, 1982 ; Hedges et al., 1984) have shown that it is impossible to identify the land-derived organic matter in aquatic systems, through the analysis of the oxidation products of lignin. This lignin together with other compounds such as tannins, polyphenols and quininones can undergo condensation reactions to form the humic material that shapes a considerable part of organic material (Kononava, 1966).

Phenolic materials are abundant in the soil and water of eutrophic environments and are the main components of soil and aquatic humic substances (Haslam, 1989). They result in adverse environmental conditions such as high biological oxygen demand, undesirable aesthetic effects, fish fainting and toxicity to fish and other aquatic life. The very resistant nature of lignins is suggestive of long term damaging effects on

the ecosystem. Several investigations have suggested that reduction of algal productivity and biomass in aquatic systems could occur due to diminished light intensity and changes in light quality. Tannins inhibit plant growth (Mahadevan et al., 1984; Herrera and Ramirez, 1996). The effect of tannins on microorganisms and plant growth is described by Mahadevan et al., (1984). Plant produced polyphenols entering the soil in litter or canopy through fall may influence the pool and fluxes of inorganic and organic soil nutrients in terrestrial ecosystem. Polyphenol concentrations increase with decreasing soil fertility (Hattenschwiter and Vitousek, 2000). In nature, phenol will form complexes with nitrogenous compounds and makes them less susceptible for microbial degradation as compared to free proteins and amino acids. This reduces mineralization and release of nutrients. Therefore, the abundance of phenolics in sediment plays an important role in nutrient cycling (Joseph and Chandrika, 2000).

AIM AND SCOPE OF THE PRESENT STUDY

The study area, Chalakudy river is a natural ecosystem. It is one of the very few rivers of Kerala, which is having relics of riparian vegetation in substantial level. The locations included dam, ferry and estuary and these areas are an important source of carbon, nutrients and organics. Waters in the vicinity of ferry and dam are often "tea coloured" due to the relatively high concentrations of dissolved organic matter that contain tannins and other phenolic compounds. The dam itself causes no pollution but the submerged vegetation and organic matter can decompose creating organic

imbalances. The distribution of biogeoorganics in the Chalakudy river is influenced by the increasing human activities, waste discharge from major industrial establishments into the river, river runoff and by the sewage through a network of large and small canals. Microbially mediated chemical dynamics exert control on material cycles in the active channel and associated riparian vegetation. The detrimental effects of pollutants not only affect the water quality but also the quality of the sediment.

Chalakudy River is an aquatic zone capable of trapping large quantities of pollutants, particularly nutrients, organics etc. Sediments can provide a sink for these materials that are derived from aquatic and terrestrial sources. A major part of organic matter in natural waters and sediments is composed of aminoacids, proteins, carbohydrates, phenolic compounds, etc. Most of these substances are derived from decaying vegetation and play a significant role in the productivity and biological cycle in the aquatic environment, either inhibitory or stimulatory. No significant attempt for systematic chemical investigation on Chalakudy river has been reported.

Hence, the present study which is the first of its kind in this region is an attempt to generate adequate information on the relative abundances, the seasonal and spatial variations as well as on the source and fate of organic compounds found associated with the dissolved, particulate and sedimentary compartments of Chalakudy river system. The study aimed at investigating variations, the relative proportion of dissolved, particulate and sedimentary fractions of these materials as well as the pollution extent so as to be able to comment on the present condition of this river-estuarine system. This thesis focuses attention on the role of biogeoorganics in

modifying the ecological and environmental condition of the dissolved, particulate and sediment compartments with their minute variability subjected to various physical, chemical and biogeochemical processes. A scheme of study encompassing all these objectives provides the frame work for the present investigation.

The scope of the present investigation are

- to attempt a characterization of the organic compounds with a view to ascertaining their role in effective management of this ecosystem
- to use them as biomarkers, by means of which, the origin and transport of organic matter across a water system can be evaluated.
- to characterise natural and affected environments
- to prevent, treat and control organic pollutants
- to make Interfacial studies involving media such as sediment, water, particulate and organism
- to look forward to environmentally friendly pathways through ecotoxicology, risk assessment, environmental technologies effecting remediation and control

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CHAPTER II

MATERIALS AND METHODS

INTRODUCTION

The Chalakudy river in Kerala originates, and continues to flow through much of the Western Ghats. The Chalakudy river is one of the few flowing rivers in India and it is the fifth largest river in Kerala. It is 144 Km long and 1704 sq km spread and is enriched by six tributaries. The river flows through one of the best patches of evergreen forests in the Western Ghats. Deep in the forest, on the way to Valpara are the two dams, Poringalkuthu and Sholayar Dams that generate hydroelectric power to the Kerala state. There are six reservoirs impounded in this basin. The famous waterfalls Athirappilly and Vazhachal are situated on this river. Chalakudy river runs through Chalakudy town which is in the Thrissur district of Kerala. The river finally merges with the Periyar river at the village of Puthanvelikkara in Ernakulam district. The Chalakudy river basin is thus a tributary of the Periyar, the largest river in Kerala. This river flows through one of the best remaining patches of ever green forests in the Western Ghats.

Downstream of these waterfalls, more than ten lakh people living in 25 panchayats and 3 municipalities directly depend on this river for their drinking, agriculture and livelihood purposes. This river is constantly under the threat of pollution, sand mining and salt water intrusion in the down stream areas all along its journey till it joins the sea. This river joins the

right arm of the Periyar river at Elanthikkara and flows down to join the sea at Azhikode in Kodungallur taluk

DESCRIPTION OF THE STUDY AREA

The following is a brief description of the characteristics of the stations where the present study was carried out. The area of investigation and the station locations are depicted in the Figure 2.1. Stations were fixed so as to obtain a fairly good coverage of the prevailing complex conditions. The basin of Chalakudy river is between 10^0 05' to 10^0 35' north latitude and 76^0 15' to 76^0 55' east longitude. This area is located in Thrissur, Ernakulam and Palakkad disricts of Kerala. The sampling sites with station numbers are given in Table 2.1.

Table 2.1: Sampling sites with station numbers

Sampling locations of Chalakudy river	Station Numbers
Poringalkuthu dam	1
Vazhachal waterfalls	2
Athirappilli	3
Ayyampuzha (PCK ferry)	4
Chalakudy town	5
Kanakkankadavu	6
Kottappuram	7
Azhikodu estuary	8

The first station is the reservoir at Poringalkuthu. The next two stations are waterfall regions, namely Vazhachal and Athirappilly. These are located in the forest area at the entrance to Sholayar ranges, and these waterfalls are tourist centers. Both these waterfalls are a part of Chalakudy river. The fourth river station is passing through the Plantation Corporation of Kerala (PCK) at Ayyampuzha, Athirappilli, and this place is 63 km from Thrissur city with 2,300 hectares of rubber plantations and factories and there is a ferry service across the river. The fifth river station is below Chalakudy bridge in Chalakudy town. The sixth station is an undisturbed area, Kanakkankadavu. Before reaching the next station, the river merges with Periyar. Station 7 is at Kottappuram where there is intrusion of seawater. Station 8 is found to be exclusively estuarine in character as Chalakudy river merges into Arabian sea. A fish hatchery is situated very close to the station 8. Sewage and waste from this fish hatchery are discharged into this area.

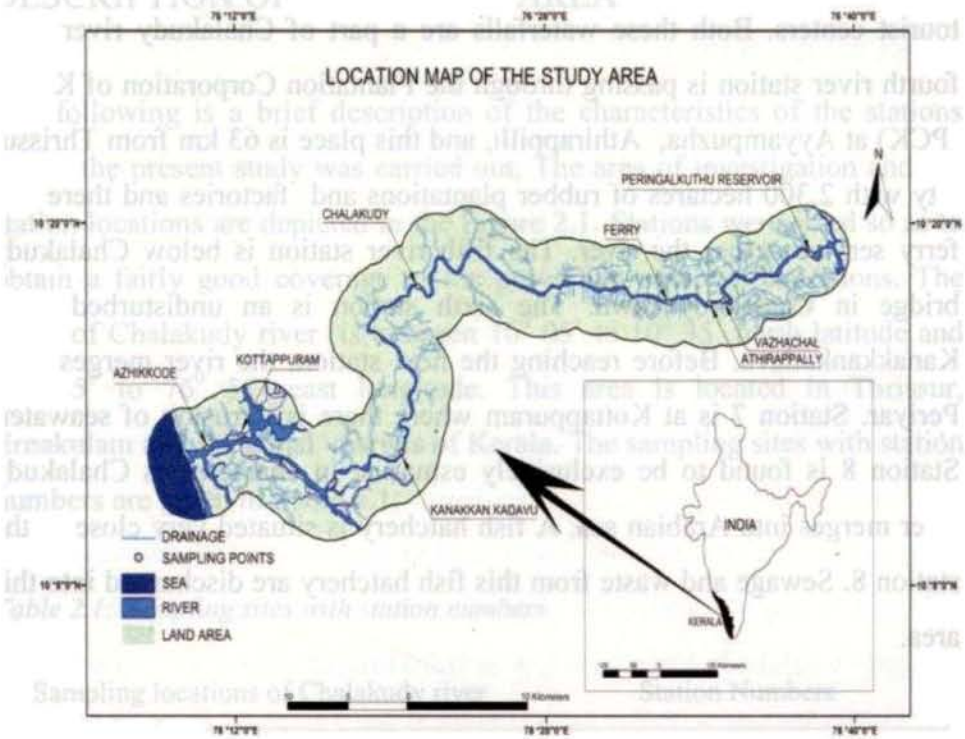

Figure 2.1 Location map of the study area

SAMPLING AND STORAGE

Surface and bottom water samples and the surficial sediments were collected from the eight stations of Chalakudy river, during the period from May 2005 to March 2006 at bimonthly intervals.

All collecting scoops, bags and containers were acid washed and rinsed thoroughly with milli.Q water before use. Surface water samples were collected using a clean plastic bucket and bottom water was taken by a modified Hi-Tech water sampler. The surficial sediment samples were collected using a van Veen grab. The water samples were then transferred carefully to precleaned polythene bottles. The sediment samples were stored in labeled plastic bags and kept deep frozen until analyses.

ANALYTICAL METHODS

General hydrographical parameters were measured immediately after sampling. pH was measured using a portable pH meter. The temperature was measured using a sensitive thermometer designed to read upto 0.05°C. The samples for determining dissolved oxygen were collected in 50 ml DO bottles and were fixed in-situ using Winkler A and Winkler B reagents. Only surface water samples were collected from stations 2 and 3 through out the period due to the low depth at these stations.

Particulate matter was separated from dissolved fraction using GF/C filters having 0.45μm pores and 47 mm diameter. Filters were preheated in a

muffle furnace at a temperature range 450^0C-500^0C for 2 hours (Strickland and Parsons, 1972). These filters containing particulate organic matter were stored in a petri dish and kept in a deep freezer. The filtered water samples were kept at 0^0 C to minimize changes due to storage.

All glass wares and plastic wares were thoroughly cleaned with acid and then with Milli-Q water. All reagents were of analytical grade. Reagent solutions and standard solutions were prepared in Milli-Q water. The physico-chemical parameters like salinity, dissolved oxygen and chemical oxygen demand were estimated by standard procedures as discussed below.

Dissolved oxygen (DO): DO was found using iodometric method. This is based on the addition of divalent manganese solution followed by strong alkali to the sample in a glass stoppered bottle. DO rapidly oxidizes and an equivalent amount of the dispersed divalent manganous hydroxide precipitate to hydroxide of higher valency state. In the presence of iodide ions in an acidic solution, the oxidized manganese reverts to the divalent state with the liberation of iodine equivalent to the original DO content, which is titrated against standard solution of thiosulphate using starch as indicator (APHA, 1998).

Salinity: Salinity of water samples was determined on the same day of the collection by Mohr-Knudsen titrimetric method (Grashoff et al., 1983) using potassium chromate indicator. The chloride ions form a precipitate with a low solubility product with silver ions.

Chemical oxygen demand: The chemical oxygen demand (COD) is used as a measure of the oxygen equivalent of the organic matter content of a sample that is susceptible to oxidation by a strong chemical oxidant. COD was determined by open reflux method, suggested in APHA (1995). The sample was refluxed in strongly acid solution with a known excess of potassium dichromate. After digestion, the remaining unreduced dichromate was titrated with ferrous ammonium sulphate to determine the amount of dichromate consumed and the oxidisable organic matter was calculated in terms of oxygen equivalent.

Sediment organic carbon (SOC): SOC was determined by chromic acid oxidation method (Gaudette and Flight, 1975), which involved the oxidation of organic matter present in sample by a known quantity of chromic acid. The amount of acid consumed was determined by back titration with 0.5N ferrous ammonium sulphate (Mohr's salt) solution using ferroin as indicator.

Moisture content: Approximately 10g of homogenized wet sediment sample was taken and the percentage of moisture in the sample was determined. The sample was kept in a hot air oven at 90° C for 48 hrs. The difference in weights of the wet and dry samples gave the moisture content.

CHN analysis: Approximately, 2 mg of sample is measured into a tin capsule (Elementar Americas, D1034) using a Sartorius M2P microbalance (readability: 0.001 mg, range: 0.1 mg - 55 g). The tin capsule is then carefully folded into a cube approximately 2-3 mm in width with forceps

on a pane of glass. The capsule was then loaded into a Perkins Elmer 2400 Series II CHNS/O analyzer for analysis. This analyzer operates by flash combusting the sample encapsulated in a tin cup at 1760 °C. The resulting gases are chemically scrubbed of the halogens and sulfur followed by separation in a gas chromatographic column prior to detection by a thermal conductivity detector.

Texture analysis: Texture analysis was conducted based on Stoke's law, which states that the settling velocity of fine sized particles is directly proportional to the size and diameter of the particles. The procedure was as follows. After removing carbonate by adding 10%HCl, the sediment samples were treated with H_2O_2 for removing organic matter. Sediment collected by filtering was used for texture analysis, which was carried out by sieving and pipetting method. A known weight of wet sediment was dispersed overnight in 0.025N sodiumhexametaphosphate (calgon) solution. The sand fraction was separated from the dispersed sediment by wet sieving using a 230 mesh (63μm) ASTM sieve (Carvar, 1971).The filtrate containing silt and clay fraction was subjected to pipette analysis (Krumbein and Pettit John, 1938; Lewis 1984)

Methodology for estimation of organic compounds

Carbohydrates: Carbohydrates were estimated by the phenol-sulphuric acid method (Dubois et. al., 1956). To 1 ml of the sample, 1 ml of 5% phenol and 5 ml of conc.H_2SO_4 were added. After cooling the test tube at room temperature, absorbance was measured spectrophotometrically at 490 nm

using a Thermospectronic Genysis 10 uv-visible spectrophotometer. Blank and standards of D-glucose were also treated similarly. Blank corrections were applied to all set of readings. A calibration curve was plotted from which the concentrations of the dissolved monosaccharides was obtained. To obtain the total dissolved carbohydrates, the sample was hydrolysed with 1N H_2SO_4 in 1:1 ratio at 100° C for 1hr and measuring the absorbance after developing colour using phenol and sulphuric acid. Carbohydrates from the sediment and particulate samples were leached with H_2SO_4 for 1hour, cooled and filtered the samples and aliquots were taken in clean test tubes and measuring the absorbance after developing colour. Monosaccharides were determined without sample hydrolysis. Polysaccharide concentrations were estimated by subtracting the concentration of monosaccharide from concentration of total carbohydrates (Burney and Sieburth, 1977)

Proteins: Proteins in dissolved phase was measured using copper reagent and folin ciocalteu phenol reagent (Lowry et al., 1951). The method adopted was as follows. The samples were treated with 1N NaOH at 80°C for 30 minutes to dissolve the proteins. After cooling and centrifuging, 1 ml of the extract was transferred to clean test tubes and 5 ml of copper reagent (mixture of 2 ml each of 2% $CuSO_4$ and 4% sodium potassium tartarate and 96 ml of 3% Na_2CO_3 in 0.1 N NaOH) were added followed by 0.5 ml of folin-ciocalteu phenol reagent (1:1 mixture) after 10 minutes. After 40 minutes, samples were analysed spectrophotometrically at 750 nm against reagent blank. A calibration curve using bovine albumin was plotted from which the concentration of proteins in the samples was obtained.

Tannin and lignin: The estimation of dissolved tannin and lignin was performed by sodium tungstate –phospho molybdate acid method (APHA, 1995). The principle involved is the determination of a blue colour on reduction of folin-ciocalteu phenol reagent by the aromatic hydroxyl groups present in tannins and lignins. The effects of Mg and Ca hydroxides and/or bicarbonates present in the sample were suppressed by the addition of trisodium citrate solution (Nair et al., 1989). To 10 ml of the sample, added in rapid succession 5 ml of 1.6 M tri-sodium citrate solution followed by 1 ml of folin-ciocalteu phenol reagent and 10 ml of carbonate-tartarate reagent (200 g Na_2CO_3 and 12 g sodium carbonate in 750 ml hot distilled water, cooled to 20°C, and dilute to 1litre) and allowed to stand for 30 minutes for colour development. Reagent blanks were similarly prepared omitting the sample. The absorbance was measured spectrophotometrically at 760 nm against blank. The concentrations of each samples were calculated from the calibration curve obtained using tannic acid standards. Sediments and particulate matter were subjected to 0.05 M NaOH leaching for 72 hours. The sediment to solution ratio was maintained at 500 mg: 250 ml. 5 ml of the supernatant liquid was withdrawn for analysis as described for water samples. The blank solution was 0.05 N NaOH.

STATISTICAL ANALYSIS

In the present study, Geostatistical Analysis was used for showing hydrogeochemical variation. Geostatistical analyses were carried out using ArcGIS, which is an integrated collection of GIS software products for building a complete geographic information. ArcGIS is an information system for geographic data. Here sample points were taken as reference locations in a landscape and created a continuous surface. Geostatistical wizard was used to generate surface using the various interpolation techniques available in it.

The monthly data on various constituents were reduced to seasonal averages of monsoon and nonmonsoon, so as to establish a reliable trend. Correlation analysis was carried out to find out the relation among different parameters. Differences in parameters with station and season were tested using 3 way ANOVA after normalizing the data using transformation, $z_i = Xi - \overline{Xi} / \sigma Xi$ where Xi is the parameter under consideration, $\overline{Xi}$ is the average of parameters and σXi is the standard deviation of the parameter over the sampling station and zi is the transformed value of the i^{th} parameter i=1,2,.....K where K is the number of above mentioned parameters (Snedecor and Cochran, 1967; Jayalakshmy, 1998). When the difference in the parameter observed is found to be significant, pair wise comparison is carried out using students 't' test (Sokal and Rohlf, 1981) and the significance is put in the form of a Trellis diagram at 5% level of significance and 1% level of significance (Tuckey, 1949).

ANALYTICAL REPRODUCIBILITY

Spectrophotometric method was followed for all organic estimations. Calibration involved comparison of the sample absorption after chemical reaction with the absorption of a standard of known concentrations which had been treated in exactly the same manner. A sequence of standards from zero to a concentration slightly beyond the expected maximum sample concentration were prepared in pure water. Sample aliquots per standard were treated as described for the respective analytical method and the absorbances were measured. Linear concentration/absorbance relationship were obtained from a plot of standard concentrations versus absorbances. The blank absorbance was determined by measuring a sample volume of pure water plus reagents against a pure water reference without reagents. Thus the terms required to calculate sample concentrations were obtained. The reliability of calibrations decreases with increasing concentration differences between the sample and standard. Consequently, the best calibration and analytical results were obtained which exactly matched sample and calibration ranges.

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CHAPTER III

HYDROGRAPHICAL PARAMETERS AND SEDIMENT CHARACTERISTICS

INTRODUCTION

The study of the hydrographical parameters has great importance in characterizing the general features of a river- estuarine system. A detailed study of the variations in the parameters such as temperature, pH, salinity and dissolved oxygen was also carried out along with the organic matter analysis of the Chalakudy River. The significant changes in the organic constituents are brought about by variations in the hydrographical features. The concentrations of many components in the aquatic systems are controlled by the factors like salinity, pH and the major and minor ionic concentrations. Hence, the study of these parameters is indeed quiet relevant in the present context. The results of the present investigations are presented and discussed in the following sections.

The temporal and spatial dynamics of certain biological, physical and chemical parameters were investigated to gain a general approach into the system, and an endeavour had also been taken to present the environmental conditions along the river, though contaminants did not always follow the mineralogy, and are strongly influenced by outlets of human activities.

MATERIALS AND METHODS

Temperature, pH, salinity, dissolved oxygen and chemical oxygen demand were analysed for both surface and bottom water samples and moisture content, CHN, grain size and organic carbon were analysed for sediments. The methods adopted are discussed in Chapter II.

RESULTS AND DISCUSSION

The results on water characteristics obtained in the present study are tabulated in Table 3.1 (for surface waters) and Table 3.2 (for bottom waters). The values of sediment characteristics are given in Table 3.3 (moisture content and sediment organic carbon) and Table 3.4 (texture and CHN analyses).

Table 3. 1 Values of hydrographical parameters along the surface waters

Parameters	Months	Stations S1	S2	S3	S4	S5	S6	S7	S8
Temperature °C	May	28.2	29.6	30.4	30.8	32.6	32	33	32.8
	July	25	25.2	25.4	27.2	27.4	28.2	29.4	29.2
	Sep	26	25.8	26.2	27.4	27.2	27.4	31.4	29.2
	Nov	27.6	26.4	27.2	27.4	28.4	27.8	30.2	30.2
	Jan	27.2	26.4	28.2	28.2	30.2	32.2	31.6	31.8
	Mar	27.2	28.2	30.2	29.8	32.2	31.8	33.6	31.6
pH	May	6.85	7.15	7.43	7.25	6.94	6.78	7.25	7.38
	July	7.41	7.12	7.15	7.1	7.02	6.67	7.35	6.97
	Sep	7.35	7.45	7.56	7.46	7.34	7.34	7.33	7.41
	Nov	7.23	7.15	7.16	7	6.79	6.7	6.84	7.19
	Jan	7.65	7.5	7.53	7.35	7.1	7.08	8.02	8.09
	Mar	7.03	7.1	7.05	7.02	7.03	6.89	7.72	7.9
Salinity (ppt)	May	0.01	0.02	0.02	0.02	0.02	0.08	16.83	27.48
	July	0.01	0.01	0.01	0.01	0.01	0.02	0.46	0.30
	Sep	0.01	0.01	0.01	0.01	0.02	0.01	0.16	2.79
	Nov	0.02	0.02	0.01	0.02	0.02	0.03	1.68	4.19
	Jan	0.01	0.01	0.01	0.01	0.03	0.06	25.33	26.52
	Mar	0.01	0.02	0.01	0.02	0.02	0.07	18.78	26.04
DO (ml/l)	May	5.33	5.06	6.2	4.64	3.79	4.68	3.16	2.77
	Jul	9.03	8.61	10.1	7.99	6.96	7.15	6.94	5.48
	Sep	8.35	8.35	9.16	8.44	6.62	6.72	6.28	5.54
	Nov	6.07	6.81	7.08	7.36	6.54	6.15	6.22	4.31
	Jan	5.59	6.62	6.71	6.94	6.25	6.71	5.45	4.5
	Mar	4.77	4.37	4.92	4.35	3.91	4.63	3.2	2.77
COD (mg/l)	May	4.78	5.95	3.72	12.5	3.73	3.93	135.58	151.2
	Jul	16.1	18	16.1	16.1	40.2	7.74	30.94	23.21
	Sep	175	39.8	63.7	23.9	222	145	30.56	45.84
	Nov	6.41	6.43	16.1	12.9	7.24	4.02	7.24	2.41
	Jan	12.9	1.61	5.63	4.02	13.7	0.8	40.2	48.24
	Mar	9.64	7.23	4.82	8.04	1.61	4.82	120.59	128.6

Table 3. 2 Values of hydrographical parameters along the bottom waters

Parameters	Months	Stations							
		B1	B2	B3	B4	B5	B6	B7	B8
Temperature °C	May	28.2	29.6	30.4	31	32.4	31.8	33	32.6
	July	25	25.2	25.4	27.2	27.4	28.2	29.4	28.8
	Sep	25.8	25.8	26.2	26.8	26.8	27.4	30.8	28.8
	Nov	28	26.4	27.2	27.4	28.4	27.8	30.2	29.8
	Jan	27.2	26.4	28.2	28.2	30.2	31.8	31.6	31.8
	Mar	28	28.2	30.2	30.2	32	32	33.6	32
pH	May	6.85	7.15	7.43	7.05	7	6.83	7.25	7.5
	July	7.22	7.12	7.15	7.43	7.02	6.95	7.35	6.97
	Sep	7.35	7.45	7.56	7.63	7.45	7.42	7.4	7.52
	Nov	7.25	7.15	7.16	7.33	6.79	6.7	6.95	7.73
	Jan	7.55	7.5	7.53	7.15	7.1	7.05	8.02	8.03
	Mar	7.13	7.1	7.05	6.79	6.93	6.9	7.72	7.92
Salinity (ppt)	May	0.01	0.02	0.02	0.05	0.17	0.08	16.83	28.78
	July	0.02	0.01	0.01	0.03	0.01	0.03	0.46	0.33
	Sep	0.02	0.01	0.01	0.01	0.02	0.01	0.39	1.50
	Nov	0.03	0.02	0.01	0.02	0.02	0.03	1.71	15.46
	Jan	0.32	0.01	0.01	0.01	0.03	0.07	25.33	25.71
	Mar	0.07	0.02	0.01	0.00	0.17	0.08	18.78	27.04
DO (ml/l)	May	5.33	5.06	6.2	4.52	4.39	4.36	3.16	2.89
	Jul	8.61	8.61	10.073	8.61	6.96	7.57	6.94	5.46
	Sep	8.35	8.35	9.16	8.35	5.37	6.35	6.28	4.86
	Nov	5.55	6.81	7.08	7.08	6.54	6.15	4.87	4.31
	Jan	5.12	6.62	6.71	6.49	6.25	6.32	5.45	4.5
	Mar	4.07	4.37	4.92	4.49	3.91	4.34	3.2	2.91
COD (mg/l)	May	4.78	5.95	3.72	13.14	5.26	4.45	136	163
	Jul	56.3	18	16.08	104.51	40.2	46.4	30.9	15.5
	Sep	87.6	39.8	63.69	129.88	260	22.9	22.5	222
	Nov	44.2	6.43	16.08	0.804	7.24	4.02	5.63	17.7
	Jan	0	1.61	5.63	0	13.7	0.8	40.2	48.2
	Mar	10.5	7.23	4.82	2.41	4.82	5.62	121	129

Temperature: Temperature of the environment is a major and even the deciding environmental factor in determining growth rate, metabolism and nutritional efficiency of aquatic life. In fact, temperature will influence all biological and chemical processes in an aquatic system. Seasonal variations are shown in Figure 3.1

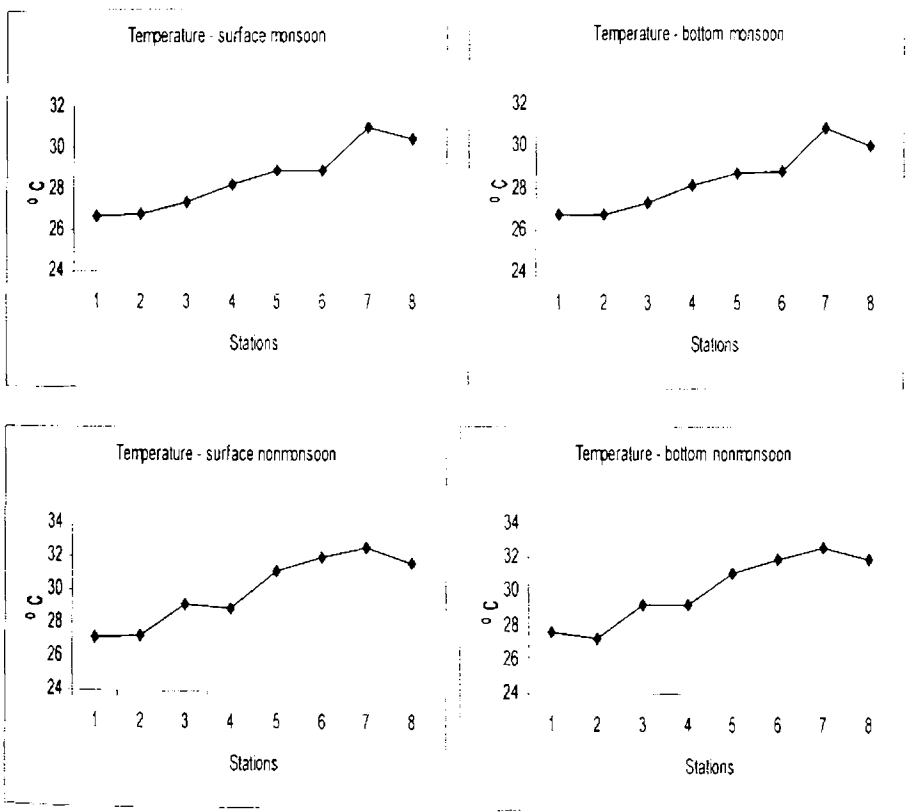

Figure 3.1 Spatial and seasonal variations of temperature

At all the 8 stations, the highest temperature for surface water samples was observed at station 7 (32.6°C) during nonmonsoon and lowest temperature

was 26.7°C at station 1 during monsoon season. For bottom water samples the lowest temperature was observed at station 1 (26.8°C) and highest temperature was observed at station 7 (32.6 °C) during nonmonsoon.

pH: pH is an another important parameter which exerts definite influence on the speciation of elements in water. The solubility of different constituents is dependent on pH. The pH also controls the growth of organisms regulating the activity of enzymes. In open ocean waters, pH ranges from 7.8 to 8.4. Variation of pH in coastal waters is caused by many factors . Estuarine pH generally varies from 7 to 7.5 in the fresher sections to between 8 and 8.6 in the more saline areas. The slightly alkaline pH of sea water is due to the natural buffering from the carbonate and bicarbonate dissolved in the water. During the monsoon season, the fresh water discharge from the rivers lowers the pH. Photosynthesis, denitrification and sulphate reduction increase pH whereas, processes such as respiration and nitrification decrease pH (Zhang, 2000). When photosynthetic reactions take place in the aquatic system, CO_2 is reduced to carbohydrate. Thus, the higher pH values for surface waters are caused by the enhanced photosynthetic activity occurring at the surface. Respiration and degradation/decomposition of organic material are the reactions that proceed in the opposite direction of the photosynthesis. Oxidation of organic matter leads to the increase in CO_2 levels and to a shift of equilibrium to the lower pH. Other factors that determine the pH of the water include bacterial activity; water turbulence; chemical constituents in runoff flowing; sewage out flows and impacts from other anthropogenic activities. Seasonal variations of pH are depicted in Figure 3.2.

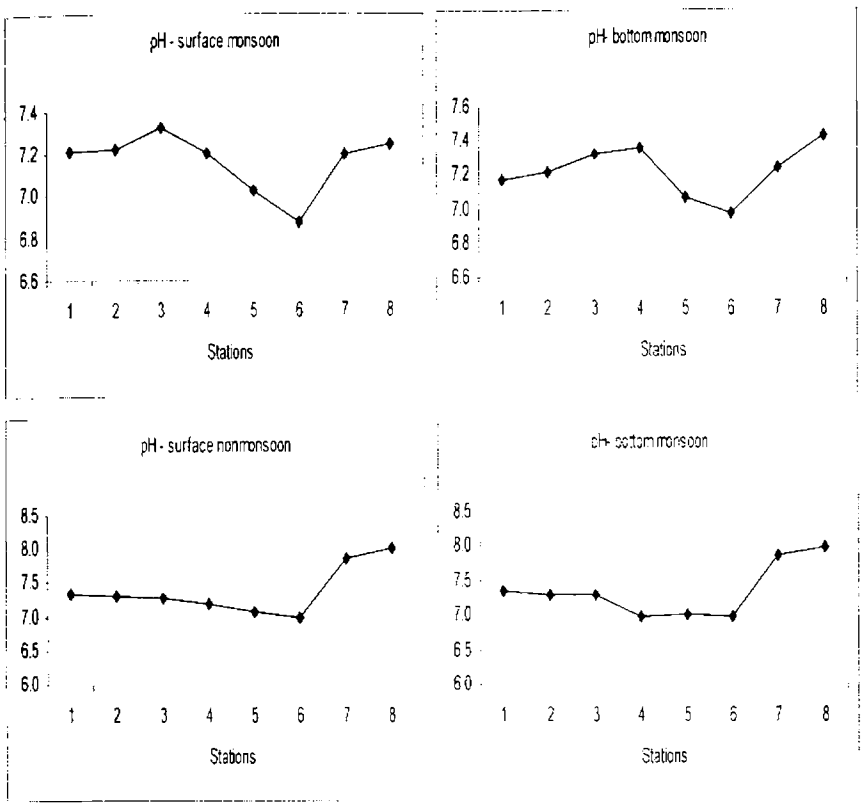

Figure 3.2 Spatial and seasonal variations of pH.

The prominent factors influencing the pH in this part of Chalakudy river are photosynthetic activity of phytoplanktons, discharge of fresh waters from different rivers and the extent of salinity changes during salt water intrusion. During the period of this study, the pH variations were in the range 6.87 to 7.99 (in surface waters) and 6.97 to 7.97(in bottom waters). The pH value of river water usually increases when it mixes with saline water. This influence of saline water intrusion in the variation of pH values were also evident in this part of the study area.

Salinity: Estuarine waters were saline, whereas in riverine waters, chloride was least. During nonmonsoon salinity increased due to evaporation and low discharge of fresh water. Evaporation rate may be the highest during nonmonsoon with low or no rain fall, which explains the highest values of salinity during this period. Salinity intrusion occurred at station 8 during monsoon and nonmonsoon seasons. Seasonal variations of salinity are depicted in Figure 3.3.

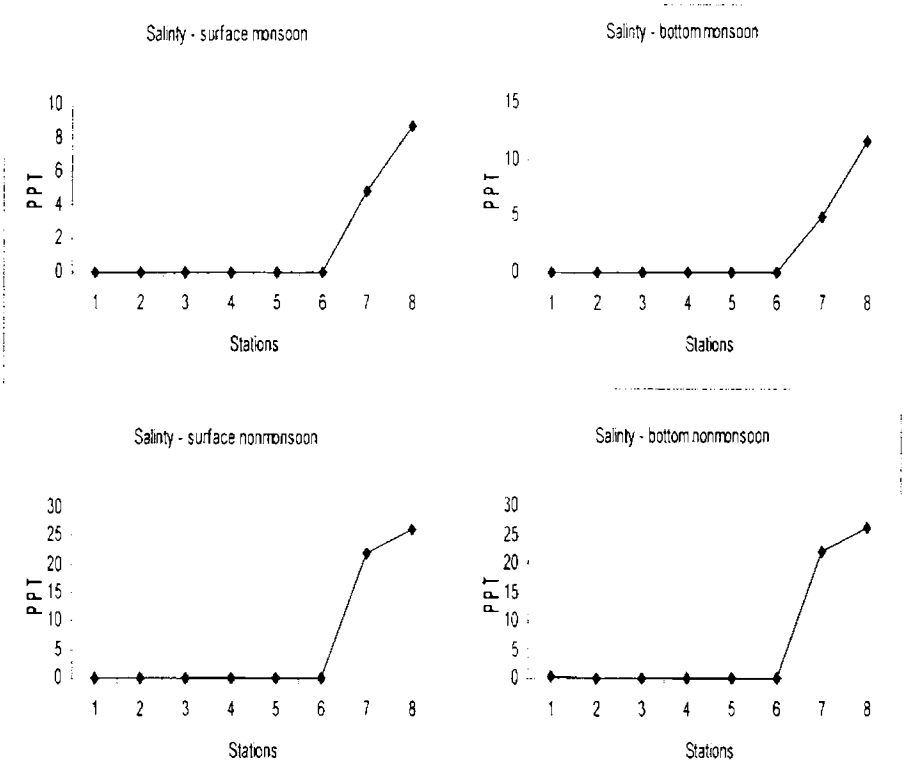

Figure 3.3 Spatial and seasonal variations of salinity.

Of all the hydrographical parameters, chloride content is perhaps the most important one being an index of the amount of dissolved solids in water.

Salinity varies with depth and from place to place. The principal natural processes, which lead to changes in the salinity are those which bring about the removal or addition of fresh water. Decrease in salinity results from atmospheric precipitation, run off from land etc.

Dissolved oxygen: Dissolved oxygen plays an important role in the aquatic environment being essential to the survival of aquatic life. Oxygen enters the water primarily through direct diffusion at the air water inter phase and through aquatic plant photosynthesis. The quantity of oxygen dissolved in water is determined by a number of factors such as temperature, salinity, partial pressure of the gas in the atmosphere, biochemical degradation of organic matter, respiration, photosynthesis, biological activity, currents and mixing process. In fact, the maximum amount of oxygen that can be dissolved in water is only about 8.3mg/l at standard temperature and pressure and is referred to as oxygen saturation, which is influenced by temperature and salinity levels.

The competing process of photosynthesis and respiration are the main causes of insitu changes in the concentration of dissolved oxygen and CO_2 in the water. Photosynthesis in the phytoplankton leads to the removal of CO_2 and to the liberation of oxygen. DO is consumed by the respiration of plants, animals and bacteria. The ultimate factor limiting the consumption of oxygen is the supply of organic matter. The oxygen is involved both in the photosynthetic and degradation processes in nature, oxygen is not a conservative element in the natural water.

The results of dissolved oxygen at surface and bottom waters of all the stations and the seasonal distribution are shown in Figure 3.4. For surface water higher content (8.18 ml/l) was observed at station 3 during monsoon. Low dissolved oxygen content (3.63 ml/l) was observed at station 8 during nonmonsoon. For bottom water samples the high dissolved oxygen content (7.14 ml/l) was observed at station 3 during monsoon and low dissolved oxygen content (3.7 ml/l) was observed in station 8 during nonmonsoon. The lowest value was observed at station 8 both for surface and bottom waters .This may be explained as the combined effect of low solubility of oxygen due to high salinity and temperature and also due to the utilization of oxygen for biodegradation of organic matter. High dissolved oxygen contents were observed during monsoon due to greater solubility of oxygen in fresh water and high turbulence.

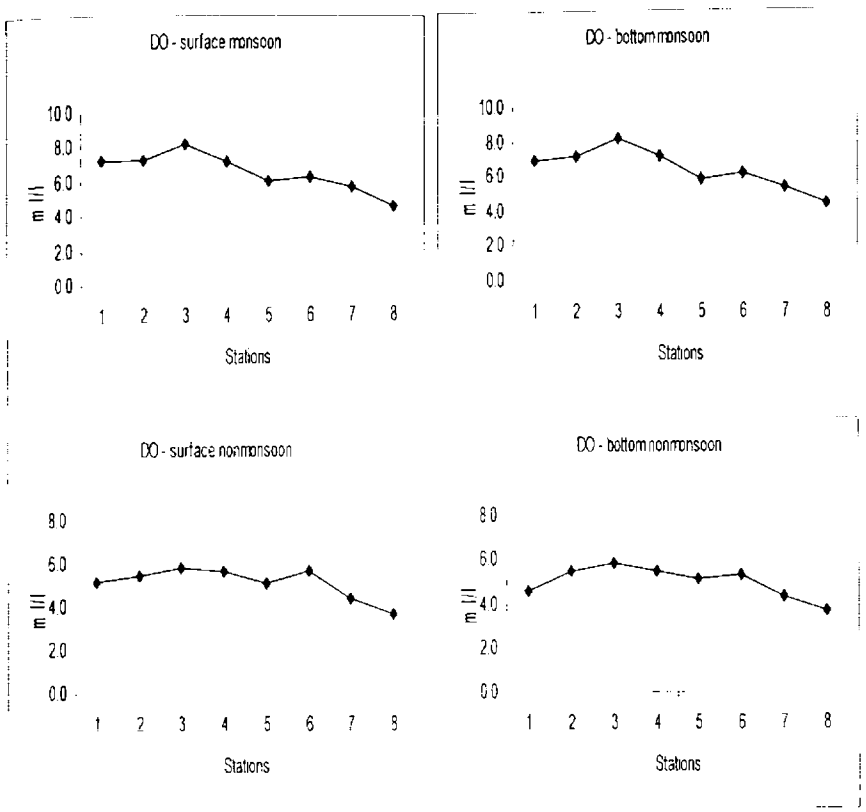

Fig.3.4 Spatial and seasonal variations of dissolved oxygen

Chemical oxygen demand: According to American society of testing of materials, COD is defined as the amount of oxygen consumed under specified condition in the oxidation of organic and inorganic matter. Most types of organic matter could be destroyed by boiling in a mixture of chromic acid and sulphuric acid. The amount of organic matter liberated is then found out by titration with ferrous ammonium sulphate and COD is calculated.

The seasonal distribution are given in Figure 3.5. For surface water, higher COD (88.43 mg/l) was observed at station 8 during nonmonsoon and low COD (2.81 mg/l) was observed at station 6 during nonmonsoon. For bottom water samples higher COD (104.43 mg/l) was observed at station 8 during monsoon and low COD was observed at station 2during nonmonsoon

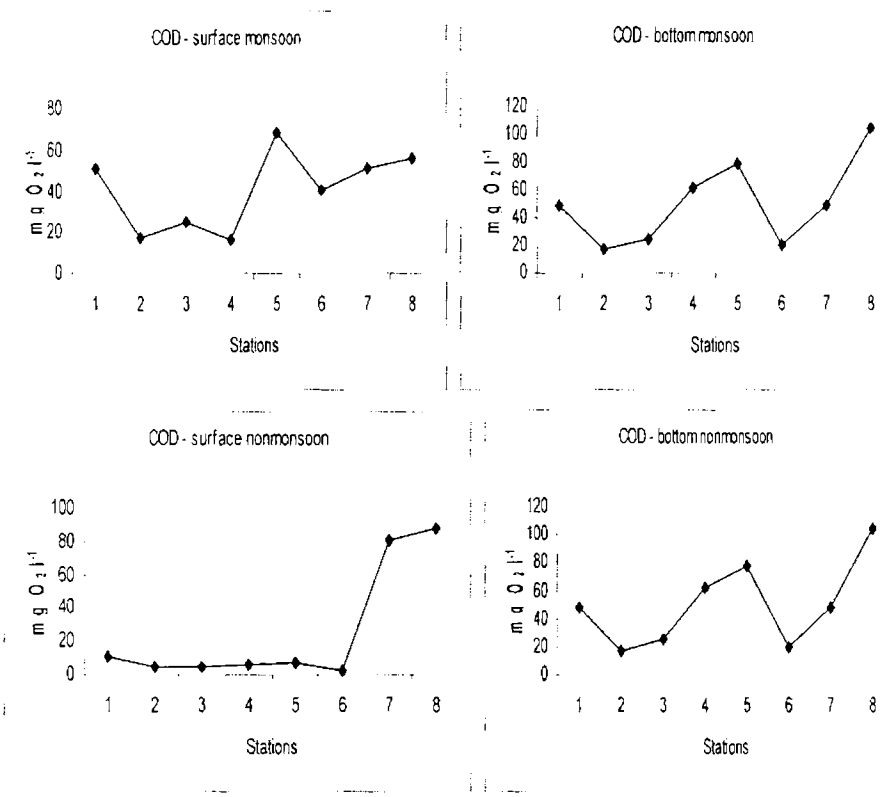

Figure 3.5 Spatial and seasonal variations of COD

Table 3.3 Distribution values of sediment parameters

Parameters	Months	Stations							
		S1	S2	S3	S4	S5	S6	S7	S8
Moisture content %	May	49.5	18.9	24.74	21.99	19.9	18	60	50
	Jul	56.8	20.9	16.55	65.31	57.3	44.9	25.7	39.3
	Sep	58.7	17.3	25.74	57.59	55.5	35.3	45.6	47.9
	Nov	39.2	18.6	21.13	34.68	44	36.6	50.6	67.3
	Jan	70.1	20.7	23.24	32.42	51.5	42.8	40.2	58.6
	Mar	51.8	20.6	21.29	29.05	39.3	29.6	58.5	51.1
SOC %	May	2.6	0.06	0.52	0.1	0.25	0.35	1.14	1.96
	Jul	4.07	0.2	0.19	3.31	3.85	1.88	0.66	1.35
	Sep	5.07	0.07	0.88	4.55	4.71	0.98	1.91	1.69
	Nov	2.62	0.06	0.177	1.14	1.85	0.6	1.53	2.83
	Jan	6.36	0.13	2.62	1.06	3.1	1.22	1.09	2.93
	Mar	3.33	0.12	0.18	0.49	0.85	0.51	2.38	1.48

Sediment moisture content: Moisture content in sediments varied from 18.9% to 60.94% and minimum value was observed at station 2 and maximum value was observed at station 1 (Figure 3.6). Seasonal and spatial variations were observed in the moisture content. Stations 2 and 3 were also characterized by minimum variability in moisture content. It was found that seasonal variations were not uniform among the stations. Higher percentage of moisture was found in the sediments from stations 1,7 and 8. Generally stations 2 and 3 recorded the lowest values in monsoon and nonmonsoon. The comparatively lower percentages of moisture contents at stations 2 and 3 were associated with the sandy nature of the sediments found at these stations. This is evident from the good negative correlation of moisture content with sand percentage (Table 3.5). Moisture content also showed a good positive correlation with organic carbon. From the above discussion,

it appears that the variation in moisture content could be attributed to the variation in sediment texture and organic carbon.

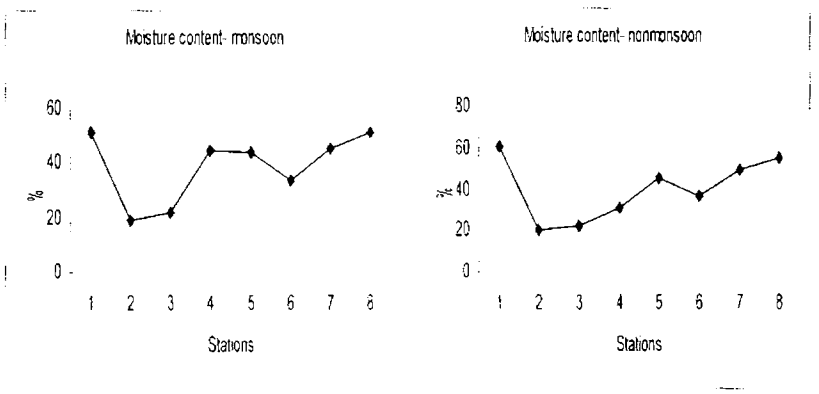

Figure 3.6 Spatial and seasonal variation of moisture content of sediment

Sediment organic carbon: The level of organic carbon in sediments is reported to be a reliable index of nutrient regeneration and the productivity of the water body. The carbon and nutrient cycles in the aquatic systems are temporally band spatially variable since they are regulated by a variety of factors such as soil type and texture, temperature and rain fall (Kristensen et al., 1992; Woodroffe, 1992; Robertson et al., 1992; Alongi et al., 1993). As the preservation and burial of organic matter in aquatic environments is a function of the rate of primary productivity, water depth, dissolved oxygen content in the water column, sedimentation rate, biological activity and sediment stability, the organic carbon contents of sediments can be a sensitive indicator of the nature of source areas and the environments of deposition (Emerson and Hedges, 1988). Long term burial of organic matter has been a key process in the formation and maintenance of an oxygen rich atmosphere (Berner, 2001), be it burial of terrestrial plants in

fresh water swamps leading to extensive coal formation (Holland, 1987) or the deposition of organic matter in marine deposits(de Haas et al., 2002). Whether the coastal system acts as net carbon sources or sinks remains debatable, largely because coastal systems varies substantially in response to external change (Hung and Kuo, 2001).

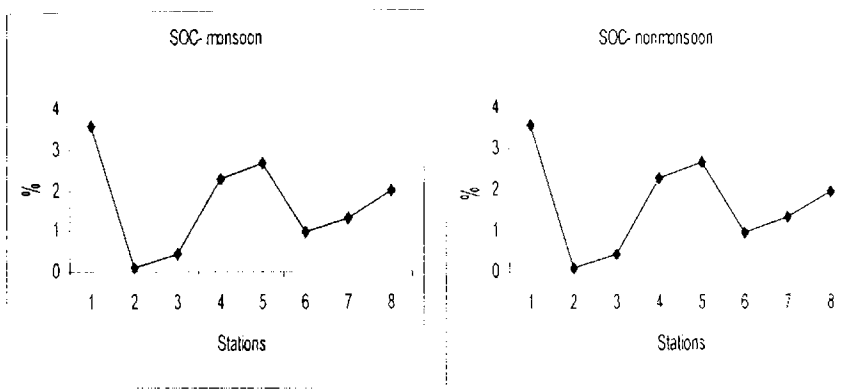

Figure 3.7 Spatial and seasonal variations of SOC

The primary purpose of this investigation was, therefore, to determine the distribution of organic carbon and the extent to which this distribution is related to other factors, primary productivity, oxygen content, bottom topography and hydrodynamic features. Total organic carbon of the sediment has a major role in keeping the fertility of soil and there by augmenting their biological productivity. Since Chalakudy river is one of the most productive aquatic ecosystems, an understanding of this carbon is prerequisite for assessing and also determining the extent of nutrients in surrounding water.

Seasonal variation showed a minimum at station 2 (0.09%) during monsoon and maximum at station 1(4.84%) during nonmonsoon (Figure 3.7). The sediments of station 2 were poor in carbon and station 1 was richer. Organic carbon is imported as an energy source for organisms in aquatic systems. Estuarine sediments are rich in organic matter than those of the adjacent sea (Nixon and Lee, 1982). The highest concentration of organic carbon at station 1 during nonmonsoon station may be due to the combined effect of ,high productivity, settling of organic 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 runoff through rivers, prevailing water currents and depth of occurrence play an important role in the accumulation of organic matter (Purandara and Dora, 1987).

Previous work done by Joseph (2002), on the distribution of organic carbon contents of sediments of Chitrapuzha river showed a range from 1.34 mg/g to 90.24 mg/g. Rini Sebastian (2002) observed organic carbon variation in mangrove sediments of Cochin from 9.83 mg/g to 152.76 mg/g.

Values obtained for SOC in the present study were slightly lower than those reported earlier, especially those at stations 2 and 3. This might be due to the sandy nature of the sediments of the area and also the enhanced oxidative degradation.

Table 3.4 Distribution values of sediment parameters

		Stations							
Months		S1	S2	S3	S4	S5	S6	S7	S8
Sand	May	25.3	95.9	92.19	19.94	47.1	46.3	78.9	41.2
	Jul	34.8	90.2	69.63	22.14	12.5	41.6	73.9	13
	Sep	34.8	90.2	69.63	22.14	12.5	41.6	73.9	13
	Nov	56.4	89.7	65.02	11.92	12.1	14.4	65.3	11.7
	Jan	56.4	89.7	65.02	11.92	12.1	14.4	65.3	11.7
	Mar	25.3	95.9	92.19	19.94	47.1	46.3	78.9	41.2
Silt	May	67.6	1.89	6.85	77.12	48.8	49.7	14.8	54
	Jul	55.9	6.21	25.46	70.51	76.3	50.2	24.8	77
	Sep	55.9	6.21	25.46	70.51	76.3	50.2	24.8	77
	Nov	40.4	9.02	33.37	85.83	84	81.6	31.4	82.1
	Jan	40.4	9.02	33.37	85.83	84	81.6	31.4	82.1
	Mar	67.6	1.89	6.85	77.12	48.8	49.7	14.8	54
Clay	May	7.11	2.25	0.96	2.94	4.18	4.03	6.34	4.83
	Jul	9.3	3.57	4.91	7.35	11.2	8.18	1.36	10.1
	Sep	9.3	3.57	4.91	7.35	11.2	8.18	1.36	10.1
	Nov	3.29	1.32	1.61	2.25	3.92	4.03	3.25	6.2
	Jan	3.29	1.32	1.61	2.25	3.92	4.03	3.25	6.2
	Mar	7.11	2.25	0.96	2.94	4.18	4.03	6.34	4.83
Carbon	May	5.64	0.27	0.33	0.71	0.93	0.83	3.45	2.24
	Jul	7.71	0.21	2.08	6.79	7.45	1.59	2.99	2.22
	Sep	7.71	0.21	2.08	6.79	7.45	1.59	2.99	2.22
	Nov	5.71	0.12	0.43	1.11	2.72	0.95	1.82	3.64
	Jan	5.71	0.12	0.43	1.11	2.72	0.95	1.82	3.64
	Mar	5.64	0.27	0.33	0.71	0.93	0.83	3.45	2.24
Hydrogen	May	2	0.35	0.35	0.42	0.29	0.5	2.1	1.56
	Jul	2.06	0.4	1.05	1.98	2.24	0.65	1.6	1.17
	Sep	2.06	0.4	1.05	1.98	2.24	0.65	1.6	1.17
	Nov	1.81	0.19	0.42	0.55	1.07	0.45	0.87	2.02
	Jan	1.81	0.19	0.42	0.55	1.07	0.45	0.87	2.02
	Mar	2	0.35	0.35	0.42	0.29	0.5	2.1	1.56
Nitrogen	May	0.51	0	0.11	0.12	0.11	0.14	0.35	0.28
	Jul	0.49	0.03	0.00	0.38	0.5	0.00	0.32	0.25
	Sep	0.49	0.03	0.00	0.38	0.5	0.00	0.32	0.25
	Nov	0.49	0.09	0.13	0.18	0.24	0.00	0.21	0.45
	Jan	0.49	0.09	0.13	0.18	0.24	0.00	0.21	0.45
	Mar	0.51	0	0.11	0.12	0.11	0.14	0.35	0.28

Grain size (texture) analysis: Grain size analysis is a fundamental procedure in sedimentology and limnology, and it gives basic information

on the sediment composition and depositional environment. Natural sediments consist of particles of different sizes and for deciding the size groups, several class intervals based on average diameter have been suggested. One such system includes the grading of particles into sand (>63 μm), silt (4-63 μm) and clay(<4 μm) sizes (Krumbein and Pettijohn, 1938). The seasonal and spatial variations of sand, silt and clay are depicted in Figure 3.8. The sediments of station 2 and 3 were mainly composed of sand particles.

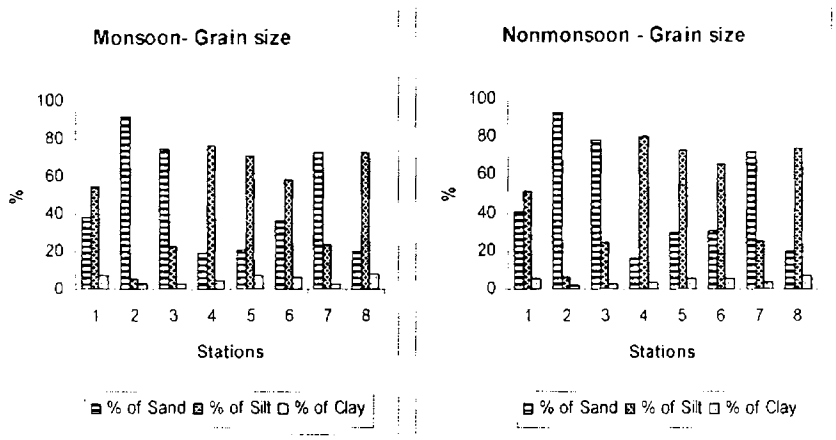

Figure 3.8 Spatial and seasonal variations of grain size

The sediment distribution pattern depends on several factors such as sediment sources, texture of the sedimentary materials supplied, bottom topography of the basin and general hydrographical features (Veerayya and Murty, 1974; Seralathan, 1986; Nair, 1992). At stations 7 and 8, the bulk of the sedimentary materials is supplied by the Periyar river, whereas at station 1 the sedimentary material is supplied from Sholayar.The percentage of clay in the present study varied from 1.32 to 8.2%.

Percentage of clay was generally higher at stations 1 and 8 during monsoon.

CHN analysis: Figure 3.9 shows spatial and seasonal variations of CHN. Higher percentage of carbon, hydrogen and nitrogen was observed at station 1 during monsoon. The percentage of carbon, hydrogen and nitrogen was lowest at station 2. The lowest percentage of carbon and hydrogen was observed during nonmonsoon and nitrogen during monsoon. In this study, high seasonal variations of C,H,N in the sediments of station 1 were observed and it could be attributed to the changes in physico-chemical 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 nonmonsoon seasons. As compared with station 1, lower values could be attributed to the sandy nature of the sediments at stations 2 and 3.

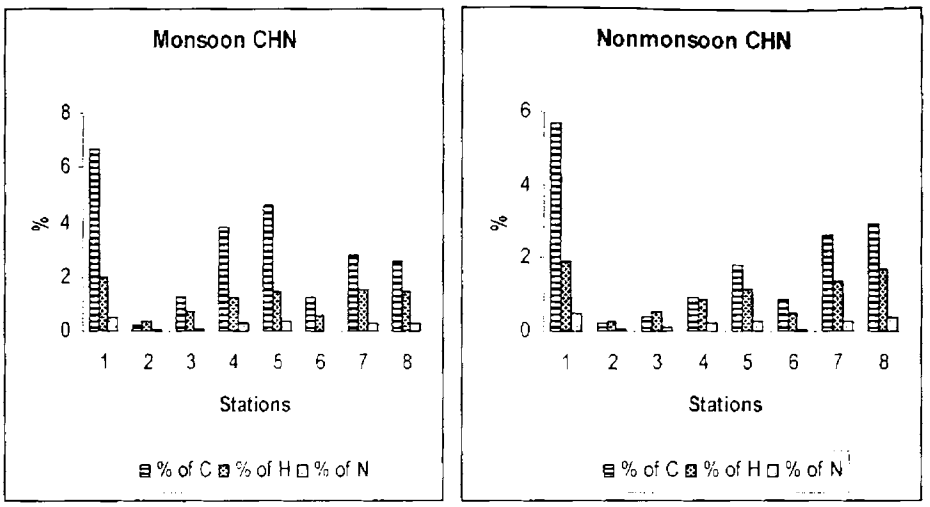

Figure 3.9 Spatial and seasonal variations of CHN

Inter parameter relationships

The geochemical and hydrogeological results helped in getting an idea about the ecosystem of Chalakudy river. On comparing the hydrographical parameters of samples from all sites, several of the hydrochemical data were significantly correlated (Table 3.5).

Table 3.5Pearson correlation matrix of hydrochemical parameters in sediments

	Moisture content	SOC	C %	H %	N %	Sand %	Silt %
SOC	0.81						
C %	0.82	0.86					
H %	0.85	0.72	0.89				
N %	0.87	0.85	0.92	0.93			
sand %	-0.52	-0.35	-0.37	-0.33	-0.40		
silt %	0.50	0.33	0.34	0.31	0.39	-1.00	
clay %	0.59	0.41	0.63	0.62	0.52	-0.53	0.48

Moisture content was positive to percentage of C, H, N, SOC, and clay. SOC was significantly interlinked to C, N and H. The percentages of C, H and N are interrelated at significant level with r values in the range 0.89 to 0.93. Clay was found to be highly related with C and H.

Some recent values of hydrographical parameters in rivers, reported globally are presented in Table 3.6

Table 3.6 Recently reported values of hydrographical parameters in rivers on worldwide

Para - meters	Aquatic system	Concentration	Reference
DO	Wuli Lake in China	7.48 ± 3.08 mg l^{-1}	Jin et. al., 2006
	Surma River, Eastern Bangladesh	5.52 -5.72 mg l^{-1}	Alam et al., 2007
pH	Surma River, Eastern Bangladesh	6.126 -6.093	Alam et al., 2007
	Oukaimeden river (Morocco)	7.6	Oudra et al., 2008
Chloride	Moselle river, France	352 ± 91 mg l^{-1}	Montarges-Pelletier et al., 2007
SOC (%)	Moselle river, France	0.77 -13.01%	Montarges-Pelletier et al., 2007

Statistical Approach

Abbreviations

NS	:	Not Significant
dof		degrees of freedom
MSS		Mean Sum of Squares
(P<0.05)		calculated F is significant at 5% level
(P<0. 01)		calculated F is significant at 1% level
(P<0.001)		calculated F is significant at 0.1% level
MDS		Multidimensional scaling

Table 3.7 Distribution of Dissolved oxygen in water

Stations	Average	std	CV%	Stations	Average	std	CV%
S1	6.523	1.591	24.40	S5	5.678	1.310	23.06
B1	6.172	1.698	27.52	B5	5.570	1.120	20.10
S2	6.637	1.554	23.41	S6	6.007	0.999	16.03
B2	6.637	1.554	23.41	B6	5.848	1.156	19.77
S3	7.357	1.751	23.80	S7	5.208	1.498	28.76
B3	7.357	1.751	23.80	B7	4.983	1.429	28.67
S4	6.620	1.577	23.82	S8	4.228	1.127	26.65
B4	6.590	1.639	24.88	B8	4.155	0.957	23.03

Dissolved oxygen averaged seasons ranged at surface between 4.23 (S8) and 7.36 (S3) and ranged between 4.16 (B8) and 7.36 (B3) at bottom seasonal variation at different station both at surface and bottom were more or less similar. At surface station seasonal variations are higher than at bottom except at station B1, B6 and B7 where it was higher than that at the surface (CV% varied between 16.63% and 28.76%) (Table 3.7).

3 way ANOVA (Table 3.8) applied to compare between station, between surface and bottom and between seasons showed significant station wise variations ($F_{(7,35)}$=185.59, P<0.001), surface and bottom variation ($F_{(1,35)}$=5.217, P<0.01) and seasonal variation ($F_{(5,35)}$= 549.15, P<0.001) along with significant station season interaction ($F_{(35,35}$= 9.175, P<0.001)as indicated by higher values at station 3 and station 1 during July and September irrespective of surface and bottom (interaction of surface and bottom with station and seasons were not significant (P>0.05).

Table 3.8: 3 way ANOVA for compairing DO in water with respect to station, surface and bottom and with respect to season

Source	dof	SS	MSS	F ratio	Remarks
Stations (A)	7	83.5481	11.9354	185.5916	(P<0.001)
Sur/Bot (B)	1	0.3354	0.3354	5.2164	(P<0.01)
Seasons (C)	5	176.569	35.3137	549.146	(P<0.001)
AB interaction	7		0.045271	0.70398	NS
BC interaction	5		0.0952	1.4806	NS
AC interaction	35		0.58999	9.1746	(P<0.001)
Error	35	2.2507	0.06431		
Total	95	37093.3			

Dendrogram drawn to group the stations showed (Figures 3.10 a and b) two distinct clusters 1. March, November and January and 2. May, July and September separating the seasons into monsoon and non monsoon seasons. Dendrogram drawn to group the station grouped the locations into two main clusters 1. (S1, B1, S3, B3) and 2. (S6, B6, B8) (S2, B2, B4, B7, S8) and (S4, S5, S7) at very high level of similarity (96%) on comparing the station at surface and bottom based on DO, show significant difference between all station and also stations S3 and B3 from station 7 ($p < 0.01$) ($t10 > 3.169$ at 1% level, $p<0.01$).

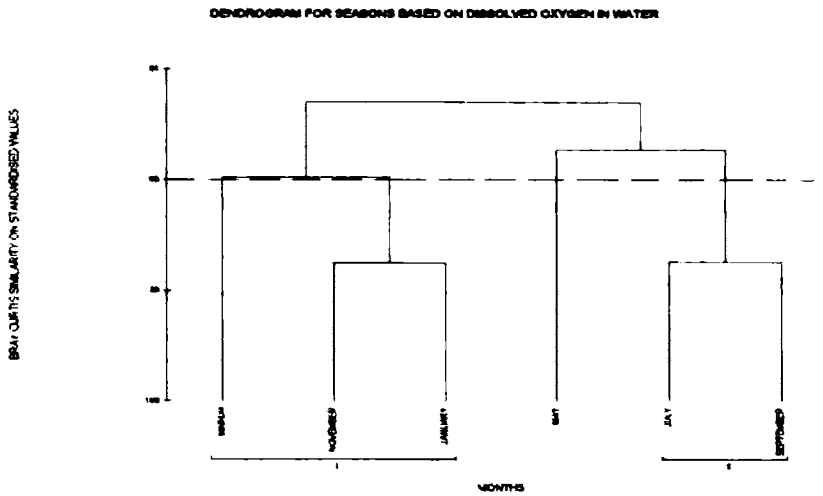

Figure 3.10 a. Dendrogram for seasons based on dissolved oxygen in water

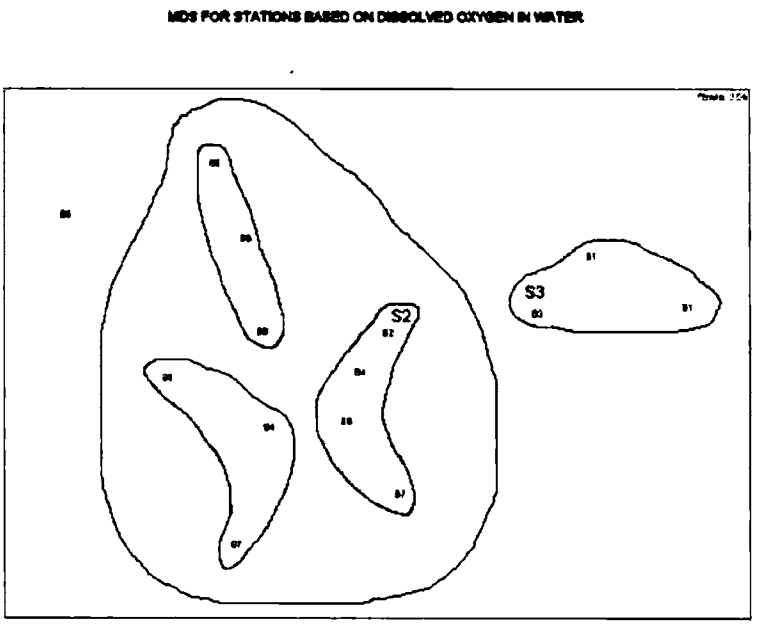

Figure 3.10 b. MDS for stations based on dissolved oxygen in water

Trellis diagram drawn to show the difference between the station based on dissolved oxygen is presented in Table 3.9

Table 3.9 Trellis diagram for students t test to compare between stations based on dissolved oxygen (• Not significant; • Significant at 10% level; • Significant at 5% level; • Significant at 1% level)

	S1	B1	S2	B2	S3	B3	S4	B4	S5	B5	S6	B6	S7	B7	S8	B8
S1		0.34	0.11	0.11	0.79	0.79	0.1	0.07	0.92	1.1	0.62	0.77	1.35	1.61	2.63	2.85
B1	•		0.45	0.45	1.08	1.09	0.43	0.4	0.51	0.66	0.19	0.35	0.95	1.2	2.13	2.31
S2	•	•		0	0.69	0.69	0.02	0.05	1.06	1.25	0.76	0.91	1.48	1.75	2.81	3.04
B2	•	•	•		0.69	0.69	0.02	0.05	1.06	1.25	0.76	0.91	1.48	1.75	2.81	3.04
S3	•	•	•	•		0	0.7	0.72	1.72	1.92	1.5	1.61	2.09	2.35	3.36	3.59
B3	•	•	•	•	•		0.7	0.72	1.72	1.92	1.5	1.61	2.09	2.35	3.36	3.59
S4	•	•	•	•	•	•		0.03	1.03	1.21	0.73	0.88	1.45	1.72	2.76	2.99
B4	•	•	•	•	•	•	•		0.97	1.15	0.68	0.83	1.39	1.65	2.65	2.89
S5	•	•	•	•	•	•	•	•		0.14	0.45	0.22	0.53	0.8	1.88	2.10
B5	•	•	•	•	•	•	•	•	•		0.65	0.39	0.43	0.72	1.89	2.15
S6	•	•	•	•	•	•	•	•	•	•		0.23	0.99	1.31	2.65	2.99
B6	•	•	•	•	•	•	•	•	•	•	•		0.76	1.05	2.24	2.52
S7	•	•	•	•	•	•	•	•	•	•	•	•		0.24	1.17	1.32
B7	•	•	•	•	•	•	•	•	•	•	•	•	•		0.93	1.08
S8	•	•	•	•	•	•	•	•	•	•	•	•	•	•		0.11
B8	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	

Table 3.10 Distribution of Temperature in water

Station	Average	std	CV%	Station	Average	std	CV%
S1	26.867	1.062	3.96	S5	29.667	2.165	7.30
B1	27.033	1.219	4.51	B5	29.533	2.162	7.32
S2	26.933	1.504	5.58	S6	29.900	2.116	7.08
B2	26.933	1.882	6.58	B6	29.833	2.047	6.86
S3	27.933	1.882	6.74	S7	31.533	1.459	4.63
B3	27.933	1.882	6.74	B7	31.433	1.485	4.73
S4	28.467	1.365	4.79	S8	30.800	1.361	4.42
B4	28.467	1.582	5.56	B8	30.633	1.555	5.08

Temperature in water averaged over seasons ranged between 26.87°C (S1) and 31.57°C (S7) at surface and between 27.63°C (B2) and 31.43°C (B7) at bottom with very low seasonal variations at all station (CV%<1.30 at surface and CV%<7.32 at bottom). Comparatively higher temperature was observed at bottom at all stations (Table 3.10).

3 way ANOVA applied to compare between station, surface and bottom and between seasons, based on temperature showed significant station wise ($F_{(7,35)}$=1576.88, $p<0.001$) surface and bottom ($F_{(1,35)}$=2.143, $p<0.05$) and season wise variations ($F_{(5,35)}$=2107.21, $p<0.001$) along with season-surface/bottom interaction ($F_{(5,35)}$= 4.0714, $p<0.001$) and station - season interaction ($F_{(35,35)}$=51.826, $P<0.001$) as indicated by higher temperature during nonmonsoon seasons than monsoon seasons particularly at stations 3-8 compared to stations 1&2 (Table 3.11).

Table 3.11: 3 way ANOVA for comparing temperature in water with respect to station, surface and bottom and seasons

Source	SS	dof	MSS	F ratio	Remarks
Stations (A)	241.461	7	34.4944	1576.88	(P<0.001)
Sur/Bot (B)	0.04687	1	0.04687	2.1429	(P<0.05)
Seasons (C)	230.477	5	46.0953	2107.21	(P<0.001)
AB interaction		7	0.0301339	1.37755	NS
BC interaction		5	0.0890625	4.0714	(P<0. 01)
AC interaction		35	1.13371	51.8265	(P<0.001)
Error	0.765625	35	0.0218750		
Total	81214.3	95			

Dendrogram drawn to group the seasons has highlighted two distinct clusters of seasons: 1. September, November 2. January, March, May and July at 98.5% similarity level (Figures 3.11 a and b). Dendrogram drawn to group the stations has produced three distinct clusters of station: 1. (S6, B6), 2. (S1, B1) and 3. station 2, 3, 4, 5& 8 with surface and bottom linked together, at 98.5% similarity level.

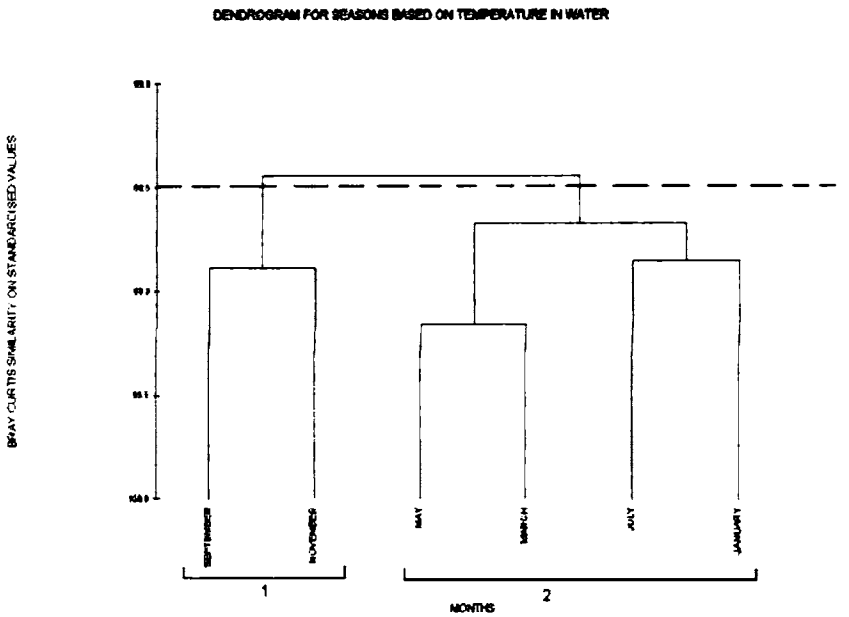

Figure 3.11 a. Dendrogram for seasons based on temperature in water

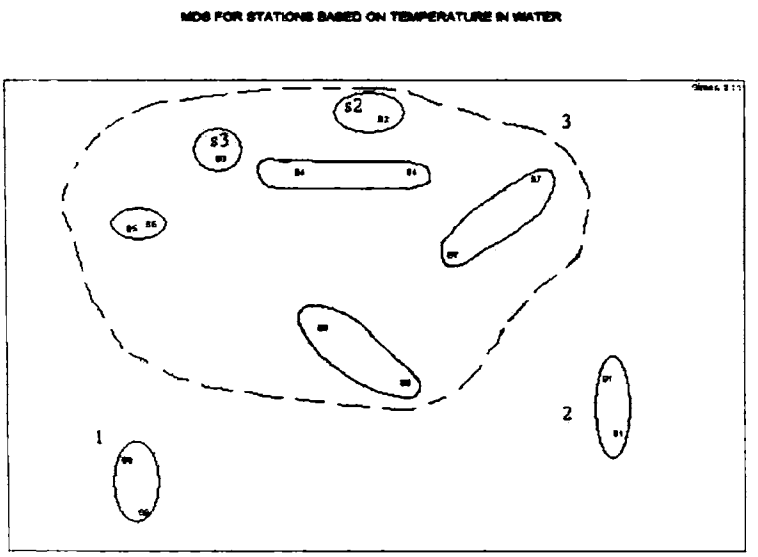

Figure 3.11 b. MDS for stations based on temperature in water

Trellis diagram drawn to show the difference between the station based on temperature showed significant difference between station (S2, S1) and (S5,S8) (t10>2.228, p<0.05) and stations (S3,S4) and (S7,B8) (Table 3.12).

Table 3.12 Trellis diagram for students t test to compare between stations based on temperature (• Not significant; • Significant at 10% level; • Significant at 5% level; • Significant at 1% level)

	S1	B1	S2	B2	S3	B3	S4	B4	S5	B5	S6	B6	S7	B7	S8	B8
S1		0.23	0.08	0.08	1.1	1.1	2.07	1.88	2.6	2.48	2.87	2.88	5.78	5.6	5.09	4.47
B1	•		0.12	0.12	0.9	0.9	1.75	1.61	2.37	2.25	2.63	2.63	5.29	5.12	4.61	4.07
S2	•	•		0	0.93	0.93	1.69	1.57	2.32	2.21	2.56	2.55	4.91	4.76	4.26	3.82
B2	•	•	•		0.93	0.93	1.69	1.57	2.32	2.21	2.56	2.55	4.91	4.76	4.26	3.82
S3	•	•	•	•		0	0.51	0.49	1.35	1.25	155	1.53	3.38	3.26	2.76	2.47
B3	•	•	•	•	•		0.51	0.49	1.35	1.25	155	1.53	3.38	3.26	2.76	2.47
S4	•	•	•	•	•	•		0	1.05	0.93	1.27	1.24	3.43	3.29	2.71	2.34
B4	•	•	•	•	•	•	•		1	0.89	1.21	1.18	3.19	3.06	2.50	2.18
S5	•	•	•	•	•	•	•	•		0.1	0.17	0.13	1.6	1.5	0.99	0.81
B5	•	•	•	•	•	•	•	•	•		0.27	0.23	1.71	1.62	1.11	0.92
S6	•	•	•	•	•	•	•	•	•	•		0.05	1.42	1.33	0.80	0.62
B6	•	•	•	•	•	•	•	•	•	•	•		1.51	1.41	0.88	0.70
S7	•	•	•	•	•	•	•	•	•	•	•	•		0.11	0.82	0.94
B7	•	•	•	•	•	•	•	•	•	•	•	•	•		0.70	0.83
S8	•	•	•	•	•	•	•	•	•	•	•	•	•	•		0.18
B8	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	

Table 3.13 Distribution of Salinity in water

Station	mean	std	CV%	Station	mean	std	CV%
S1	0.013	0.002	15.30	S5	0.018	0.004	22.82
B1	0.076	0.109	143.81	B5	0.069	0.071	103.27
S2	0.014	0.003	20.87	S6	0.044	0.025	56.49
B2	0.014	0.003	20.87	B6	0.048	0.027	56.35
S3	0.013	0.002	14.61	S7	10.542	10.177	95.97
B3	0.013	0.002	14.61	B7	10.584	10.075	95.18
S4	0.014	0.003	23.39	S8	14.554	12.186	83.73
B4	0.020	0.015	72.49	B8	11.100	11.791	71.59

Salinity in water arranged over the seasons ranged between 0.013 (S3) and 14.554 (S8) at surface and between 0.13 (B3) and 16.470 (B8). At surface stations, seasonal variations was low at station S1&S2- S5 (CV<22.82%) and very high at station S7 (CV= 95.97%). But at bottom high seasonal variation was felt at station (B1,B5-B8) (56.35≤ CV% ≤ 143.87%) (Table 3.13).

3 way ANOVA applied to compare between stations, surface / bottom, seasons and their first order interactions (Table 3.14), showed high station wise difference ($F_{(7,35)}$=330.41, P<0.001) and season wise difference ($F_{(5,35)}$= 101.59, P<0.001) with moderate surface and bottom variation. Station- season interaction effect was very high ($F_{(35, 35)}$ =45.375, P<0.001) indicated by high salinity during nonmonsoon seasons and low salinity during monsoon seasons, particularly at stations 7 and 8 irrespective of surface and bottom.

Table 3.14: 3 way ANOVA for salinity in water with respect to station, surface and bottom and seasons

Source	SS	dof	MSS	F ratio	Remarks
Stations (A)	3192.68	7	456.098	330.41	(P<0.001)
Sur/Bot (B)	1.6267	1	1.6267	1.1784	NS
Seasons (C)	701.210	5	140.242	101.595	(P<0. 001)
ABinteraction		7	1.34365	0.9734	NS
BCinteraction		5	1.3353	0.9673	NS
ACinteraction		35	62.6354	45.3745	(P<0. 001)
Error	48.3143	35	1.3804		
Total	7185.98	95			

Dendrogram drawn to group the months based on salinity has grouped the January to July together separating November and September which shows low similarity between them as well as with the cluster (similarity <60%). Station wise grouping showed two distinct groups of stations *viz* 1. (S6, B6, S7, B7, S8, B8) and 2. (S3, B3,S4,S2,,B2,S1,S5) at 80% level of similarity , separating B1 and B5 and B4, with B4 more similar to cluster 2 and B5 to cluster 1, which are stations with least average salinity (Figures 3.12 a and b).

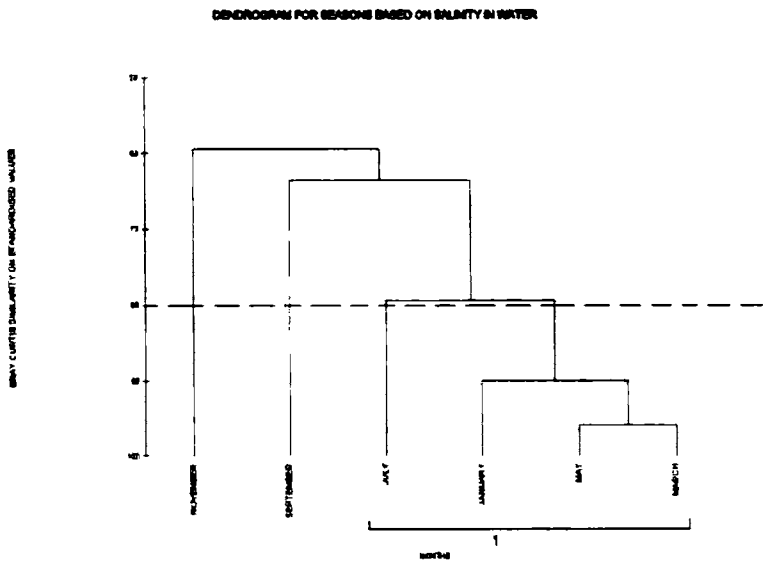

Figure 3.12 a. Dendrogram for seasons based on salinity in water

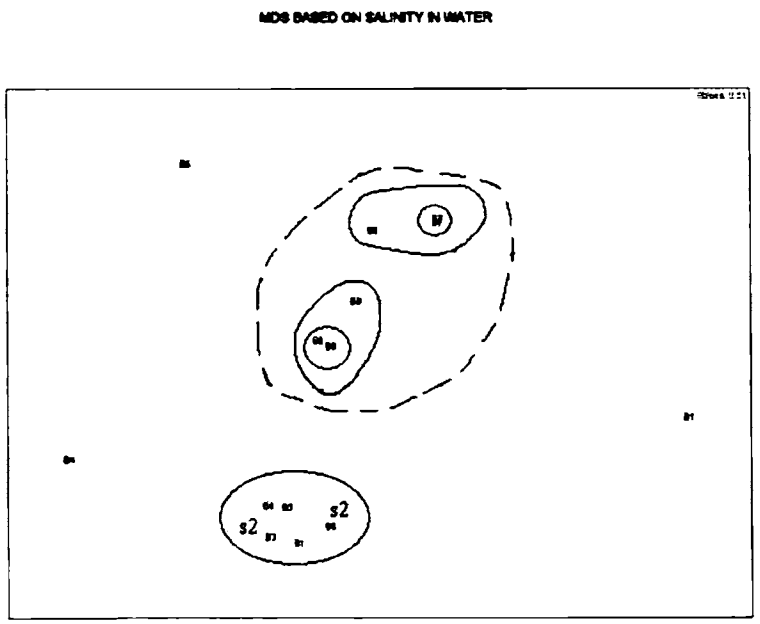

Figure 3.12 b. MDS for stations based on salinity in water

Trellis diagram drawn to compare between stations based on salinity showed highly significant difference between all stations, station 1 to 5, at surface and bottom with station 6 to 8, at surface and bottom ((t10 >2.228, p<0.05) (Figure 3.15).

Table 3.15 Trellis diagram for students t test to compare between stations based on salinity (• Not significant; • Significant at 10% level; • Significant at 5% level; • Significant at 1% level)

	S1	B1	S2	B2	S3	B3	S4	B4	S5	B5	S6	B6	S7	B7	S8	B8
S1		1.29	0.83	0.83	0.07	0.07	0.51	1.13	2.45	1.76	2.8	2.91	2.33	2.35	2.67	3.12
B1	•		1.27	1.27	1.29	1.29	1.27	1.13	1.19	0.13	0.64	0.55	2.31	2.33	2.66	3.11
S2	•	•		0	0.9	0.9	0.24	0.92	1.61	1.73	2.67	2.79	2.33	2.35	2.67	3.12
B2	•	•	•		0.9	0.9	0.24	0.92	1.61	1.73	2.67	2.79	2.33	2.35	2.67	3.12
S3	•	•	•	•		0	0.56	1.14	2.52	1.77	2.81	2.92	2.33	2.35	2.67	3.12
B3	•	•	•	•	•		0.56	1.14	2.52	1.77	2.81	2.92	2.33	2.35	2.67	3.12
S4	•	•	•	•	•	•		0.98	1.77	1.73	2.71	2.83	2.33	2.35	2.67	3.12
B4	•	•	•	•	•	•	•		0.37	1.5	1.84	2.03	2.33	2.34	2.67	3.12
S5	•	•	•	•	•	•	•	•		1.61	2.33	2.49	2.33	2.35	2.67	3.12
B5	•	•	•	•	•	•	•	•	•		0.74	0.6	2.31	2.33	2.66	3.11
S6	•	•	•	•	•	•	•	•	•	•		0.27	2.32	2.34	2.66	3.12
B6	•	•	•	•	•	•	•	•	•	•	•		2.32	2.34	2.66	3.12
S7	•	•	•	•	•	•	•	•	•	•	•	•		0.01	0.57	0.85
B7	•	•	•	•	•	•	•	•	•	•	•	•	•		0.57	0.85
S8	•	•	•	•	•	•	•	•	•	•	•	•	•	•		0.25
B8	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	

Table 3.16 Distribution of pH in water

Station	Average	std	CV%	Station	average	std	CV%
S1	7.253	0.260	3.58	S5	7.037	0.167	2.37
B1	7.225	0.213	2.94	B5	7.048	0.203	2.88
S2	7.245	0.164	2.27	S6	6.910	0.236	3.41
B2	7.245	0.164	2.27	B6	6.975	0.226	3.24
S3	7.313	0.200	2.74	S7	7.418	0.372	5.01
B3	7.313	0.200	2.74	B7	7.448	0.342	4.59
S4	7.197	0.171	2.37	S8	7.490	0.389	5.19
B4	7.230	0.272	3.76	B8	7.612	0.346	4.54

Distribution of pH in water averaged over seasons showed higher value at bottom stations (S4 to S8) than the stations B4 to B8 where as at S1 to S3, higher or equal values than at B1 to B3 separately were observed. pH values were highly consistent with respect to seasons as indicated by very low coefficient of variations, both at surface and bottom (CV%<5.19%) (Table 3.16). 3 way ANOVA (Table 3.17) applied to compare between stations, surface and bottom and between seasons showed significant station wise variation ($F_{(7,35)}$=54.4158, P<0.001), surface and bottom difference, ($F_{(1,35)}$=2.3798, P<0.05) and season wise difference ($F_{(5,35)}$=64.823, p<0.001) along with high station season interaction ($F_{(35,35)}$ = 10.869, p<0.001) as indicated by lowest pH value at S1,B1,S6 and B6 during May and higher values during January at S1, B1, S7, B7, S8 and B8 and high values during September at S3, B3, S4 and B4.

Dendrogram drawn to group the seasons based on pH value to group the seasons based on pH value has grouped the seasons into two clusters: 1. January and March 2. May to November thus distinctly grouping dry season and wet season separately (Figures 3.13 a and b) at 98.5% similarity level. Stations grouped based on the same index of similarity, at 98% level of similarity showed two distinct clusters 1. Stations 7 and 8 2. (B4, stations 1,2, S4, and stations 3,5 and 6) showing the significant difference between station7&8 and other stations.

Table 3.17: 3 way ANOVA for pH in water with respect to station, surface and bottom and seasons

Source	SS	dof	MSS	F ratio	Remarks
Stations (A)	3.20508	7	0.4578	54.4158	(P<0.001)
Sur/Bot (B)	0.0200195	1	0.02002	2.3798	(P<0.05)
Seasons (C)	2.72656	5	0.5453	64.8226	(P<0.001)
AB interaction		7	0.00662	0.7877	NS
BC interaction		5	0.016895	2.0083	(P<0. 05)
ACinteraction		35	0.09143	10.8690	(P<0.001)
Error	0.2944	35	0.008413		
Total	5052.10	95			

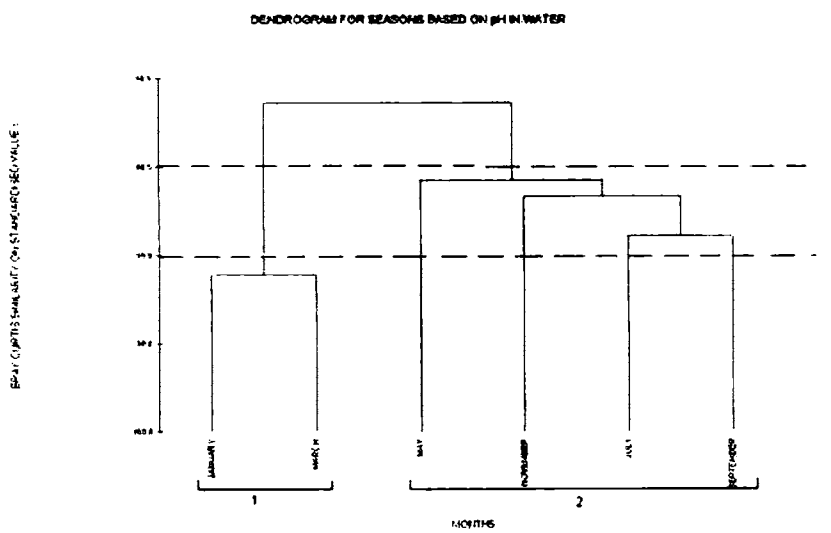

Figure 3.13 a. Dendrogram for seasons based on pH in water

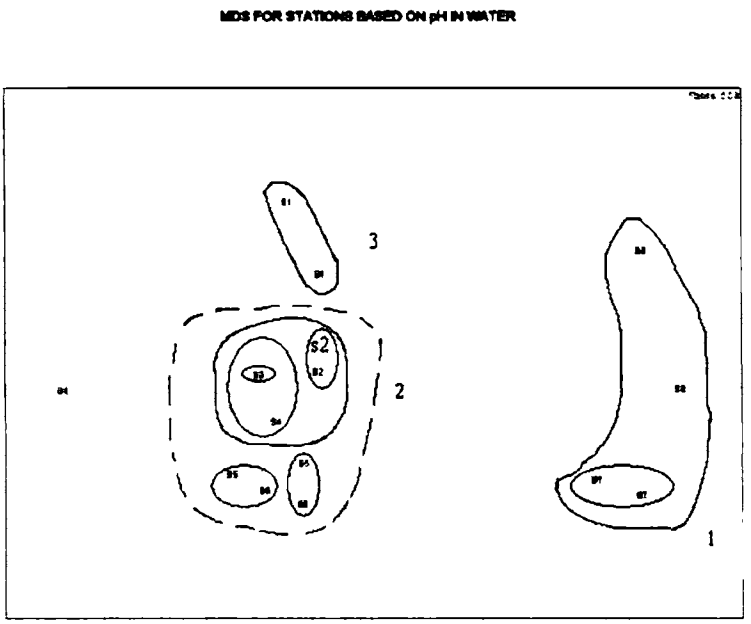

Figure 3.13 b. MDS for stations based on pH in water

Trellis diagram shown to show the significant station wise differences (Table 3.18) showed high differences between stations 2 and 3, 5 and 6 and both at surface and bottom ((t10 >2.28, p<0.05), S5,S6 and B3,B4 (t10 ≥2.28, p<0.05) and B1-B4 and stations B5-B8 (t10 ≥2.28, p<0.05).

Table 3.18 Trellis diagram for students t test to compare between stations based on pH (• Not significant; • Significant at 10% level; • Significant at 5% level; • Significant at 1% level)

	S1	B1	S2	B2	S3	B3	S4	B4	S5	B5	S6	B6	S7	B7	S8	B8
S1		0.19	0.06	0.06	0.41	0.41	0.41	0.14	1.57	1.39	2.19	1.81	0.81	1.02	1.13	1.85
B1	•		0.17	0.17	0.68	0.68	0.23	0.03	1.55	1.34	2.22	1.8	1.01	1.24	1.34	2.13
S2	•	•		0	0.59	0.59	0.46	0.11	1.99	1.68	2.61	2.16	0.95	1.2	1.30	2.14
B2	•	•	•		0.59	0.59	0.46	0.11	1.99	1.68	2.61	2.16	0.95	1.2	1.30	2.14
S3	•	•	•	•		0	0.99	0.55	2.37	2.08	2.92	2.5	0.56	0.76	0.90	1.67
B3	•	•	•	•	•		0.99	0.55	2.37	2.08	2.92	2.5	0.56	0.76	0.90	1.67
S4	•	•	•	•	•	•		0.23	1.5	1.25	2.2	1.75	1.21	1.47	1.54	2.41
B4	•	•	•	•	•	•	•		1.36	1.2	1.99	1.61	0.92	1.12	1.23	1.95
S5	•	•	•	•	•	•	•	•		0.1	0.98	0.49	2.1	2.42	2.40	3.35
B5	•	•	•	•	•	•	•	•	•		0.99	0.54	1.95	2.25	2.25	3.14
S6	•	•	•	•	•	•	•	•	•	•		0.45	2.58	2.9	2.85	3.75
B6	•	•	•	•	•	•	•	•	•	•	•		2.28	2.58	2.56	3.45
S7	•	•	•	•	•	•	•	•	•	•	•	•		0.13	0.30	0.85
B7	•	•	•	•	•	•	•	•	•	•	•	•	•		0.18	0.75
S8	•	•	•	•	•	•	•	•	•	•	•	•	•	•		0.52
B8	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	

Table 3.19 Distribution of COD in water

Station	Average	std	CV%	Station	average	std	CV%
S1	37.485	61.677	164.54	S5	48.002	78.672	163.89
B1	33.880	31.713	93.60	B5	55.158	92.310	167.36
S2	13.178	12.909	97.96	S6	27.746	52.548	189.392
B2	13.178	12.909	97.96	B6	14.039	16.154	115.068
S3	18.337	20.916	114.07	S7	60.852	48.761	80.131
B3	18.337	20.916	114.07	B7	59.243	49.962	84.334
S4	12.902	6.235	48.33	B8	66.593	54.438	81.147
B4	41.791	53.993	129.20	B8	99.103	77.636	78.338

Distribution of COD in water (Table 3.19), arranged over seasons showed high seasonal variability at all stations with least variation at S4 (CV=48.33%), and highest variation at S1 (CV= 164.54%), COD was at lower level at stations S2, B2, S3, B3, S4, S6, B6 and S7

(12.90≤COD≤27.746) and higher values at S1& B4 and stations 5,7& 8(31.713≤COD≤99.103). At the bottom samples, COD varied over a larger range with least COD at B2 (12.904) and highest value at B8 (99.103). Seasonal variations was higher at bottom stations B1, B2, B3, B4, B5&B6 (93.60≤CV%≤167.36). Bottom COD values are higher than the corresponding surface values (Table 3.20) at station 4, 5, 7 and 8. 3 way ANOVA (Table 3.20) applied to compare spatially and seasonally based on COD values, it is obtained that COD values vary highly with respect to stations ($F_{(7,35)}$=7.715, p≤0.001) and seasons ($F_{(5,35)}$=18.152, p≤0.001 but not with respect to surface and bottom(p>0.05) with high station season interaction ($F_{(35,35)}$=4.045, p<0.001 as indicated by very high value during September at stations S1-S6 and during May and March at station 7 and 8 both surface and bottom and low values during January to May at stations1,2,3-6 at surface and bottom. Depth wise variation in COD is not significant (p>0.05).

Table 3.20: 3 way ANOVA for comparing COD in water with respect to station, surface and bottom, and seasons

Source	SS	dot	MSS	F ratio	Remarks
Stations (A)	49101.9	7	7014.55	7.7148	(P<0.001)
Sur/Bot (B)	923.906	1	923.906	1.0161	NS
Seasons (C)	82523.1	5	16504.6	18.1520	(P<0.001)
AB interaction		7	787.790	0.8664	NS
BC interaction		5	289.297	0.3182	NS
AC interaction		35	3646.40	4.0104	(P<0.001)
Error	31823.6	35	909.246		
Total	443026.0	95			

Dendrogram drawn to group the seasons showed two distinct clusters of months: 1. low COD values months 2. High COD values months at 55% level of similarity (Figure 3.14). Clusters of stations obtained at 80% level of similarity are:1. Stations 7&8 (surface and bottom) 2. [(S6, S1, S5, B5) (S4, B1, S2, B2, S3, B3), B4, B6] (Figure 3.14).

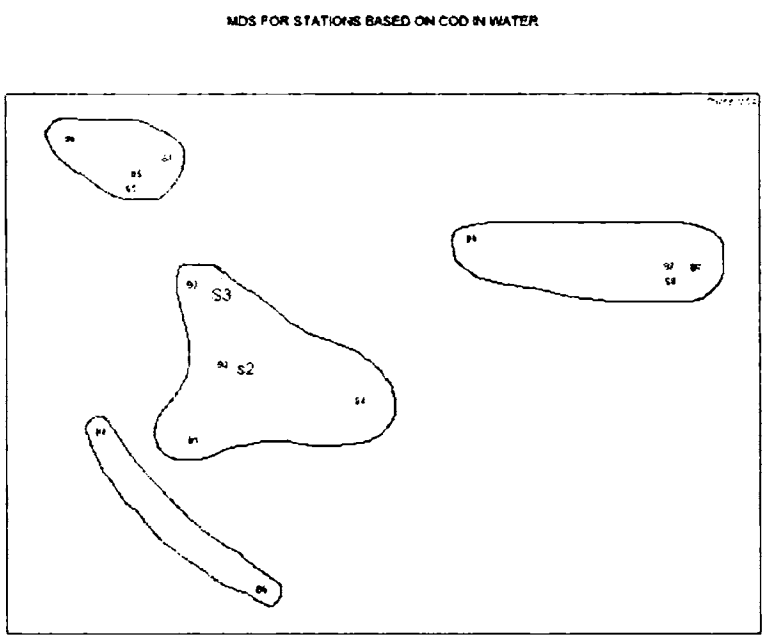

Figure 3.14 MDS for stations based on COD in water

Trellis diagram drawn to compare between stations showed S2, B4, S4, B6 are significantly different from ($t(10) > 1.812$, $P < 0.10$) (Table 3.21).

Table 3.21 Trellis diagram for students t test to compare between stations based on COD (• Not significant; • Significant at 10% level; • Significant at 5% level; • Significant at 1% level)

	S1	B1	S2	B2	S3	B3	S4	B4	S5	B5	S6	B6	S7	B7	S8	B8
S1		0.12	0.86	0.86	0.66	0.66	0.89	0.12	0.24	0.36	0.27	0.82	0.66	0.61	0.79	1.39
B1	•		1.35	1.35	0.91	0.91	1.45	0.28	0.37	0.49	0.22	1.25	1.04	0.96	1.16	1.74
S2	•	•		0	0.47	0.47	0.04	1.15	0.98	1.01	0.6	0.09	2.11	2	2.13	2.44
B2	•	•	•		0.47	0.47	0.04	1.15	0.98	1.01	0.6	0.09	2.11	2	2.13	2.44
S3	•	•	•	•		0	0.56	0.91	0.81	0.87	0.37	0.36	1.79	1.69	1.85	2.25
B3	•	•	•	•	•		0.56	0.91	0.81	0.87	0.37	0.36	1.79	1.69	1.85	2.25
S4	•	•	•	•	•	•		1.19	0.99	1.02	0.63	0.15	2.18	2.06	2.19	2.48
B4	•	•	•	•	•	•	•		0.15	0.28	0.42	1.1	0.59	0.53	0.72	1.36
S5	•	•	•	•	•	•	•	•		0.13	0.48	0.95	0.31	0.27	0.43	1.03
B5	•	•	•	•	•	•	•	•	•		0.58	0.98	0.12	0.09	0.24	0.81
S6	•	•	•	•	•	•	•	•	•	•		0.56	1.03	0.97	1.15	1.70
B6	•	•	•	•	•	•	•	•	•	•	•		2.04	1.93	2.07	2.40
S7	•	•	•	•	•	•	•	•	•	•	•	•		0.05	0.18	0.93
B7	•	•	•	•	•	•	•	•	•	•	•	•	•		0.22	0.97
S8	•	•	•	•	•	•	•	•	•	•	•	•	•	•		0.77
B8	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	

Table 3.22 Distribution of sand, silt and clay

	Sand			Silt			Clay		
station	mean	std	CV%	mean	std	CV%	mean	std	CV%
S1	38.837	12.979	33.42	54.597	11.44	20.42	6.567	2.483	37.82
S2	91.91	2.803	3.050	5.707	2.932	51.39	2.380	0.923	38.79
S3	75.61	11.872	15.70	21.893	11.117	50.78	2.493	1.729	69.36
S4	18.00	4.392	24.40	77.82	6.274	8.06	4.180	2.259	54.05
S5	23.897	16.373	68.52	69.677	15.110	21.69	6.427	3.363	53.33
S6	34.083	14.078	41.31	60.503	14.926	24.67	5.413	1.953	36.14
S7	72.677	5.581	7.68	23.673	6.827	28.84	3.650	2.053	56.24
S8	21.973	13.619	61.98	70.993	12.231	17.23	7.033	2.219	31.55

Sand percentage averaged over seasons varied between 18.00 (station 4) and 91.91 (station 2) with seasonal variation ranging between 2.80% (station 2) and 68.52% (station 5). Silt percentage averaged over

seasons varied between 5.70% (station 2) and 77.82% (station 4) with seasonal variation ranging between 8.06 (station 4) with seasonal variation ranging between 8.06 (station 4) and 51.39 (station 2). Clay concentration ranged between 2.38(station 2) and 7.03 (station 8) with seasonal variation ranging between 31.55% (station 8) and 69.36% (station 3). At stations 2, 3 and 7 sand was the dominant sediment structure where as at stations 1,4,5,6 and 8, silt concentration was the dominant sediment structure where as clay concentration was very less in all stations (Table 3.22).

Table 3.23: 3 way ANOVA for comparing sand, silt and clay concentration in sediments with respect to stations, sediment structure and seasons

Source	SS	dof	MSS	F ratio	Remarks
Stations (A)		7			
Sand, silt and clay (B)	58773.5	2	29386.7	259.613	(P<0.001)
Seasons (C)		5			
AB interaction		14	4672.72	41.2805	(P<0.01)
BC interaction		10	408.764	3.6112	(P<0.05)
AC interaction		35			
Error	7923.61	70	113.194		
Total	296201.0	143			

3way ANOVA applied to compare the sediment structure between stations and between seasons and between sediment type showed high significant variation between the sediment types ($F_{(2,70)}$=259.613 p<0.001) and high season-sediment type interaction ($F_{(10,70)}$=3.611,p<0.05) and high station sediment type interaction ($F_{(14,70)}$=41.28, p<0.001 as indicated by least sand concentration at stations 4,5 and 8 particularly during July, September, November and

January and high values for silt during these months at these three stations clay concentration is comparatively higher at station 4,5 and 8 during July and September (Table 3.23).

Dendrogram drawn to group the seasons based on sediment structure has divided the study period into three clusters: 1.March, May 2. July, September and 3. November and January. All the three cases (Figures 3.15 a to f) are at 85% of similarity level. Based on sand (Figures 3.15 a and b) the stations are grouped as Cluster 1. station1, station 5 Cluster 2. stations 2, 3, 4, 6 7. Station 1 is quite different from other stations at 80% level of similarity. Cluster 1 have the maximum seasonal variability where as cluster 2 stations have seasonal variations CV %< 41.31%. Based on silt, two distinct clusters are obtained: 1. stations 2and 3, 2. Stations 4, 5, 6, 7and 8. Cluster 1 stations have same seasonal variations, CV~51% where as cluster 2 stations have seasonal variations, CV<28.84%. Station 1 is not associated with any of the two clusters (Figures 3.15 c and d) at 80% level of similarity. Based on clay, only a single cluster containing all stations other than station 7 is obtained at 85% level of similarity. The seasonal variations for the clay distribution at stations in cluster 1 is almost similar, CV<40% except at station 3 where a seasonal variation of 69.36% is observed. Stations 4,5 have similar seasonal variation, ~54%, so also station 1 and station 2 it being ~38%, station 3 and station 7 are having higher seasonal variation (Figures 3.15 e and f).

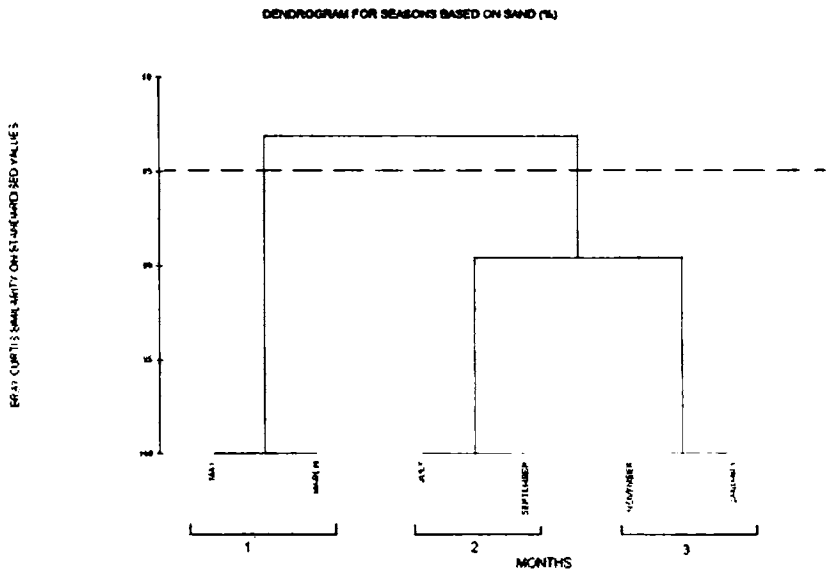

Figure 3.15 a. Dendrogram for seasons based on sand

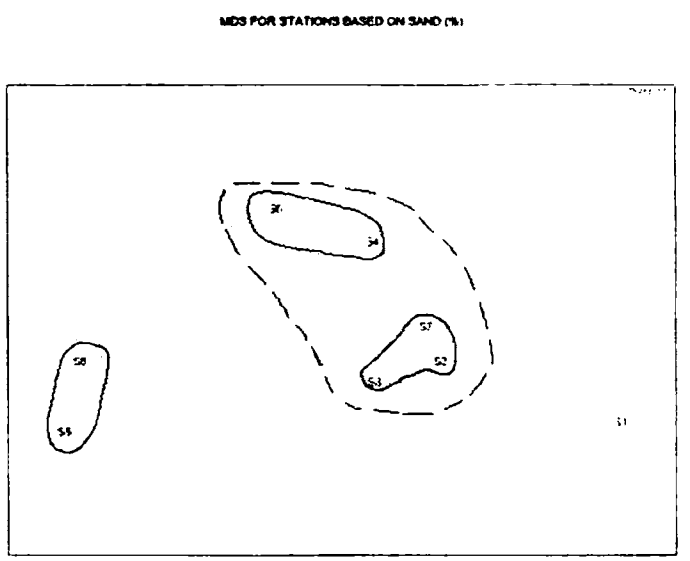

Figure 3.15 b. MDS for stations based on sand

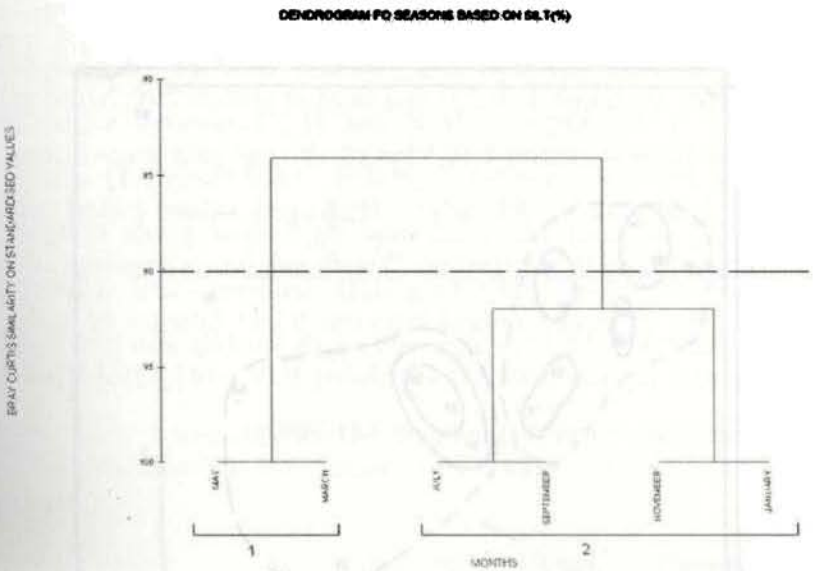

Figure 3.15 c. Dendrogram for seasons based on silt

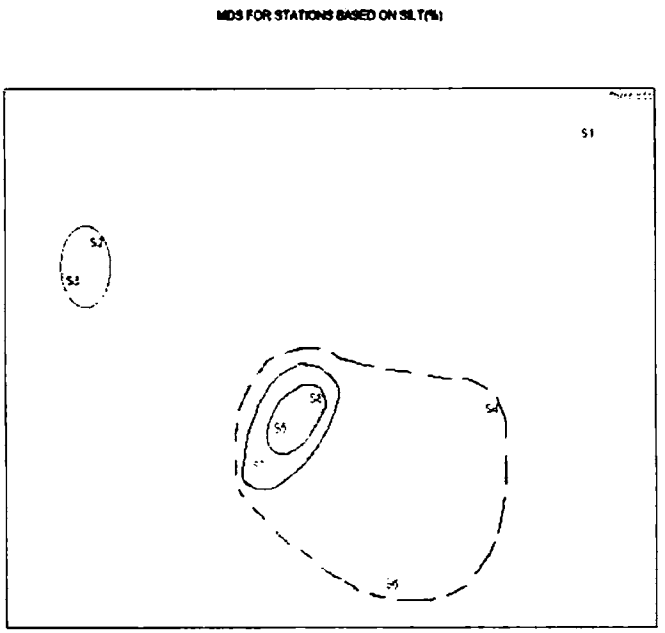

Figure 3.15 d. MDS for stations based on silt

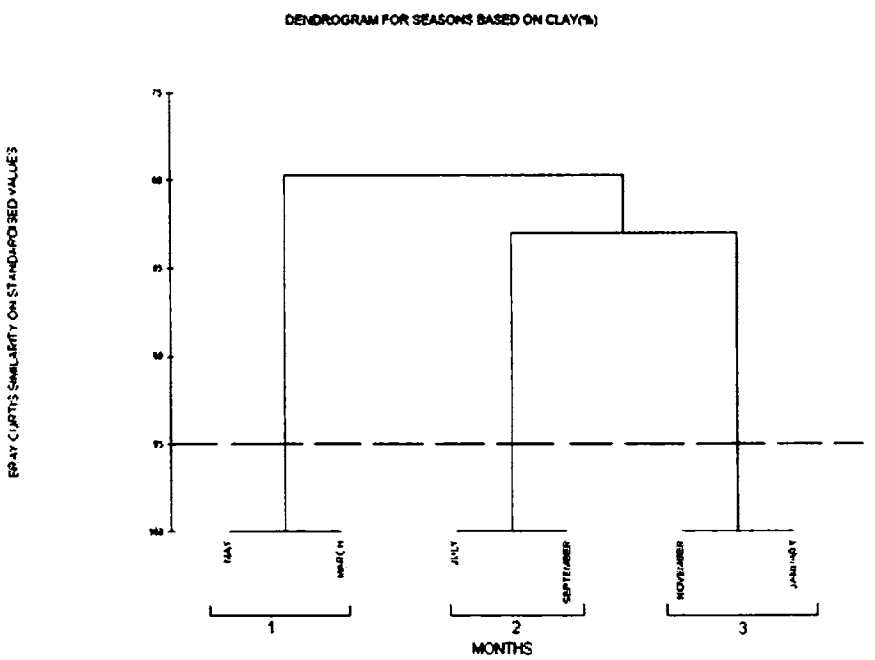

Figure 3.15 e. Dendrogram for seasons based on clay

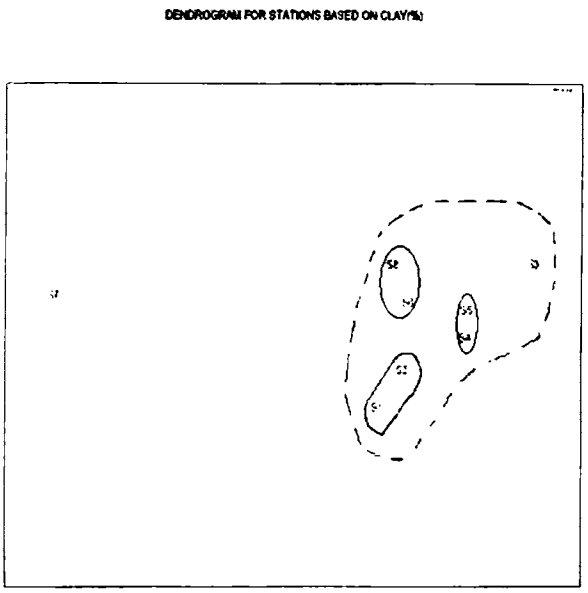

Figure 3.15 f. MDS for stations based on clay

Table 3.24 Distribution of carbon, nitrogen and hydrogen

	carbon			hydrogen			nitrogen		
station	mean	std	CV%	mean	std	CV%	mean	std	CV%
S1	6.353	0.960	15.10	1.957	0.107	5.45	0.497	0.009	1.90
S2	.200	0.062	30.82	0.313	0.090	28.59	0.040	0.037	93.54
S3	0.947	0.802	84.76	0.607	0.315	51.89	0.080	0.057	71.44
S4	2.870	2.777	96.75	0.983	0.707	71.87	0.227	0.111	49.04
S5	3.700	2.751	74.34	1.200	0.801	66.78	0.283	0.162	57.23
S6	1.123	0.334	29.70	0.533	0.085	15.93	0.047	0.066	141.42
S7	2.753	0.686	24.92	1.523	0.505	33.16	0.293	0.060	20.52
S8	2.700	0.665	24.62	1.583	0.347	21.94	0.323	0.088	26.96

Distribution of carbon, hydrogen and nitrogen averaged over seasons, showed that carbon was the highest at all stations compared to hydrogen and nitrogen and nitrogen was at the least level, invariably at

all stations (Table 3.24). Seasonal variations were felt maximum for carbon followed by nitrogen and then by hydrogen, generally carbon was maximum at station 1 (6.35) and least at station 2 (0.20) with least seasonal variation at station 1 (CV%=15.10) and maximum seasonality at stations 3 & 4 (CV> 84.76%). Hydrogen values varied between 1.957 (station 1) and 0.313 (station 2) with maximum seasonal variation (CV %=5.45). Nitrogen ranged between 0.047 (station 6) and 0.497 (station 1) with highest seasonal variability (CV =141.42%) at station 6 and least seasonal variation at station 1 (1.90%)

3 way ANOVA (Table 3.25) applied to compare between the three components, between stations and between seasons, showed high difference between C, H and N ($F_{(2,70)}$=149.113, p<0.001) between stations ($F_{(7,70)}$=29.8917, p<0.001) between seasons ($F_{(5,70)}$=9.3410, p<0.001) along with high specificity for location (F(14,70)=5.421, p<0.001) and seasons, ($F_{(10,70)}$=4.7993, p<0.001) station season specificity was also not negligible, $F_{(35,70)}$=2.6264, p<0.05).

Table 3.25: 3 way ANOVA for comparing between carbon, hydrogen and nitrogen (in 8 stations in 6 seasons) with respect to 3 components stations and seasons

Source	SS	dof	MSS	F ratio	Remarks
C,H&N (A)	136.468	2	68.2341	149.1130	(P<0.001)
Stations (B)	95.7412	7	13.6773	29.8917	(P<0.001)
Seasons (C)	21.3704	5	4.2741	9.3410	(P<0. 01)
AB interaction		14	5.42135	11.8483	(P<0.001)
BC interaction		35	1.2018	2.6264	(P<0.05)
AC interaction		10	2.1960	4.7993	(P<0.01)
Error	32.0294	70	0.4576		
Total	667.954	143			

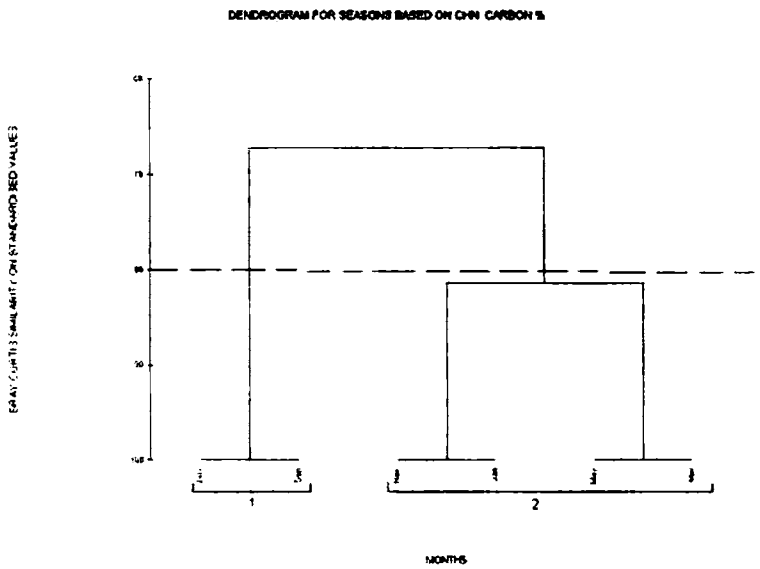

Figure 3.16 a. Dendrogram for seasons based on carbon

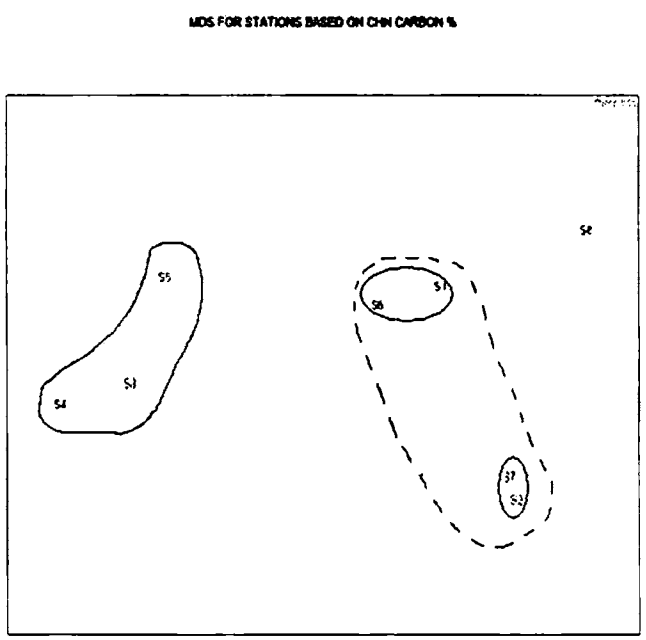

Figure 3.16 b. MDS for stations based on carbon

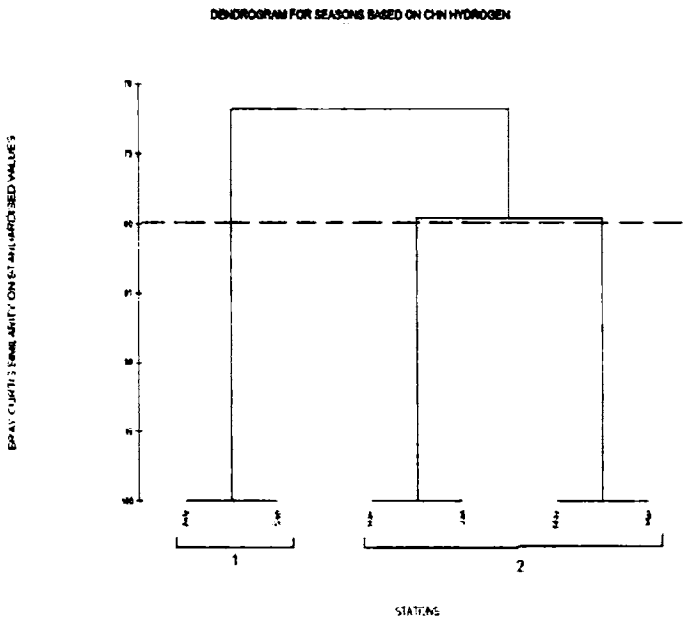

Figure 3.16 c. Dendrogram for seasons based on hydrogen

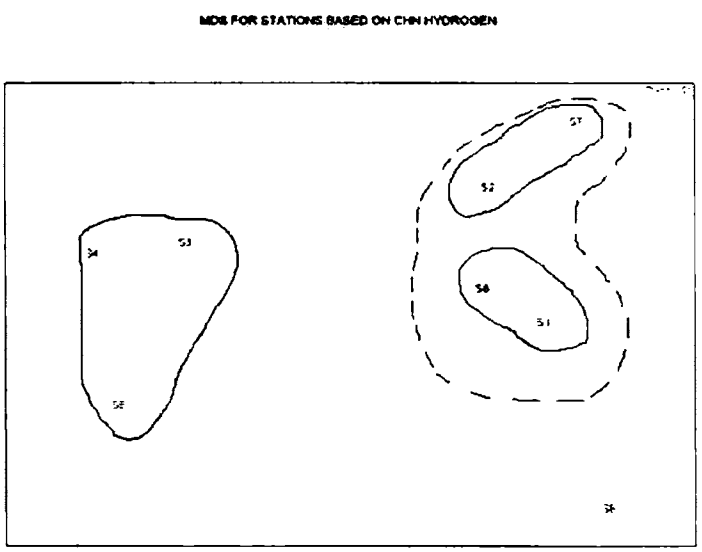

Figure 3.16 d. MDS for stations based on hydrogen

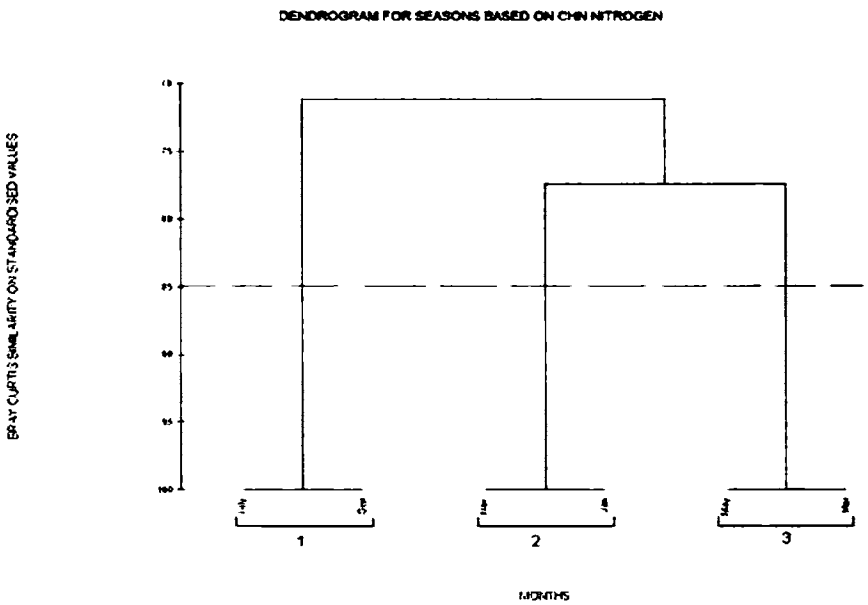

Figure 3.16 e. Dendrogram for seasons based on nitrogen

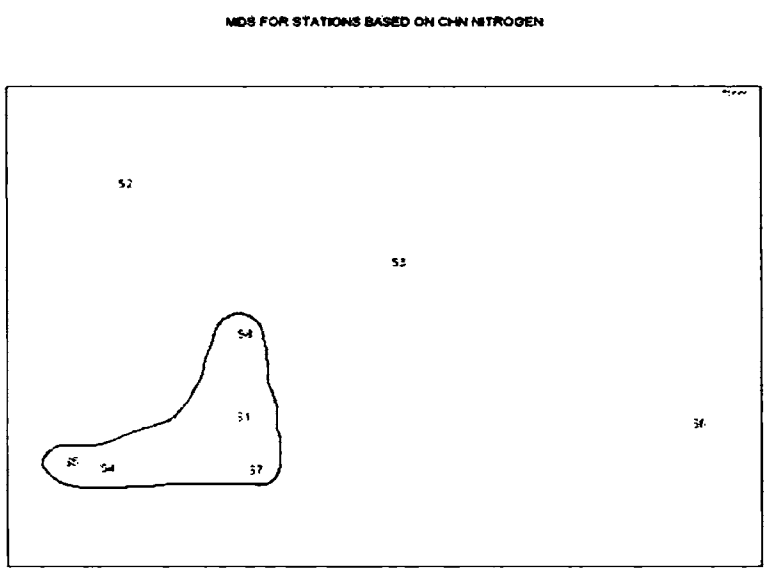

Figure 3.16 f. MDS for stations based on nitrogen

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CHAPTER IV

PROTEINS: PHASES-COUPLED SPATIOTEMPORAL VARIABILITY

INTRODUCTION

Rivers are obvious and visible pathways for terrestrial runoff. Rivers deliver both particulate and dissolved organic matter to coastal regions via estuaries. An accurate characterization of the nature and quantities of organic material delivered as well as the transformations of the organic matter in the estuary, is central to understand the functioning of these systems in their present form.

Natural organic matter (NOM) has been widely studied in all aquatic environments for decades but still, much of its structure and properties is not fully understood. NOM which is present in every drop of natural water, in every particle of suspended material can be conveniently classified into two categories, particulate organic matter (POM) and dissolved organic matter (DOM) based on its filter passing properties. The latter embraces material having a diameter greater than 0.45μm, whereas the former includes the dissolved matter together with colloidal materials that passes through 0.45μm membrane filter. The quantity of dissolved organic matter greatly exceeds that of suspended or particulate organic matter (Romankevich, 1984). Dissolved organic matter, the supply and loss of

which are generally balanced, is converted into a suspended state when utilized by organisms as structural material.

A significant proportion of NOM is believed to comprise of refractory, chemically heterogenous copolymers often called humic substances (Aiken et al., 1985). Humic substances are known to be important binding agents for trace elements and organic contaminants in both fresh and marine waters (Mantoura et al., 1978; Tipping and Hurley, 1992).

Dissolved organic carbon (DOC) in marine and fresh water ecosystems is one of Earth's largest actively cycled reservoirs of organic matter (Bushaw et al., 1996). The oxidation of organic matter affects the redox potential, which, inturn can have dramatic effects on biological and chemical processes (Breck, 1974). Thus, dissolved organic substances play a vital role in biological, chemical and geological processes (Hayase and Shinozuka, 1995).

Enrichment of DOC in the water column occurs through degradation / transformation of particulate organic carbon (POC), either in the water column or in bottom sediments by leaching processes, desorption of particulate organic carbon due to modification of environmental conditions (salinity, pH etc.) and diffusion from interstitial water. Elimination processes of dissolved organic matter in estuarine environment include flocculation, adsorption and degradation (Mannino and Harvey, 1999). Microbial dissolution is undoubtedly important in the decomposition of cellulose, hemicellulose, proteins and lignin in the sense that these macro molecules must be broken down into monomers which can enter the cell.

Dissolved organic matter is known to be an important light absorbing component of natural waters and hence has an important role in aquatic photochemical processes. Photochemical oxidation of biologically refractory DOM may form geologically labile products, thereby providing a potentially important removal mechanism for this pool of DOM. Photochemical transformations of DOM occur upon direct absorption of UV and visible light by organic chromophore in aquatic environments. The significance of chromophoric dissolved organic matter to biogeochemical processes has been studied by many researchers with respect to photochemical reactivity (Zafiriou et al., 1984; Moffett and Zika, 1987; Mopper et al., 1991), light attenuation and optical characteristics, which can affect primary production rates (Blough et al., 1993; Nelson et al., 1998; Rochelle-Newall and Fisher, 2002a,b) and the fueling of microbial respiration by photo degraded chromophoric dissolved organic matter (Miller and Moran, 1997; Benner and Biddanda, 1998; Opsahl and Benner, 1998; Reche et al., 1998). Chromophoric dissolved organic matter has also been used as a tracer for terrestrial sources of DOM to the estuarine systems (Zimmerman and Rommets, 1974; Chen and Bada, 1992; De sousa Sierra et al., 1997; Coble, 1996; Chen, 1999). Because of its photochemical reactivity, much of the chromophoric dissolved organic matter entering into the estuarine systems are removed through direct photochemical transformation as well as photodegradation in conjunction with microbial respiration, before it reaches the marine environment (Miller and Moran, 1997; Benner and Biddanda, 1998; Opsahl and Benner, 1998).

Biogeochemical as well as photochemical processes create unique environments for biogeochemical and photochemical activities.

Particulate matter comprises a large fraction of the organic material in estuarine and coastal waters. The organic fraction of particulate matter includes mainly living organisms and other decay and metabolic products (Riley and Chester, 1971). In surface layers, variation in composition of organic matter may be due to the variation of phytoplankton species or to variable ratios of constituents of particulate matter. In deep waters, detritus is the principal constituent of particles and the variations are due to the differential decomposition of the material (Montegut and Montegut, 1983). Particulate organic matter is produced by aquatic organisms through photosynthesis utilizing inorganic carbon and nutrients. Phytoplankton, benthic algae and vascular plants are the predominant groups of autotrophs, supplying most of the insitu primary production. Sinking through the water column, particulate organic matter is oxidized by microbial activity, utilizing dissolved oxygen and releasing inorganic carbon and nutrients to the water column, a process known as remineralisation. Protein in the phytoplankton (up to 75%) of the particulate nitrogen (Nguyen and Harvey, 1997) are rapidly recycled in the water column (Harvey et al., 1995)

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.

Organic matter is composed of labile and refractory compounds whose relative importance might have profound implications for organic matter diagenesis and turn over (Rowe and Deming, 1985). Conversely, the refractory fraction of organic matter is largely composed of complex macro molecules which are degraded slowly, subjected to burial and thus lost in short term for the benthic food webs (Fabiano and Danovaro, 1994). This residual fraction of the organic carbon is that part of which is not accounted for by lipids, proteins and carbohydrates and consists of complex molecules like tannin and lignin, humic substances etc.

A small and perhaps variable component of dissolved organic matter consists of the compounds typically associated with the general biochemical machinery of living organisms. Included in this group are proteins, carbohydrates, amino acids, lipids etc. Carbohydrates and amino acids are biochemical components comprising substantial portion of living biomass (80% of algal carbon and 65% of terrestrial plant carbon) and are important components of DOM in fresh water, in estuaries and in the oceans. Many of these compounds are essential in life processes and probably undergo fairly rapid biological transformations and degradation and hence are labile (Fichez, 1991; 1995; Cividanes et al., 2002).

MATERIALS AND METHODS

Proteins in dissolved as well as sedimentary and particulate phases were measured using copper and folin-ciocalteu phenol reagents, as discussed in Chapter II.

RESULTS AND DISCUSSION

Analysis of proteins in various environmental compartments were done bimonthly and the results were discussed in hereunder. The temporal changes in concentrations of dissolved, particulate and sedimentary phases of proteins are illustrated in Tables 4.1 to 4.3.

Dissolved protein (DP)

Table 4.1 Bimonthly distribution of dissolved proteins (mg/l) in the surface and bottom waters of Chalakudy river

		Stations							
Months		S1	S2	S3	S4	S5	S6	S7	S8
Surface waters	May	1.59	0.82	0.72	0.82	1.01	0.99	1.51	1.83
	July	1.01	0.05	0.09	0.43	0.59	0.43	0.83	0.99
	Sep	1.10	0.06	0.10	0.52	0.62	0.50	0.77	1.10
	Nov	1.40	0.69	0.51	0.69	0.98	0.62	1.13	1.57
	Jan	1.31	0.71	0.66	0.78	1.10	0.79	1.26	1.17
	Mar	1.57	0.71	0.69	1.12	1.32	1.08	1.20	1.94
		Stations							
		B1	B2	B3	B4	B5	B6	B7	B8
Bottom waters	May	1.59	0.82	0.72	1.17	1.21	1.25	1.71	2.14
	July	0.82	0.05	0.09	0.24	0.59	0.38	0.83	1.23
	Sep	0.50	0.06	0.10	0.64	0.70	0.41	0.79	1.15
	Nov	1.25	0.69	0.51	0.89	1.07	0.62	1.17	1.91
	Jan	1.11	0.71	0.66	0.82	1.10	0.56	1.26	1.52
	Mar	1.64	0.71	0.69	1.25	1.17	1.41	1.20	2.36

Surface monsoon: In monsoon, the surface distribution profile of dissolved protein (Figure 4.1) showed slightly higher concentrations at the reservoir station 1 which there after showed a zigzag trend up to station 6. Beyond this station, concentration showed a slight hike with the maximum at the saline station 8.

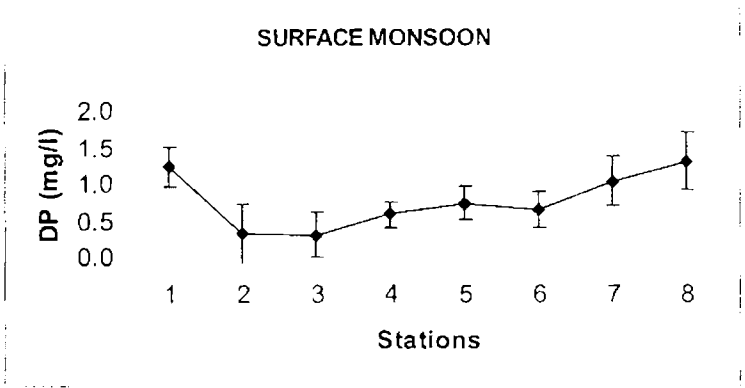

Figure 4.1 Distribution of dissolved protein (DP) (mg/l) in surface waters during monsoon.

Surface nonmonsoon: The nonmonsoonal trend in surface followed more or less a similar trend as that in monsoon (Figure 4.2). Near to stations 1 and 5, slightly higher values were seen compared with the stations 2, 3, 4 and 6. From the estuarine station 7 onwards a slight increase in concentration was seen, where the maximum was at the end station 8.

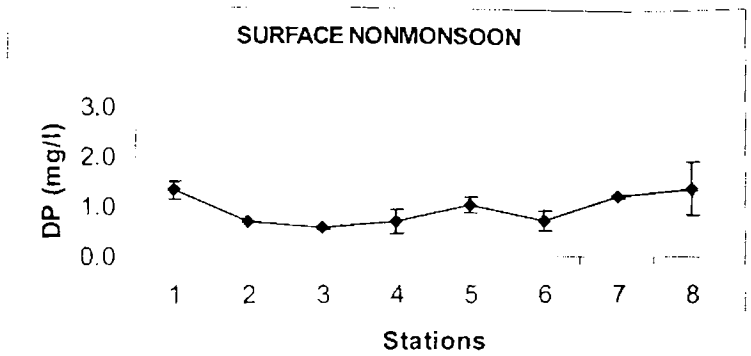

Figure 4.2 Distribution of dissolved protein (DP) in surface waters during nonmonsoon.

Bottom monsoon: In monsoon, the distribution profile of dissolved proteins in bottom waters were in an irregular manner up to station 6 (Figure 4.3); similar to surface monsoonal trend. For stations 7 and 8 which were in the down stream end, a gradual increase in concentrations was observed. In short, the diamensional characters of dissolved proteins were not significantly influenced by the depth-wise variability.

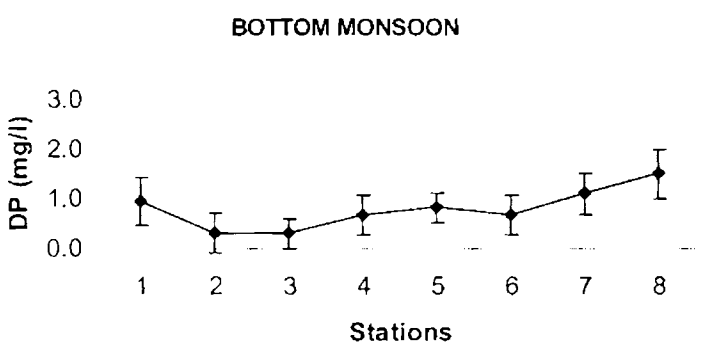

Figure 4.3 Distribution of dissolved protein (DP) (mg/l) in bottom waters during monsoon.

Bottom nonmonsoon: As observed in the monsoon season, the nonmonsoonal dissolved protein concentrations were also in a random pattern upto station 6 (Figure 4.4). From the station 7 on wards, the concentration gradually increased towards the coastal region.

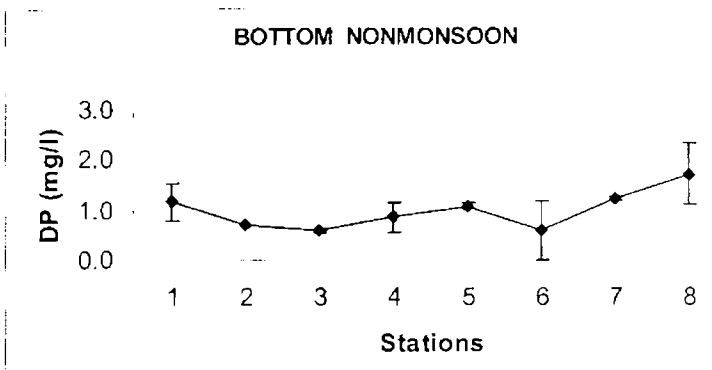

Figure 4.4 Distribution of dissolved protein (DP) (mg/l) in bottom waters during nonmonsoon.

General: In the distribution profile (Figure 4.5) of dissolved proteins, nonmonsoon values were higher than monsoon values, for the surface stations. For the bottom stations also, exactly the same trend was observed where nonmonsoon season recorded the maximum values. At waterfalls stations 2 and 3, comparatively lower values were observed both seasonally and temporally. At the reservoir and confluence stations (1 and 8), dissolved protein concentrations were found to be higher than the rest of the stations, both spatially and seasonally. In short, the station-wise specificity is the most important factor in determining the levels of dissolved proteins rather than seasonality.

It has been proved difficult to distinguish between marine plankton remains and terrigenous organic matter delivered by nearby major rivers (Onstad et al., 2000). The concept of dissolved organic carbon as encountered in the context of estuarine and marine research needs to be carefully defined and related to current perspectives on the dissolved organic carbon generated in the upstream areas and delivered to the estuary. Riverine dissolved organic carbon is produced primarily by leaching of leaf litter with in the stream, and by ground water inflows which have infiltrated through organic rich areas of the soil. It is composed primarily of humic substances (Ertel et al., 1986) with lesser amounts of polysaccharides, carbohydrates and amino acids (Volk et al., 1997). Part of this material can be taken up by bacteria (O' Connel et al., 2000) and upto about 10% of the riverine DOC can be respired on passing through the estuary (Moran et al., 1999). Riverine DOC has a major impact on coastal DOC dynamics and forms part of the microbial food web there (Zweifel et al., 1995).

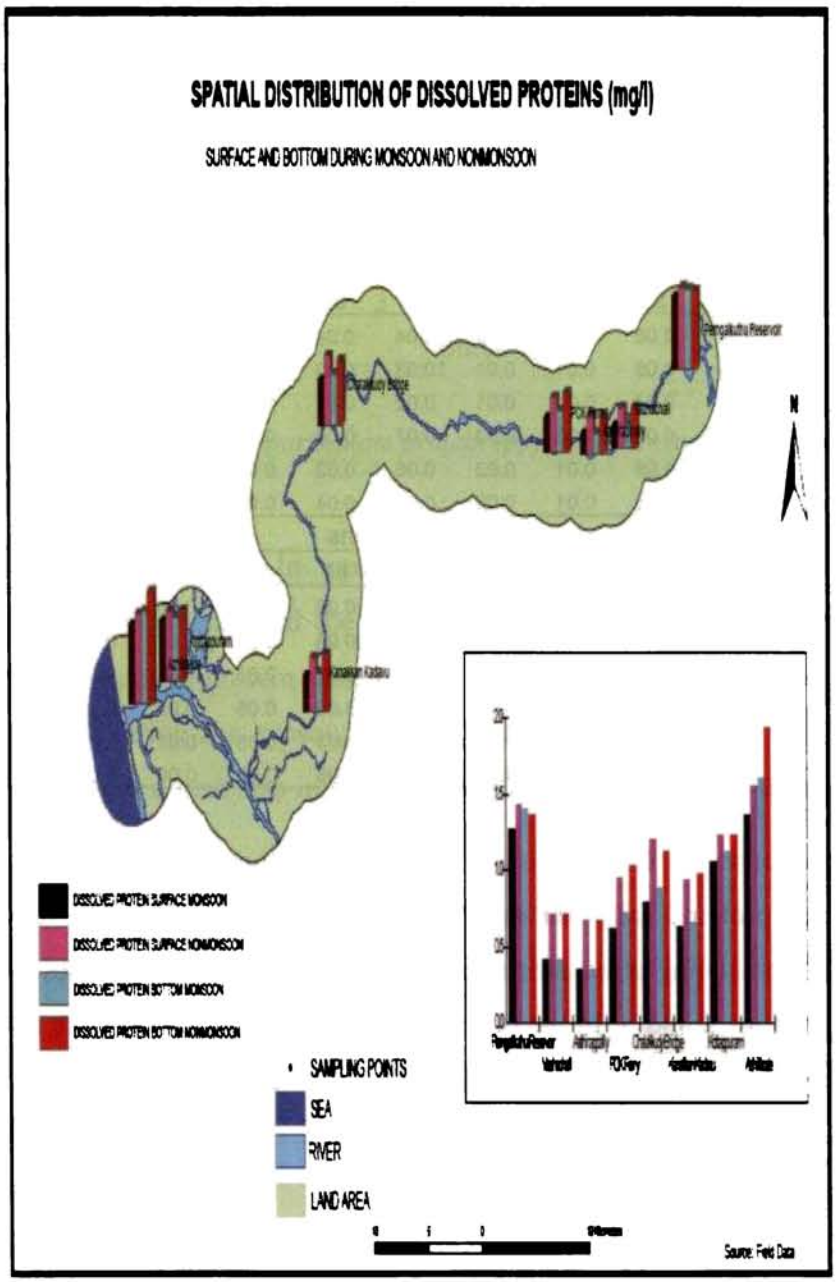

Figure 4.5 Spatial distribution of dissolved proteins in mg/l.

Particulate protein (PP)

Bimonthly distribution of particulate proteins in mg/l in the surface and bottom waters of Chalakudy river are given in Table 4.2

Table 4.2 Bimonthly distribution of particulate proteins (mg/l) in the surface and bottom waters of Chalakudy river

		Stations							
		S1	S2	S3	S4	S5	S6	S7	S8
Surface waters	May	0.06	0.01	0.01	0.04	0.04	0.03	0.06	0.07
	July	0.05	0.01	0.01	0.03	0.03	0.02	0.04	0.05
	Sep	0.04	0.01	0.01	0.02	0.02	0.02	0.04	0.04
	Nov	0.09	0.02	0.02	0.07	0.05	0.05	0.08	0.09
	Jan	0.08	0.01	0.03	0.06	0.03	0.05	0.07	0.07
	Mar	0.06	0.01	0.02	0.04	0.04	0.03	0.06	0.07
		Stations							
		B1	B2	B3	B4	B5	B6	B7	B8
Bottom waters	May	0.06	0.01	0.01	0.24	0.05	0.05	0.06	0.09
	July	0.05	0.01	0.01	0.04	0.03	0.03	0.04	0.05
	Sep	0.04	0.01	0.01	0.02	0.03	0.03	0.05	0.04
	Nov	0.09	0.02	0.02	0.08	0.06	0.05	0.08	0.13
	Jan	0.08	0.01	0.03	0.06	0.03	0.05	0.07	0.09
	Mar	0.07	0.01	0.02	0.05	0.06	0.05	0.06	0.08

Surface monsoon: In monsoon, surface distribution (Figure 4.6) of particulate proteins followed an irregular pattern, the highest observed concentrations being at estuarine stations. Lowest monsoonal values were near to stations 2 and 3. In the down stream part, a gradual increase in the concentration was seen, more precisely after station 6.

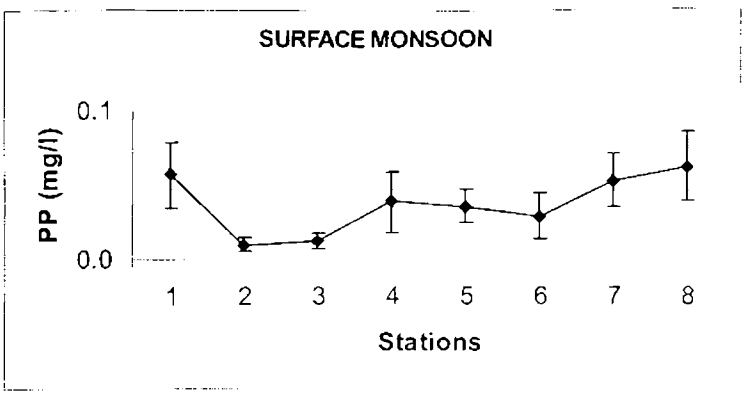

Figure 4.6 Distribution of particulate protein (pp) (mg/l) in surface waters during monsoon.

Surface nonmonsoon: In nonmonsoon also, surface distribution of particulate protein showed the typical irregular pattern (Figure 4.7). The highest particulate protein values were reported in the up stream region, while considering the seasonal as well as spatial variations. The lowest observed values were also in the waterfalls region i.e., stations 2 and 3.

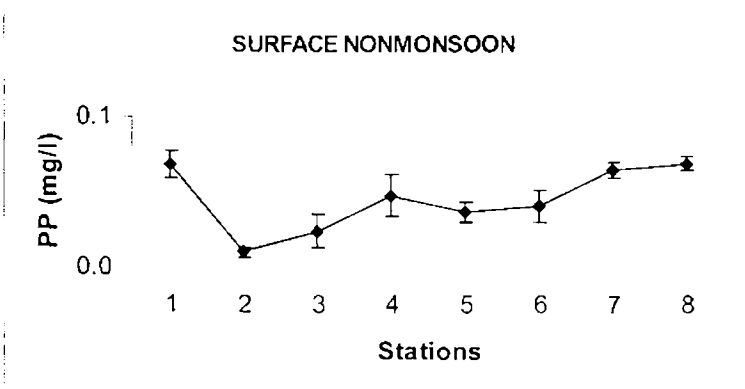

Figure 4.7 Distribution of particulate protein (PP) (mg/l) in surface waters during nonmonsoon.

Bottom monsoon: In monsoon, bottom particulate protein concentrations never displayed a wide variation from the surface monsoon values (Figure 4.8). As observed for the surface stations, here also the lowest observed concentration was at station 2 and the highest at station 4. From station 2 onwards, particulate protein concentrations showed a gradual increasing trend towards the downstream.

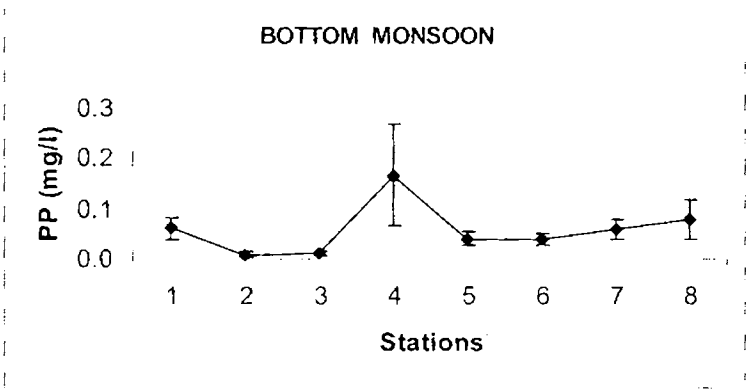

Figure 4.8 Distribution of particulate protein (mg/l) in bottom waters during monsoon.

Bottom nonmonsoon: In nonmonsoon, particulate protein distribution showed a gradual increase from station 2 to the estuarine end, except an odd hike at the ferry station 4 (Figure 4.9). At stations 2 and 3, comparitively low values were observed. Enrichment of particulate protein in the bottom water of the reservoir station (1) during nonmonsoon season also indicated the availability of organic pools in dams.

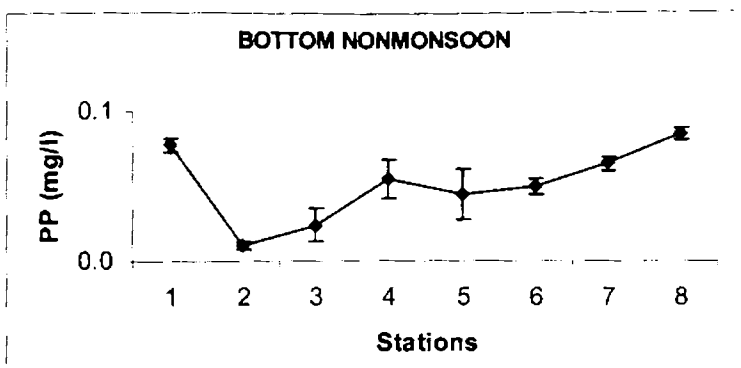

Figure 4.9 Distribution of particulate protein (mg/l) in bottom waters during nonmonsoon.

General: While discussing the particulate protein distributions at stations 2 and 3, no wide variations in concentration were observed, both spatially and seasonally (Figure 4.10). At stations 1, 6 and 8 nonmonsoonal values were slightly higher than monsoonal values. At station 4, the surface nonmonsoonal values showed a sudden hike and this was the highest reported particulate protein concentrations in the study area.

Variation of particulate proteins in the present investigation showed a maximum value at station 8 (0.08 mg/l) for bottom water samples during nonmonson and a minimum at station 2 (0.01mg/l). The high protein content at station 8 may be due to the high productivity and the low value at the waterfalls station 2 could be attributed to the increase in the turbulent character of river system which removes the particulate organic matter as readily as it forms and hence proteins.

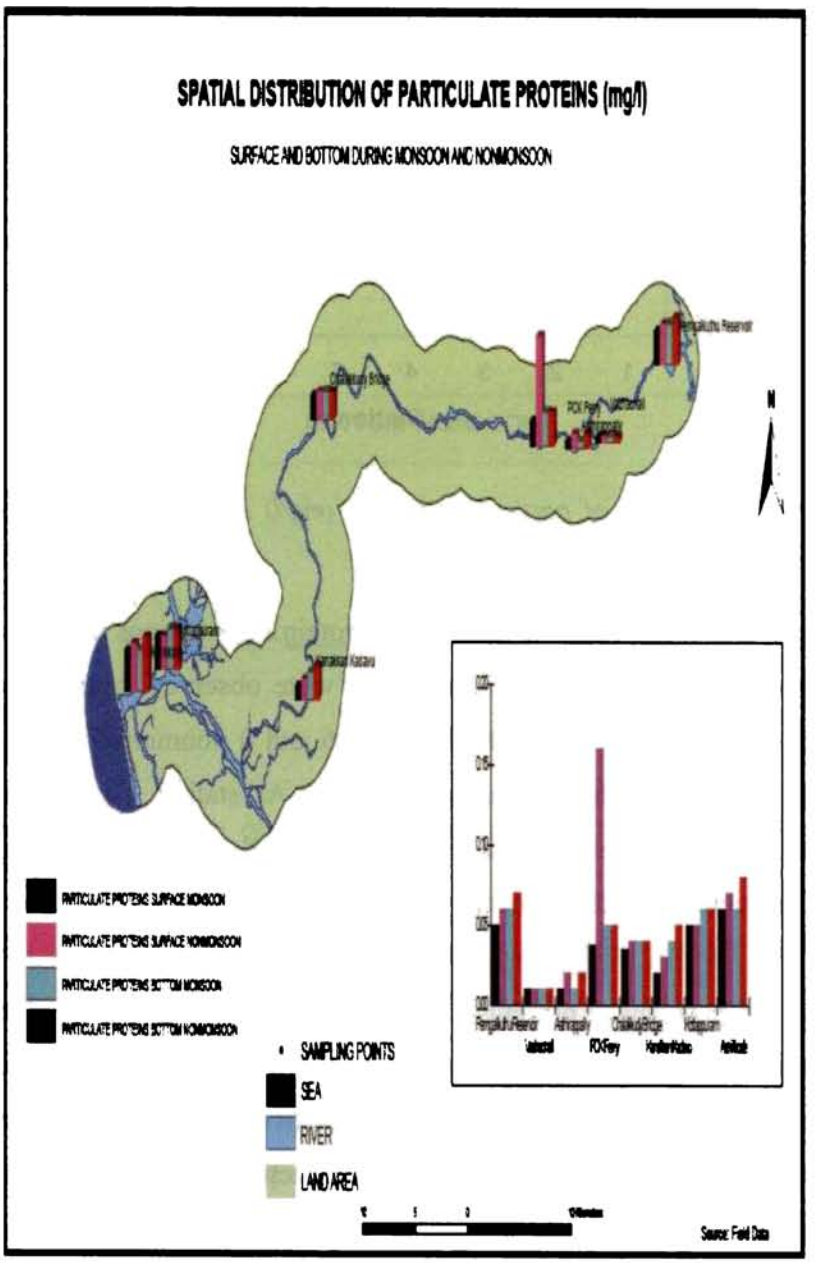

Figure 4.10 Spatial distribution of particulate proteins in mg/l.

Sedimentary protein (SP)

Bimonthly distribution of sedimentary proteins in mg/g in the sediments of Chalakudy river are presented in Table 4.3

Table 4.3 Bimonthly distribution of sedimentary proteins (mg/g) in the sediments of Chalakudy river

	Stations							
	S1	S2	S3	S4	S5	S6	S7	S8
May	8.58	0.95	1.30	5.91	2.82	3.08	4.23	9.34
July	4.35	0.39	0.58	3.79	0.78	1.09	1.27	5.15
Sep	3.97	0.43	0.69	3.04	0.69	1.77	1.30	4.58
Nov	6.84	0.69	0.92	3.08	1.27	2.32	2.90	7.51
Jan	5.24	0.56	0.81	3.88	1.07	2.70	2.52	6.81
Mar	9.87	0.82	1.09	6.84	2.32	4.60	4.60	10.20

Monsoon: The monsoonal distribution of sedimentary protein showed an irregular distribution pattern (Figure 4.11). Reservoir and estuarine stations recorded comparatively higher concentrations of sedimentary proteins. Waterfalls stations (2 and 3) in the upstream portion recorded the lowest values. Station 4 which was also in the upstream region recorded slightly higher concentrations.

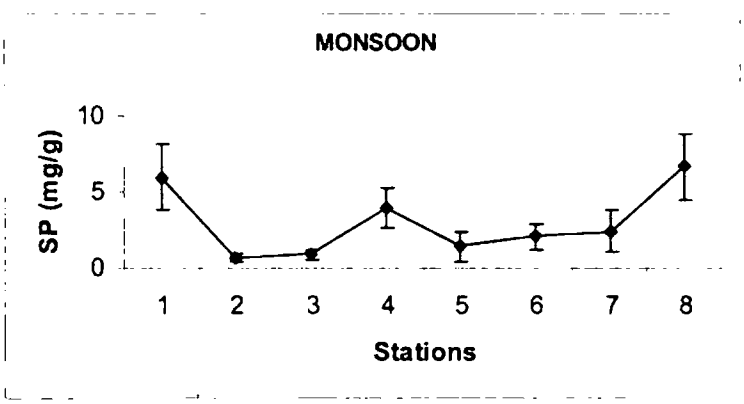

Figure 4.11 Distribution of proteins in sediments (SP) (mg/g) during monsoon.

Nonmonsoon: The nonmonsoonal sedimentary protein distribution depicted the same trend as that in the monsoonal distribution; the highest observed concentrations being at stations 1 and 8 (Figure 4.12). In this season, the lowest observed value was at station 2. On generalizing the distribution of sedimentary protein through out the entire stream, the pattern was found to be similar to that of dissolved/ particulate phases.

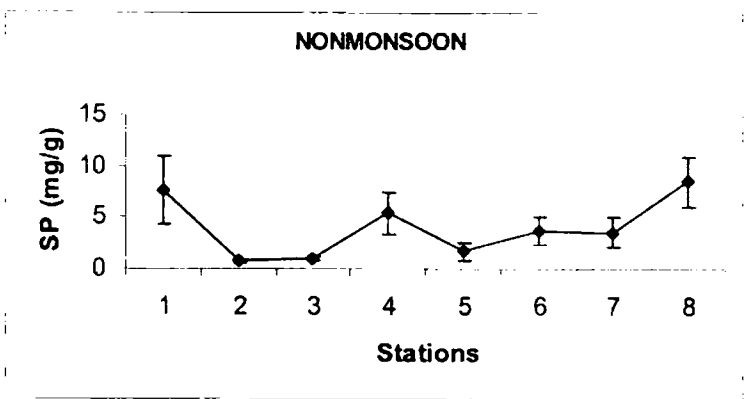

Figure 4.12 Distribution of proteins in sediments (SP) (mg/g) during nonmonsoon.

General: While discussing the general trend in the distribution of sedimentary proteins (Figure 4.13), nonmonsoon values were higher than monsoon values through out the study area. At stations 1,4,6,7 and 8 nonmonsoon sedimentary protein concentrations widely varied from monsoon concentrations.

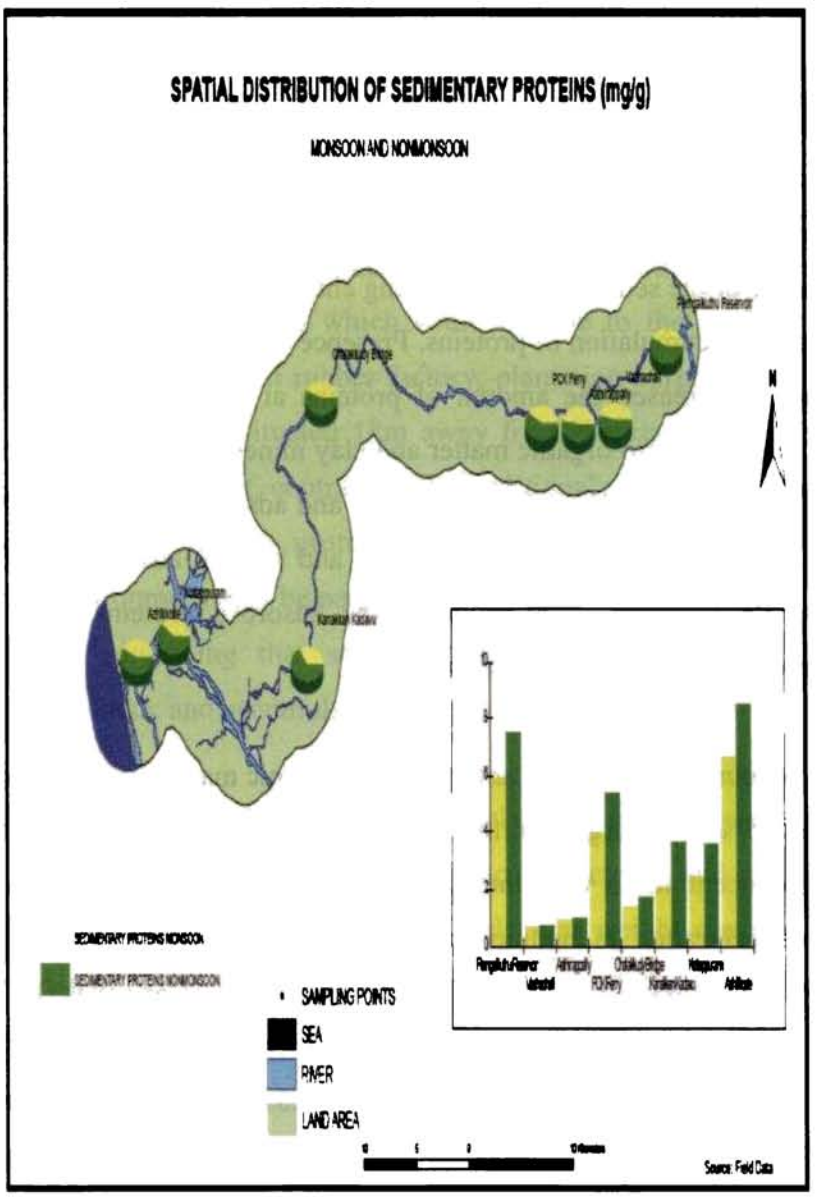

Figure 4.13 Spatial distribution of sedimentary proteins in mg/g

Rivers can bring about the distribution of the large quantities terrestrially derived organic matter, to the sediments. In the present study the highest protein concentration (8.5 mg/g) was observed at station 8 during non-monsoon and the lowest (0.61 mg/g) at station 2 during monsoon. The low protein content at station 2 may be due to the low organic matter and high sandy nature of the sediment. High flowing character of the river at this site restricted the accumulation of proteins. Presence of high organic matter and clay content increased the amount of proteins at station 8. Proteins are strongly adsorbed onto organic matter and clay minerals. Low tidal activity provides a suitable condition for the settling and adsorption of protein onto the sediments. The proteins were strongly and rapidly adsorbed by clay minerals and sediments, and much of the adsorbed proteins were not readily desorbed (Ding and Henrichs, 2002).

Proteins account for more than about 50% of organic matter (Romankevich, 1984) and 85% of the organic nitrogen of marine organisms. At all stations, monsoon concentrations were the least. Leaching might have increased the protein concentration in nonmonsoon seasons. Photochemical processes may also be important in cycling of some biochemical compounds (Keiber and Mopper, 1987). For surface water samples, the lowest value for dissolved proteins was recorded at station 3 (0.35 mg/l) during monsoon season and the highest value was recorded at station 8 (1.55mg/l) during nonmonsoon. The high values at station 8 during both monsoon and non-monsoon seasons also reflect the enhanced biological activity, especially in the estuarine region. The decomposition of phytoplankton and other vegetation and sewage which contain enormous amounts of proteinaceous

materials contribute to protein concentration. Generally, higher concentration of protein was found at station 1 during both seasons. For surface water samples, station 1 recorded a maximum value of 1.43 mg/l during nonmonsoon and for bottom water samples, the value was 1.37 mg/l. Comparatively higher concentration of proteins was found at station 4 during nonmonsoon season which could be due to the settling of plant materials discharged from rubber factory, plantation corporation of Kerala (PCK ferry) which is situated 1km away from the station 4. There is an increasing evidence that, contrary to the traditional view of proteins as very labile molecules, certain protein species of bacterial origin present in aquatic environment may be particularly resistant to degradation (Nagata et al., 1996) suggesting that some protein components are resistant to enzymatic attack and accumulate in water.

Although high molecular organic materials were refractory to microbial attack, they tend to adhere onto the surface of detritus and consequently, particles are easily formed from high molecular weight materials. Partial hydrolysis of macromolecules such as proteins and other compounds may take place on the detrital surfaces under the influence of bacterial enzymes and consequently, a portion of macromolecules may be transformed into low molecular weight compounds easily utilized by aquatic organisms (Ogura, 1977). Macromolecular DOM may not be directly utilized by aquatic organisms, but they may be transformed into smaller compounds on detrital surfaces by bactririal activity and take part in food chains in aquatic systems.

Previous studies have shown that adsorption of polymeric organic materials such as proteins to surfaces can occur very rapidly and that the adsorption can have substantial effects on the degradation rates of organic material (van Loosedrecht et al., 1990; Fletcher, 1991; Keil and Kirchman, 1994) and the dissolved organic matter adsorbed to colloids was less easily degraded than freshly dissolved organic matter. Marine colloids and sub micron particles provide large surface areas which could have substantial implications for biochemical cycling in aquatic environment. Effect of surface area on degradation of organic matter could be stimulative, neutral, or even inhibitory (van Loosdrecht et al, 1990, Fletcher, 1991). But the results appear to vary depending on several factors, including concentration of organic matter on the surface and the nature of the interactions between organic matter and surfaces (van Loosdrecht et al., 1990; Griffith and Fletcher, 1991).

Proteolytic enzymes bound to bacterial cells are suggested to be responsible for high turn over of dissolved proteins (Hollibough and Azam, 1983). To utilized absorbed proteins, bacteria need to remove protein molecules from the surface. Hydrolysis of adsorbed proteins are initiated only when the affinity of bacterial proteases or 'protein binding proteins' that bind to proteineous substrates exceeds the bond strength between proteins and surfaces (Nagata and Krichman, 1996).

Mechanisms underlying the variation in degradability of dissolved proteins and other dissolved organic components in aquatic systems are not well understood. One hypothesis is that labile protein is transformed into less

labile protein due to abiotic modifications including, adsorption, condensation and photochemical reactions (Keil and Krichmann, 1994; Nagata and Krichman, 1996). Recent research has suggested that association of proteins with other organic components may affect greatly the degradability of proteins in water (Keil and Krichmann, 1994; Nagata and Krichman, 1996). Because of the slow turn over and close association of proteins with other macromolecules including proteins probably have more chances to be modified geochemically which may result in the formation of refractory proteins (Keil and Krichmann, 1994). This process is significantly enhanced by radiation, especially in the ultraviolet range (300-400 nm) (Keil and Krichmann, 1994) while originally refractive dissolved organic matter becomes labile upon uv exposure (Lindell et al.,1995,1996; Wetzel et al., 1995, Graneli et al., 1996, Kaiser and Herndl 1997, Reitener et al.,1997). However, not only the light but also the sorption processes of labile organic matter onto sediments contribute to its refractory nature (Keil et al. 1994; Hedges and Keil, 1995). Thus, structures of macromolecular organic complexes and their interactions with bacterial assemblages could substantially influence storage, turn over and transport of organic matter especially proteins. The overall distribution of proteins in dissolved, particulate and sedimentary phases are pictured in Figure 4.14.

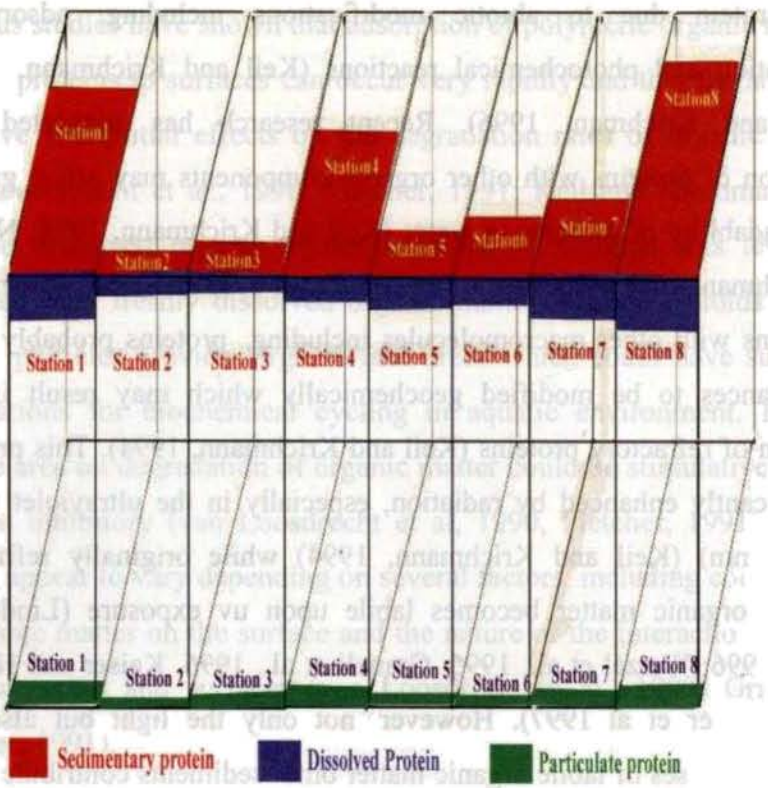

Figure 4.14 Overall distribution of proteins in dissolved, particulate and sedimentary phases.

Role of hydrographical parameters on protein distribution profile

On examining the influence of hydrographical as well as sedimentological parameters on the distribution of proteins, certain significant correlations were observed based on Pearson's correlation coefficient values. Dissolved oxygen was found to be negatively correlated to dissolved as well as particulate protein (Figure 4.15 and 4.16). Sedimentary proteins showed good positive correlation with SOC, clay, silt and nitrogen ((Figure 4.17).

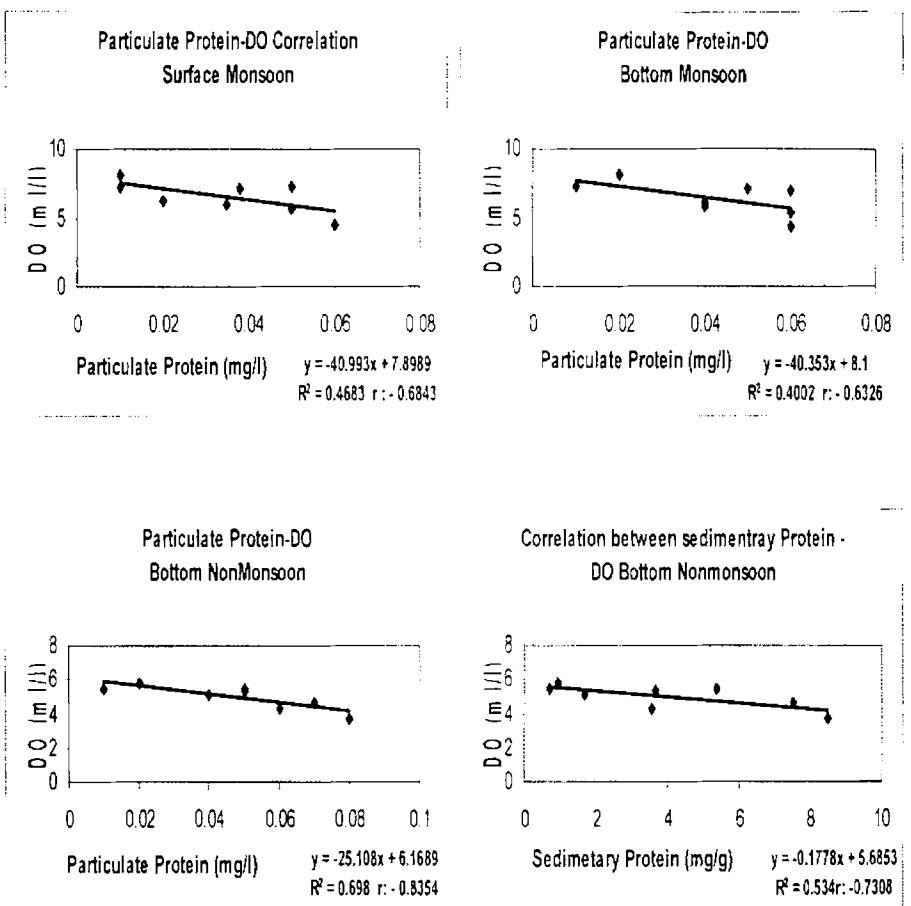

Figure 4.16 Correlation of particulate protein with DO.

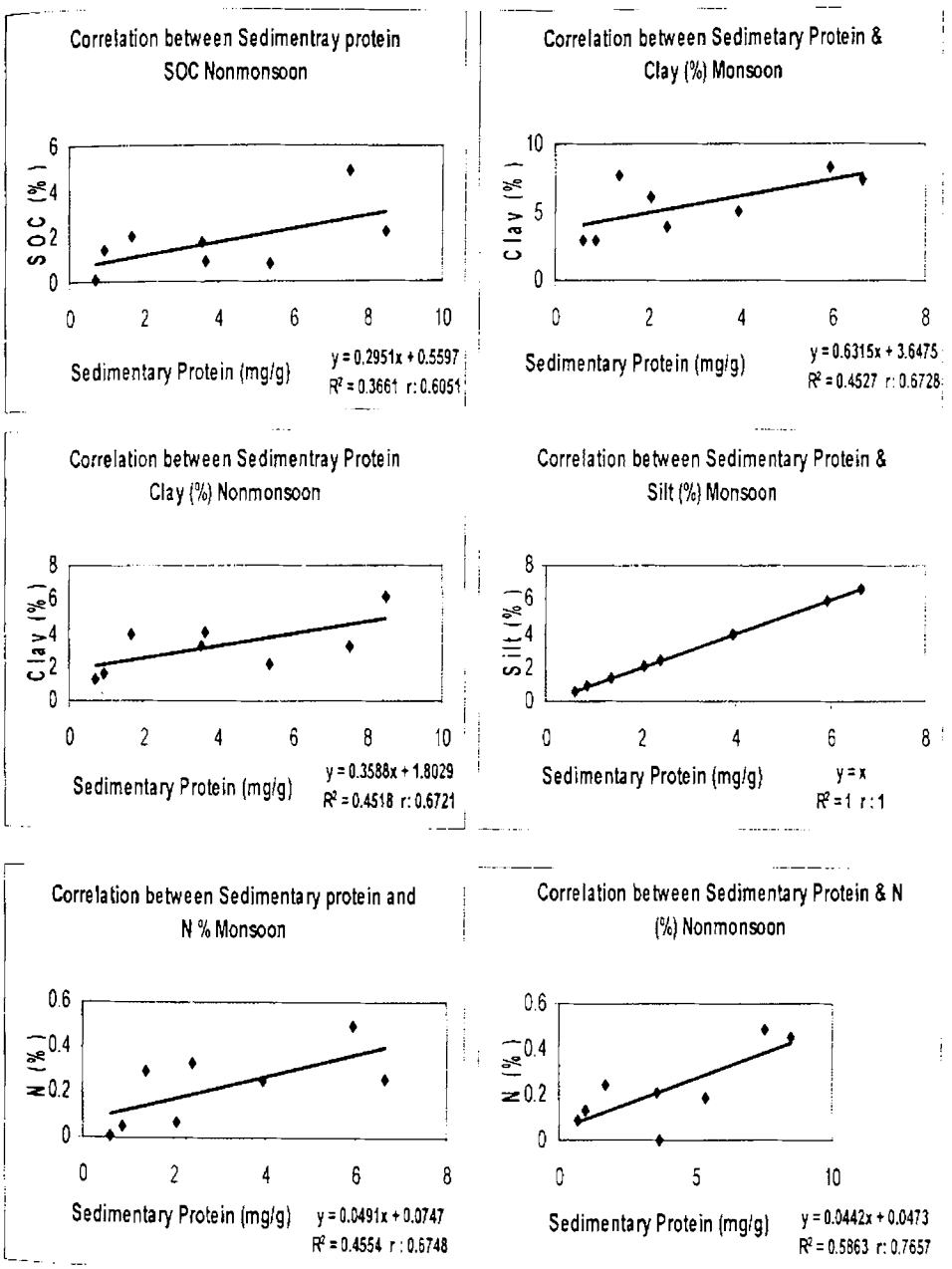

Figure 4.17 Correlation of sedimentary protein with various sedimental parameters

Statistical Approach

Abbreviations

NS	:	Not Significant
dof		degrees of freedom
MSS		Mean Sum of Squares
(P<0.05)		calculated F is significant at 5% level
(P<0. 01)		calculated F is significant at 1% level
(P<0.001)		calculated F is significant at 0.1% level
MDS		Multidimensional scaling

Table 4.4 Distribution of dissolved proteins

Station	Average	std	CV%	Station	average	std	CV%
S1	1.329	.219	16.50	S5	0.936	0.258	27.61
B1	1.154	.403	34.91	B5	0.974	0.238	24.50
S2	.508	.323	63.62	S6	0.736	0.240	32.67
B2	.508	.323	63.62	B6	0.772	0.406	52.59
S3	.460	.267	58.02	S7	1.117	0.251	22.49
B3	.460	.267	58.02	B7	1.161	0.305	26.30
S4	.727	.223	30.69	S8	1.433	0.369	25.75
B4	.834	.336	40.34	B8	1.719	0.452	26.32

Distribution of dissolved proteins (Table 4.4) averaged over seasons showed very low proteins at stations 2 to 3 (ô proteins <0.508) and comparatively higher values at S1, S7, S8 with high seasonal variation at S2, S3 (CV %> 58.02) and consistent - seasonal values at stations S1, S4, S5-S8 (CV %< 32.67). Bottom proteins showed an increasing trend from B3 toB8 with higher values from B2-B7 to B8 (1.154≤proteins≤1.719) with

(CV %) seasonal variations ranging between 22.50% (B7) and 63.62% (CV% for B2)

3way ANOVA (Table 4.5)applied for station wise, seasonal and depth wise comparison showed significantly high spatial ($F_{(7,35)}$=210.305, $p<0.001$), seasonal ($F_{(5,35)}$=189.70, $p<0.001$) and surface/bottom difference ($F_{(1,35)}$=5.1197, $p<0.01$) with all interactions significantly high ($F>3.3528$, $p<0.05$) as indicated by least values at stations 2 & 3 during July and September at all stations and highest values during March and May at all stations and surface/bottom difference being high at station 4 to S8.

Table 4.5 3 way ANOVA for comparing dissolved protein in water with respect to station, surface and bottom, and seasons

Source	SS	dof	MSS	F ratio	Remarks
Stations (A)	12.1289	7	1.7327	210.3046	(P<0.001)
Sur/Bot (B)	0.04218	1	0.04218	5.1197	(P<0.01)
Seasons (C)	7.8150	5	1.5630	189.700	(P<0.001)
AB interaction		7	0.04903	5.9510	(P<0.01)
BC interaction		5	0.02762	3.3528	(P<0.05)
AC interaction		35	0.03333	4.0456	(P<0.001)
Error	0.28838	35	0.008239		
Total	104.355	95			

Dendrogram drawn separated July and September (cluster 1) from January to May and November (cluster 2) at 90% level of similarity (Figure 4.18 a). Clustering carried out for stations separated stations 2 and 3 from rest 6 stations (Figure 4.18 b) at 90% level of similarity other than station B6

which is differing from the rest of the stations, because at this stations July to January show more consistency in protein distribution while March and May show 1.33 as the average which is nearly three times the average protein observed during other months.

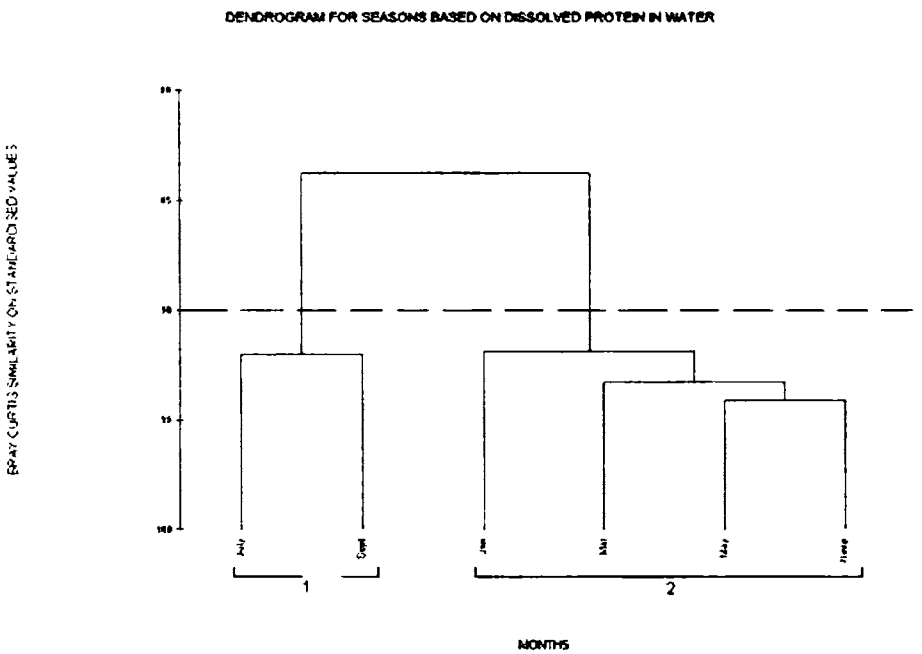

Figure 4.18 a. Dendrogram for seasons based on dissolved protein in water

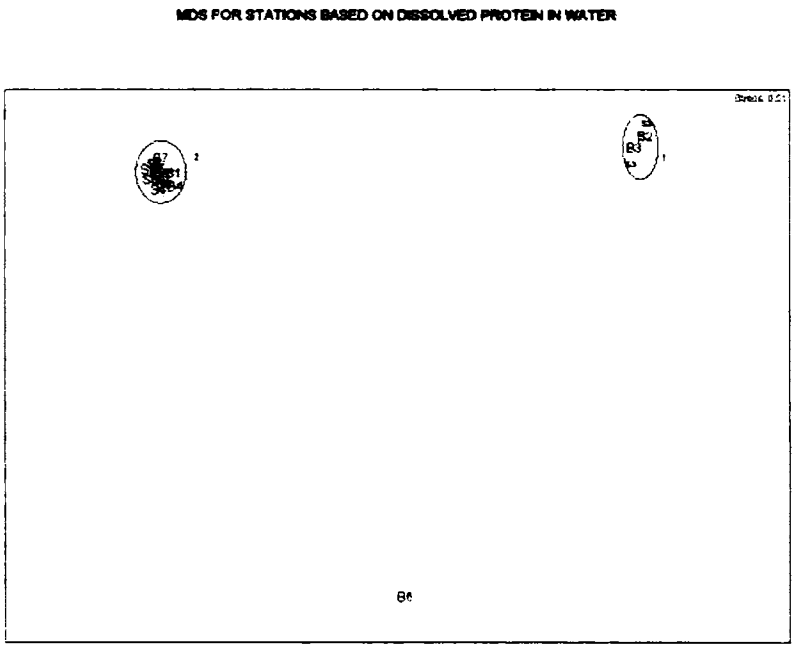

Figure 4.18 b. MDS for stations based on dissolved protein in water

Trellis diagram drawn to compare between stations showed significant difference between stations S1 and B1 with stations S2 to B6 ($t_{10}>3.169$, $p<0.01$) and stations 2 to 4, different from that of stations 1 to 8 ($t_{10}>20228$, $p<0.05$) at surface and bottom and stations 5 to 6 from that of S8 and B8 ($t_{10}>3.169$, $P<0.01$) (Table 4.6) at surface and bottom for stations 5 and 6.

Table 4.6: Trellis diagram for students t test to compare between stations based on dissolved protein (• Not significant; • Significant at 10% level; • Significant at 5% level; • Significant at 1% level)

	S1	B1	S2	B2	S3	B3	S4	B4	S5	B5	S6	B6	S7	B7	S8	B8
S1		0.85	4.7	4.7	5.63	5.63	4.31	2.06	2.59	2.45	4.08	2.7	1.42	0.99	0.54	1.73
B1	•		2.8	2.8	3.21	3.21	2.07	1.36	1.02	0.86	1.99	1.49	0.17	0.03	1.14	2.09
S2	•	•		0	0.26	0.26	1.24	1.56	2.31	2.59	1.26	1.14	3.33	3.28	4.22	4.87
B2	•	•	•		0.26	0.26	1.24	1.56	2.31	2.59	1.26	1.14	3.33	3.28	4.22	4.87
S3	•	•	•	•		0	1.71	1.95	2.86	3.21	1.72	1.43	4.01	3.86	4.78	5.36
B3	•	•	•	•	•		1.71	1.95	2.86	3.21	1.72	1.43	4.01	3.86	4.78	5.36
S4	•	•	•	•	•	•		0.6	1.37	1.69	0.06	0.22	2.6	2.07	3.66	4.40
B4	•	•	•	•	•	•	•		0.54	0.76	0.53	0.27	1.51	1.61	2.68	3.51
S5	•	•	•	•	•	•	•	•		0.24	1.27	0.76	1.13	1.26	2.47	3.36
B5	•	•	•	•	•	•	•	•	•		1.57	0.96	0.93	1.08	2.34	3.26
S6	•	•	•	•	•	•	•	•	•	•		0.17	2.45	2.45	3.54	4.29
B6	•	•	•	•	•	•	•	•	•	•	•		1.62	1.71	2.70	2.48
S7	•	•	•	•	•	•	•	•	•	•	•	•		0.25	1.58	2.60
B7	•	•	•	•	•	•	•	•	•	•	•	•	•		1.27	2.28
S8	•	•	•	•	•	•	•	•	•	•	•	•	•	•		1.09
B8	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	

Table 4.7 Distribution of particulate protein

station	**mean**	std	CV%	station	Mean	**std**	CV%
S1	0.061	0.017	27.68	S5	0.036	0.008	23.43
B1	0.067	0.018	26.80	B5	0.042	0.012	28.96
S2	0.101	0.004	37.79	S6	0.032	0.013	40.15
B2	0.010	0.004	37.79	B6	0.042	0.010	24.00
S3	0.016	0.008	50.56	S7	0.056	**0.014**	**25.32**
B3	0.016	0.008	50.56	B7	0.060	**0.014**	**23.50**
S4	0.041	0.017	40.33	S8	0.064	**0.017**	**26.75**
B4	0.130	0.184	141.74	B8	**0.080**	**0.028**	**35.17**

Distribution of particulate proteins arranged over seasons (Table 4.7) showed comparatively higher values at station 1 and station 8 at surface and a steady increase in value from station 2 to station 8 (0.010-0.064)

with seasonal variation between 23.43% and 50.56%. A similar trend was observed for bottom samples also. With highest variations over seasons at station 4, B4 (CV%=141.74%). Maximum protein at surface was 0.061 and minimum was 0.010 at station 2. The corresponding values at bottom were 0.080 (station 8) and 0.010 (station 2).

Table 4.8 3 way ANOVA for comparing particulate protein with respect to stations, surface and bottom and seasons

Source	SS	dof	MSS	F ratio	Remarks
Stations (A)	0.060199	7	0.008599	3.4015	(P<0.05)
Sur/Bot (B)	0.00630505	1	0.0063051	2.4941	4.12 (P>0.05)
Seasons (C)	0.026396	5	0.0052793	2.0883	2.49 (P>0. 05)
AB interaction		7	0.0026496	1.0481	(P>0.05)
BC interaction		5	0.0026525	1.0493	(P>0.05)
AC interaction		35	0.0026767	1.0588	(P>0.05)
Error	0.08848	35	0.002528		
Total	0.52576	95			

3 way ANOVA (Table 4.8) applied to compare between stations, surface and bottom and between seasons based on particulate proteins showed high station wise difference ($F_{(7,35)}$=3.40, p<0.05), but low significance for surface and bottom difference ($F_{(1,35)}$=2.49, p<0.12) and low significance for seasonal difference, ($F_{(5,35)}$ =2.0883, p<0.09). No significant station season specificity was observed (p>0.05).

Dendrogram drawn to group the months showed that May is different from other months as indicated by the single cluster containing the

months September, January, November, July and March at 90% level of similarity. Stations were grouped into single cluster excluding station 4 at bottom were seasonal variation was the maximum. Stations 5, 1, 7 and 2 showed consistent values of proteins both at surface and bottom (Figure 4.19).

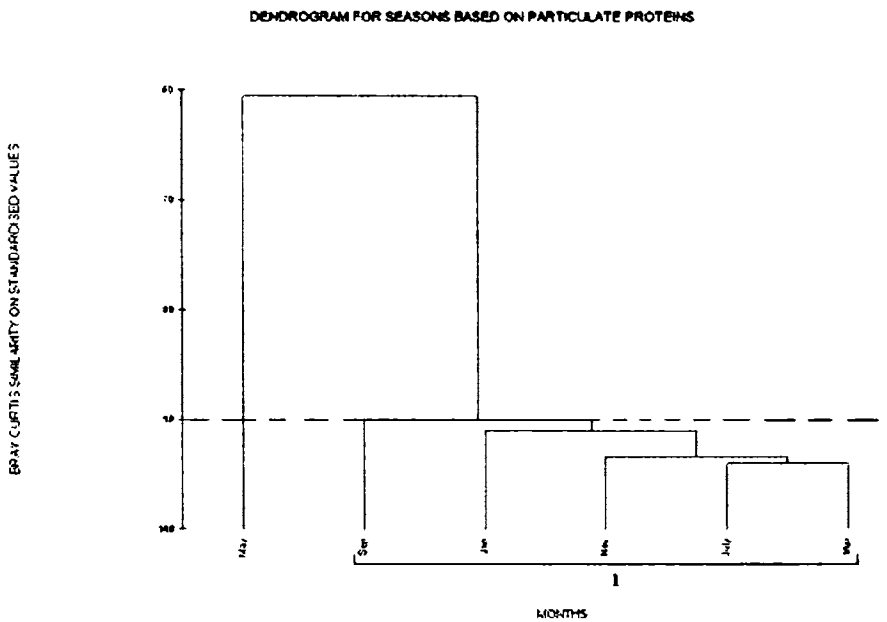

Figure 4.19 Dendrogram for seasons based on particulate protein in water

Table 4.9: Trellis diagram for students t test to compare between stations based on particulate protein (• Not significant; • Significant at 10% level; • Significant at 5% level; • Significant at 1% level)

	S1	B1	S2	B2	S3	B3	S4	B4	S5	B5	S6	B6	S7	B7	S8	B8
S1		0.55	6.61	6.61	5.33	5.33	1.83	0.84	2.96	2.03	2.96	2.03	0.42	0.05	0.34	1.31
B1	•		6.96	6.96	5.75	5.75	2.32	0.77	3.49	2.57	3.45	2.65	0.99	0.64	0.21	0.88
S2	•	•		0	1.58	1.58	4.12	1.46	6.33	5.65	3.74	6.72	7.06	7.76	6.92	5.53
B2	•	•	•		1.58	1.58	4.12	1.46	6.33	5.65	3.74	6.72	7.06	7.76	6.92	5.53
S3	•	•	•	•		0	3.03	1.38	3.75	3.93	2.37	4.49	5.47	6.06	5.65	4.87
B3	•	•	•	•	•		3.03	1.38	3.75	3.93	2.37	4.49	5.47	6.06	5.65	4.87
S4	•	•	•	•	•	•		1.07	0.66	0.05	0.93	0.12	1.54	1.93	2.15	2.64
B4	•	•	•	•	•	•	•		1.14	1.07	1.18	1.06	0.89	0.85	0.79	0.60
S5	•	•	•	•	•	•	•	•		0.91	0.48	1.1	2.79	3.33	3.33	3.36
B5	•	•	•	•	•	•	•	•	•		1.17	0.07	1.75	2.21	2.39	2.78
S6	•	•	•	•	•	•	•	•	•	•		1.33	2.77	3.23	3.30	3.42
B6	•	•	•	•	•	•	•	•	•	•	•		1.81	2.3	2.46	2.81
S7	•	•	•	•	•	•	•	•	•	•	•	•		0.41	0.78	1.66
B7	•	•	•	•	•	•	•	•	•	•	•	•	•		0.42	1.40
S8	•	•	•	•	•	•	•	•	•	•	•	•	•	•		1.05
B8	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	

Trellis diagram drawn (Table 4.9) to compare between stations showed high difference in protein values between stations S1 and station 8. S2,S3,S5 and S6 similarly for B1 with B2,B3,B5,B6, stations S2,B2,S3 and B3 are different from S5,B5,S6,B6,B7,S7,S8 and B8. Also B4, S5, B5 and S6 are different from S7, B7, S8 and B8 ($t10>3.169$, $p<0.01$).

Table 4.10 Distribution of carbon equivalents of proteins

Station	average	std	CV%
1	3.173	1.066	33.60
2	0.314	0.099	31.51
3	0.440	0.119	26.93
4	2.167	0.706	32.59
5	0.731	0.391	53.54
6	1.271	0.540	42.50
7	1.374	0.631	45.97
8	3.560	0.998	28.03

Distribution of proteins average over seasons showed that proteins varied between 0.314 (station 2) and 3.560 (station 8). Maximum seasonal variation was observed at station 5 (CV%=53.54). Stations with higher proteins have comparatively lower seasonal variations (Table 4.10).

Table 4.11 3 way ANOVA for comparing between carbon equivalent of protein with respect to station and seasons

Source	SS	dof	MSS	F ratio	Remarks
protein (A)	18.0161	1	18.0161	279.579	(P<0.001)
Stations (B)	55.9159	7	7.9879	123.975	(P<0.001)
Seasons (C)	16.1577	5	3.2315	50.1542	(P<0.001)
AB interaction		7	2.0881	32.4075	(P<0.001)
BC interaction		35	0.18565	2.8813	(P<0.05)
AC interaction		5	0.4211	6.5357	(P<0.01)
Error	2.2552	35	0.06444		
Totai	252.754	95			

3 way ANOVA (Table 4.11) applied to compare proteins, between stations and between seasons showed significant difference in protein concentration ($_{(F(1,35)}$=279.579, p<0.001) between stations ($F_{(7,35)}$=123.975, p<0.001) and between seasons ($F_{(5,35)}$=50.154, p<0.001). Protein distribution depicted a season station interaction, with higher values at station 1 and station 8 almost all the months and very low values during July, September and November at stations 2, 3, 5 and 7.

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CHAPTER V

CARBOHYDRATES: PHASES-COUPLED SPATIOTEMPORAL VARIABILITY

INTRODUCTION

In the water column organic matter exists in dissolved and particulate forms. 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 the initial input in the form of large particles such as fecal pellets or marine snow reaches the sediment floor (Asper, 1987).

Carbohydrates are polyhydroxy aldehydes/ ketones or compounds that can be hydrolysed to these compounds. Carbohydrates form an important reactive fraction of organic matter in water and sediment 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 with polymers, and there are several important polymeric sugars that decompose and enter into the aquatic system. The important polymers 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 the aquatic environment.

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

On the other hand, soils contain carbohydrate rich organic debris that are not readly soluble in water. Stevenson (1982) stated that as much as 5 to 25% of soil organic matter is carbohydrates, 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 soils, during wet seasons into streams and rivers. Since simple sugars are easily utilized 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 the algal population and usually, concentration of carbohydrates decreases with depth as the algal population decreases. Seasonal and temporal

variations in the carbohydrates were reported in different water systems, since they are among the most important biopolymers in fresh water systems (Buffle, 1990: Sigleo, 1996; Mannino and Harvey, 2000)

Carbohydrates are the largest identified fraction of organic matter in the aquatic systems, accounting for 20 – 30% in the surface water (Pakulski and Benner, 1994; Benner et al., 1992; Skoog and Benner, 1997) and occur as monosaccharides, oligosaccharides and polysaccharides. They are the versatile molecules that serve as energy, storage and structural components of cells. In aquatic systems, chemical energy is stored in the form of phytoplankton derived carbohydrates, and this in turn provides energy to the non photosynthesizing organisms through the process of glycolysis and respiration (Witter and Luther, 2002). Glucose and to a lesser extent the other dissolved neutral monosaccharide components probably fuel a large fraction of bacterial respiration (Rich et al., 1996). Carbohydrates, especially free glucose, have been shown to be biologically reactive molecules (Skoog and Benner, 1997). They are found to vary geographically and seasonally, and are primarily derived from phytoplankton and vascular plants.

The present study focuses on the spatial as well as temporal variations of dissolved, particulate and sedimentary carbohydrates in the different selected stations of Chalakudy river.

MATERIALS AND METHODS

Carbohydrates were estimated by the phenol- sulphuric acid method as described in Chapter II. The analyses were carried out in the dissolved,

particulate and sedimentary phases. Monosaccharides and polysaccharides were estimated.

RESULTS AND DISCUSSION

The temporal changes in the concentrations of dissolved, particulate and sedimentary monosaccharides and polysaccharides are illustrated in Tables 5.1 to 5.6.

Monosaccharides in the dissolved phase(DMS)

The concentration profile of dissolved monosaccharides reflects the balance among dissolved, particulate and sedimentary carbohydrates via solubilisation.

Table 5.1 Bimonthly distribution of dissolved monosaccharides (mg/l) in the surface and bottom waters of Chalakudy river

		Stations							
	Months	S1	S2	S3	S4	S5	S6	S7	S8
Surface waters	May	1.33	0.86	0.93	1.01	1.03	1.04	1.15	1.52
	July	0.61	0.59	0.53	0.75	0.83	0.78	1.17	1.12
	Sep	0.11	0.11	0.68	0.59	0.72	0.66	1.09	1.30
	Nov	1.25	0.78	0.86	0.96	0.99	0.99	1.36	1.44
	Jan	1.19	0.64	0.76	0.79	1.10	0.78	1.22	1.59
	Mar	1.19	0.66	0.80	1.12	1.29	1.19	1.39	1.45
		Stations							
		B1	B2	B3	B4	B5	B6	B7	B8
Bottom waters	May	1.33	0.86	0.93	1.22	1.19	1.12	1.59	1.80
	July	0.76	0.59	0.53	0.71	0.83	0.87	1.17	1.21
	Sep	0.62	0.11	0.68	0.65	0.81	0.78	1.11	1.11
	Nov	1.17	0.78	0.86	1.10	1.10	0.99	1.10	1.52
	Jan	1.03	0.64	0.76	0.93	1.10	1.20	1.22	1.63
	Mar	1.28	0.66	0.80	1.40	1.33	1.01	1.39	1.66

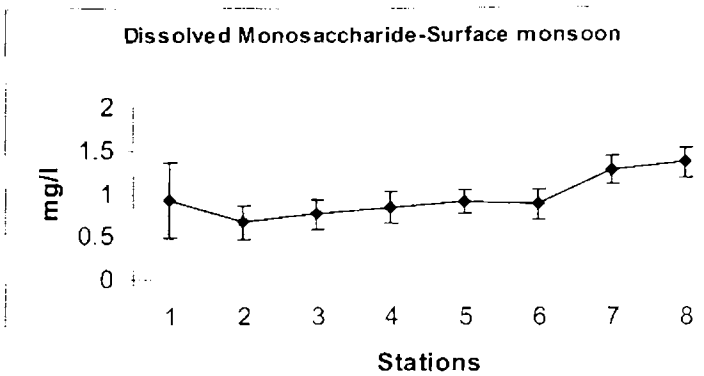

Figure 5.1 Distribution of dissolved monosaccharides (mg/l) in surface waters during monsoon.

Surface monsoon: The surface distribution pattern of dissolved monosaccharides in the monsoon showed (Figure 5.1) more or less an irregular pattern in the upstream portion where comparatively low values were observed near to stations 2 and 3. The down stream portion of the river showed a gradual increase in concentration beyond station 6 where the highest recorded values were at the estuarine stations 7 and 8.

Surface nonmonsoon: In the nonmonsoon season (Figure 5.2), comparatively lower values were seen near to stations 2 and 3, whereas station 5 showed a slightly higher dissolved monosaccharide concentration towards the down stream end. A gradual increase in concentration was observed towards the estuarine end, where the highest value was at the Azhikkode area (station 8).

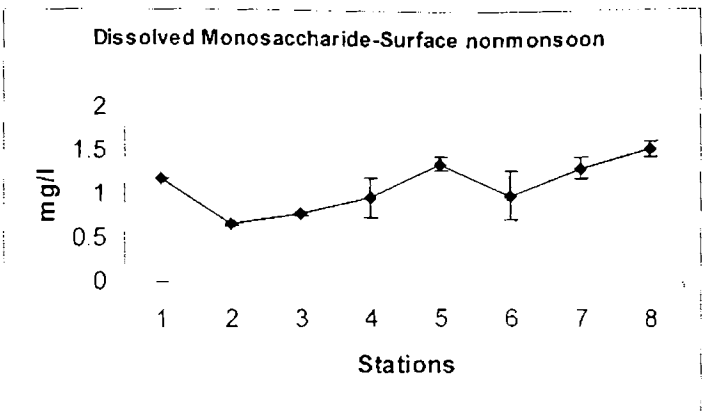

Figure 5.2 Distribution of dissolved monosaccharides (mg/l) in surface waters during nonmonsoon.

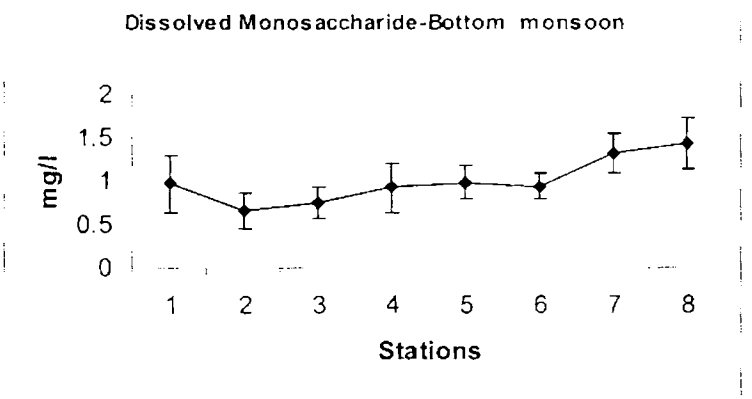

Figure 5.3 Distribution of dissolved monosaccharides (mg/l) in bottomwaters during monsoon.

Bottom monsoon: No specific pattern was observed in the distribution of dissolved monosaccharide in bottom waters upto station 6 (Figure 5.3). Beyond this station, a gradual increase was observed in the distribution of monosaccharides towards the estuarine end. Comparatively lower values

were observed near to the waterfall stations 2 and 3. The highest observed concentrations were the confluence regions of the estuarine systems.

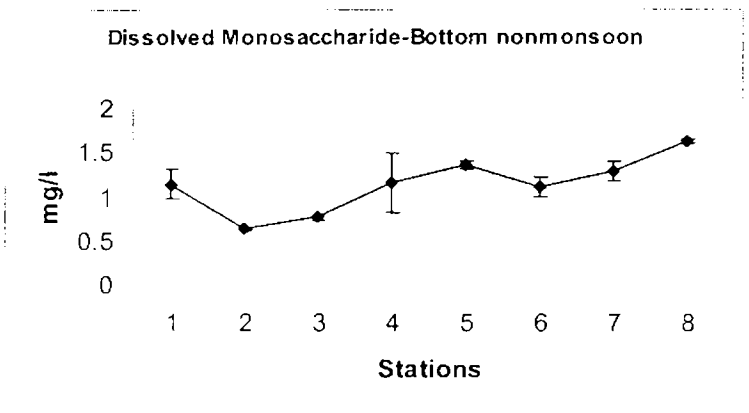

Figure 5.4 Distribution of dissolved monosaccharides (mg/l) in bottom waters during nonmonsoon.

Bottom nonmonsoon: The nonmonsoonal distribution (Figure 5.4) of dissolved monosaccharides in bottom water was exactly similar to that observed in the monsoon season. Here also, upto station 6, the distribution profile exhibited an irregular variability. Beyond station 6 (Kanakkankadavu), a gradual increase in concentration was observed towards the down stream end where the highest concentration was at the estuarine end.

The presented bimonthly data showed a highest monosaccharide concentration of 1.52 mg/l at station 8 during nonmonsoon for surface water samples and 1.64 mg/l at station 8 during nonmonsoon for bottom water samples. The concentration profile of dissolved carbohydrates

reflects the balance between the production of dissolved carbohydrates via solubilisation/hydrolysis from particulate organic carbon and consumption of carbohydrates by fermentative bacteria. Once hydrolysed, most monosacharides would likely to be remineralised rapidly (Sawyer and King, 1993; Rich et al., 1996). The major monosaccharide utilisers were reported to be the micro heterotrophs, namely, bacteria, yeasts and possibly some algae. Their concentrations were found to be highly variable with respect to tidal cycle (Millero and Sohn, 1992). Although carbohydrates are the important constituents of dissolved organic matter (usually 10-20 %), relatively little is known about them in estuarine and coastal ecosystems. Leaf material from vascular plants is an important source of organic carbon in a variety of coastal and estuarine ecosystems (Valeila et al., 1984) and a potentially important source of dissolved and particulate carbohydrates. The observed enrichment of dissolved carbohydrates at station 8 may be mainly due to the leaching of dead and decayed leaf litter. Due to the variation in tidal flow, the leaf litter remains accumulated in station 8, which will lead to an increase in concentration of carbohydrates. The waste products from fish hatchery unit situated very close to the station 8, can also contribute to the increased level of carbohydrates at this station.

While discussing the general trend (Figure5.5), both spatially and seasonally at most of the stations (1,4,5,6,7 and 8) the nonmonsoonal values were higher than the monsoonal values for both surface and bottom samples. At stations 2 and 3 no wide variations were observed in the dissolved monosaccharide concentrations, seasonally.

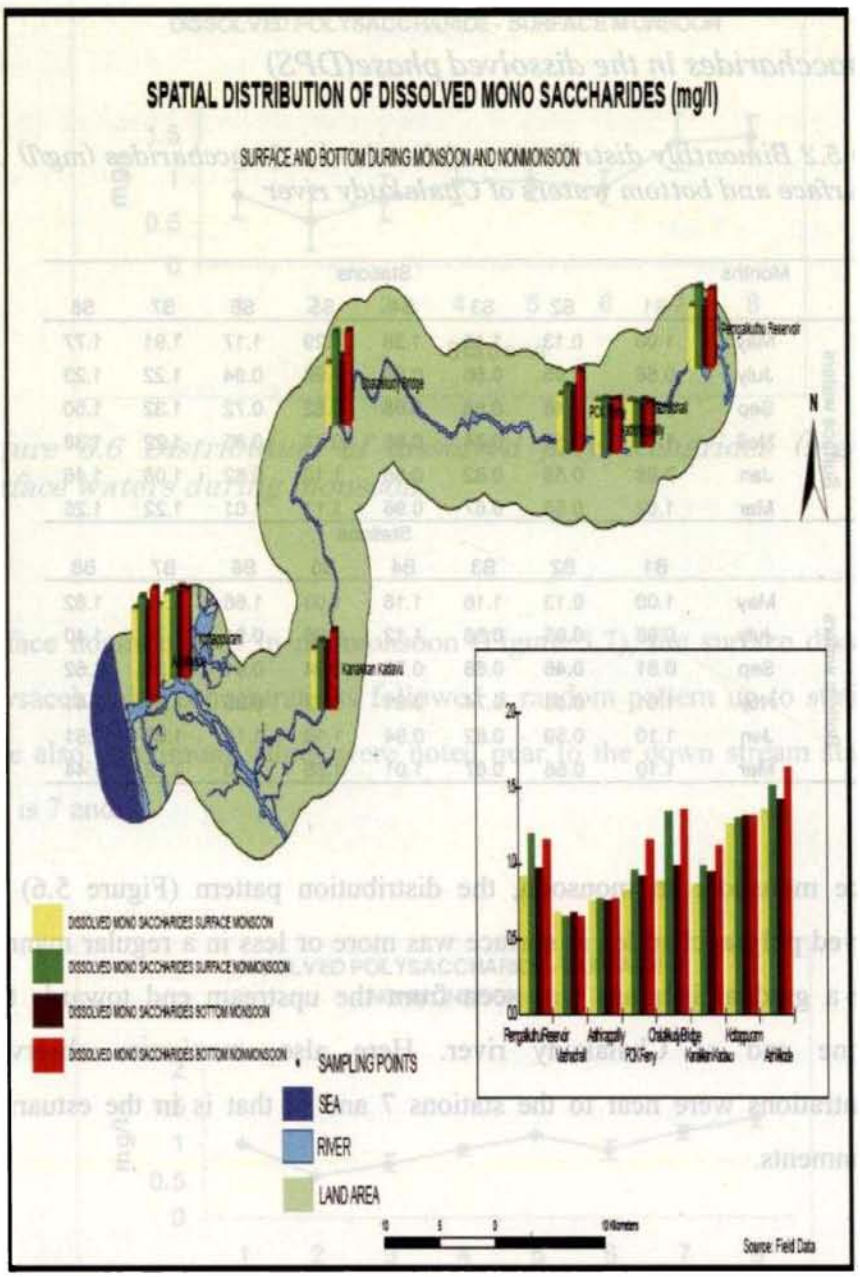

Figure 5.5 Spatial distribution of dissolved monosaccharides in mg/l.

Polysaccharides in the dissolved phase(DPS)

Table 5.2 Bimonthly distribution of dissolved polysaccharides (mg/l) in the surface and bottom waters of Chalakudy river

	Months	Stations							
		S1	S2	S3	S4	S5	S6	S7	S8
Surface waters	May	1.00	0.13	1.16	1.28	1.29	1.17	1.91	1.77
	July	0.58	0.95	0.56	0.98	0.96	0.84	1.22	1.23
	Sep	0.57	0.46	0.68	0.68	0.82	0.72	1.32	1.50
	Nov	1.12	0.58	0.74	0.86	0.83	0.85	1.22	1.38
	Jan	0.98	0.59	0.82	0.86	1.10	0.82	1.08	1.46
	Mar	1.02	0.56	0.67	0.96	1.13	1.01	1.22	1.25
		Stations							
		B1	B2	B3	B4	B5	B6	B7	B8
Bottom waters	May	1.00	0.13	1.16	1.16	1.03	1.66	1.79	1.82
	July	0.68	0.95	0.56	1.12	0.96	0.91	1.79	1.40
	Sep	0.81	0.46	0.68	0.75	0.94	0.91	1.26	1.62
	Nov	1.01	0.58	0.74	0.91	0.92	0.85	1.30	1.41
	Jan	1.10	0.59	0.82	0.94	1.10	1.10	1.08	1.51
	Mar	1.10	0.56	0.67	1.01	1.50	1.10	1.22	1.44

Surface monsoon: In monsoon, the distribution pattern (Figure 5.6) of dissolved polysaccharides in surface was more or less in a regular manner where a gradual increase was seen from the upstream end towards the estuarine end of Chalakudy river. Here also, maximum observed concentrations were near to the stations 7 and 8, that is in the estuarine environments.

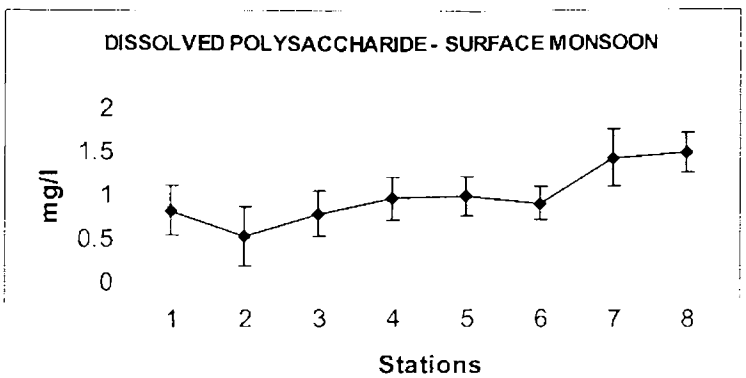

Figure 5.6 Distribution of dissolved polysaccharides (mg/l) in surface waters during monsoon.

Surface nonmonsoon: In nonmonsoon (Figure 5.7), the surface dissolved polysaccharides concentrations followed a random pattern up to station 6. Here also, maximum values were noted near to the down stream stations, that is 7 and 8.

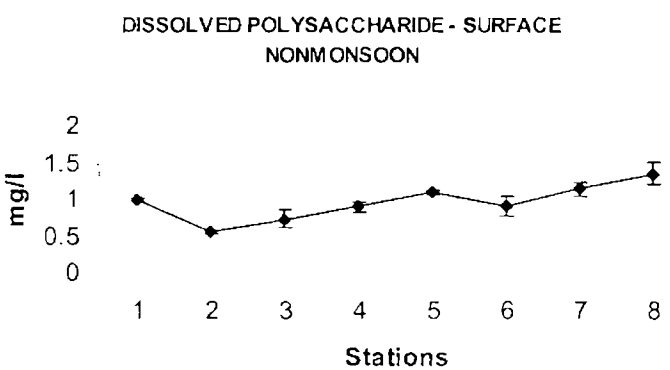

Figure 5.7 Distribution of dissolved polysaccharides (mg/l) in surface waters during nonmonsoon.

Bottom monsoon: In monsoon, the part of the study area up to station 6 showed randomness in the concentration gradient (Figure 5.8). In the down stream part of the study area a gradual increase was observed in the dissolved polysaccharide concentration where the maximum values were near to stations 7 and 8.

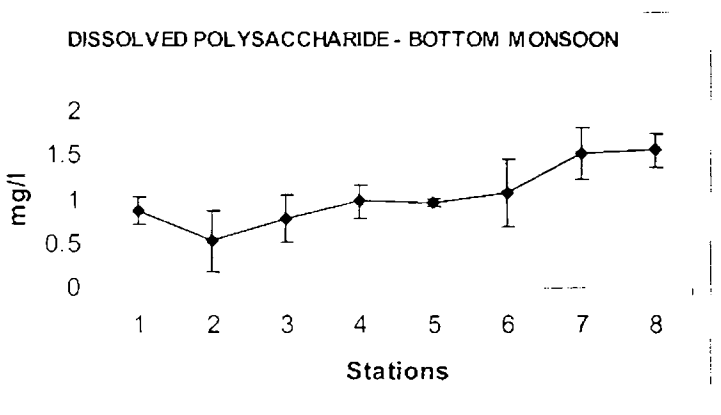

Figure 5.8 Distribution of dissolved polysaccharides (mg/l) in bottom waters during monsoon.

Bottom nonmonsoon: In nonmonsoon also the bottom distribution profile of dissolved polysaccharides was irregular up to station 6 (Figure 5.9). In this season also a gradual increase in concentrations was seen only beyond station 6 towards the sea side, the maximum being at station 8.

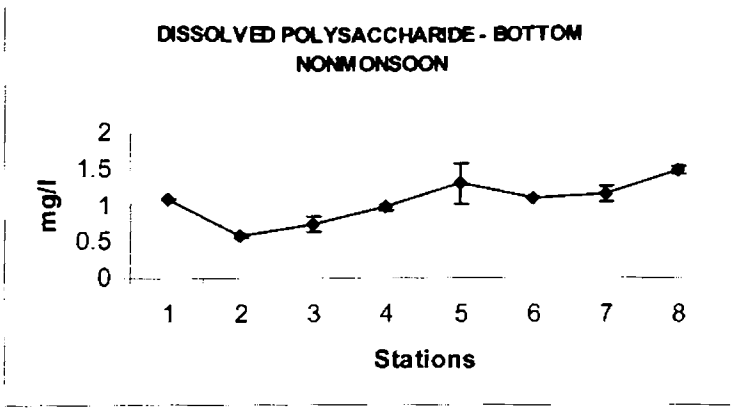

Figure 5.9 Distribution of dissolved polysaccharides (mg/l) in bottom waters during nonmonsoon.

While discussing the general trend in the dissolved polysaccharide concentrations both spatially and seasonally, the lowest values were at station 2 (Figure 5.10). At stations 7 and 8, which were at the down stream end, comparatively high values were observed when compared with the rest of the stream. At stations 1, 2, 5 and 6, nonmonsoonal values were slightly higher than monsoonal values at surface. At stations 7 and 8, the monsoonal values of the dissolved polysaccharides exceeded the nonmonsoonal values. For bottom samples, upto station 6 nonmonsoonal values were slightly higher than monsoonal values. At stations 7 and 8 monsoon recorded slightly higher concentrations than nonmonsoon season.

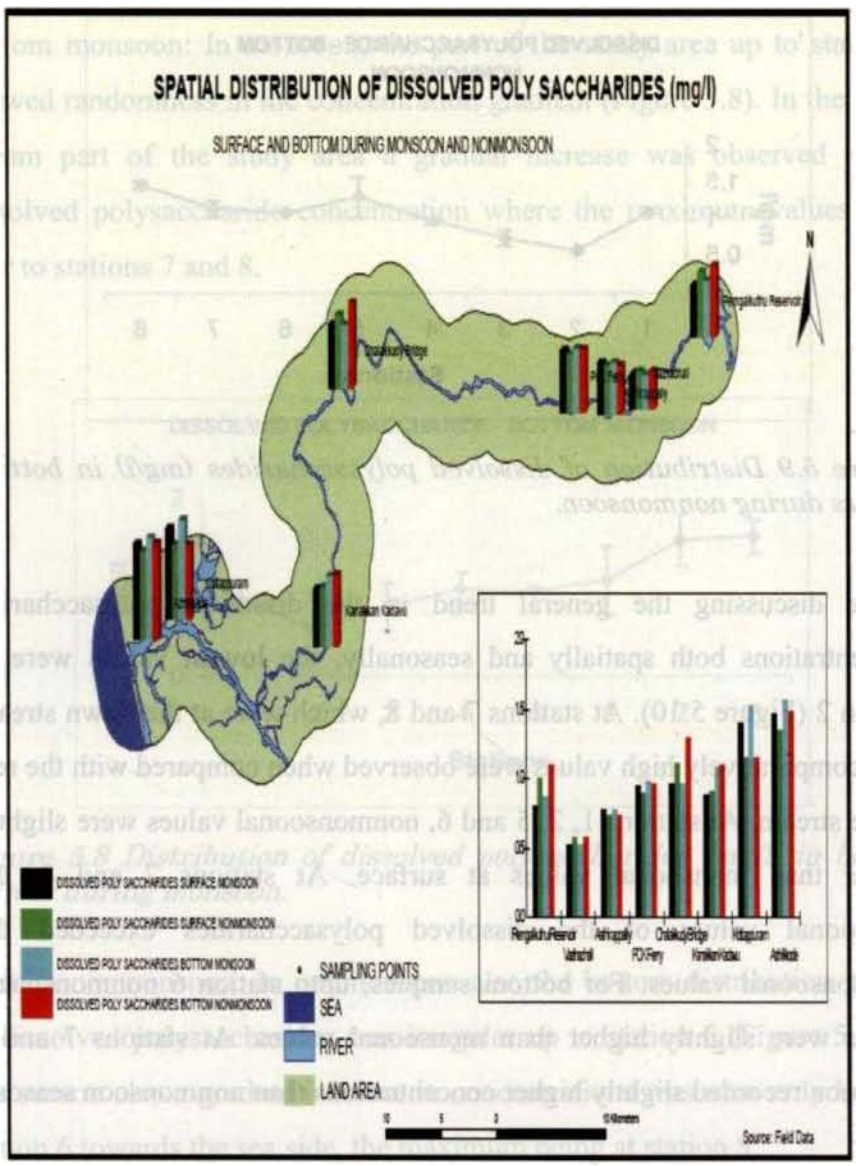

Figure 5.10 Spatial distribution of dissolved polysaccharide in mg/l

The present study showed the maximum value 1.56 mg/l at station 8 during monsoon for bottom water samples and 1.47 mg/l at station 8 during monsoon for surface water samples. The lowest value was recorded in station 2. Comparatively high value was recorded at station 7 (Kottappuram), where Chalakkudy river merges with Periyar river. The highest concentration observed in this station could be due to the combined effect of various contributing factors such as high productivity, transport of organic matter and biogenic production caused by nutrient rich water. The observed low value of carbohydrate at station 2 may be due to the dilution and oxidative degradation of organic matter.

Monosaccharides in the particulate phase (PMS)

Carbohydrates are the structural and storage components of both marine and terrestrial organisms. In particulate samples, the contribution of carbohydrate carbon to the particulate organic carbon may vary from10-30% (Hernes et al., 1996; Sigelo, 1996). Phytoplankton and the detritus largely determine the carbohydrate composition of particulate matter.

Table 5.3 Bimonthly distribution of particulate monosaccharides (mg/l) in the surface and bottom waters of Chalakudy river

		Stations							
		S1	S2	S3	S4	S5	S6	S7	S8
Surface waters	May	0.14	0.00	0.06	0.09	0.10	0.12	0.16	0.18
	July	0.11	0.00	0.03	0.03	0.06	0.09	0.13	0.13
	Sep	0.10	0.00	0.04	0.03	0.04	0.09	0.12	0.12
	Nov	0.26	0.01	0.11	0.16	0.13	0.15	0.20	0.39
	Jan	0.16	0.01	0.09	0.16	0.13	0.13	0.16	0.29
	Mar	0.11	0.00	0.06	0.14	0.11	0.11	0.14	0.17
		Stations							
		B1	B2	B3	B4	B5	B6	B7	B8
Bottom waters	May	0.14	0.00	0.06	0.18	0.14	0.14	0.16	0.24
	July	0.13	0.00	0.03	0.05	0.06	0.13	0.13	0.16
	Sep	0.13	0.00	0.04	0.04	0.06	0.11	0.12	0.14
	Nov	0.32	0.01	0.11	0.16	0.15	0.15	0.28	0.41
	Jan	0.23	0.01	0.09	0.18	0.13	0.15	0.16	0.38
	Mar	0.18	0.00	0.06	0.16	0.12	0.14	0.14	0.17

Surface monsoon: In monsoon, the surface distribution of particulate monosaccharide showed more or less a gradual increase beyond station 2. (Figure 5.11). Maximum observed concentration being near to station 8, the lowest observed concentration was near to station 2. The dam station (station 1) also reported slightly high value.

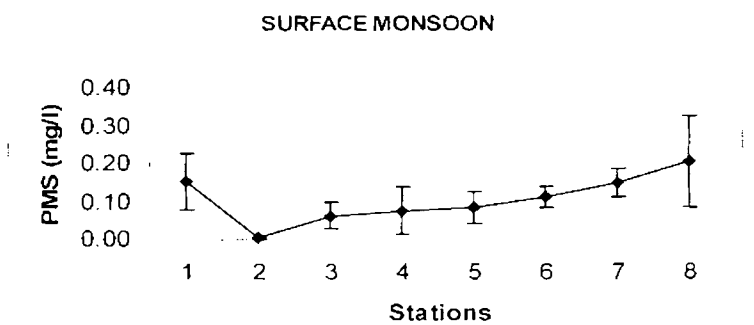

Figure 5.11 Distribution of particulate monosaccharides (mg/l) in surface waters during monsoon.

Surface nonmonsoon: In nonmonsoon season, particulate monosaccharide distribution in surface depicted an irregular pattern, the lowest being near to station 2 and the highest near to station 8 (Figure 5.12). After the middle stream portion i.e., after station 5, a gradual increase in concentrations was observed.

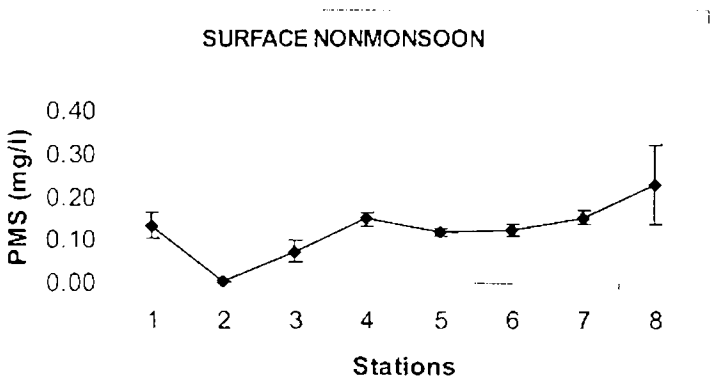

Figure 5.12 Distribution of particulate monosaccharides (mg/l) in surface waters during nonmonsoon.

Bottom monsoon: In monsoon (Figure 5.13), particulate monosaccharide concentration was found to be low at station 2, whereas the highest observed concentration was at station 8. The monsoonal values were slightly lower than the nonmonsoonal values. Spatially, bottom stations recorded slightly higher values than surface both in monsoon and nonmonsoon

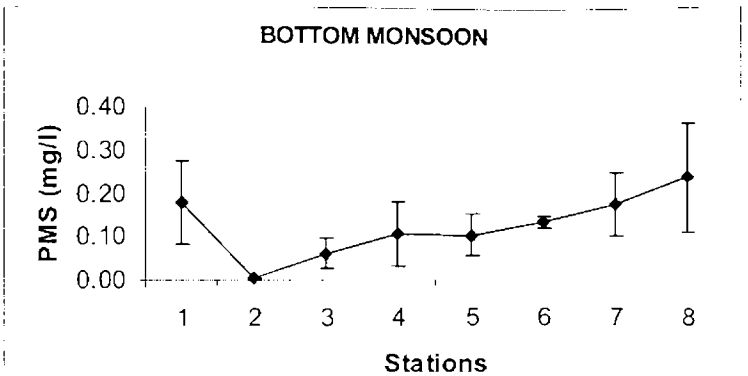

Figure 5.13 Distribution of particulate monosaccharides (mg/l) in bottom waters during monsoon.

Bottom nonmonsoon: In the distribution of particulate monosaccharide, the pattern was more or less an irregular in the upper stream half (Figure 5.14). Comparatively low value were seen near to stations 2 and 3. In the down stream portion beyond station 6, a gradual increasing trend was seen in particulate monosaccharide distribution. Comparatively higher concentrations were seen at dam station 1 and the estuarine station 8.

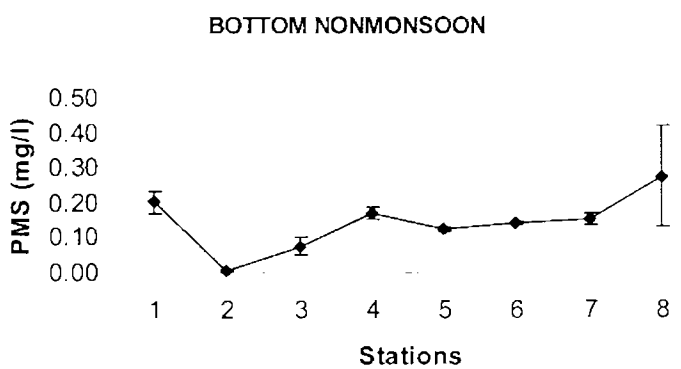

Figure 5.14 Distribution of particulate monosaccharides (mg/l) in bottom waters during nonmonsoon.

In the present study, particulate monosaccharide showed a maximum of 0.27 mg/l at station 8 during nonmonsoon and the lowest was observed at station 2 (0.003 mg/l) during monsoon (Figure 5.15). In the general distribution of particulate monosaccharide, both in surface and bottom, nonmonsoon recorded slightly higher concentrations than monsoon, a gradual increasing trend in concentration was observed from stations 2 to 8 where the maximum was at station 8 both spatially and seasonally. The station 2 i.e, the waterfalls region is characterized by high rate of water turbulence which facilitated the oxidative decomposition of organic materials to a large extent. Except at station 7, higher particulate monosaccharide concentrations were seen in bottom stations and in the nonmonsoon season. The higher estuarine concentration in nonmonsoon may be due to the combined effect of several factors- high productivity, transport of organic matter (estuarine/terrestrial), anthropogenic input, high rate of sedimentation and decomposition (both aeroboic and anaerobic) and subsequent preservation due to ambient conditions prevalent in the ecosystem such as pH, salinity, DO, Eh etc.

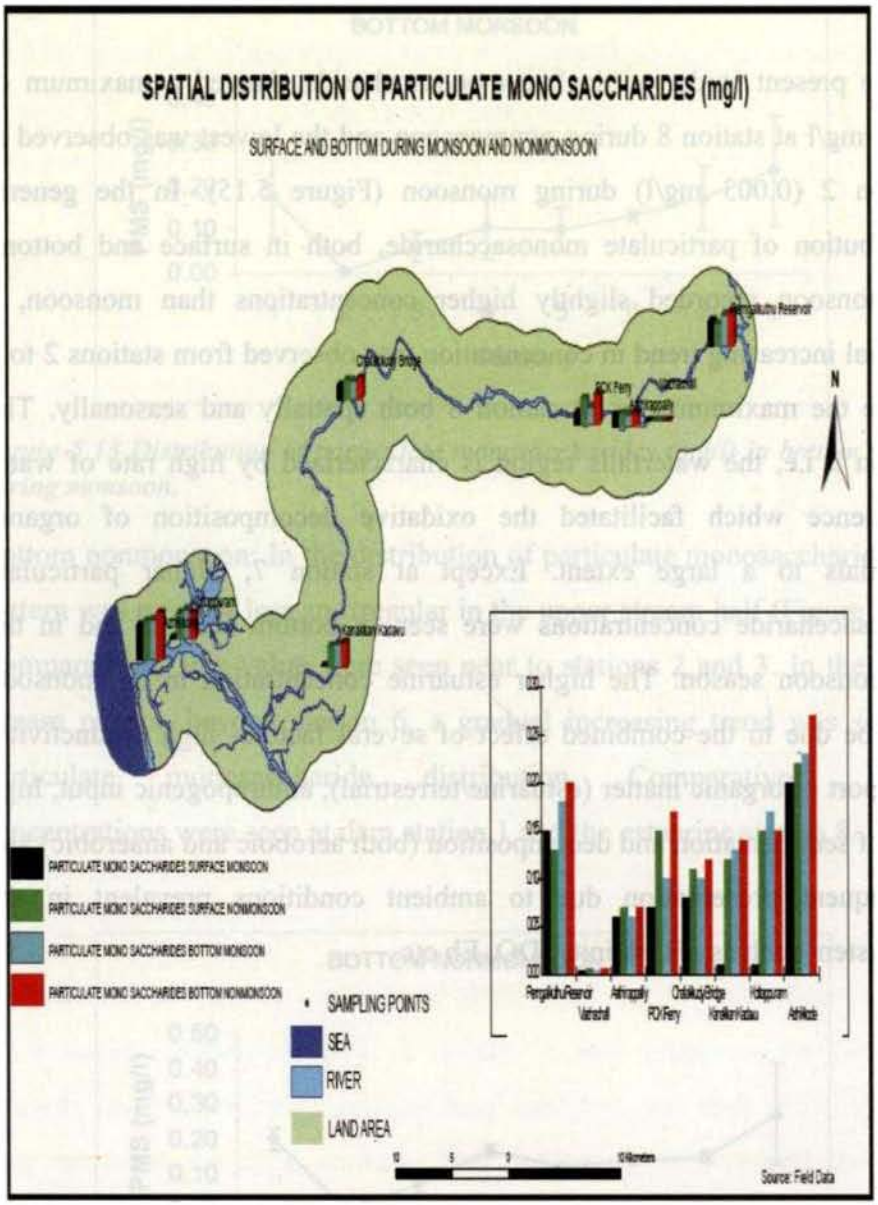

Figure 5.15 Spatial distribution of particulate monosaccharide in mg/l.

Polysaccharides in the particulate phase (PPS)

Table 5.4 Bimonthly distribution of particulate polysaccharides (mg/l) in the surface and bottom waters of Chalakudy river

		Stations							
		S1	S2	S3	S4	S5	S6	S7	S8
Surface waters	May	0.16	0.01	0.03	0.12	0.11	0.12	0.18	0.23
	July	0.14	0.00	0.01	0.08	0.05	0.10	0.12	0.12
	Sep	0.14	0.01	0.01	0.12	0.02	0.12	0.12	0.12
	Nov	0.39	0.05	0.06	0.17	0.14	0.16	0.25	0.40
	Jan	0.30	0.03	0.08	0.16	0.13	0.14	0.23	0.34
	Mar	0.29	0.01	0.05	0.14	0.09	0.14	0.14	0.26
		Stations							
		B1	B2	B3	B4	B5	B6	B7	B8
Bottom waters	May	0.16	0.01	0.03	0.16	0.13	0.16	0.22	0.31
	July	0.16	0.00	0.01	0.11	0.05	0.12	0.12	0.17
	Sep	0.16	0.01	0.01	0.13	0.06	0.12	0.14	0.14
	Nov	0.35	0.05	0.06	0.19	0.12	0.16	0.29	0.46
	Jan	0.38	0.03	0.08	0.17	0.13	0.15	0.23	0.45
	Mar	0.36	0.01	0.05	0.15	0.14	0.12	0.14	0.39

Surface monsoon: In monsoon (Figure 5.16), surface distribution of particulate polysaccharides depicted a random pattern upto station 5. Beyond this station, a steady increase was seen towards the lower stream end, maximum observed concentration being at station 8. Here also, as seen earlier, lowest value was at station 2.

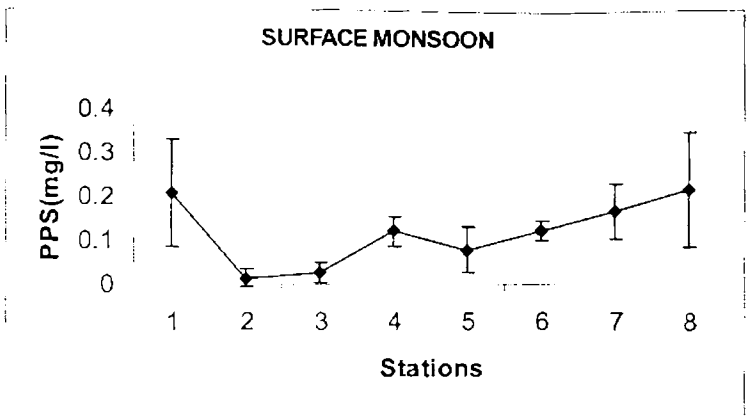

Figure 5.16 Distribution of particulate polysaccharides (mg/l) in surface waters during monsoon.

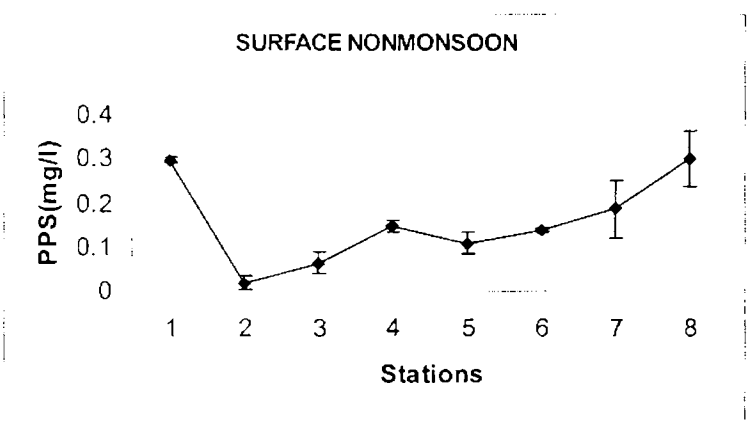

Figure 5.17 Distribution of particulate polysaccharides (mg/l) in surface waters during nonmonsoon.

Surface nonmonsoon: The nonmonsoonal distribution profile of particulate polysaccharides was exactly the same as that in monsoon, i.e, highly irregular distribution trend upto station 5 (Figure 5.17). Towards the lower end of the stream, a steady increase was seen in particulate ploysaccharides distribution, the maximum being at station 8.

Bottom monsoon: The monsoon bottom distribution profile (Figure 5.18) of particulate polysaccharide was also irregular upto station 5. Beyond this station, a gradual increase was observed, maximum being near 8. Stations 2 and 3 in the upper stream side recorded comparatively low particulate polysaccharide concentrations.

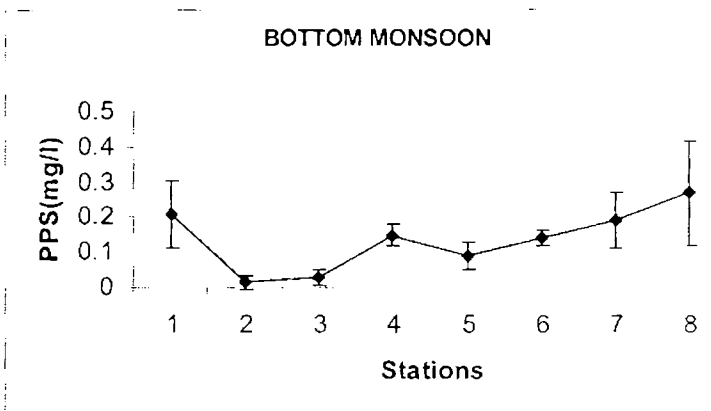

Figure 5.18 Distribution of particulate polysaccharide (mg/l) in bottom waters during monsoon.

Bottom nonmonsoon: In nonmonsoon, the bottom distribution pattern (Figure 5.19) of particulate polysaccharide showed a showed a stagely different distributional features in which stations 4 to 6 maintained a uniformity in the values. As seen in the monsoonal distribution pattern, here also lowest concentrations were seen near to stations 2 and 3. Dam and estuarine stations continued to keep their peak values.

Considering the general trend in particulate polysaccharide distribution, both seasonally and temporally, nonmonsoonal values were slightly higher than monsoonal values (Figure 5.20). The lowest observed concentrations were near to the stations 2 and 3 and the highest being near to the stations 1 and 8. At stations 1 and 8, bottom nonmonsoonal values showed a slight

increase in particulate polysaccharide concentration. In the present study particulate polysaccharides showed a maximum of (0.42 mg/l) at station 8 during nonmonsoon and the lowest was observed at station 2 (0.015 mg/l) during monsoon.

The highest concentration of particulate polysacharides observed in the estuary (station 8) could be due to combined effects of high productivity, transport of organic matter, anthropogenic input etc. in addition to this, decay and decomposition of floating plants in this station can also contributed to an increase in concentration of carbohydrates.

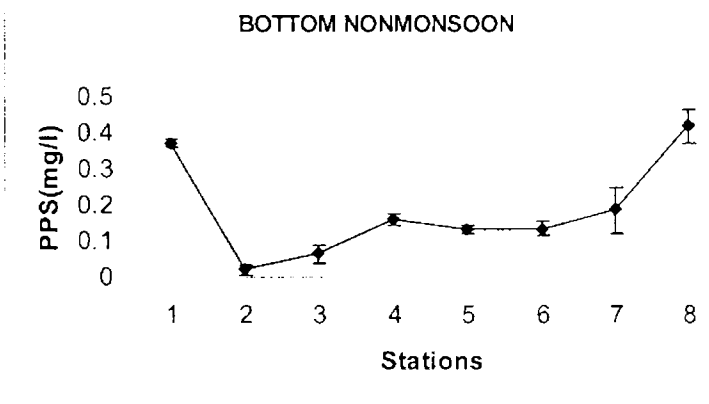

Figure 5.19 Distribution of particulate polysaccharides (mg/l) in bottom waters during nonmonsoon.

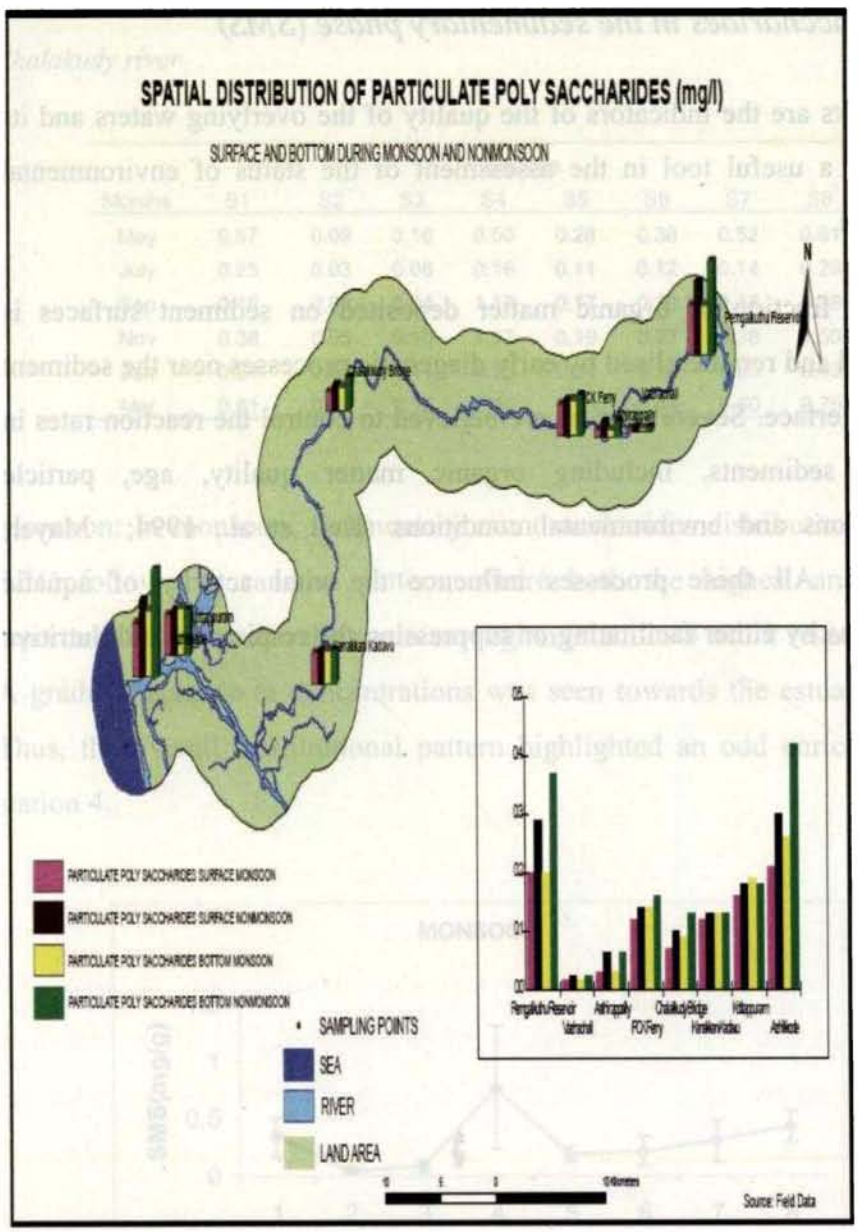

Figure 5.20 General distribution trend of polysaccharides in particulate matter in mg/l.

Monosaccharides in the sedimentary phase (SMS)

Sediments are the indicators of the quality of the overlying waters and its study is a useful tool in the assessment of the status of environmental pollution.

A large fraction of organic matter deposited on sediment surfaces is degraded and remineralised by early diagenetic processes near the sediment water interface. Several factors are believed to control the reaction rates in surface sediments, including organic matter quality, age, particle associations and environmental conditions (Keil et al., 1994; Mayer, 1994a,b). All these processes influence the vital activity of aquatic organisms by either facilitating or suppressing the respiratory and nutritive systems.

Table 5.5 Bimonthly distribution of monosaccharides (mg/l) in the sediments of Chalakudy river

	Stations							
Months	S1	S2	S3	S4	S5	S6	S7	S8
May	0.57	0.09	0.16	0.50	0.28	0.38	0.52	0.61
July	0.25	0.03	0.06	0.16	0.11	0.12	0.14	0.29
Sep	0.18	0.03	0.04	1.17	0.17	0.10	0.18	0.38
Nov	0.38	0.05	0.10	1.27	0.19	0.27	0.38	0.50
Jan	0.34	0.05	0.11	0.25	0.17	0.24	0.33	0.43
Mar	0.61	0.07	0.18	0.50	0.34	0.44	0.50	0.79

Monsoon: In monsoon, sedimentary monosaccharides distribution (Figure 5.21) followed a random pattern, where both the highest and lowest reported values were in the upstream region (stations 4 and 2 respectively). A gradual increase in concentrations was seen towards the estuarine end. Thus, the overall distributional pattern highlighted an odd enrichment at station 4.

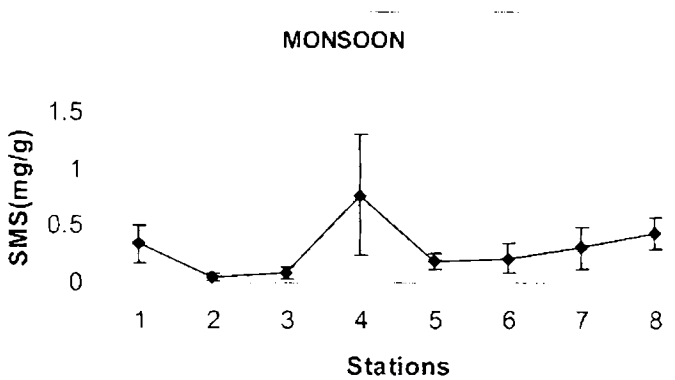

Figure 5.21 Distribution of monosaccharides in sediments (mg/g) during monsoon.

Nonmonsoon: As seen in the monsoon, the lowest observed concentration (Figure 5.22) of monosaccharide was at station 2. Iin this season, the highest reported value was at station 8 i.e ., Azhikode. Here also after station 5, a gradual increase in concentration was seen towards the seaside.

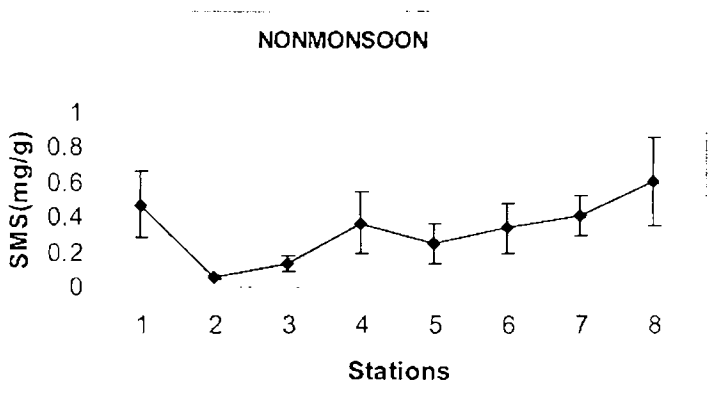

Figure 5.22 Distribution of monosaccharide in sediments (mg/g) during nonmonsoon.

On generalizing the distributional characteristics of sedimentary monosaccharides, the nonmonsoonal values were higher than the monsoonal values except at station 4 (Figure 5.23). In this mid-station monsoon recorded slightly higher value than nonmonsoon. At station 2 also, the seasonal variation in concentration was negligible where monsoon and non monsoon recorded almost the same sedimentary monosaccharide concentrations.

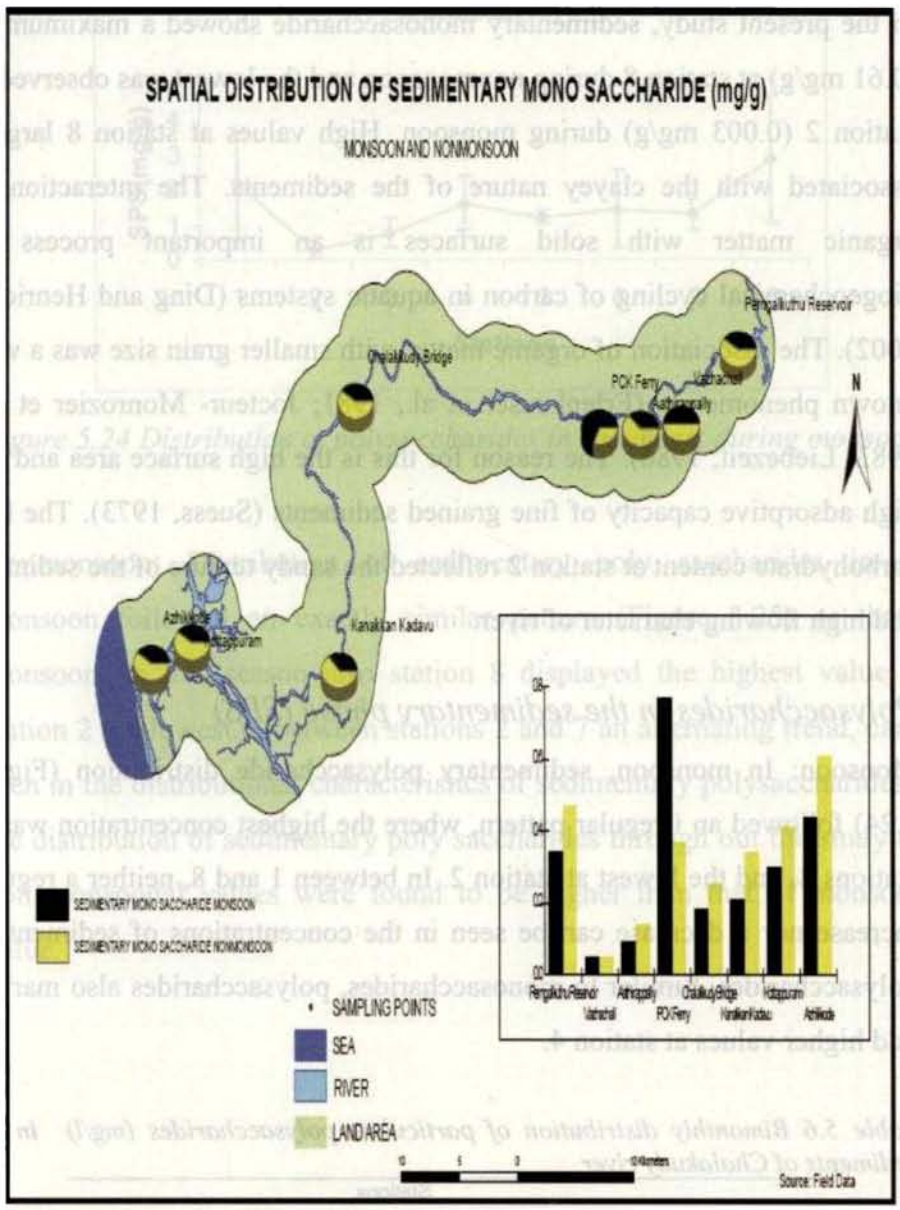

Figure 5.23 Spatial distribution of sedimentary monosaccharides in mg/g.

In the present study, sedimentary monosaccharide showed a maximum of (0.61 mg/g) at station 8 during nonmonsoon and the lowest was observed at station 2 (0.003 mg/g) during monsoon. High values at station 8 largely associated with the clayey nature of the sediments. The interaction of organic matter with solid surfaces is an important process in biogeochemical cycling of carbon in aquatic systems (Ding and Henrichs, 2002). The association of organic matter with smaller grain size was a well known phenomenon (Erlenkeuser et al., 1981; Jocteur- Monrozier et al., 1983; Liebezeit, 1986). The reason for this is the high surface area and the high adsorptive capacity of fine grained sediments (Suess, 1973). The low carbohydrate content at station 2 reflected the sandy texture of the sediment and high flowing character of river.

Polysaccharides in the sedimentary phase (SPS)

Monsoon: In monsoon, sedimentary polysaccharide distribution (Figure 5.24) followed an irregular pattern, where the highest concentration was at stations 8, and the lowest at station 2. In between 1 and 8, neither a regular increase nor a decrease can be seen in the concentrations of sedimentary polysaccharides. Similar to monosaccharides, polysaccharides also marked odd higher values at station 4.

Table 5.6 Bimonthly distribution of particulate polysaccharides (mg/l) in the sediments of Chalakudy river

	Stations							
Months	S1	S2	S3	S4	S5	S6	S7	S8
May	4.48	0.72	1.39	2.77	1.46	3.12	1.89	5.59
July	1.02	0.13	0.47	1.15	1.02	0.86	1.03	1.78
Sep	1.24	0.11	0.59	1.20	1.14	0.82	1.02	1.86
Nov	1.91	0.29	0.62	1.38	1.30	1.03	1.25	2.19
Jan	2.12	0.47	0.76	1.46	1.42	1.52	1.03	3.27
Mar	3.51	0.69	1.03	2.18	1.48	2.26	1.75	4.73

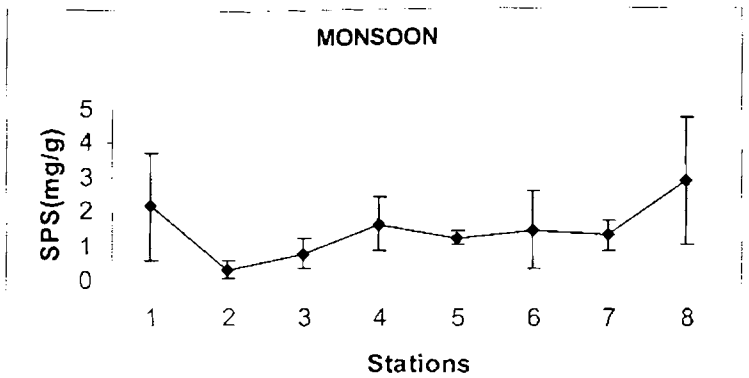

Figure 5.24 Distribution of polysaccharides in sediments during monsoon.

Nonmonsoon: Distribution of sedimentary poly saccharides in non monsoon followed an exactly similar pattern (Figure 5.25) as that in monsoon. In this season also station 8 displayed the highest value and station 2 the lowest.in between stations 2 and 7 an alternating trend, can be seen in the distributional characteristics of sedimentary polysaccharides. In the distribution of sedimentary poly saccharides through out the study area non monsoonal values were found to be higher than that of monsoonal value.

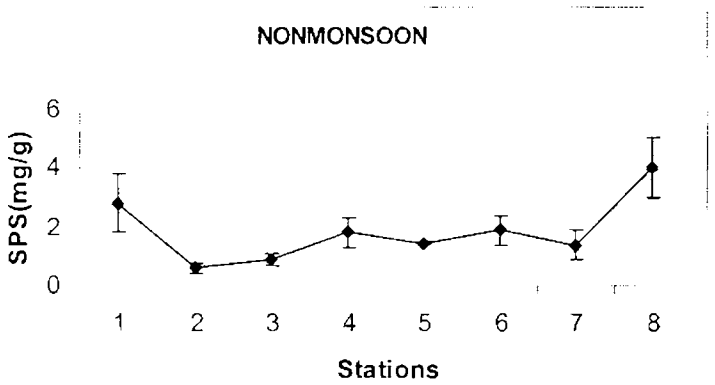

Figure 5.25 Distribution of polysaccharides in sediments during nonmonsoon.

In the present study, sedimentary polysaccharide showed a maximum of (4 mg/g) at station 8 during nonmonsoon and the lowest was observed at station 2 (0.31mg/g) during monsoon (Figure 5.26). High values at station 8 might be due to the combined effect of several contributory factors: high productivity, transport of organic matter, anthropogenic input, high rate of sedimentation, decomposition etc. Carbohydrates were the most abundant fraction of the organic matter in the sediments. This might be attributed to the quality of organic matter settling into the sediments and its consequent transformation by benthic organisms. Carbohydrates represent an important food source for heterotrophic organisms and are rapidly recycled (Gagosian and Lee, 1981; Ittekkot et al., 1984). The low carbohydrate contents at station 2 might be due to sandy texture of the sediment.

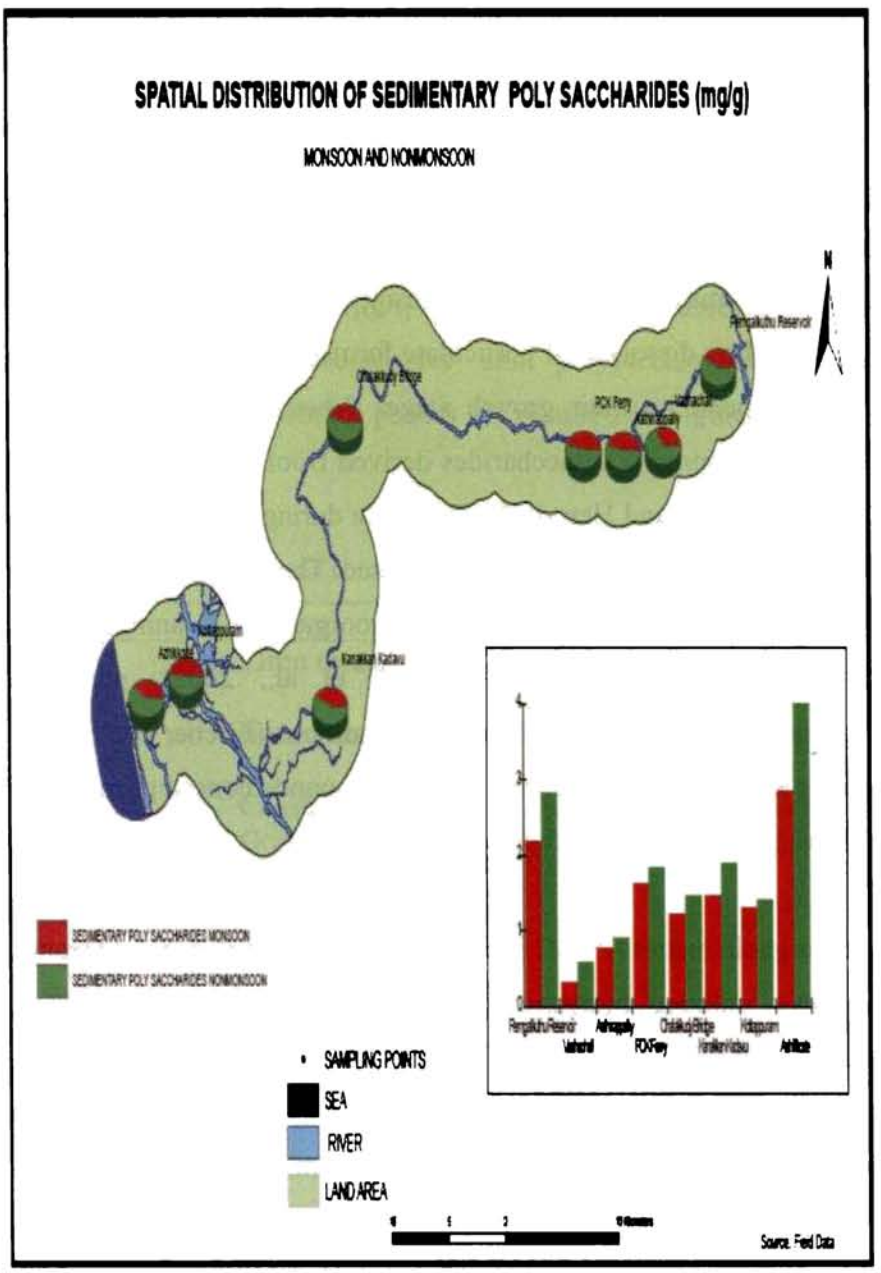

Figure 5.26 Spatial distribution of sedimentary monosaccharides in mg/g.

In aquatic environments, bacterioplankton release considerable quantities of cell material (Stoderegger and Herndl, 1998), usually referred to as extracellular polysaccharides or exopolysaccharides. The structure and function of these polysaccharides are still poorly understood, in spite of their importance for the limnology of tropical areas in which the organic carbon released may contribute significantly to the pool of organic compounds, in their dissolved or particulate forms. The substances released by plankton depend on their growth stage. When metabolically active, plankton release mainly polysaccharides derived from renewal of cell wall capsules (Stoderegger and Herndl, 1998), while during the senescent stage, intracellular structures are preferentially released. The compositions of such extracellular polymers vary with type of microorganisms (Vaningelgem et al., 2004), nutrient availability (Ricciardi et al., 2002), phase of microorganisms growth and environmental conditions (Fischer et al., 2003; Bahat-Samet et al., 2004). In general, such compounds consist primarily of high-molecular weight, hydrated polysaccharides.

Particulate organic matter (POM) is produced by aquatic organisms through photosynthesis utilizing inorganic carbon and nutrients. Phytoplankton, benthic algae and vascular plants are the predominant group of autotrophs, supplying the most of the insitu primary production. Phytoplankton produces organic particles in the water column; microphytobenthos production takes place on the bottom. Sinking through the water column, particulate organic matter is oxidized by microbial activity, utilizing dissolved oxygen and releasing inorganic carbon and nutrients to the water column, a process known as remineralization.

Carbohydrates are much higher in vascular plants than in algae (Cowie and Hedges, 1984). Carbohydrates values were 0.37 mg/g to 5.35 mg/g in the harbor and coastal sediments of Vishakapattanam (Sarma and Rao, 1988). Lecerda et al., (1995) reported variation of carbohydrates in the core sediments of Avicennia soil in south eastern Brazil (1.41 mg/g to 3.83 mg/g) and that of Rizophora soil (2.44 mg/g to 2.50 mg/g). Some reported values of carbohydrates (μg/l) are produced in Table 5.7. The overall distribution of monosaccharides and polysaccharides in dissolved, particulate and sedimentary phases are pictured in Figure 5.27 and Figure 5.28 respectively.

Table 5.7 Earlier reported values of Carbohydrates (μg/l)

No	System	Range	Reference
1	Elron estuary	90- 1080	William et al., 1991
2	Narragansett Bay	122-156	Johnson et al., 1977
3	Coastal waters, Goa	0.5-29	Kamat, 1976

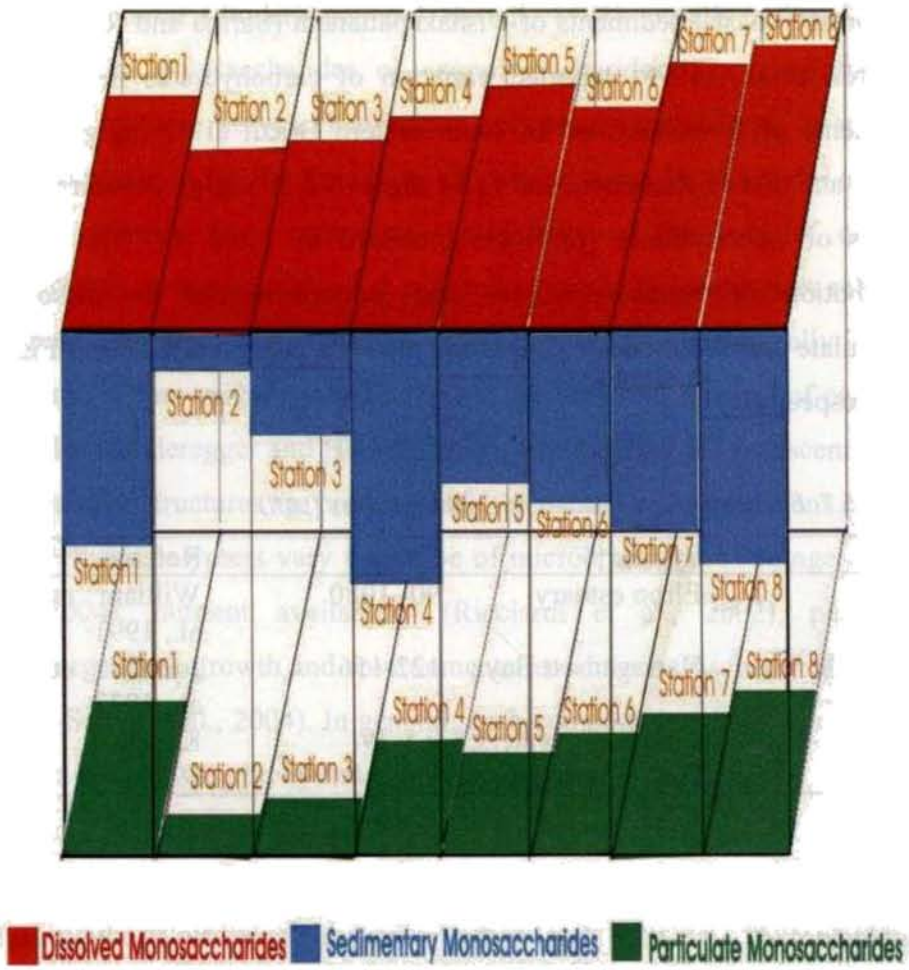

Figure 5.27 Overall distribution of monosaccharides in dissolved, particulate and sedimentary phases.

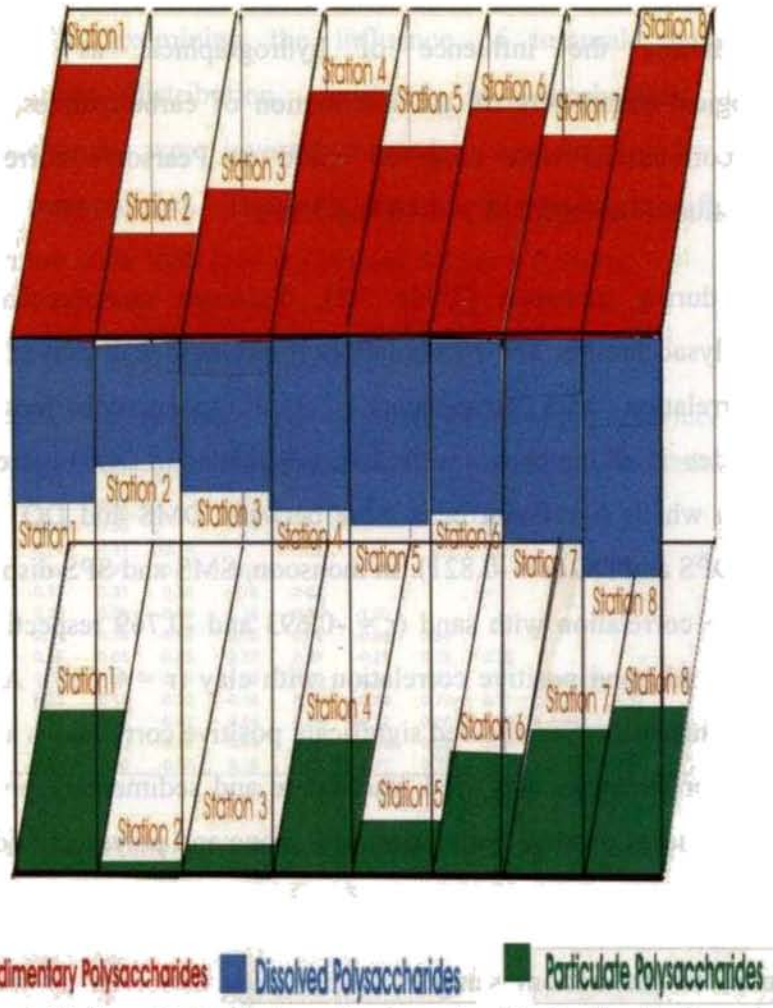

Figure 5.28 Overall distribution of polysaccharides in dissolved, particulate and sedimentary phases.

Role of hydrographical parameters on carbohydrate distribution profile

While examining the influence of hydrographical as well as sedimentological parameters on the distribution of carbohydrates, some significant correlations were observed based on Pearson's correlation coefficient values (Tables 5.8, 5.9, 5.10 and 5.11).

In surface, during monsoon (Table 5.8), dissolved monosaccharides, dissolved polysaccharides and particulate polysaccharides displayed good positive correlation with temperature. Both monosaccharides and polysaccharides in all the phases were inversely related to DO (Figure 5.27 and 5.28), in which significant ones were between DMS and DO ($r = -0.851$), and DPS and DO ($r = -0.821$). In monsoon, SMS and SPS displayed good negative correlation with sand ($r = -0.693$ and -0.769 respectively). The SPS showed good positive correlation with clay ($r = 0.765$). All the organic constituents studied showed significant positive correlations among themselves. For example, dissolved, particulate and sedimentary proteins displayed significant positive correlation with mono and polysaccharides in all the three phases.

In monsoon, in the bottom samples (Table 5.9), dissolved as well as particulate fraction of monosaccharides and polysaccharides displayed significant positive correlation with temperature. All the forms of carbohydrate in the dissolved as well as sedimented phases displayed positive correlation with COD of the water samples. Both monosaccharides and polysaccharides in the dissolved, particulate and sedimental phases displayed negative correlation with DO. Here the significant correlations

were between DO and DMS (r = -0.985), DO and PMS (r= -0.731), DO and DPS (r = -0.848), DO and PPS (r = -0.732) and DO and SPS (r = 0.616). On examining the influence of textural characteristics on carbohydrate distribution, sediment monosaccharides as well as polysaccharides were inversely related to sand fraction (r= -0.693 and -0.769 respectively). The silt fraction displayed significant positive correlation with SMS (r = 0.728) and SPS (r = 0.769).

Table 5.8 Correlation matrix among different parameters of surface monsoon

	Temp	pH	DO	COD	SOC	Sand	Silt	Clay	DMS	PMS	SMS	DPS	PPS
pH	0.22												
chloride	0.77	0.24											
DO	0.85	0.32											
COD	0.79	-0.41	-0.76										
SOC	0.02	-0.07	-0.21	0.01									
Sand	-0.17	0.31	0.38	-0.16	0.82								
Silt	0.20	0.30	-0.39	0.16	0.81	-1.00							
Clay	0.14	-0.38	-0.48	0.26	0.85	-0.86	0.84						
DMS	0.86	0.08	-0.85	0.57	0.27	-0.26	0.28	0.35					
PMS	0.07	0.32	-0.35	0.06	0.65	-0.65	0.63	0.71	0.47				
SMS	0.25	0.12	-0.22	0.14	0.52	-0.69	0.73	0.31	0.31	0.39			
DPS	0.93	0.03	-0.82	0.64	0.25	-0.32	0.36	0.29	0.96	0.39	0.41		
PPS	0.93	0.03	-0.82	0.64	0.25	-0.32	0.36	0.29	0.96	0.39	0.41	1.00	
SPS	0.41	0.00	-0.62	0.18	0.67	-0.77	0.77	0.77	0.70	0.84	0.60	0.65	0.65

Table 5.9 Correlation matrix among different parameters of bottom monsoon

	Temp	pH	DO	COD	SOC	Sand	Silt	Clay	DMS	PMS	SMS	DPS	PPS
pH	0.10												
chloride	0.69	0.56											
DO	-0.84	-0.02											
COD	0.51	0.43	-0.69										
SOC	0.02	-0.05	-0.25	0.60									
Sand	-0.15	0.00	0.36	-0.68	-0.82								
Silt	0.18	0.02	0.37	0.69	0.81	-1.00							
Clay	0.13	-0.24	-0.49	0.63	0.85	-0.86	0.84						
DMS	0.86	0.29	-0.90	0.72	0.35	-0.37	0.40	0.43					
PMS	0.61	0.17	-0.73	0.65	0.58	-0.58	0.59	0.66	0.89				
SMS	0.24	0.47	-0.20	0.53	0.52	-0.69	0.73	0.31	0.39	0.45			
DPS	0.93	0.26	-0.85	0.62	0.21	-0.32	0.35	0.30	0.97	0.84	0.40		
PPS	0.59	0.25	-0.73	0.67	0.60	-0.61	0.63	0.63	0.88	0.97	0.59	0.82	
SPS	0.38	0.30	-0.62	0.74	0.67	-0.77	0.77	0.77	0.74	0.92	0.60	0.66	0.93

Table 5.10 Correlation matrix among different parameters of surface nonmonsoon

	Temp	pH	DO	COD	SOC	Sand	Silt	Clay	DMS	PMS	SMS	DPS	PPS
pH	0.32												
chloride	0.60	0.94											
DO	-0.51	-0.88											
COD	0.58	0.95	-0.94										
SOC	-0.18	0.21	-0.31	0.16									
Sand	0.51	0.16	0.18	-0.07	-0.03								
Silt	0.49	-0.19	-0.15	0.04	0.01	-1.00							
Clay	0.63	0.44	-0.76	0.62	0.36	-0.66	0.63						
DMS	0.59	0.54	-0.83	0.70	0.54	-0.53	0.50	0.87					
PMS	0.56	0.54	-0.70	0.68	0.39	-0.68	0.66	0.82	0.83				
SMS	0.40	0.56	-0.71	0.66	0.56	-0.54	0.51	0.81	0.82	0.95			
DPS	0.66	0.59	-0.84	0.75	0.47	-0.58	0.55	0.89	0.99	0.90	0.86		
PPS	0.18	0.57	-0.68	0.59	0.75	-0.35	0.32	0.73	0.77	0.83	0.95	0.78	
SPS	0.22	0.48	-0.66	0.53	0.57	-0.55	0.52	0.85	0.73	0.84	0.92	0.76	0.92

Table 5.11 Correlation matrix among different parameters of bottom nonmonsoon

	Temp	pH	DO	COD	SOC	Sand	Silt	Clay	DMS	PMS	SMS	DPS	PPS
pH	0.35												
DO	-0.48	-0.81											
COD	0.65	0.92	-0.86										
SOC	-0.13	0.25	-0.51	0.12									
Sand	-0.53	0.25	0.21	-0.07	-0.03								
Silt	0.51	-0.28	-0.18	0.04	0.01	-1.00							
Clay	0.67	0.44	-0.81	0.63	0.36	-0.66	0.63						
DMS	0.69	0.43	-0.81	0.66	0.40	-0.70	0.68	0.90					
PMS	0.69	0.43	-0.81	0.66	0.40	-0.70	0.68	0.90	1.00				
SMS	0.47	0.50	-0.83	0.62	0.56	-0.54	0.51	0.81	0.87	0.87			
DPS	0.70	0.36	-0.78	0.59	0.45	-0.72	0.69	0.94	0.98	0.98	0.83		
PPS	0.19	0.54	-0.85	0.53	0.75	-0.37	0.34	0.76	0.75	0.75	0.92	0.74	
SPS	0.28	0.45	-0.78	0.50	0.57	-0.55	0.52	0.85	0.78	0.78	0.92	0.78	0.96

In surface, during nonmonsoon (Table 5.10), dissolved monosaccharides as well as polysaccharides displayed significant positive correlation with temperature. pH also showed a direct correlation with all the carbohydrate forms in the three phases. COD of the water column showed a direct relation with all the carbohydrate forms in the three phases. While examining the influence of textural characteristics in carbohydrate distribution, in nonmonsoon, sand displayed significant negative correlation with carbohydrate. On the other hand, clay content showed a positive

correlation with all the carbohydrate forms studied here. The labile as well as refractory organic constituents showed significant positive correlation among themselves. For example, dissolved proteins displayed high positive correlation with both DMS and DPS in all the three phases. Sedimentary proteins also showed highly significant positive correlation with mono and polysaccharides in the dissolved, particulate and sedimentary phases. The carbohydrate fractions also displayed strong positive correlations among themselves.

For the bottom samples, in nonmonsoon (Table 5.11), dissolved as well as particulate monosaccharides and polysaccharides displayed good positive correlation with temperature. All the carbohydrate forms were inversely related to the DO of water samples, the significant ones being DMS and DO (r= -0.895), PMS and DO (r = -0.731), DPS and DO (r = -0.848), PPS and DO (r = -0.732) and SPS and DO (r = -0.616). SMS and SPS were inversely related to sand fraction of sediment texture (r = -0.693 and -0.769 respectively) whereas they showed positive correlation with silt (r = 0.728 and 0.769 respectively). Here also, the organic fractions studied displayed significant positive correlations among themselves. Dissolved, particulate as well as sedimentary proteins displayed significant positive correlation with mono and polysaccharides in the three phases (Figures 5.29, 5.30)

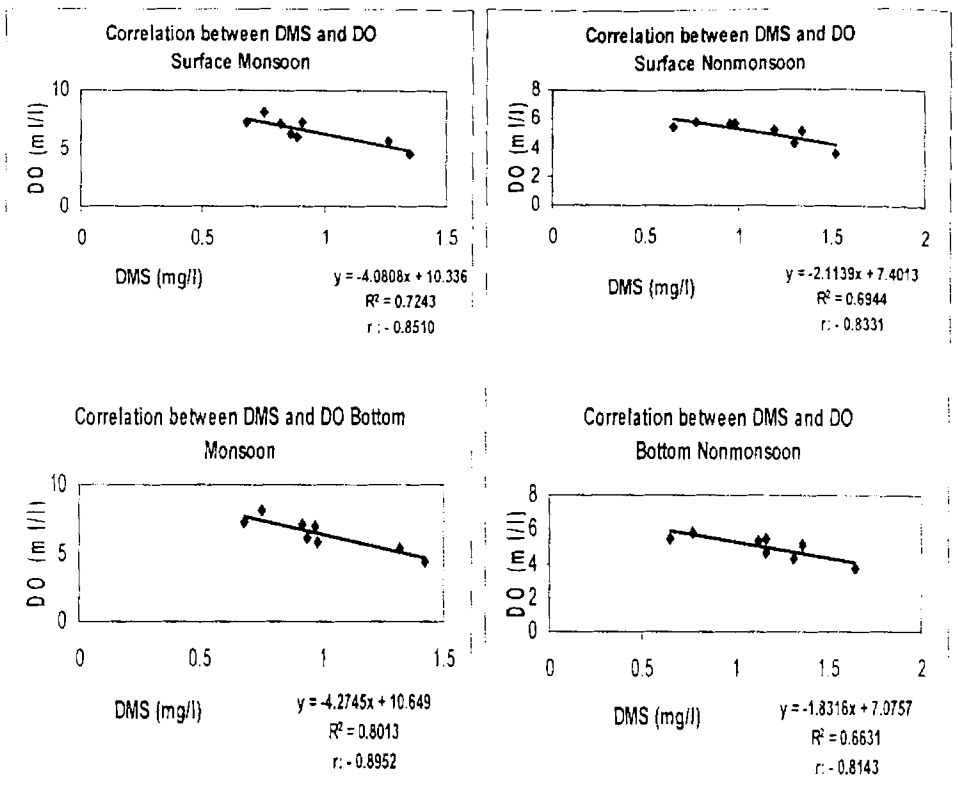

Figure 5.29 Correlation of dissolved monosaccharide with DO.

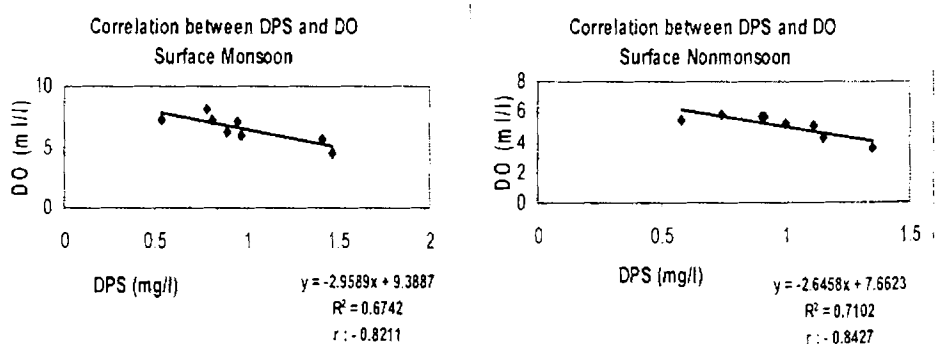

Figure 5.30 Correlation of dissolved polysaccharide with DO.

Protein/Carbohydrate ratio

In the dissolved phase(Table 5.12), both in monsoon and nonmonsoon, protein/carbohydrate ratios were less than one for surface as well as bottom stations. In surface, highest ratio was at station 1 for both seasons. In bottom, station 1 recorded the highest ratio in monsoon whereas station 8 recorded the highest in nonmonsoon. In the particulate phase(Table 5.12), station 2 recorded the highest, and station 3 the lowest in monsoon. In nonmonsoon also, highest observed concentration was at station 2. In this season station 8 recorded the lowest protein/carbohydrate ratio. In bottom samples, highest monsoonal protein/carbohydrate ratio was at station 4 and lowest at station 6.

Table 5.12 Protein: Carbohydrate ratios in dissolved and particulate matter

	Water - Protein:Carbohydrate		Particulate matter - Protein:Carbohydrate	
Stations	Monsoon	Nonmonsoon	Monsoon	Nonmonsoon
S1	0.738	0.653	0.143	0.143
S2	0.339	0.577	0.556	0.400
S3	0.229	0.444	0.114	0.154
S4	0.345	0.514	0.200	0.172
S5	0.425	0.494	0.233	0.190
S6	0.360	0.492	0.154	0.160
S7	0.397	0.502	0.294	0.182
S8	0.486	0.540	0.146	0.115
B1	0.565	0.606	0.158	0.123
B4	0.384	0.484	0.667	0.152
B5	0.459	0.425	0.211	0.160
B6	0.327	0.441	0.115	0.185
B7	0.393	0.500	0.139	0.182
B8	0.537	0.622	0.143	0.116

Table 5.13 Protein: Carbohydrate ratios in sediments

	Sediment-Protein:Carbohydrate	
Stations	Monsoon	Nonmonsoon
S1	2.372	2.287
S2	1.694	1.095
S3	1.024	0.922
S4	1.653	2.447
S5	0.993	0.994
S6	1.241	1.637
S7	1.522	1.978
S8	2.018	1.844

In the sedimentary phase (Table 5.13), both in monsoon and nonmonsoon, protein/carbohydrate ratio was greater than one at all stations except at station 5 (for both seasons) and at station 3 (only in nonmonsoon). Protein/carbohydrate ratio greater than two was recorded at station 1 (in both monsoon and nonmonsoon), station 4 (nonmonsoon) and station 8 (in monsoon). In nonmonson, station 4 recorded the highest protein/carbohydrate ratio (2.447) and station 3 the lowest (0.922) ratio. The highest observed ratio in monsoon was at station 1 (2.372). Station 5 recorded the lowest ratio in monsoon.

In the dissolved as well as particulate phases, protein/carbohydrate ratios were less than one. Such dominance of carbohydrates versus proteins is a typical feature of detrital-heterotrophic environments (Danovaro, 1996). Since proteins are mobilized more rapidly than carbohydrates, low value of protein/carbohydrate ratio indicate the presence of aged (i.e.not freshly produced) organic detritus. In the sedimentary phase, protein/carbohydrate ratios were greater than one both in monsoon and nonmonsoon seasons.

Statistical Approach

Abbreviations

NS	:	Not Significant
dof		degrees of freedom
MSS		Mean Sum of Squares
(P<0.05)		calculated F is significant at 5% level
(P<0. 01)		calculated F is significant at 1% level
(P<0.001)		calculated F is significant at 0.1% level
MDS		Multidimensional scaling

Table 5.14 Distribution of dissolved monosaccharide

station	mean	std	CV%	station	Mean	std	CV%
S1	1.007	0.338	33.60	S5	1.044	0.238	22.77
B1	1.032	0.262	25.43	B5	1.111	0.226	20.30
S2	0.656	0.143	21.75	S6	0.905	0.182	20.125
B2	0.656	0.143	21.75	B6	1.000	0.142	14.159
S3	0.759	0.129	16.96	S7	1.280	0.129	10.045
B3	0.759	0.129	16.96	B7	1.313	0.164	12.46
S4	0.870	0.178	20.42	S8	1.403	0.154	11.00
B4	1.002	0.267	26.68	B8	1.497	0.233	15.57

Distribution of dissolved monosaccharides (Table 5.14) averaged over seasons showed an increasing trend in the element both at surface and bottom from station 1 to station 8 ranging between 0.652 (station 2) to 1.403 (station 8) at surface and between 0.652 (B2) to 1.497 (B8) at

bottom. Seasonal variations decreased from station 1 to station 8 at surface and bottom.

3 way ANOVA applied (Table 5.15) to compare between seasons, seasons and surface and bottom showed station wise ($F_{(7,35)}$=129.94, $p<0.001$) surface and bottom ($F_{(1,35)}$=11.81, $p<0.001$) and season wise ($F_{(5,35)}$=87.43, $p<0.001$) with high station-season interaction. ($F_{(35,35)}$=3.9359, $p<0.05$) as indicated by high values at station 1,7 & 8 during January to May and September to November and lower values observed during July at stations S3 and B3. Dendrogram drawn showed two clusters of seasons: 1. July and September stations with comparatively lower values and 2. March, May and November, the seasons with high values (Figures 5.31 a and b).

Table 5.15 3 way ANOVA for comparing dissolved monosaccharide with respect to station, surface and bottom and seasons

Source	SS	dof	MSS	F ratio	Remarks
Stations (A)	5.7231	7	0.081759	129.9391	(P<0.001)
Sur/Bot (B)	0.07431	1	0.07431	11.8102	(P<0.001)
Seasons (C)	2.75065	5	0.55013	87.4322	(P<0.001)
ABinteraction		7	0.0070823	1.1256	NS
BCinteraction		5	0.003013	0.4787	NS
ACinteraction		35	0.02476	3.9359	(P<0.05)
Error	0.22022	35	0.0062921		
Total	109.254	95			

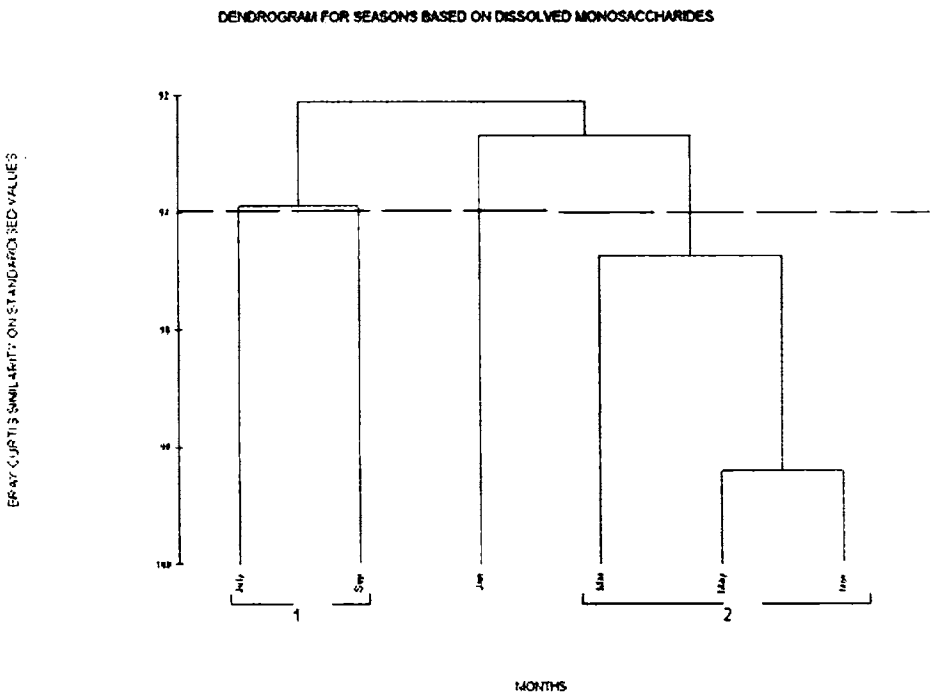

Figure 5.31 a. Dendrogram for seasons based on dissolved monosaccharide in water

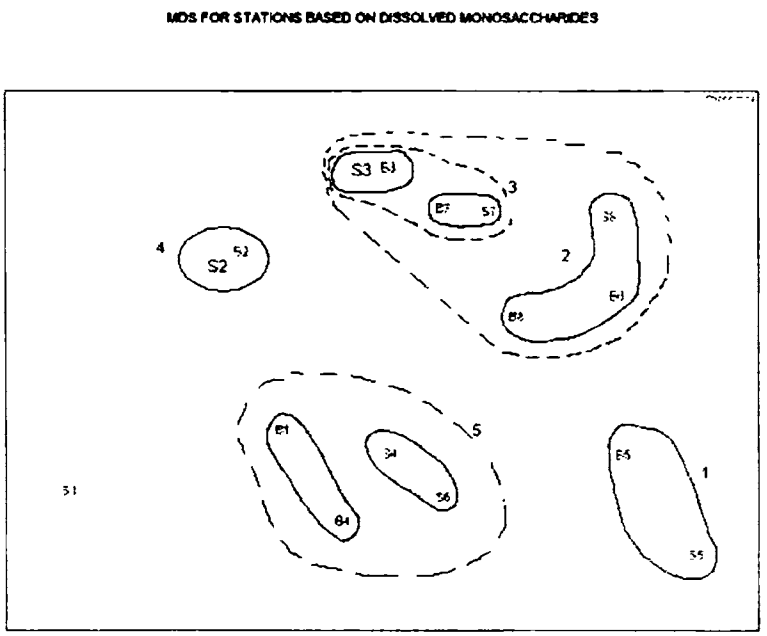

Figure 5.31 b. MDS for stations based on dissolved monosaccharide in water

Trellis diagram drawn to determine significant station wise differences showed high differences between station 2 and 3 with stations 5,6,7 and 8 and station 6 with station 7 and 8, both at surface and bottom (Table 5.16) ($t(10) \geq 3.169$, $p<0.01$).

Table 5.16: Trellis diagram for students t test to compare between stations based on dissolved monosaccharide (• Not significant; • Significant at 10% level; • Significant at 5% level; • Significant at 1% level)

	S1	B1	S2	B2	S3	B3	S4	B4	S5	B5	S6	B6	S7	B7	S8	B8
S1		0.13	2.14	2.14	1.53	1.53	0.8	0.02	0.2	0.57	0.59	0.04	1.69	1.83	2.39	2.67
B1	•		2.81	2.81	2.08	2.08	1.14	0.18	0.08	0.51	0.89	0.24	1.9	2.04	2.73	2.96
S2	•	•		0	1.2	1.2	2.1	2.55	3.13	3.81	2.41	3.82	7.27	6.77	7.95	6.88
B2	•	•	•		1.2	1.2	2.1	2.55	3.13	3.81	2.41	3.82	7.27	6.77	7.95	6.88
S3	•	•	•	•		0	1.13	1.83	2.35	3.03	1.46	2.81	6.4	5.95	7.17	6.20
B3	•	•	•	•	•		1.13	1.83	2.35	3.03	1.46	2.81	6.4	5.95	7.17	6.20
S4	•	•	•	•	•	•		0.92	1.31	1.87	0.31	1.28	4.18	4.1	5.07	4.78
B4	•	•	•	•	•	•	•		0.26	0.69	0.67	0.02	2.1	2.22	2.91	3.12
S5	•	•	•	•	•	•	•	•		0.46	1.04	0.36	1.95	2.09	2.84	3.04
B5	•	•	•	•	•	•	•	•	•		1.59	0.93	1.46	1.63	2.39	2.66
S6	•	•	•	•	•	•	•	•	•	•		0.92	3.76	3.73	4.67	4.47
B6	•	•	•	•	•	•	•	•	•	•	•		3.28	3.24	4.31	4.08
S7	•	•	•	•	•	•	•	•	•	•	•	•		0.36	1.37	1.82
B7	•	•	•	•	•	•	•	•	•	•	•	•	•		0.89	1.44
S8	•	•	•	•	•	•	•	•	•	•	•	•	•	•		0.75
B8	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	

Table 5.17 Distribution of particulate monosaccharide

station	mean	std	CV%	station	Mean	std	CV%
S1	0.148	0.053	36.15	S5	0.095	0.034	36.05
B1	0.188	0.070	37.19	B5	0.109	0.036	32.65
S2	.004	0.002	49.80	S6	0.116	0.0321	17.99
B2	0.004	0.002	49.80	B6	0.136	0.011	17.99
S3	0.065	0.027	41.85	S7	0.151	0.026	17.58
B3	0.065	0.027	41.85	B7	0.167	0.054	32.37
S4	0.101	0.057	56.05	S8	0.213	0.095	44.81
B4	0.061	0.061	47.95	B8	0.250	0.108	43.21

Distribution of particulate monosaccharides averaged over seasons showed high values of monosaccharides at surface was at station

8(0.213) and least values at station 2(0.004). An increasing trend from station 2 to station 8 is observed in its distribution with the same pattern for seasonal variation (17.58≤CV% ≤56.05%). At bottom same trend as observed at surface was obtained with maximum (0.0250) at station 8 and least value at station 2 (0.004). Seasonal variation also showed a similarity with surface values (17.99≤CV%≤49.80%) (Table 5.17).

3 way ANOVA applied to compare stations, seasons and surface and bottom based on monosccharide distribution showed significant station wise ($F_{(7,35)}$=198.54, $p<0.001$) season wise ($F_{(5,35)}$=105.29, $p<0.001$) and surface and bottom difference ($F_{(1,35)}$=31.65, $p<0.001$) together with station- surface/bottom interaction ($F_{(7,35)}$=2.412, $p<0.05$) and station- season interaction ($F_{(35,35)}$=10.138, $p<0.001$) as indicated by higher values at bottoms of station 4 to 8 and higher values during November monsoon seasons at stations 1 to 3 (Table 5.18).

Table 5.18 3 way ANOVA for comparing between elements, dissolved (DM) and particulate (PM) monosaccharides at surface, between station and between seasons

Source	SS	dof	MSS	F ratio	Remarks
Elements DM and PM (A)	18.5456	1	18.5456	1688.92	(P<0.001)
Stations (B)	2.0167	7	0.2881	32.9199	(P<0.001)
Seasons (C)	0.8520	5	0.1704	19.4719	(P<0.001)
AB interaction		7	0.1162	13.2768	(P<0.001)
BC interaction		35	0.01034	1.1818	NS
AC interaction		5	0.09330	10.6607	(P<0.001)
Error	0.3063	35	0.008751		
Total	5250.75	95			

Dendrogram drawn (Figures 32 a and b) to group the seasons has divided the seasons into 3 clusters as 1. July, September- the months with lower values 2. May and March- the periods with modulate values and 3. November, January- the periods with higher values at 92% level of similarity (Figure 5.32). stations were grouped into 3 clusters

1. B4, S5, B5

2. B6,S6,S7 and

3. S2, B2, S3, B3, S8, B8, B1, S1, B7

The grouping of the bottom station with surface and bottom of other stations clarifies the difference between surface and bottom values as well as the station-surface/bottom interaction.

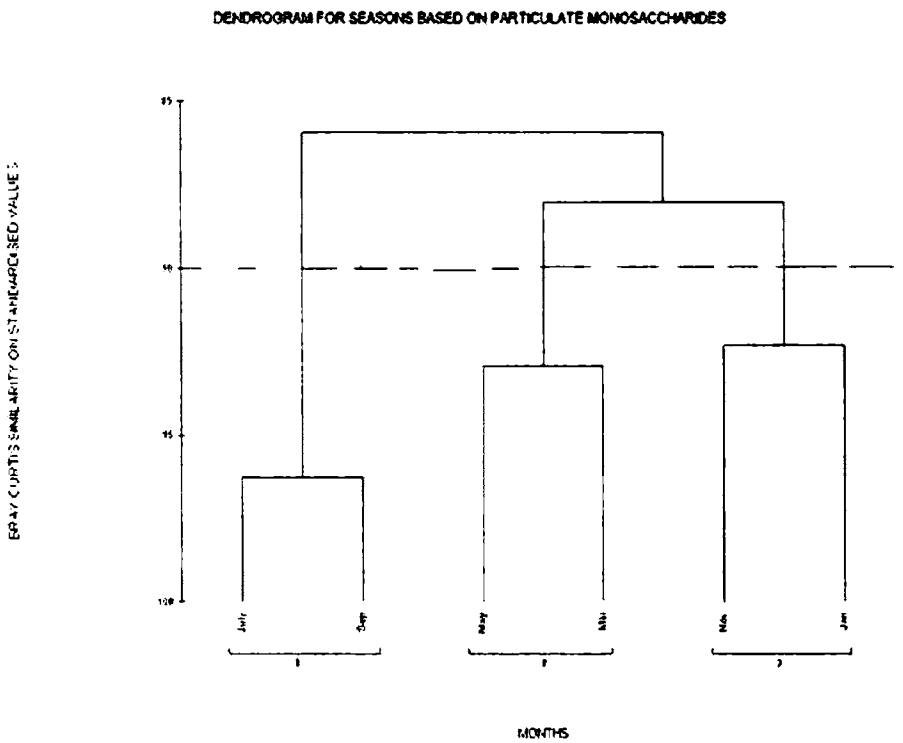

Figure 5.32 a. Dendrogram for seasons based on particulate monosaccharide in water

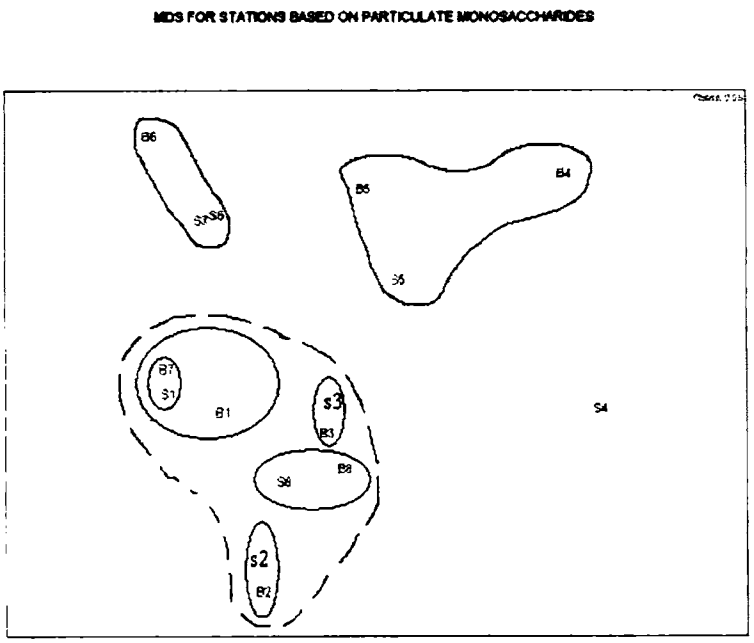

Figure 5.32 b. MDS for stations based on particulate monosaccharide in water

The Trellis diagram shows the significance of the difference between stations. Station 1 is significantly different from station 2 and 3 both at surface and bottom ($t(10) \geq 3.169$, $P<0.01$). Similarly station 2 is different from other stations ($t(10)>3.169< p<0.01$). So also station 3 from that of station 6- station 8 ($t(10) \geq 3.169$, $p<0.01$). Difference between station 6 to 8 is only at a lower level ($t(10) \geq 2.228$, $p<0.05$) (Table 5.19).

Table 5.19: Trellis diagram for students t test to compare between stations based on particulate monosaccharide (• Not significant; • Significant at 10% level; • Significant at 5% level; • Significant at 1% level)

	S1	B1	S2	B2	S3	B3	S4	B4	S5	B5	S6	B6	S7	B7	S8	B8
S1		0.13	2.14	2.14	1.53	1.53	0.8	0.02	0.2	0.57	0.59	0.04	1.69	1.83	2.39	2.67
B1	•		2.81	2.81	2.08	2.08	1.14	0.18	0.08	0.51	0.89	0.24	1.9	2.04	2.73	2.96
S2	•	•		0	1.2	1.2	2.1	2.55	3.13	3.81	2.41	3.82	7.27	6.77	7.95	6.88
B2	•	•	•		1.2	1.2	2.1	2.55	3.13	3.81	2.41	3.82	7.27	6.77	7.95	6.88
S3	•	•	•	•		0	1.13	1.83	2.35	3.03	1.46	2.81	6.4	5.95	7.17	6.20
B3	•	•	•	•	•		1.13	1.83	2.35	3.03	1.46	2.81	6.4	5.95	7.17	6.20
S4	•	•	•	•	•	•		0.92	1.31	1.87	0.31	1.28	4.18	4.1	5.07	4.78
B4	•	•	•	•	•	•	•		0.26	0.69	0.67	0.02	2.1	2.22	2.91	3.12
S5	•	•	•	•	•	•	•	•		0.46	1.04	0.36	1.95	2.09	2.84	3.04
B5	•	•	•	•	•	•	•	•	•		1.59	0.93	1.46	1.63	2.39	2.66
S6	•	•	•	•	•	•	•	•	•	•		0.92	3.76	3.73	4.67	4.47
B6	•	•	•	•	•	•	•	•	•	•	•		3.28	3.24	4.31	4.08
S7	•	•	•	•	•	•	•	•	•	•	•	•		0.36	1.37	1.82
B7	•	•	•	•	•	•	•	•	•	•	•	•	•		0.89	1.44
S8	•	•	•	•	•	•	•	•	•	•	•	•	•	•		0.75
B8	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	

Table 5.20 Distribution of dissolved polysaccharide

station	mean	std	CV%	station	Mean	std	CV%
S1	0.879	0.219	24.86	S5	1.022	0.168	16.49
B1	0.950	0.156	16.36	B5	1.075	0.199	18.53
S2	0.544	0.242	44.45	S6	0.902	0.147	16.30
B2	0.544	0.242	44.45	B6	1.089	0.23	25.04
S3	0.770	0.191	24.84	S7	1.329	0.270	20.30
B3	0.770	0.191	24.83	B7	1.407	0.279	19.86
S4	0.936	0.184	19.67	S8	1.432	0.181	12.63
B4	0.982	0.137	13.99	B8	1.153	0148	9.67

Distribution of dissolved polysaccharides averaged over seasons was least at surface station 2 (0.544), maximum at station 8 (1.432) at surface. Seasonal variation was maximum at station 2 (44.45%) and

least at station 7 (12.63%). Bottom values were maximum at station 8 (1.533) and minimum at station 2 (0.544) with corresponding values for seasonal variation as station 2 (44.45%) and station 8 (9.67%) respectively (Table 5.20).

Table 5.21 3 way ANOVA for comparing dissolved polysaccharides with respect to station, surface and bottom and seasons

Source	SS	dof	MSS	F ratio	Remarks
Stations (A)	7.6658	7	1.09512	106.6391	(P<0.001)
Sur/Bot (B)	0.108269	1	0.108269	10.5429	(P<0.001)
Seasons (C)	0.99528	5	0.19906	19.3835	(P<0.001)
AB interaction		7	1.0018577	1.0573	NS
BC interaction		5	0.0093202	0.9076	NS
AC interaction		35	0.077314	7.5286	(P<0.001)
Error	0.35943	35	0.0102694		
Total	109.952	95			

3 way ANOVA carried out (Table 5.21) to study the station wise, season wise and surface/bottom comparison showed very high station wise ($F_{(7,35)}$=106.64, p<0.001), surface/bottom difference ($F_{(1,35)}$=10.56, p<0.001) and seasonal difference ($F_{(5,35)}$=19.38, p<0.001) with low station-surface/bottom interaction ($F_{(7,35)}$=1.06, p>0.05) and station season interaction ($F_{(35,35)}$=7.53, p<0.001) as indicated by the high dissolved polysaccharides during May at almost all stations and lowest values during July and September only one cluster 1. September, March, November and January are grouped with July and May independent of this cluster, at 90% similarity level (Figures 5.33 a and b). Three clusters of stations were obtained

cluster 1. S2, B2

cluster 2. B5, S1, B1 and

cluster 3. B7, S5, S6, S4, B4, B6, S3, B3, S7, S8, B8)

showing the indifference of station 2 from other stations which has the maximum seasonal variation, both at surface and bottom (Figures 5.33 a and b).

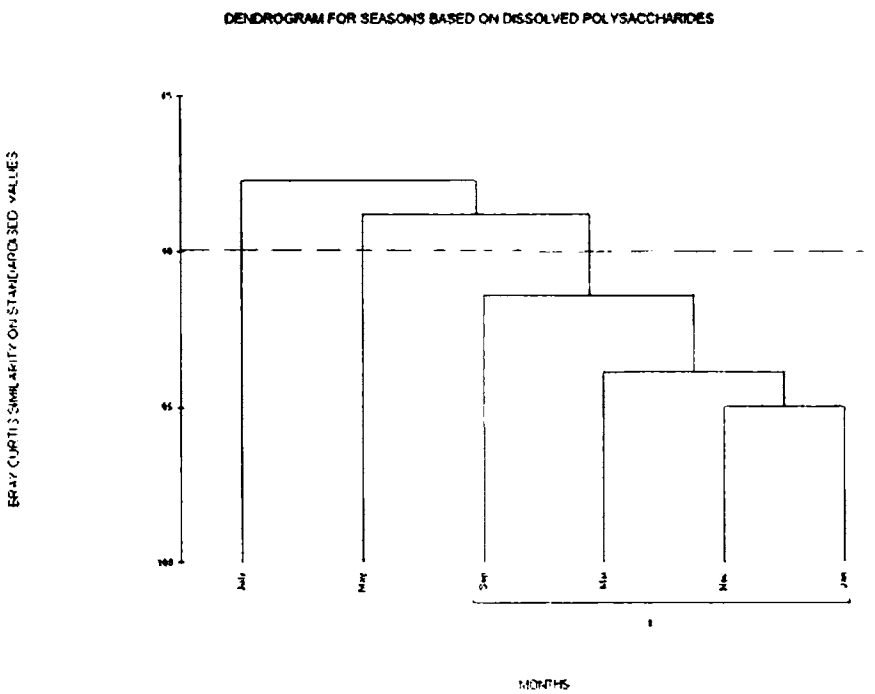

Figure 5.33 a. Dendrogram for seasons based on dissolved polysaccharide in water

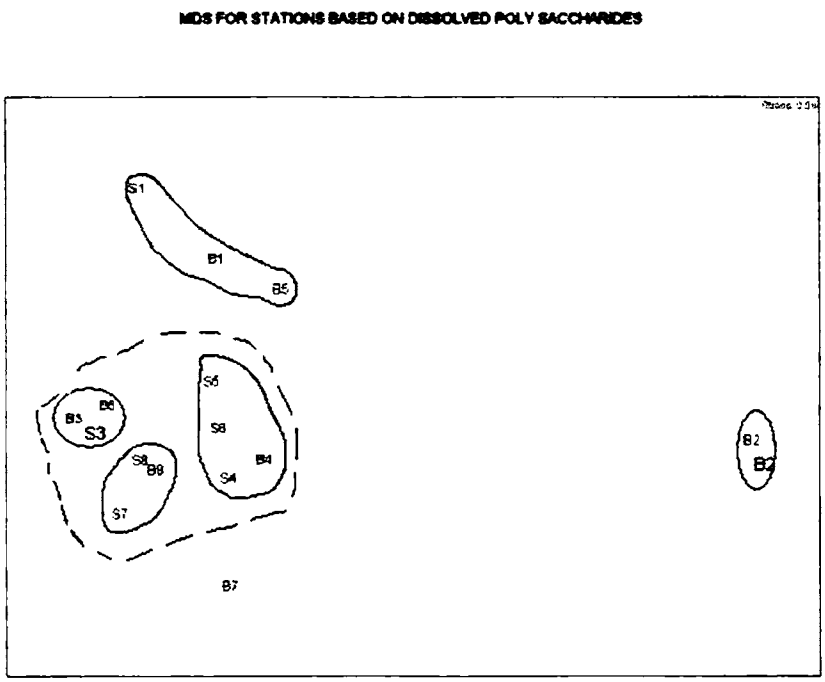

Figure 5.33 b. MDS for stations based on dissolved polysaccharide in water

Trellis diagram drawn (Table 5.22) to show the station wise difference, indicated the high difference between station 1 and station 2 ($t(10)>2.228$, $p<0.05$) and difference between stations 1 to 6 from station 7 and 8 ($t(10)>3.169$, $p<0.01$).

Table 5.22: Trellis diagram for students t test to compare between stations based on dissolved polysaccharide (• Not significant; • Significant at 10% level; • Significant at 5% level; • Significant at 1% level)

	S1	B1	S2	B2	S3	B3	S4	B4	S5	B5	S6	B6	S7	B7	S8	B8
S1		0.59	2.3	2.3	0.84	0.84	0.44	0.89	1.16	1.48	0.19	1.34	2.89	3.32	4.35	5.54
B1	•		3.16	3.16	1.63	1.63	0.13	0.34	0.7	1.11	0.51	0.99	2.72	3.19	4.51	6.07
S2	•	•		0	1.64	1.64	2.88	3.52	3.63	3.79	2.83	3.34	4.84	5.22	6.57	7.79
B2	•	•	•		1.64	1.64	2.88	3.52	3.63	3.79	2.83	3.34	4.84	5.22	6.57	7.79
S3	•	•	•	•		0	1.4	2.01	2.21	2.47	1.22	2.14	3.78	4.20	5.62	7.05
B3	•	•	•	•	•		1.4	2.01	2.21	2.47	1.22	2.14	3.78	4.20	5.62	7.05
S4	•	•	•	•	•	•		0.45	0.77	1.15	0.33	1.04	2.69	3.15	4.29	5.65
B4	•	•	•	•	•	•	•		0.41	0.86	0.89	0.78	2.56	3.05	4.42	6.10
S5	•	•	•	•	•	•	•	•		0.46	1.2	0.47	2.16	2.64	3.71	5.10
B5	•	•	•	•	•	•	•	•	•		1.57	0.09	1.69	2.16	2.96	4.12
S6	•	•	•	•	•	•	•	•	•	•		1.35	3.19	3.57	5.08	6.76
B6	•	•	•	•	•	•	•	•	•	•	•		1.4	1.82	2.34	3.20
S7	•	•	•	•	•	•	•	•	•	•	•	•		0.45	0.71	1.49
B7	•	•	•	•	•	•	•	•	•	•	•	•	•		0.17	0.90
S8	•	•	•	•	•	•	•	•	•	•	•	•	•	•		0.97
B8	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	

Table 5.23 Distribution of particulate polysaccharide

station	mean	std	CV%	station	Mean	std	CV%
S1	0.238	0.097	40.686	S5	0.089	0.042	46.70
B1	0.262	0.103	39.38	B5	0.104	0.036	34.05
S2	0.017	0.016	96.97	S6	0.129	0.018	13.71
B2	0.017	0.016	96.97	B6	0.137	0.018	13.27
S3	0.040	0.026	64.63	S7	0.174	0.053	30.50
B3	0.040	0.026	64.63	B7	0.189	0.062	32.77
S4	0.129	0.028	21.90	S8	0.245	0.104	42.58
B4	0.152	0.024	16.05	B8	0.319	0.128	40.17

Distribution of particulate polysaccharides averaged over seasons showed a maximum value of 0.245 at station 8 and a maximum value of

0.017 at station 2 at surface. Seasonal variation ranged between 13.71% at station 6 and 96.37% at station 2. Bottom values ranged between 0.016 (station2) and 0.319 (station 6) and 96.37% (station 2) a steady increase from station 2 to station 8 was observed in particulate polysaccharides values (Table 5.23).

3 way ANOVA applied to compare between stations, seasons and surface and bottom showed significant difference between stations ($F_{(7,35)}$ =328.84, $p<0.001$) between surface and bottom ($F_{(1,35)}$=30.055, $p<0.001$) and between seasons ($F_{(5,35)}$=127.724, $p<0.001$) with high station-surface/bottom interaction ($F_{(7,35)}$=5.27, $p<0.01$) and station-season interaction (($F_{(35,35)}$=13.46, $p<0.001$) as indicated by high values of polysaccharides during November, January and March and during July and September lower values at all stations (Table 5.24)

Table 5.24 3 way ANOVA for comparing particulate polysaccharide with respect to station, surface and bottom and seasons

Source	SS	dof	MSS	F ratio	Remarks
Stations (A)	0.732197	7	0.10460	328.8378	0.1%
Sur/Bot (B)	0.0095601	1	0.009560	3.055	0.1%
Seasons (C)	0.203139	5	0.040628	127.724	0.1%
AB interaction		7	0.00167714	5.2725	1.0%
BC interaction		5	0.0003432	1.0789	NS
AC interaction		35	0.0042799	13.4550	0.1%
Error	0.0111332	35	0.000318091		
Total	3.07553	95			

Dendrogram drawn to group the seasons showed two clusters 1. march, November and January, the months with higher values and 2. July and

September, the months with lower values of polysaccharides (Figures 5.34 a and b).

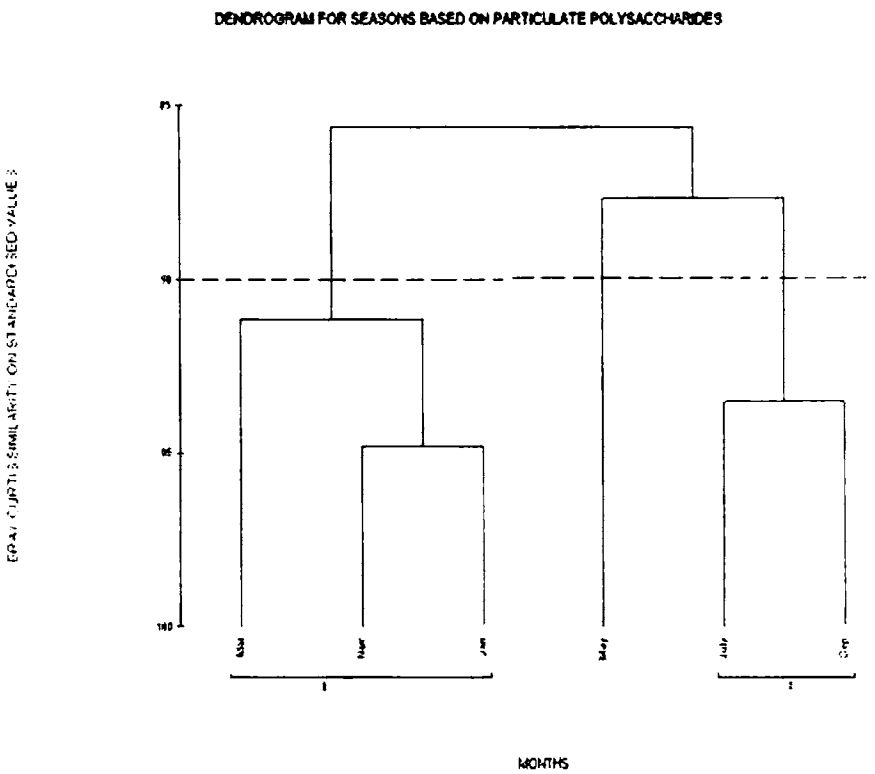

Figure 5.34 a. Dendrogram for seasons based on particulate polysaccharide in water

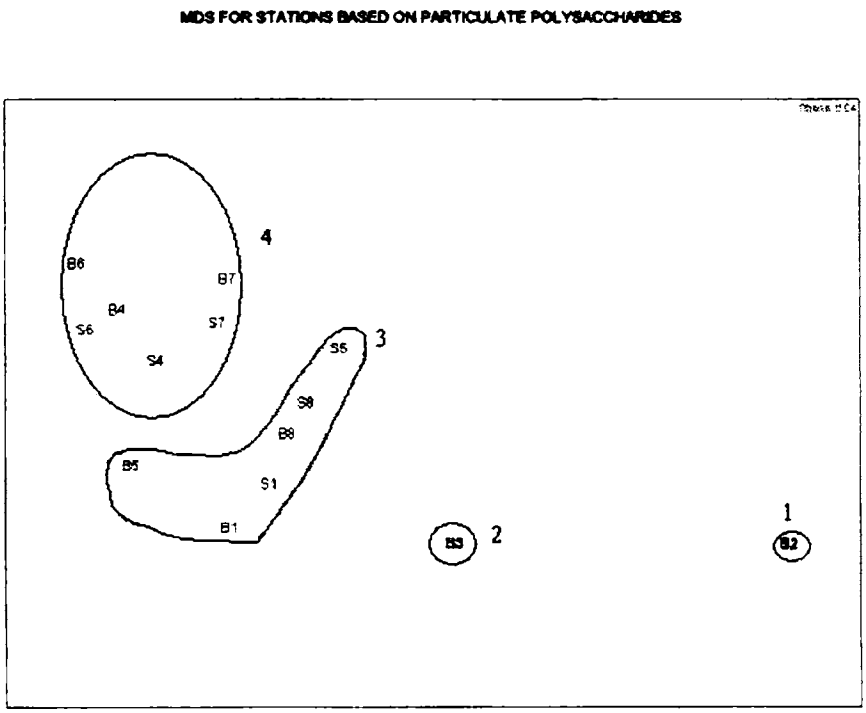

Figure 5.34 b. MDS for stations based on particulate polysaccharide in water

Trellis diagram showed significant difference between station 1and station 3-6 ($t(10) \geq 2.228$, $p<0.05$) and stations 2 and 3 with stations 4 to 8 ($t(10) \geq 3.169$,$P<0.001$). Difference observed between station 6 and station 7and station 8 are also not negligible ($t(10) \geq 1.812$, $p<0.10$) (Table 5.25).

Table 5.25: Trellis diagram for students t test to compare between stations based on particulate polysaccharide (• Not significant; • Significant at 10% level; • Significant at 5% level; • Significant at 1% level)

	S1	B1	S2	B2	S3	B3	S4	B4	S5	B5	S6	B6	S7	B7	S8	B8
S1		0.37	5.04	5.04	4.41	4.41	2.41	1.92	3.16	2.9	2.48	2.29	1.3	0.95	0.11	1.13
B1	•		5.25	5.25	4.66	4.66	2.77	2.31	3.47	3.22	2.84	2.66	1.69	1.34	0.25	0.78
S2	•	•		0	1.71	1.71	7.71	10.3	3.62	5.01	10.4	11	6.33	6.02	4.83	5.23
B2	•	•	•		1.71	1.71	7.71	10.3	3.62	5.01	10.4	11	6.33	6.02	4.83	5.23
S3	•	•	•	•		0	5.18	7.01	2.22	3.25	6.29	6.82	5.06	4.95	4.26	4.77
B3	•	•	•	•	•		5.18	7.01	2.22	3.25	6.29	6.82	5.06	4.95	4.26	4.77
S4	•	•	•	•	•	•		1.36	1.79	1.23	0.04	0.52	1.66	1.97	2.39	3.23
B4	•	•	•	•	•	•	•		2.93	2.48	1.74	1.1	0.83	1.25	1.94	2.86
S5	•	•	•	•	•	•	•	•		0.63	1.96	2.37	2.82	3	3.1	3.82
B5	•	•	•	•	•	•	•	•	•		1.37	1.84	2.44	2.66	2.85	0.36
S6	•	•	•	•	•	•	•	•	•	•		0.75	1.81	2.1	2.46	3.29
B6	•	•	•	•	•	•	•	•	•	•	•		1.47	1.8	2.28	3.14
S7	•	•	•	•	•	•	•	•	•	•	•	•		0.42	1.36	2.34
B7	•	•	•	•	•	•	•	•	•	•	•	•	•		1.03	2.04
S8	•	•	•	•	•	•	•	•	•	•	•	•	•	•		1.00
B8	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	

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CHAPTER VI

TANNIN AND LIGNIN: PHASES-COUPLED SPATIOTEMPORAL VARIABILITY

INTRODUCTION

Organic matter is composed of labile and refractory compounds whose relative importance might have profound implications for organic matter diagenisis and turn over (Rowe and Deming, 1985; Fabiano et al., 1995; Cauwet et al., 2002). Conversely, the refractory fraction of organic matter is largely composed of complex macromolecules (like humic and fulvic acids and complex polymers) which are degraded slowly, subjected to burial and thus, lost temporarily for the benthic food webs (Fabiano and Danovaro, 1994). This residual fraction of the organic carbon is that part of which is not revealed by lipids, proteins and carbohydrates and consists of complex molecules like tannin and lignin, humic substances etc.

Suspended particulate matter is one of the main forms in which various materials, including nutrients, hydrophobic organic micropollutants, and heavy metals are transferred from land to marine environments (Hong et al., 1999; Turner and Millward, 2002; Che et al., 2003). Occupying a position between the land and marine environments, estuaries are often a nexus for material exchange and biochemical processes. Increasing amount of nutrients and organic pollutants, supplied by rivers in the form of suspended particulate matter can affect coastal environments adversely. Understanding the nature and behaviour of suspended particulate matter in

estuarine systems, therefore, allows for better estimates of the transport of terrigenous and anthrpogenic materials to marine environments.

More the suspended solids, more the tannin and lignin formed in the dissolved phase. Concentrations of dissolved organic nutrients are influenced by local plant production, decomposition and sorption equilibrium with particulate matter and sediments. Dissolved organic matter concentrations also depend on flushing of organic matter during rain events. Dissolved organic carbon is one of the largest pools of reactive carbon in the oceans (Hedges, et al., 1997). A better understanding of oceanic dissolved organic carbon dynamics as well as biogeochemical processes with in and DOC transport through estuaries and coastal seas is essential to better constrain global carbon models (Bauer and Druffel, 1998; Cauwet et al., 2002). Through high discharge rates and material loading, large rivers and their plumes contribute substantial dissolved and particulate materials to continental margins and subsequently to the oceans Meybeck, 1982; Dagg et al., 2004). Many studies have revealed the strong affinity of hydrophobic contaminants for soil or sediment particulate organic matter (Karickhoff, 1981; Luthy et al., 1997; Chiou et al., 2000) and for dissolved organic matter (Burkhard, 2000; Kopinke et al., 2001). In natural waters, like estuaries, contaminants such as polyaromatic hydrocarbons may therefore be free, bound to DOM, or sorbed to suspended particulate matter and sediments.

Chemical biomarkers, such as lignin phenols, amino acids, sugars and fatty acids, offer another approach for indentifying the sources and digenetic pathways of dissolved organic matter (Hedges and Ertel, 1982; Dauwe and

Middelburg, 1998; Amon and Benner, 2003). In particular, lignin is a macromolecule that has been widely used to trace and quantify land-derived refractory organic matter in marine (Hedges and Mann, 1979) and river environments (Bianchi et al., 2004). However, recent studies have shown that lignin composition is also controlled by hydrologic and soil mineral sorption process in drainage basin (Kaiser et al., 2001; Kaiser et al., 2004; Dalzell et al., 2005; Houel et al., 2006).

Chemical tracers, such as lignin-derived phenols and stable carbon isotopes, have been applied in coastal environments to identify source and fate of DOM and particulate organic matter. Lignin is a unique tracer for vascular plant material, even suitable to distinguish vegetation types, e.g., between woody angiosperms, gymnosperms or nonwoody vascular plants (Hedges and Mann, 1979). Phenolic compounds especially lignin are unique constituents of vascular plants that is typically found to be resistant to microbial degradation (Benner et al., 1986). Therefore, lignin can be useful as biomarkers for vascular plant derived organic matter in heterogenous samples such as sediments, dissolved organic matter etc. (Meyers-Schulte and Hedges, 1986; Hamilton and Hedges, 1988). Phenolic compounds, including tannins, are a significant component of plant secondary metabolites. Tannins occur in plant leaves, roots, wood, bark, fruits and buds (Kraus et al., 2003), and are estimated to be the fourth most abundant compound types produced by vascular plant tissue after cellulose, hemicellulose and lignin (Hernes and Hedges, 2000). The nutritional quality of dissolved organic matter declines with the increase in lignin and cellulose contents. The seasonal changes in the concentrations of natural phenolic material in aquatic ecosystem may be driven by climatic patterns

that control hydrologic transport of detrital organic matter from water shed. If climate patterns shift significantly because of global scale changes, the associated changes in concentration of natural phenolic material could seriously affect the functional relationships of the aquatic ecosystems.

Particulate matter adsorbs various organic contaminants such as tannin and lignin, and carries these particle reactive contaminants to the ocean. Particulate matter discharged from rivers is transported through the coastal water column and finally deposited in coastal and open ocean sediments. Particle reactive tannin and lignin undergo various chemical and biological transformations in the water column before their burial in the bottom sediments, where they are preserved under relatively stable conditions.

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 sediments. Organic matter exists in particulate and dissolved forms with in the water column. Initial input of the organic matter consists of all major classes of naturally occurring organic compounds such as carbohydrates, proteins, amino acids, 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). 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. After reaching the sediments, significant modification of organic matter takes place due to the activities of benthic organisms.

Phenolic compounds (tannin and lignin) are one of the major groups of secondary metabolites in plants. Other sources in sediments are flavonoids leached from plant debrius and those synthesized by soil micro organisms. Lignin is a main component of wood and occurs in the cell walls of all vascular plant tissue. Leaves and other herbaceous plant tissues, however often contains varying amounts of other components, such as cyclitols, tannins and the aliphatic constituents of cuticles, that can account for substantial fraction of total organic matter (Kolattukudy and Espelie, 1985). Waters in the vicinity of decaying leaves are often tea coloured due to the relatively higher concentrations of dissolved organic matter that contain tannins and other phenolic compounds (Benner et al., 1990).

It is probably because of its hetero polymeric structure of phenyl propanoid that lignin is hardly accessible to most microorganisms, building a relatively stable biopolymer. These features make lignin a unique tracer for vascular plant matter, suitable even for chemotaxonomic distinction between angiosperms, gymnosperms and nonwoody vascular plants (Hedges and Mann, 1979).

MATERIALS AND METHODS

The estimations of dissolved, particulate and sedimented tannin and lignin were performed by sodium tungstate–phospho molybdate acid method as described in Chapter II.The principle involved is the determination of a blue colour on reduction of follin-ciocalteu phenol reagent by the aromatic hydroxyl groups present in the tannin and lignin. The effects of Mg and Ca hydroxides and / or bicarbonates present in the sample were suppressed by the addition of trisodium citrate solution.

RESULTS AND DISCUSSION

Tannin and lignin in the dissolved phase (DTL)

The bimonthly values of tannin and lignin in the dissolved phase of Chalakudy river are given in Table 6.1.

Surface monsoon: In surface waters, the monsoonal trend in dissolved tannin and lignin distribution pattern was largely irregular upto station 6 (Figure 6.1). A gradual increase was observed beyond this station towards the lower end, the maximum being near to the saline stations 7 and 8. In monsoon, maximum surface concentration (1.13 mg/l) was at the estuarine station 8 and minimum (0.13 mg/l) at station 2. The observed concentration range for this particular season in surface was 0.13-1.13 mg/l.

Table 6.1 Bimonthly distribution of dissolved tannin and lignin in the surface and bottom waters of Chalakudy river

	Months	Stations							
		S1	S2	S3	S4	S5	S6	S7	S8
Surface waters	May	1.14	0.24	0.36	0.56	0.68	1.09	0.94	1.46
	July	0.53	0.04	0.03	0.32	0.38	0.68	0.68	0.95
	Sep	0.68	0.06	0.04	0.46	0.36	0.56	0.58	0.81
	Nov	1.06	0.19	0.28	0.36	0.46	0.85	0.81	1.32
	Jan	1.12	0.10	0.19	0.46	0.58	0.95	0.74	1.09
	Mar	1.42	0.32	0.51	0.68	0.81	1.39	1.29	1.54
		Stations							
		B1	B2	B3	B4	B5	B6	B7	B8
Bottom waters	May	1.14	0.24	0.36	0.53	0.74	1.12	0.92	1.15
	July	0.95	0.04	0.03	0.46	0.38	0.74	0.68	1.09
	Sep	0.94	0.06	0.04	0.51	0.41	0.57	0.61	0.74
	Nov	0.92	0.19	0.28	0.44	0.58	0.85	0.80	1.39
	Jan	1.04	0.10	0.19	0.41	0.58	0.68	0.74	1.12
	Mar	1.14	0.32	0.51	0.95	0.94	1.51	1.29	1.61

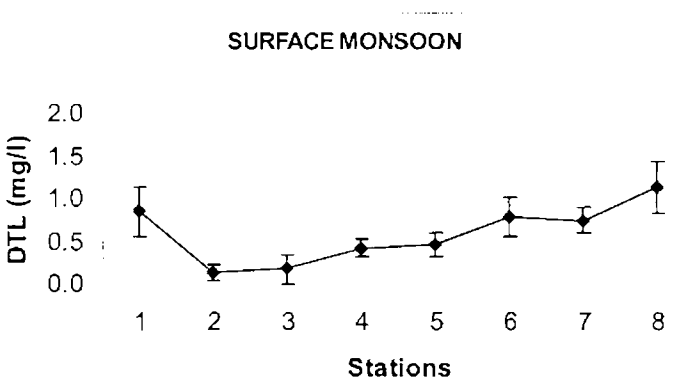

Figure 6.1 Distribution of dissolved tannin and lignin in surface waters during monsoon.

Surface nonmonsoon: In nonmonsoon, the distribution trend was highly irregular throughout the entire stiudy area, where highest concentration was near to the estuarine station 8 (Figure 6.2). At station 2, the values were slightly lower than the rest of the stations. The tannin and lignin concentrations displayed a variation of 0.21-1.69 mg/l. In this season, the reservoir station 1 also displayed an appreciable concentration of tannin and lignin type refractory compounds.

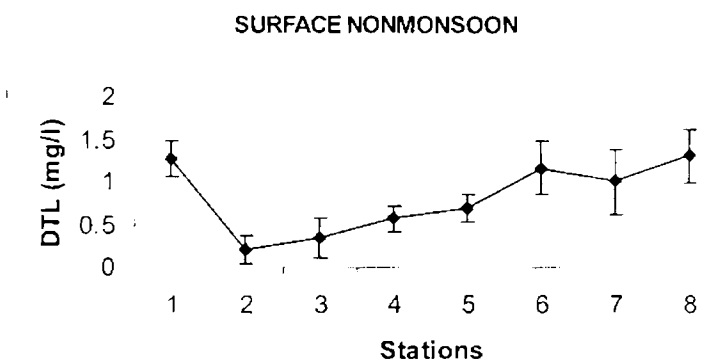

Figure 6.2 Distribution of dissolved tannin and lignin in surface waters during nonmonsoon.

Bottom monsoon: In monsoon, the bottom distribution gradient of dissolved tannin and lignin followed a zig zag trend upto station 5 (Figure 6.3). This was exactly similar to that observed for surface stations in monsoon. Comparatively low concentrations were observed near to stations 2 and 3 and the highest value was at the confluence station 8 of Azhikkode. The concentration range displayed for this season was 0.13-1.15 mg/l. Like monsoon, here also, the bottom dam water (station 1) showed its enrichment of refractory organic material.

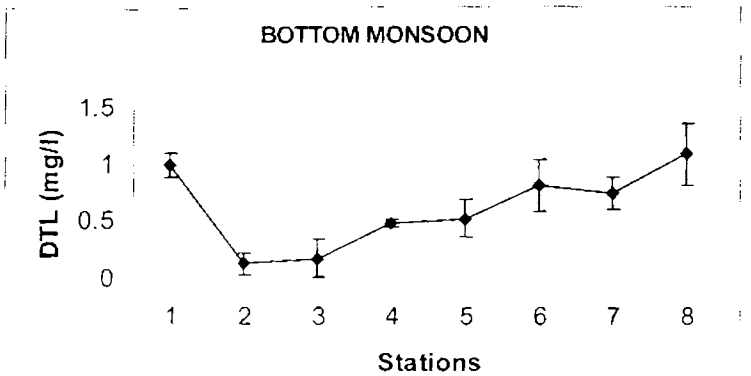

Figure 6.3 Distribution of dissolved tannin and lignin in bottom waters during monsoon.

Bottom nonmonsoon: The nonmonsoonal distribution pattern in bottom samples (Figure 6.4) followed an exactly similar trend as that in monsoon. Here also, the mid-riverine stations 2 and 3 showed comparatively low values. The estuarine end member stations still continued to exhibit its replenishment with dissolved tannin and lignin like substances. In this season, station 8 displayed the maximum concentration of tannin and lignin (1.40 mg/l) whereas the minimum was at the waterfalls station 2 (0.21 mg/l).

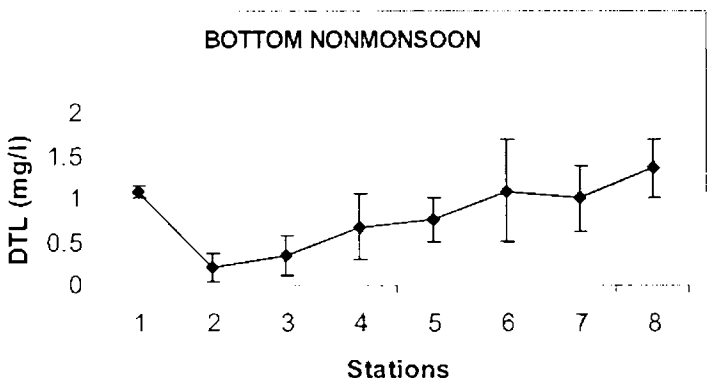

Figure 6.4 Distribution of dissolved tannin and lignin in bottom waters during nonmonsoon.

While discussing the general trend (Figure 6.5) in the dissolved tannin and lignin distribution pattern for both surface and bottom stations, nonmonsoonal values were slightly higher than monsoonal values, throughout the entire study area. At the town station 5, nonmonsoon season recorded exceedingly higher concentration in the surface sample. For all other stations, no wide fluctuations were observed in the distribution of dissolved tannin and lignin temporally.

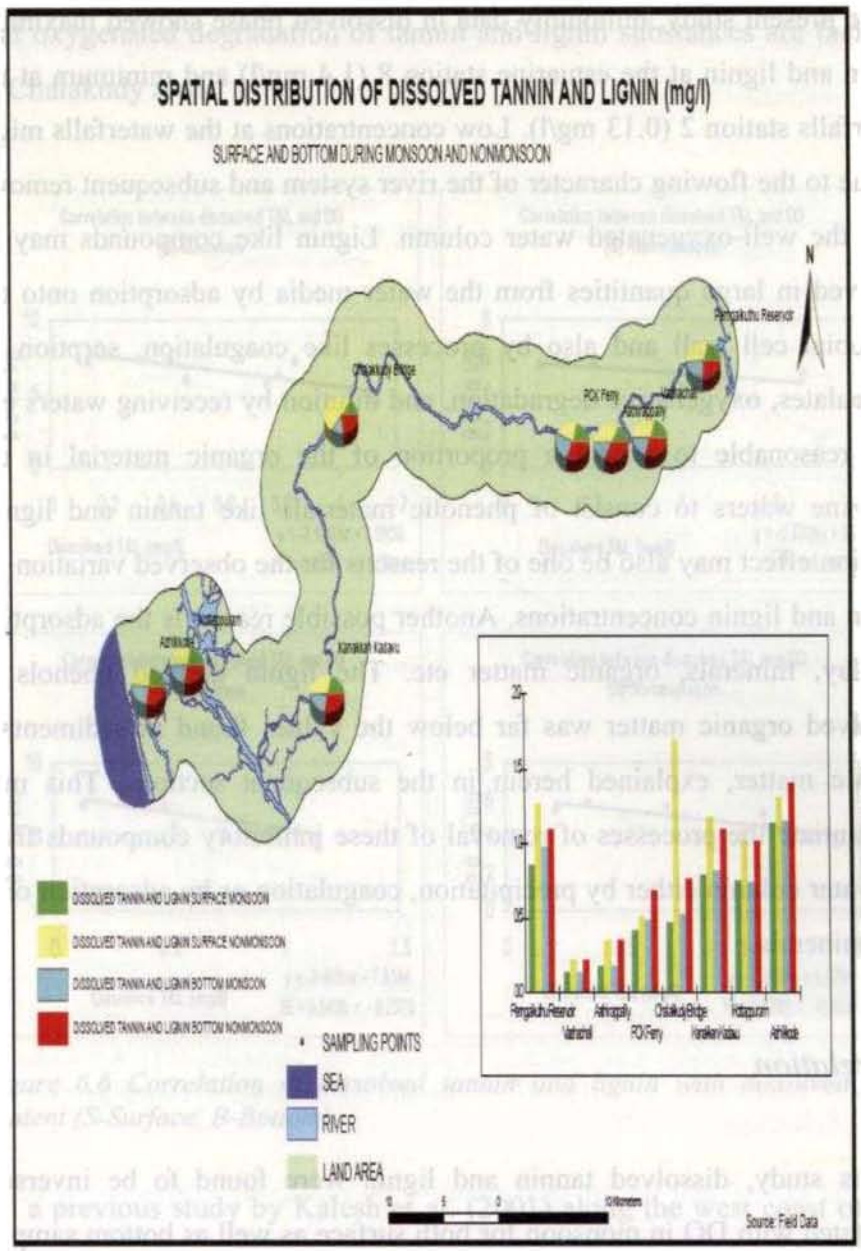

Figure 6.5 General distribution trend of tannin and lignin in dissolved state.

In the present study, bimonthly data in dissolved phase showed maximum tannin and lignin at the estuarine station 8 (1.4 mg/l) and minimum at the waterfalls station 2 (0.13 mg/l). Low concentrations at the waterfalls might be due to the flowing character of the river system and subsequent removal from the well-oxygenated water column. Lignin like compounds may be removed in large quantities from the water media by adsorption onto the microbial cell wall and also by processes like coagulation, sorption on particulates, oxygenative degradation, and dilution by receiving waters etc. It is reasonable to expect a proportion of the organic material in the estuarine waters to consist of phenolic materials like tannin and lignin. Dilution effect may also be one of the reasons for the observed variation of tannin and lignin concentrations. Another possible reason is the adsorption by clay, minerals, organic matter etc. The lignin derived phenols in dissolved organic matter was far below the values found in sedimentary organic matter, explained herein in the subsequent sections. This may substantiate the processes of removal of these inhibitory compounds from the water column either by precipitation, coagulation or by adsorption onto clay minerals.

Correlation

In this study, dissolved tannin and lignin were found to be inversely correlated with DO in monsoon for both surface as well as bottom samples ($r = -0.7714$, $p > 0.01$; $r = -0.7373$, $p > 0.02$). In nonmonsoon also, in the bottom samples, dissolved tannin and lignin displayed inverse correlation with DO ($r = -0.8237$, $p > 0.01$) (Figure 6.6). This feature revealed the fact

that oxygenated degradation of tannin and lignin substances are facilitated in Chalakudy river.

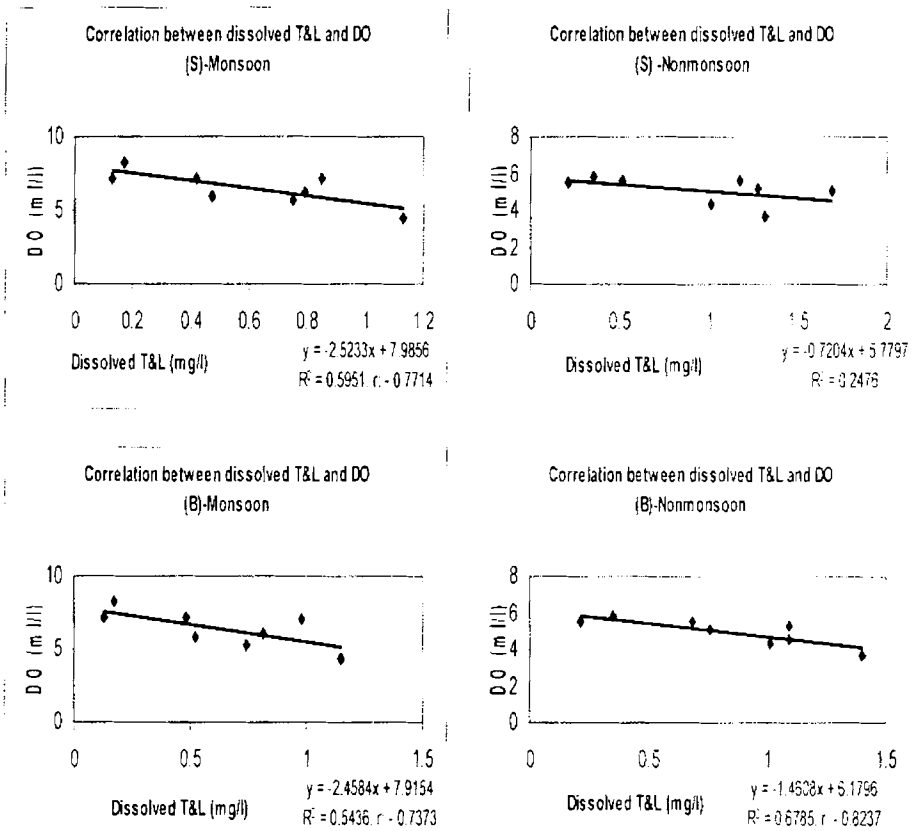

Figure 6.6 Correlation of dissolved tannin and lignin with dissolved oxygen content (S-Surface, B-Bottom).

In a previous study by Kalesh et al. (2001) along the west coast of India, tannin and lignin levels varied between 80 µg/l and 147 µg/l were reported. They found a positive and negative correlation with oxygen in surface and bottom waters respectively and a negative and positive correlation with salinity at low water depths and in deep waters respectively. This indicates

that substances such as lignins behave more conservatively in higher salinity waters.

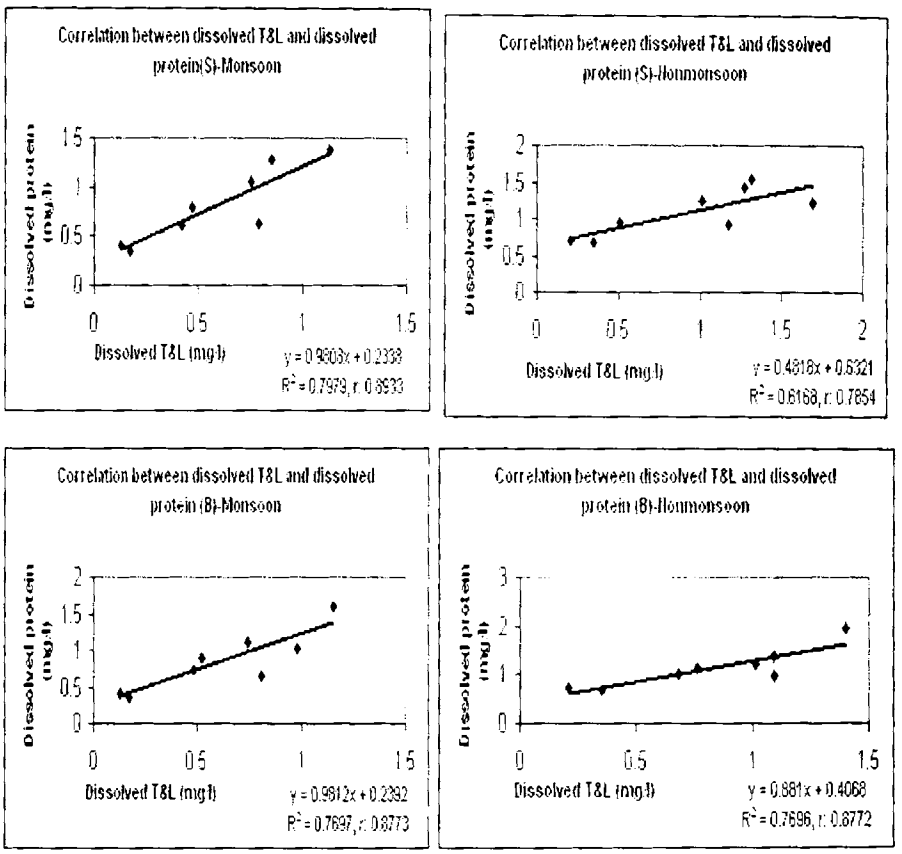

Figure 6.7 Correlation of dissolved tannin and lignin with dissolved proteins(S-Surface, B-Bottom).

Dissolved tannin and lignin was found to be positively correlated with all other labile organic constituents studied in the dissolved phase, i.e. dissolved protein (Figure 6.7), dissolved monosaccharides (Figure 6.8) and dissolved polysaccharides (Figure 6.9). This might be due to the accumulation of these compounds by low rate of degradation in the

presence of these phenolic compounds. Direct relationship between them also suggests same source of origin of these components (Rini, 2002).

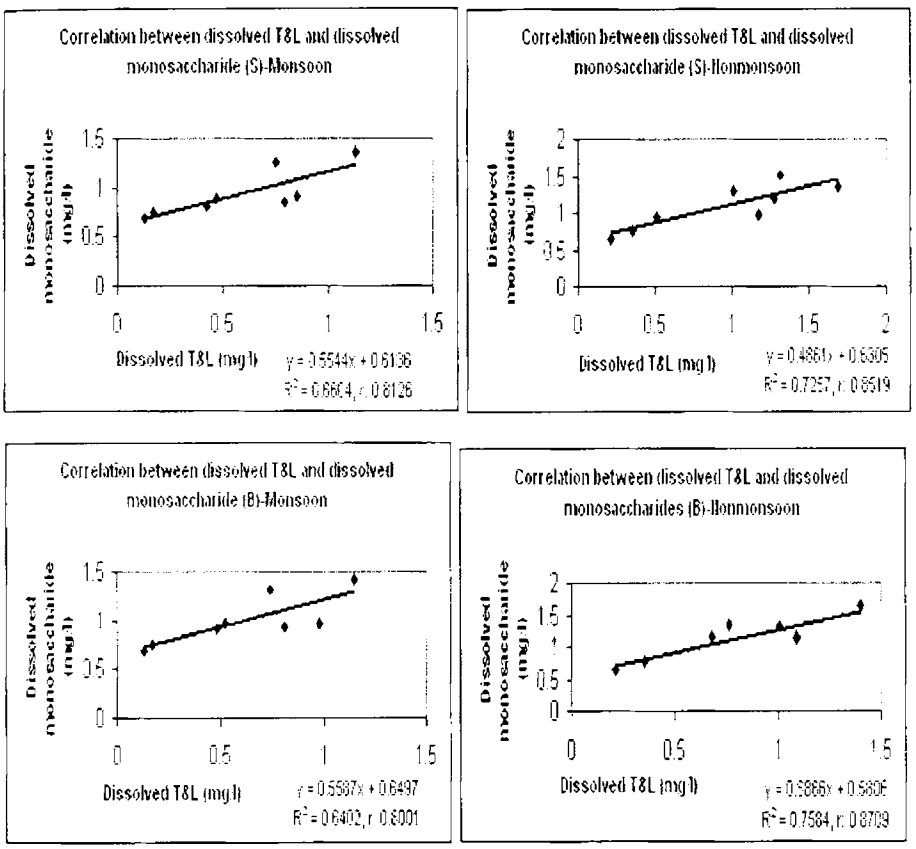

Figure 6.8 Correlation of dissolved tannin and lignin with dissolved monosaccharides (S-Surface, B-Bottom).

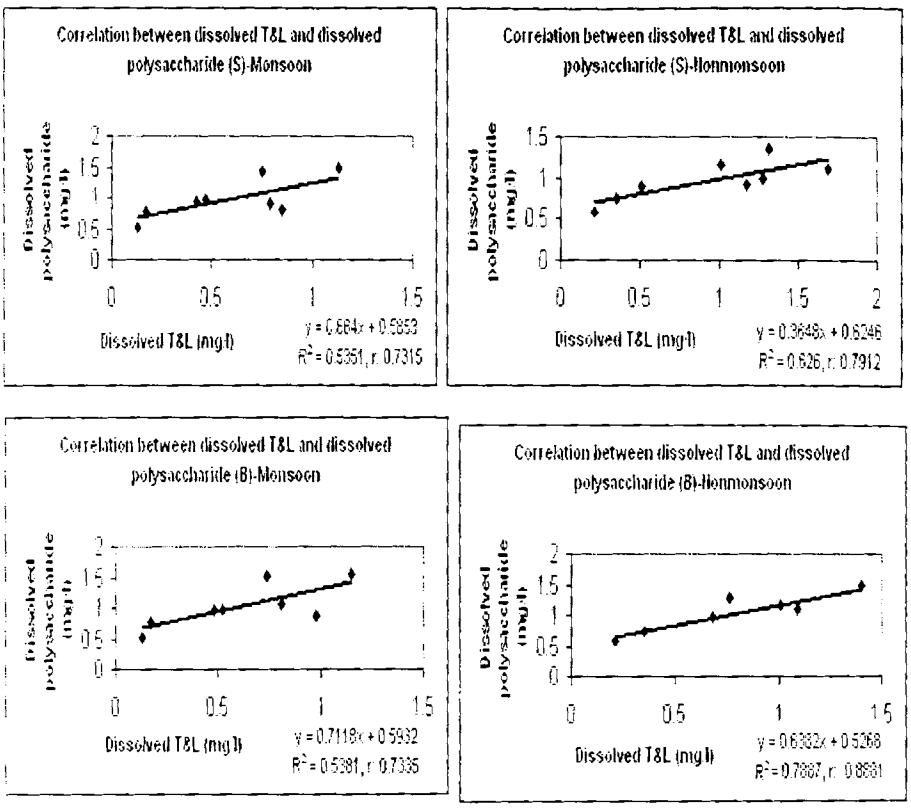

Figure 6.9 Correlation of dissolved tannin and lignin with dissolved polysaccharides(S-Surface, B-Bottom).

Tannin and lignin in the particulate phase (PTL)

The physicochemical and biological parameters of estuarine waters are dynamic both spatially and temporally. Drastic changes in salinity occur during the tidal mixing of fresh and salt waters, activities of primary and secondary producers are high, and dissolved and particulate matter of terrestrial, autochthonous and marine origin are present with adequate light penetration and nutrient supplies, fresh, autochthonous organic matter is present through photosynthetic activity (Tada et al., 2001). However,

relatively little is known about the composition and behaviour of estuarine suspended particulates with regard to bulk chemical structure, quantitative contributions of terrestrial and autochthonous materials, and transformation by active biological processes.

Table 6.2 Bimonthly distribution of tannin and lignin in the particulates of surface and bottom waters of Chalakudy river

		Stations							
	Months	S1	S2	S3	S4	S5	S6	S7	S8
Surface particulates	May	0.68	0.07	0.08	0.11	0.10	0.22	0.58	0.71
	July	0.21	0.07	0.03	0.03	0.03	0.04	0.13	0.33
	Sep	0.15	0.05	0.02	0.03	0.03	0.05	0.15	0.38
	Nov	0.42	0.04	0.06	0.08	0.07	0.14	0.39	0.54
	Jan	0.37	0.03	0.07	0.06	0.06	0.08	0.22	0.48
	Mar	0.58	0.09	0.07	0.12	0.09	0.29	0.52	0.68
		Stations							
		B1	B2	B3	B4	B5	B6	B7	B8
Bottom particulates	May	0.68	0.07	0.08	0.11	0.12	0.29	0.67	0.75
	July	0.25	0.07	0.03	0.04	0.03	0.04	0.13	0.38
	Sep	0.19	0.05	0.02	0.04	0.03	0.05	0.16	0.36
	Nov	0.51	0.04	0.06	0.08	0.13	0.14	0.42	0.56
	Jan	0.39	0.03	0.07	0.07	0.06	0.10	0.22	0.51
	Mar	0.65	0.09	0.07	0.13	0.13	0.31	0.52	0.71

To date, not much information is available on the contribution of lignin to the suspended particulate fraction in aquatic systems. It was in this context that field studies were under taken to measure the concentration and variation of the lignin in suspended particulates of Chalakudy River, so as to learn how this material is modified during its transit through this important environmental compartment (Table 6.2).

Surface monsoon: In surface particulates, tannin and lignin distribution pattern in monsoon was in a more or less uniform pattern from station 2

onwards upto station 6 (Figure 6.10). To the lower end of the study area, a sudden increase in concentration was seen, the maximum observed value (0.49 mg/l) was at the estuarine end of station 8. The minimum observed concentration was at station 3 (0.04 mg/l).

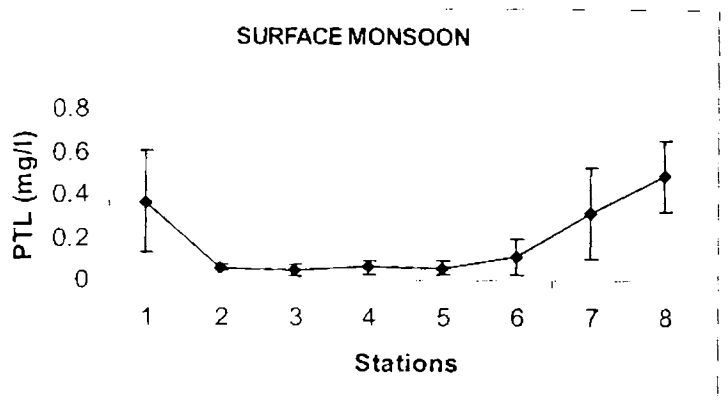

Figure 6.10 Distribution of tannin and lignin in surface particulates during monsoon.

Surface nonmonsoon: The nonmonsoonal trend (Figure 6.11) in the distribution of particulate tannin and lignin in surface followed an exactly similar trend as that in monsoon. In between stations 2 and 5, no wide fluctuations were observed in concentrations. Estuarine and reservoir stations reported comparatively high particulate tannin and lignin concentrations, reflecting the maximum concentration at station 8 (0.58 mg/l).

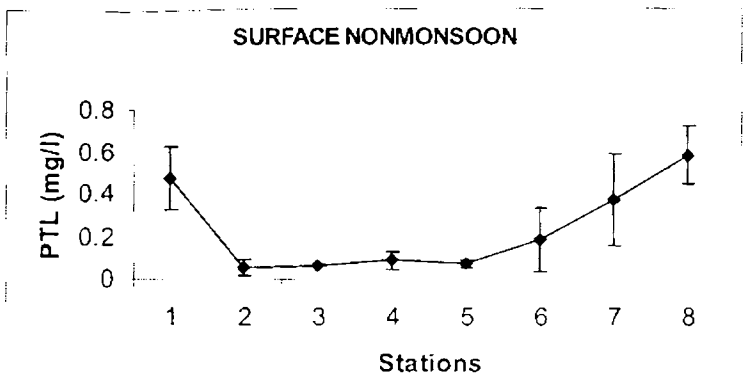

Figure 6.11 Distribution of tannin and lignin in surface particulate during nonmonsoon.

Bottom monsoon: In monsoon, bottom particulate tannin and lignin concentrations displayed no wide variations from stations 2 to 5 (Figure 6.12). Irrespective of the depth-profile of surface and bottom, suspensates of riverine and saline stations (1, 7 and 8) retained the high concentrations of tannin and lignin. A gradual increasing trend in particulate tannin and lignin concentrations was seen in the down stream end i.e., after station 6. The minimum observed concentration was 0.04 mg/l (at station 3).

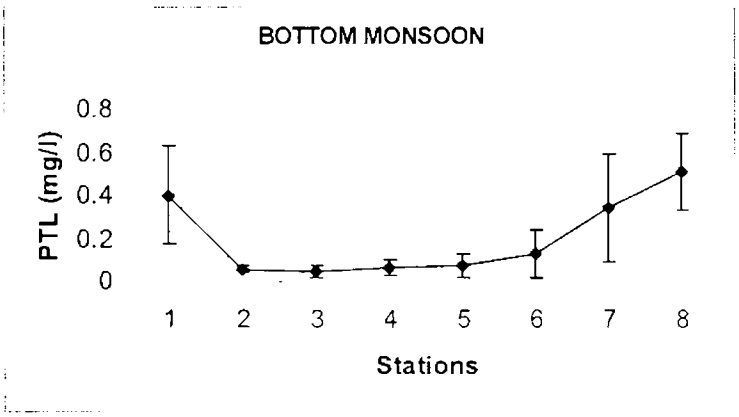

Figure 6.12 Distribution of tannin and lignin in bottom particulates during monsoon.

Bottom nonmonsoon: The nonmonsoonal trend of tannin and lignin in bottom suspensates depicted the same behavior as that in monsoon (Figure 6.13). Here also, the middle stream portion displayed almost a uniform trend in concentration. The observed concentration range for this season was 0.05-0.61 mg/l. In this season too, thestation 8 reported the maximum tannin and lignin concentration (0.61 mg/l) and minimum was at station 2 (0.05 mg/l).

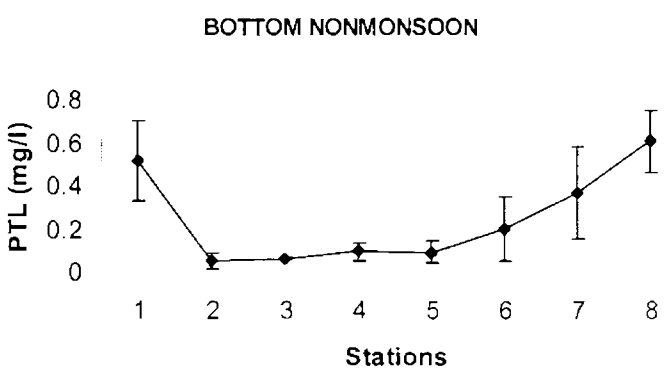

Figure 6.13 Distribution of tannin and lignin in bottom particulates during nonmonsoon.

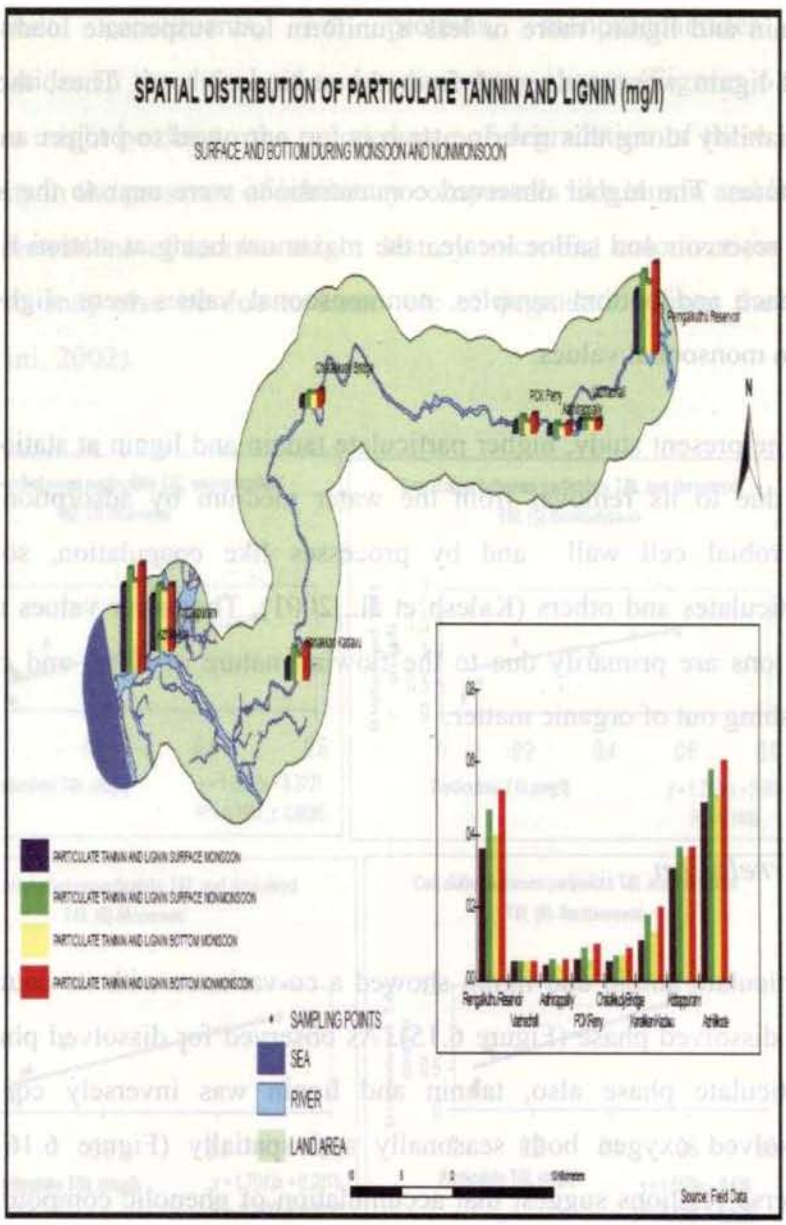

Figure 6.14 General distribution trend of tannin and lignin in particulate matter.

Considering the general trend (Figure 6.14) in the distribution of particulate tannin and lignin, more or less a uniform low suspensate loads of tannin and lignin were concerned from the stations 2 to 6. Thus, the seasonal variability along this riverine strap is too narrowed to project any specific features. The higher observed concentrations were near to the stations in the reservoir and saline locale, the maximum being at station 8. For both surface and bottom samples, nonmonsoonal values were slightly higher than monsoonal values.

In the present study, higher particulate tannin and lignin at station 8 might be due to its removal from the water medium by adsorption onto the microbial cell wall and by processes like coagulation, sorption on particulates and others (Kalesh et al., 2001). The lower values at riverine stations are primarily due to the flowing nature of river, and continuous flushing out of organic matter.

Correlation

Particulate tannin and lignin showed a co-variance with its counterpart in the dissolved phase (Figure 6.15). As observed for dissolved phase, in the particulate phase also, tannin and lignin was inversely correlated to dissolved oxygen both seasonally and spatially (Figure 6.16). These inverse relations suggest that accumulation of phenolic compounds occurs at a faster rate under anaerobic conditions. If there is availability of oxygen, rate of degradation of phenolic compounds is much faster (Rini, 2002).

Here, particulate tannin and lignin displayed positive correlations with other labile constituents, i.e. proteins, monosaccharides and polysaccharides in the dissolved and sedimentary phases (Figures 6.17 to 6.22). This might be due to the reduced rate of degradation of these labile constituents in the presence of inhibitory compounds like tannin and lignin, high concentrations of tannins might destroy microbial colonization (Lee, 1999). This may also be due to same rate of degradation from the same source (Rini, 2002).

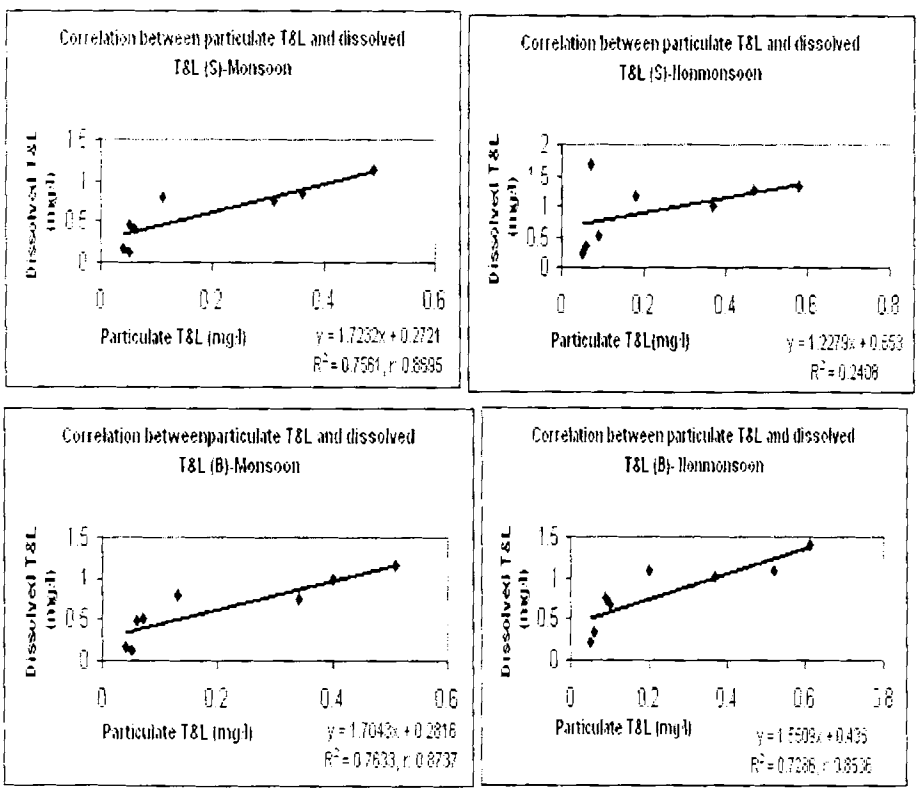

Figure 6.15 Correlation of particulate tannin and lignin with dissolved tannin and lignin (S-Surface, B-Bottom).

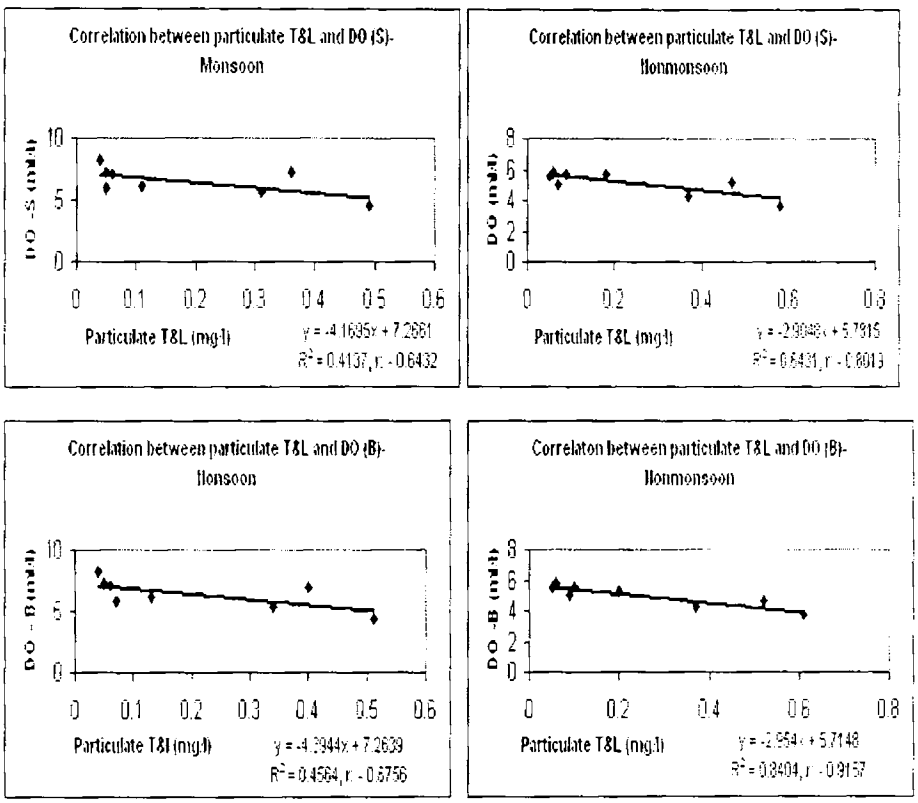

Figure 6.16 Correlation of particulate tannin and lignin with dissolved oxygen (S-Surface, B-Bottom).

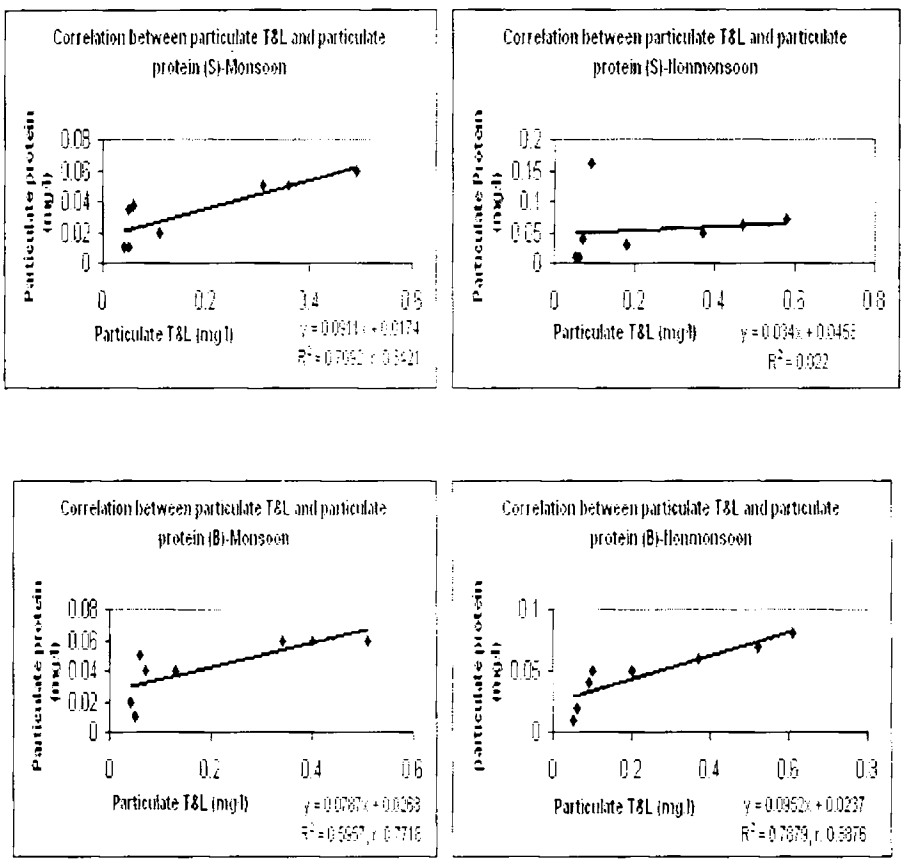

Figure 6.17 Correlation of particulate tannin and lignin with particulate protein (S-Surface, B-Bottom).

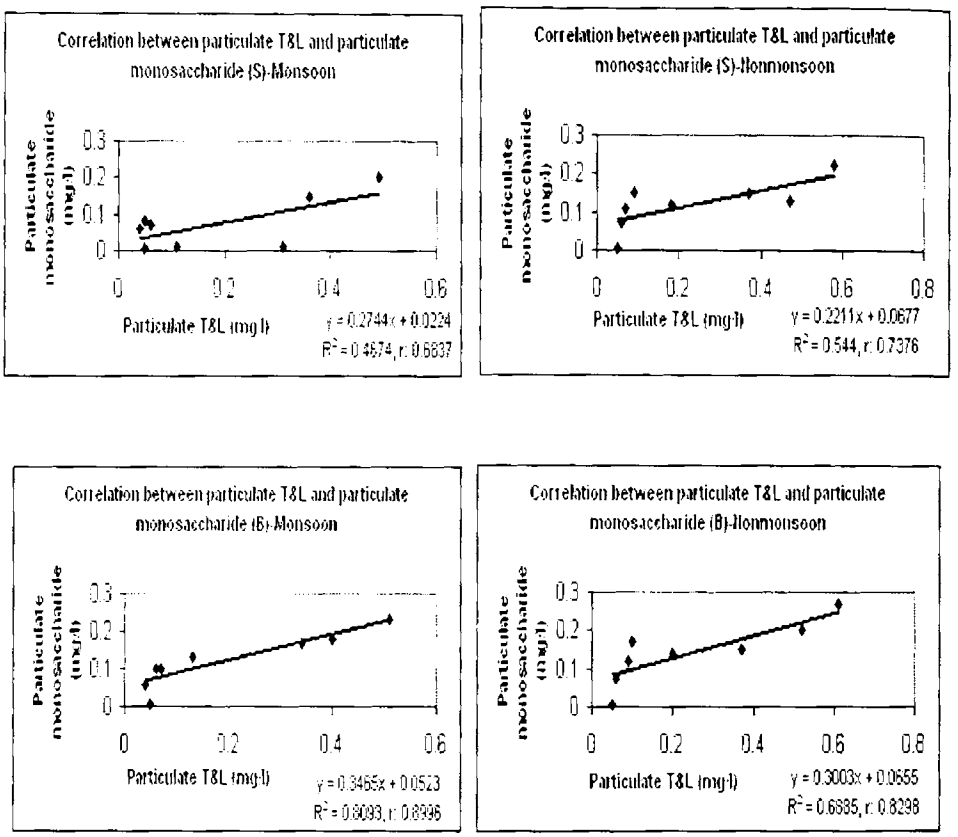

Figure 6.18 Correlation of particulate tannin and lignin with particulate monosaccharide (S-Surface, B-Bottom).

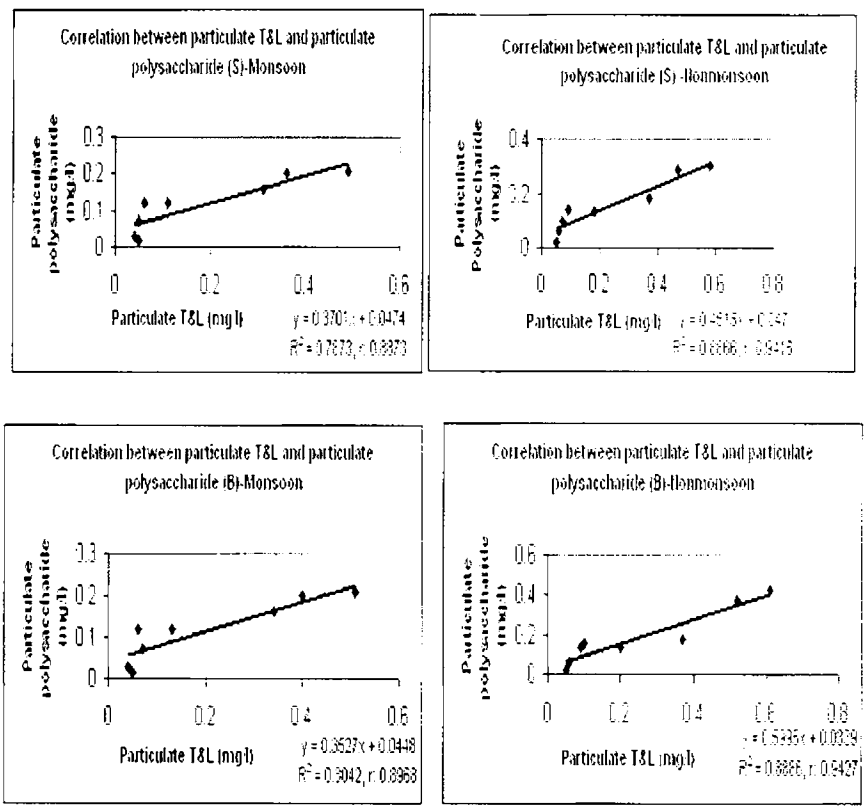

Figure 6.19 Correlation of particulate tannin and lignin with particulate polysaccharide (S-Surface, B-Bottom).

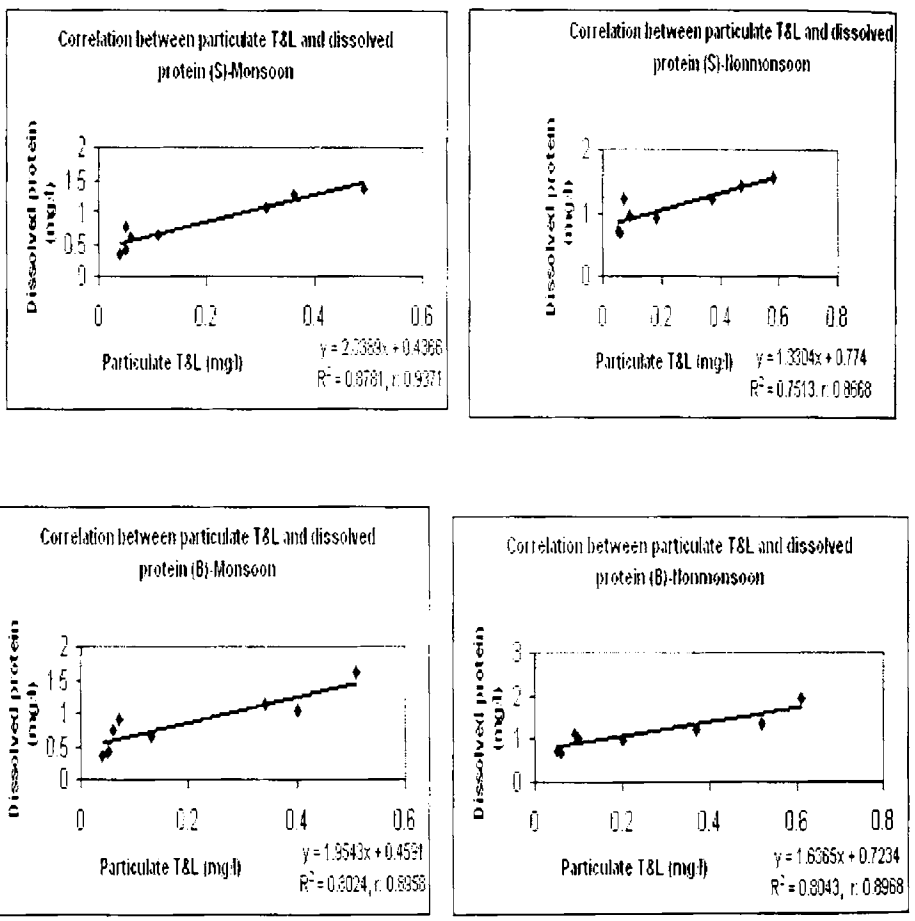

Figure 6.20 Correlation of particulate tannin and lignin with dissolved protein (S-Surface, B-Bottom).

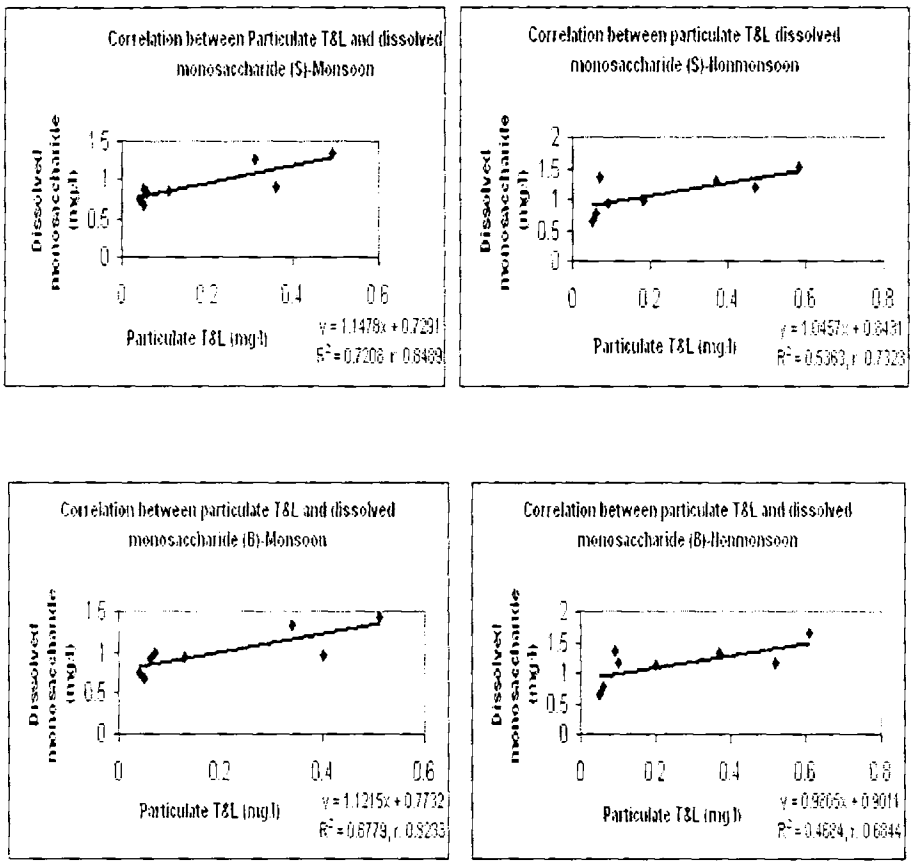

Figure 6.21 Correlation of particulate tannin and lignin with dissolved monosaccharide (S-Surface, B-Bottom).

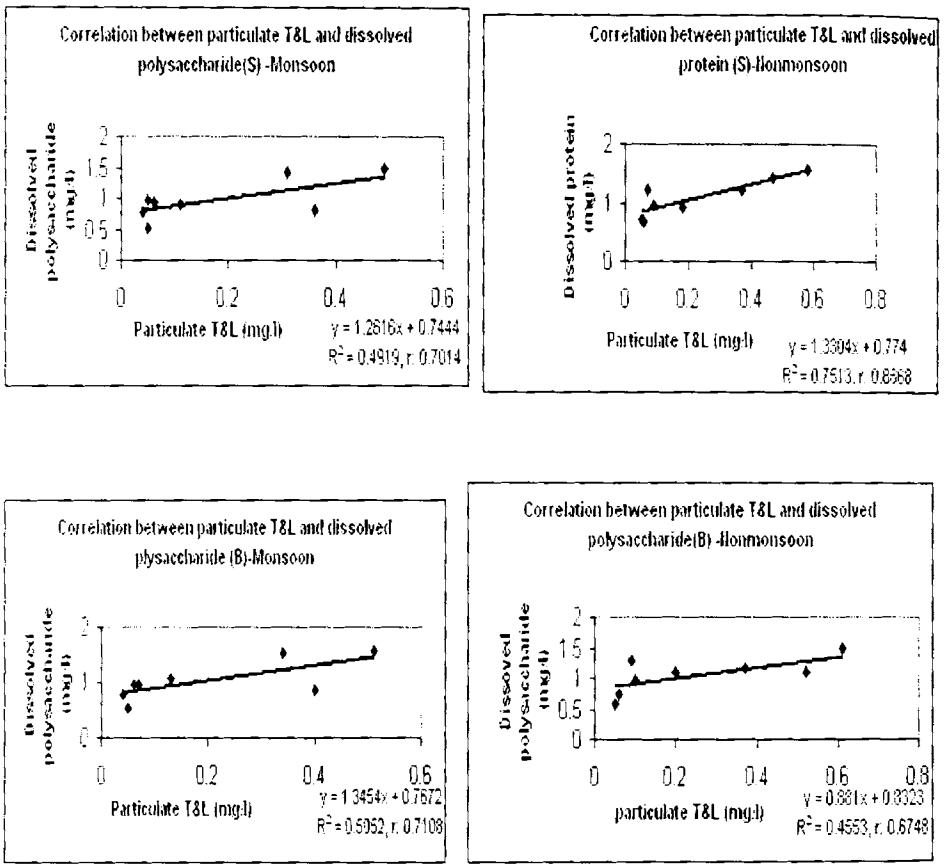

Figure 6.22 Correlation of particulate tannin and lignin with dissolved polysaccharide (S-Surface, B-Bottom).

Tannin and lignin in the sedimentary phase (STL)

The present study reports (Table 6.3) on the seasonal variation of phenolics in the sediments of eight stations of Chalakudy River along with other environmental parameters.

Table 6.3 Bimonthly distribution of sedimentary tannin and lignin (mg/g) in the sediments of Chalakudy river

Months	S1	S2	S3	S4	S5	S6	S7	S8
May	1.59	0.59	0.78	1.31	1.06	1.22	1.12	1.71
July	1.09	0.13	0.24	1.01	0.87	1.11	0.88	1.32
Sep	1.13	0.19	0.35	0.98	0.64	0.99	0.96	1.26
Nov	1.38	0.37	0.56	1.23	0.97	1.16	1.05	1.65
Jan	1.26	0.21	0.41	1.18	0.88	1.24	1.12	1.46
Mar	1.64	0.46	0.61	1.42	1.35	1.16	1.22	1.84

Monsoon: In monsoon, sedimentary tannin and lignin distribution pattern (Figure 6.23) was highly irregular, where catchment and estuarine mouth stations (1 and 8) respectively reported slightly higher concentrations. Similar to the fluvial tannin and lignin loads, stations 2 and 3 located in the upstream portion also record comparatively low values in sediments. A uniform variation in the concentration cannot be seen in the distribution of sedimentary tannin and lignin, because high values were observed near to station 1- the first station in the up stream portion, and at station 8- the last station in the downstream region. The range of concentration observed for this season was 0.32-1.48 mg/g.

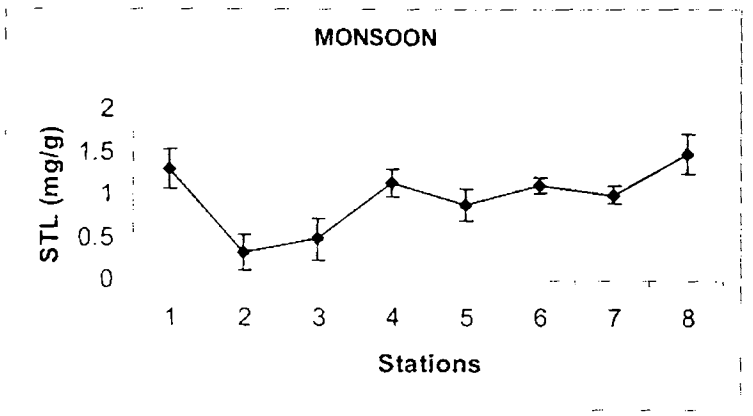

Figure 6.23 Distribution of tannin and lignin in sediments during monsoon.

Nonmonsoon: The nonmonsoonal trend (Figure 6.24) in the distribution of sedimentary tannin and lignin was same as that in monsoon season. The middle stream stations (stations 4-7) did not show a wide variation in concentration. As seen in monsoon, nonmonsoonal values were also low at the stations 2 and 3. In this season, stations 1 and 8 recorded comparatively higher concentrations of sedimentary tannin and lignin (stations 1 and 8 respectively being the upper most and lower most regions in the study area). The maximum reported value for this season was 1.65 mg/g (at station 8), minimum being 0.33 mg/g (at station 2).

The increased tannin and lignin concentrations observed at the dam site (station 1) could therefore be attributed to the influence of gravitational settling of organics occurring in this region. Salinity induced flocculation at the confluence region lead to increased value of tannin and lignin in the sediments of estuarine mouth station (i.e., 8). The lower levels of tannin and lignin noticed at the waterfall stations were the consequence of the

increased particle size which decreases the adsorption/ incorporation of organics and also the oxygenated decomposition of organic matter under the increased cycles of water turbulation. These stations were fresh water dominated and the textural characteristics of the sediments were sandy in nature.

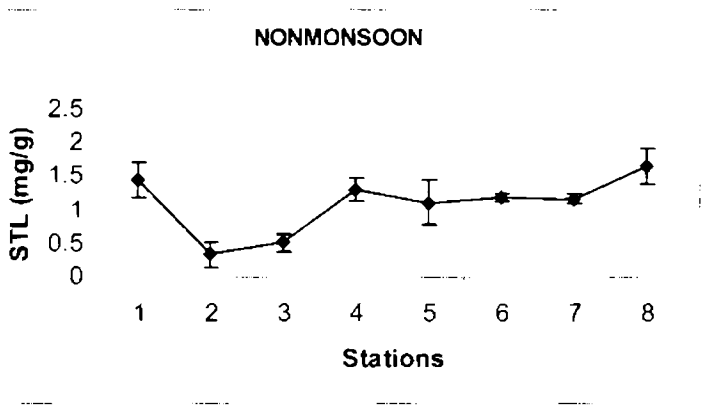

Figure 6.24 Distribution of tannin and lignin in sediments during nonmonsoon.

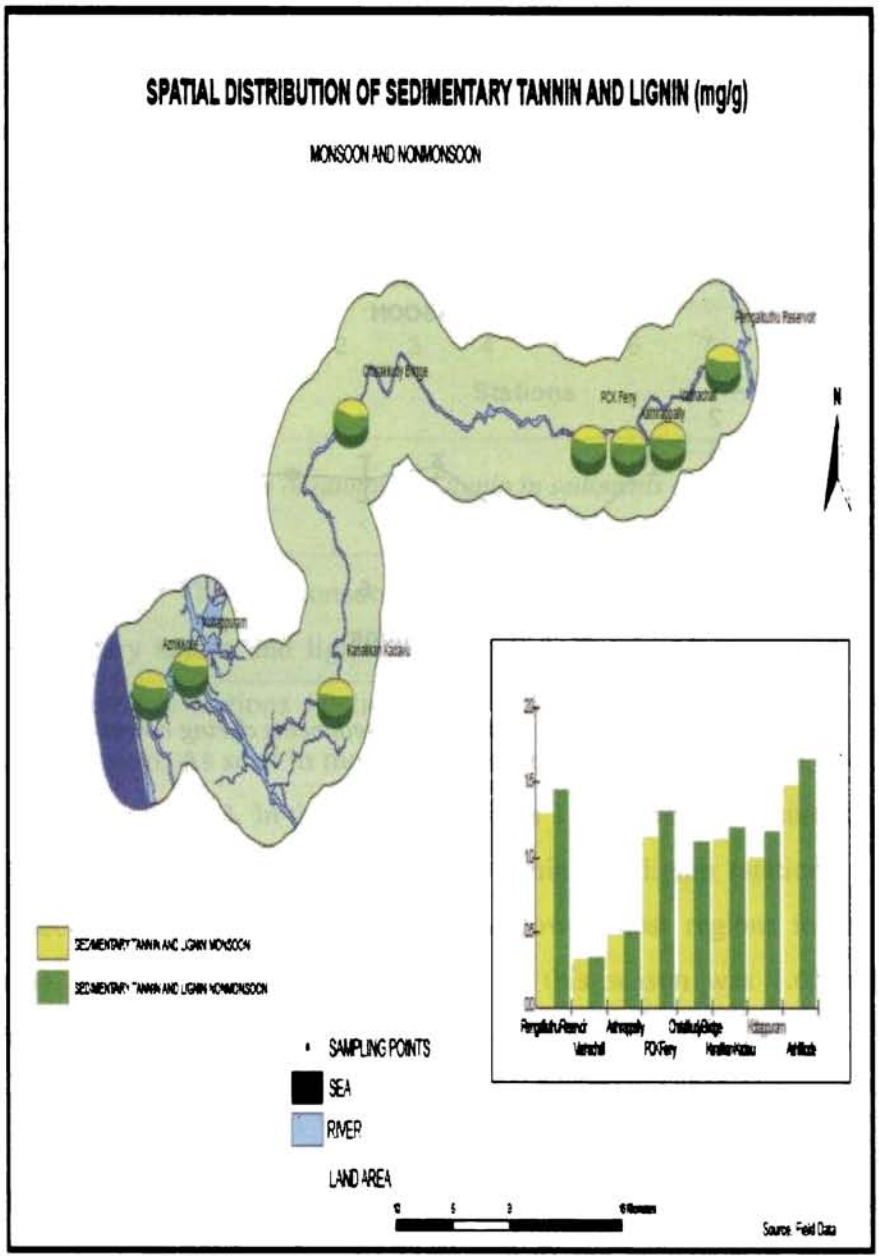

Figure 6.25 General distribution trend of tannin and lignin in sedimentary phase.

In the distributional profile of sedimentary tannin and lignin (Figure 6.25), nonmonsoonal values were found to be higher than that of monsoonal values through out the study area. The low monsoonal values can be explained as a result of renewal of sediment by high run off or as due to the dilution of sedimentary lignins by lignin deficient organic materials. The overall distribution of tannin and lignin in dissolved, particulate and sedimentary phases are pictured in (Figure 6.26). Here, the waterfall stations (2 & 3) displayed comparatively low tannin and lignin concentrations. Estuarine sediments are mainly composed of silty-clay or clayey-silt, whereas the riverine sediments are predominantly sandy. This could be the prime reason for the lower concentration of tannin and lignin in the riverine stations compared to estuarine stations. Earlier reported values of tannin and lignin are given in Table 6.4.

Table 6.4 Reported values of tannin and lignin

No	System	water	sediment	Reference
1	Cochin backwaters	0.6-25 mg/l		Nair et al., 1990
2	Mangrove leaves	3.28-20.020 mg/l		Kathiresan, K. and Veeran 1990
3	Cochin Estuary		.05-10.56mg/g	Nair 1992
4	West coast of Arabian sea	0.08-0.147 mg/l		Kalesh et al 2001
5	Mangroves	0.112-.82mg/l	1.22- 6.841mg/g	Rini 2002
6	Mangroves in Kochi	0.187-1.676 mg/l		Nisha 2002
7	Mangrove leaves		13.71 to 90.56 mg/g	Lin et al., 2006

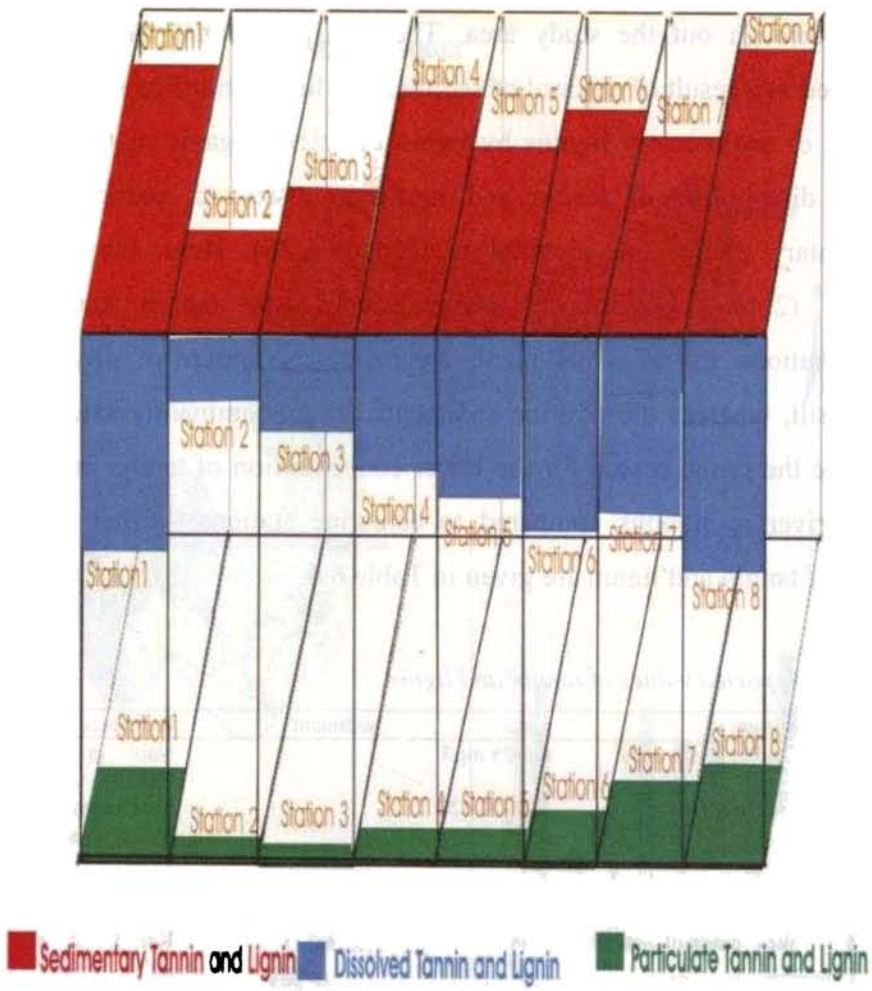

Figure 6.26 Overall distribution of tannin and lignin in dissolved, particulate and sedimentary phases.

Correlation

In this study, sedimentary tannin and lignin was inversely related to the percentage of sand, whereas it displayed positive correlations with silt and clay fractions (Figure 6.27 to 6.29). The grain size of the sediments plays a significant role in controlling the distribution of organic compounds. Clayey-silt and silty-clay sediments were capable of loading more organics than the sandy ones. Different significant correlations as related to dissolved, particulate and sedimentary tannin and lignin are shown in figures 6.27 to 6.41.

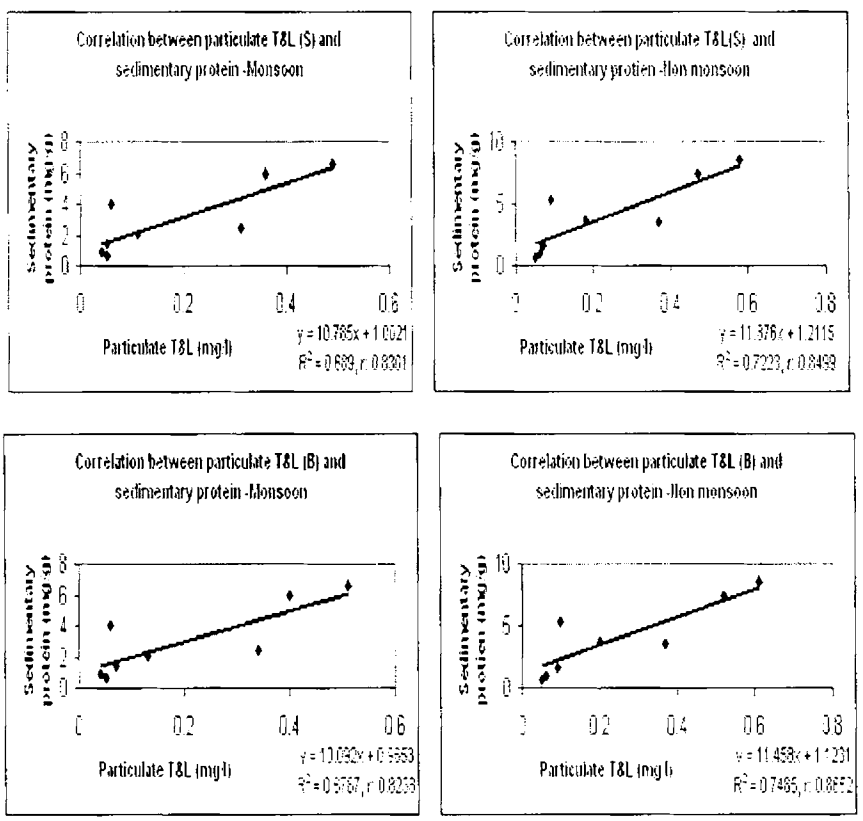

Figure 6.27 Correlation of particulate tannin and lignin with sedimentary protein (S-Surface, B-Bottom).

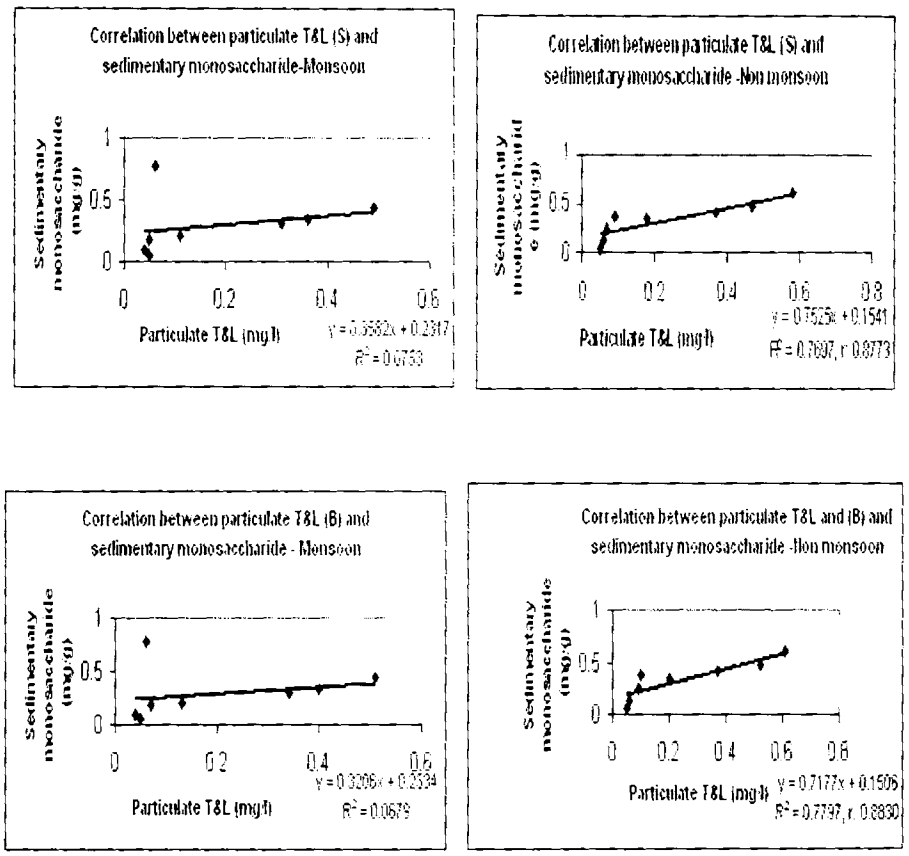

Figure 6.28 Correlation of particulate tannin and lignin with sedimentary monosaccharide (S-Surface, B-Bottom).

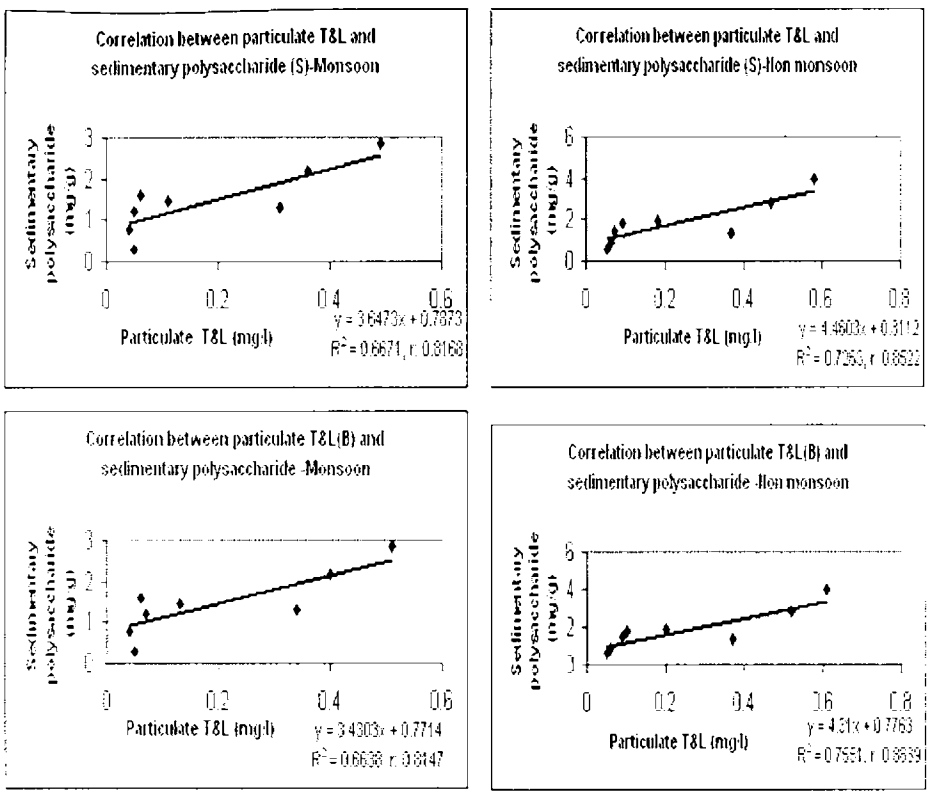

Figure 6.29 Correlation of particulate tannin and lignin with sedimentary polysaccharide (S-Surface, B-Bottom).

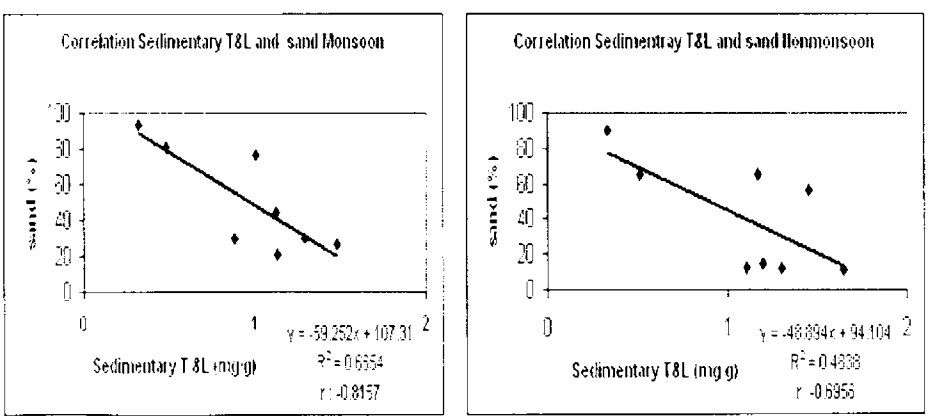

Figure 6.30 Correlation of sedimentary tannin and lignin with sand

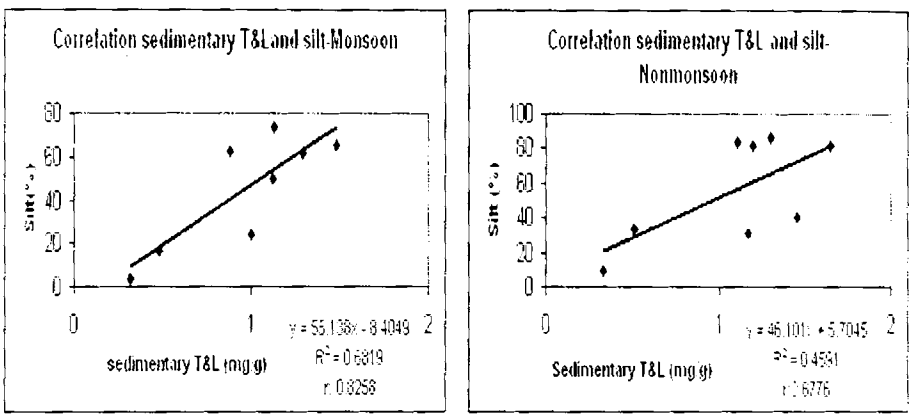

Figure 6.31 Correlation of sedimentary tannin and lignin with silt.

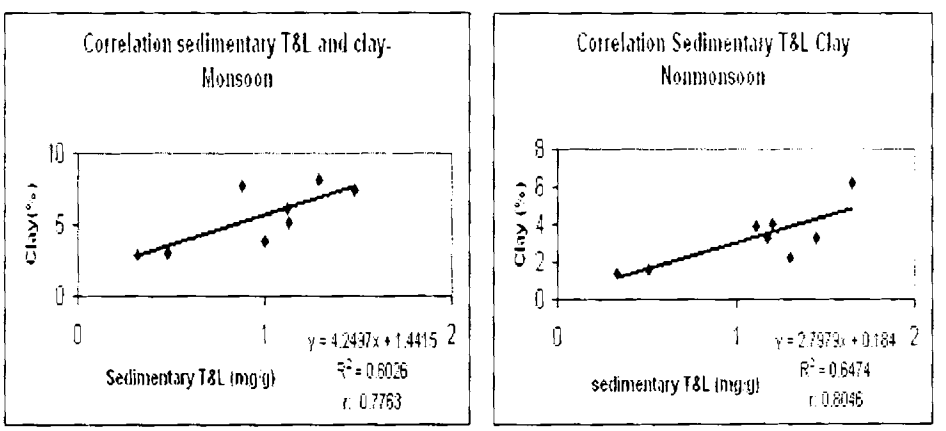

Figure 6.32 Correlation of sedimentary tannin and lignin with clay.

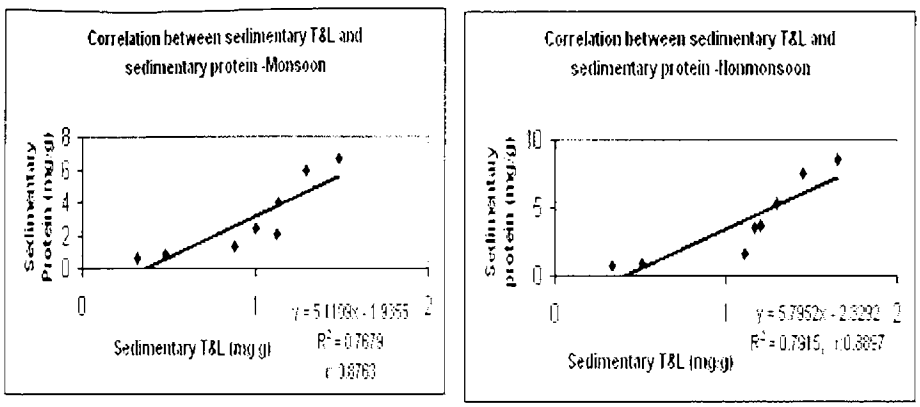

Figure 6.33 Correlation of sedimentary tannin and lignin with sedimentary protein.

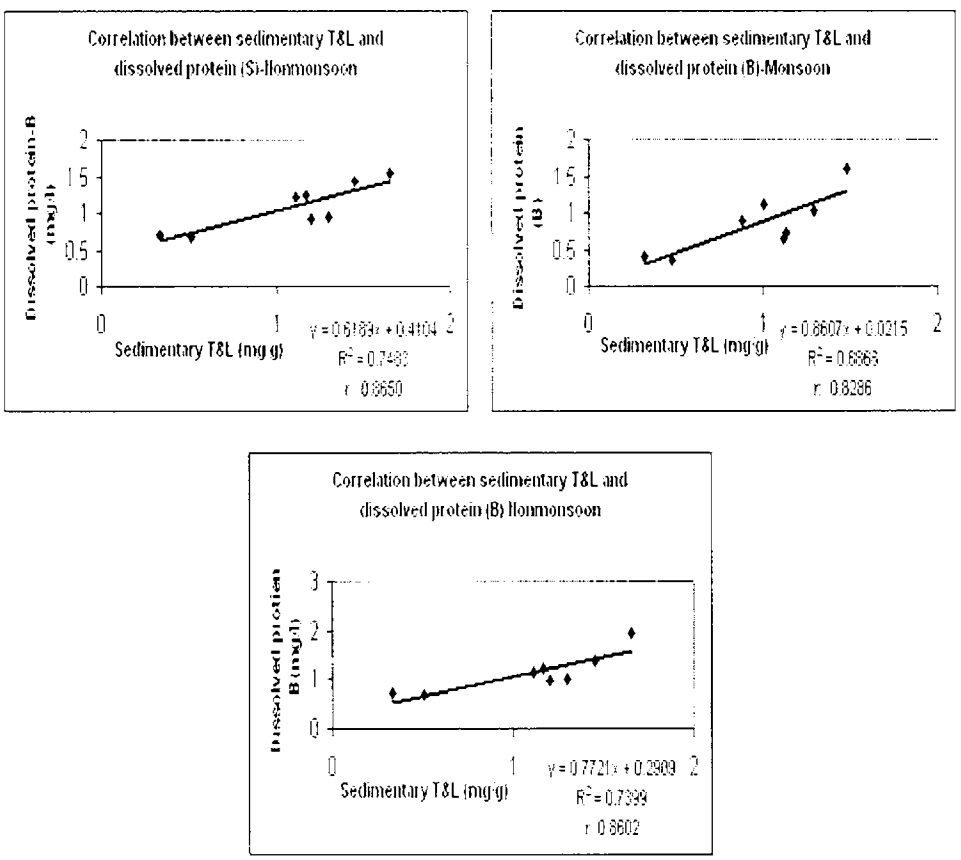

Figure 6.34 Correlation of sedimentary tannin and lignin with dissolved protein (S-Surface, B-Bottom).

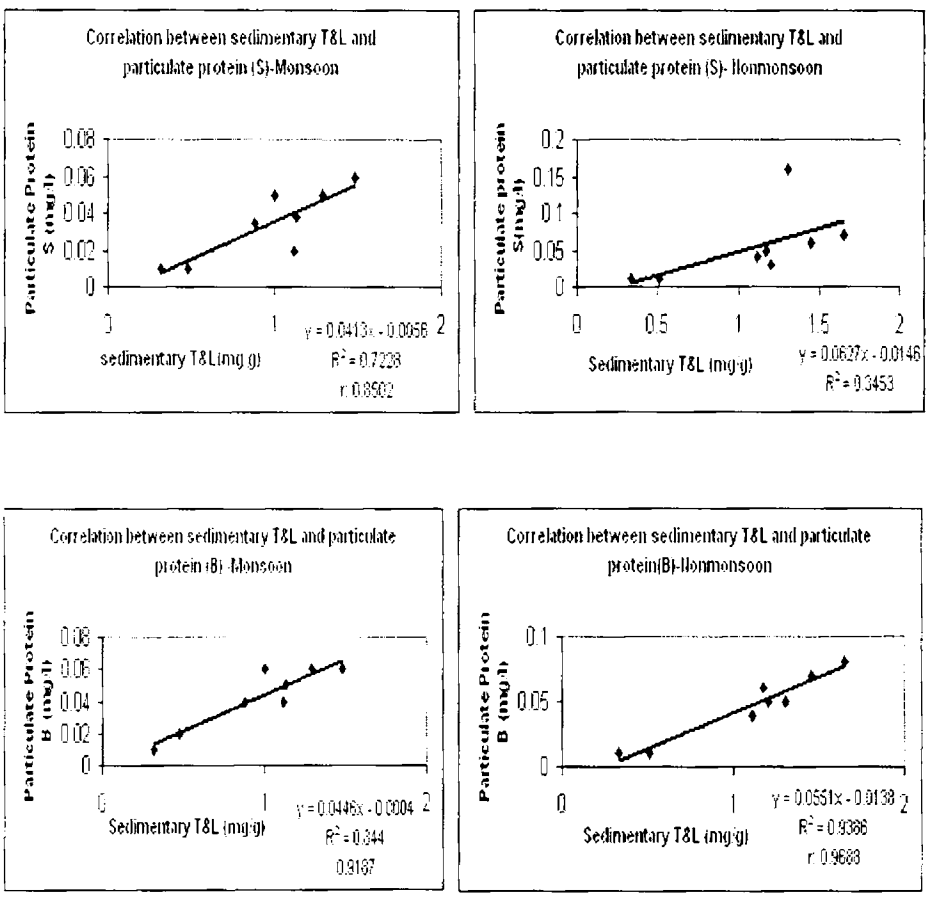

Figure 6.35Correlation of sedimentary tannin and lignin with particulate protein.

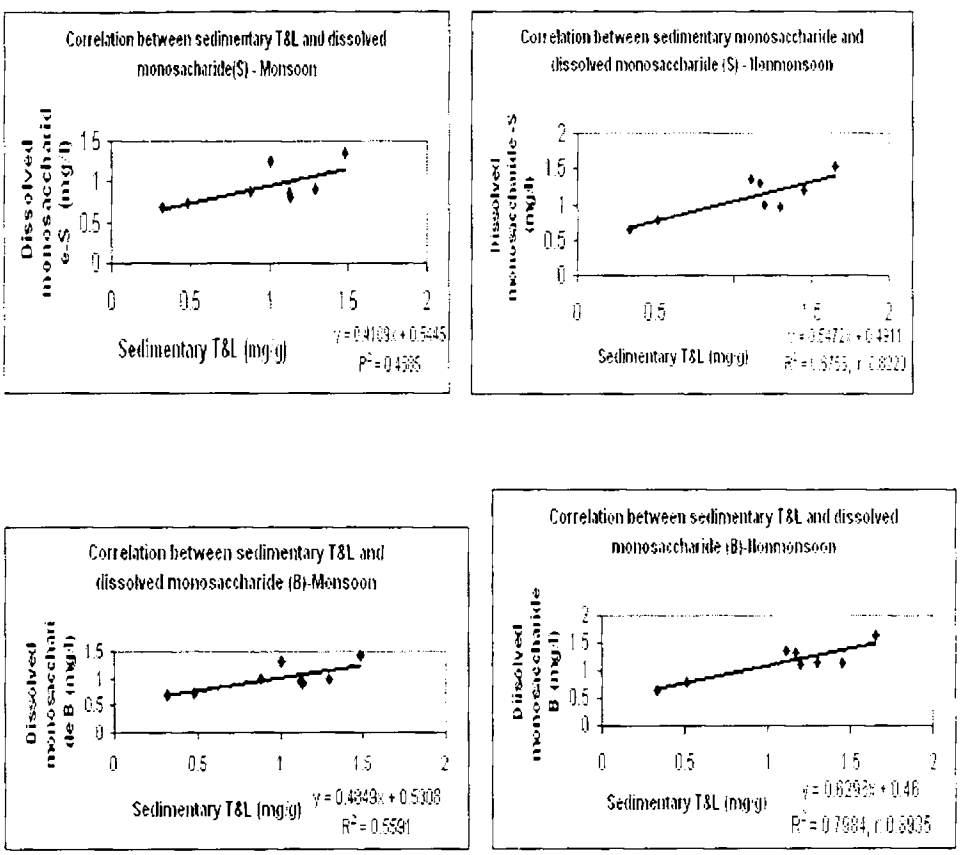

Figure 6.36 Correlation of sedimentary tannin and lignin with dissolved monosaccharide.

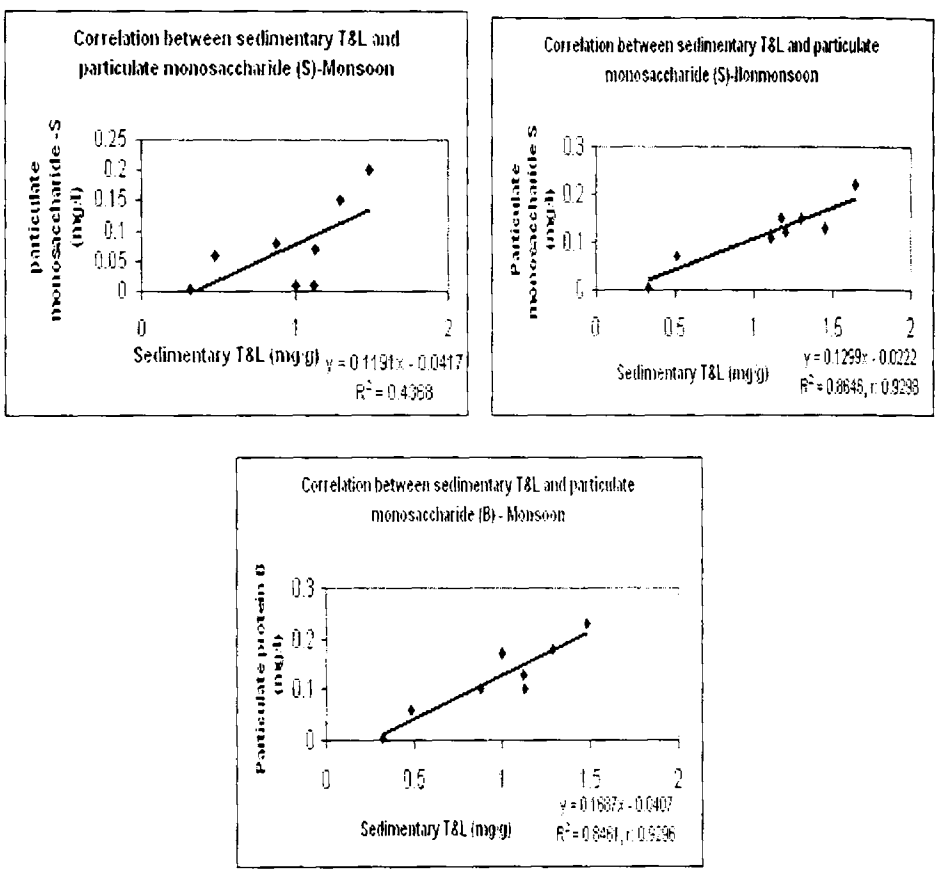

Figure 6.37 Correlation of sedimentary tannin and lignin with particulate monosaccharide.

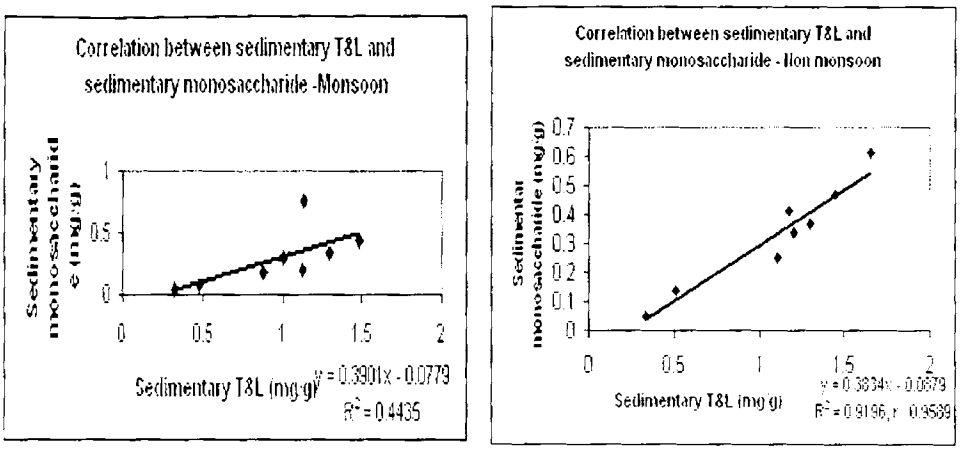

Figure 6.38 Correlation of sedimentary tannin and lignin with sedimentary monosaccharide.

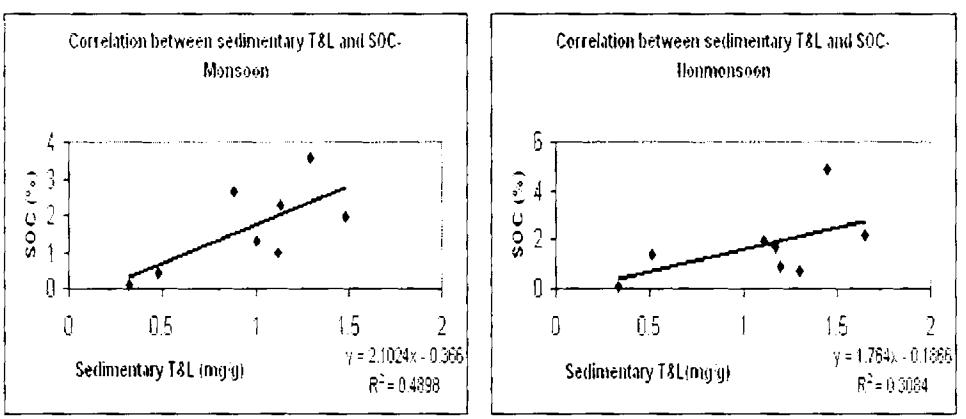

Figure 6.39 Correlation of sedimentary tannin and lignin with SOC.

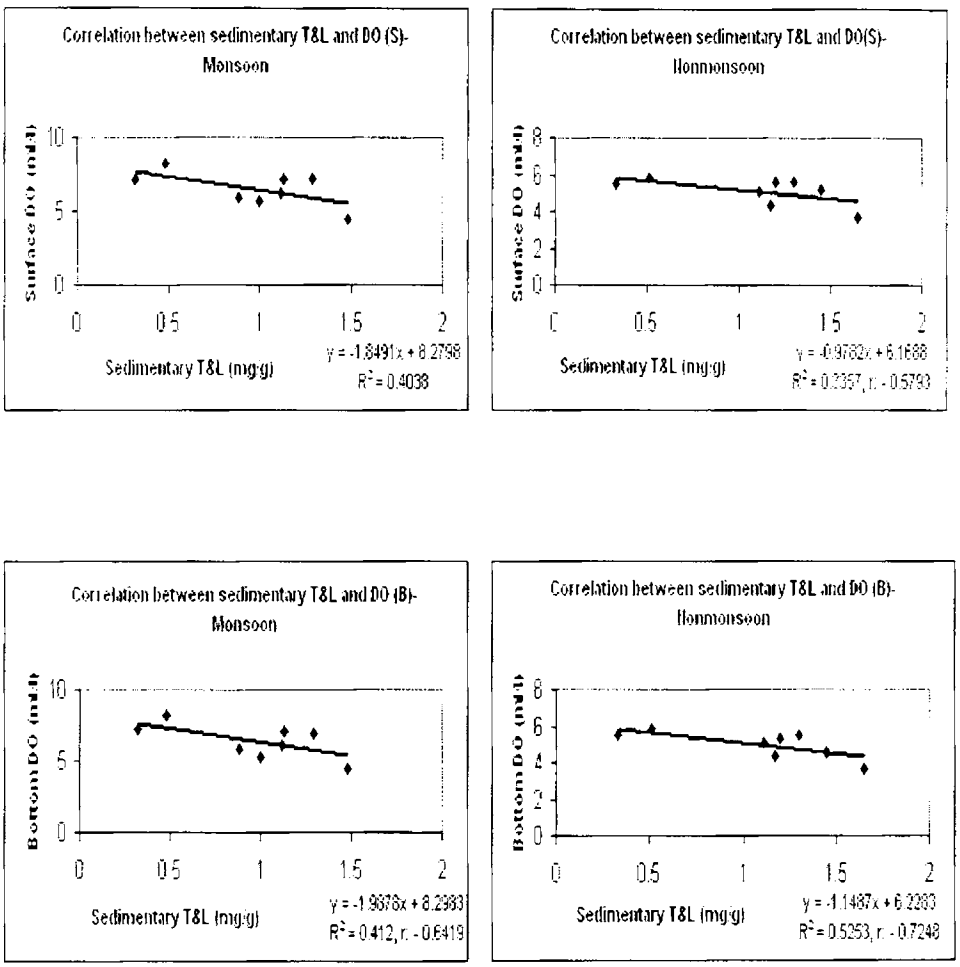

Figure 6.40 Correlation of sedimentary tannin and lignin with dissolved oxygen (S-Surface, B-Bottom).

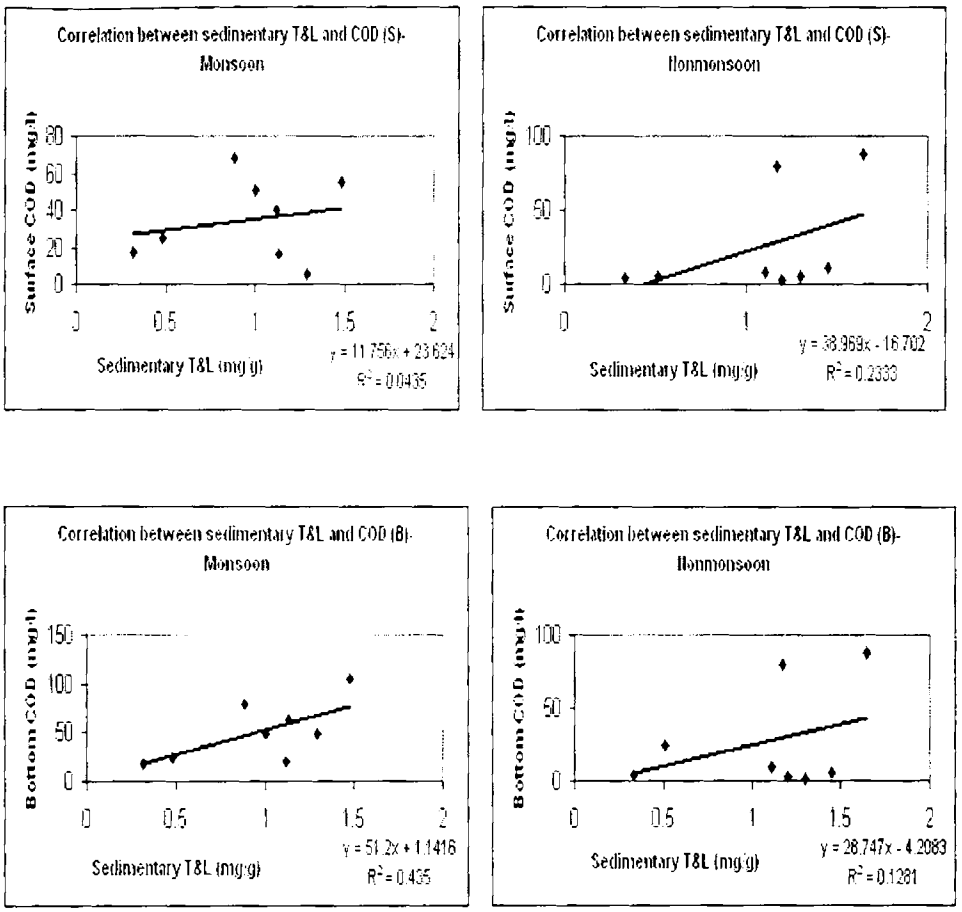

Figure 6.41 Correlation of sedimentary tannin and lignin with COD (S-Surface, B-Bottom).

Hydroxylated aromatic compounds of terrestrial origin are found in the low range of concentration at stations 1 to 6. Stations 7 and 8 showed comparatively higher values. The slight enhancement in the concentration on these estuarine stations mainly contributed by the fish hatchery unit situated near to station 8. The distribution of sediment organic carbon in

and around bar mouth region noticeably differs from other stations and also with the distribution of tannin and lignin. The study reveals the presence of tannin and lignin like substances more in the estuarine regions than the freshwater regions. The removal of lignin from the water media may by itself be a complex phenomena accountable by either one or a combination of the following processes

a) Coagulation
b) Formation of lingo sulphonates
c) Sorption on particulates
d) Limited bacterial oxidation
e) Diution by receiving waters
f) Formation of compounds undetectable to the analytical methods.

Summarizing the general observations, in all the compartments i.e. dissolved, sedimental and particulate phases, tannin and lignin concentrations were found to be higher in the estuarine region compared to riverine stations. Lower concentrations observed in the riverine stations can be the consequence of increased particle size which decreased the adsorption/incorporation of organics from terrestrial origin. In nature phenol will form complexes with nitrogenous compound like proteins and free amino acids and makes them less susceptible for microbial degradation. This reduces mineralization and release of nutrients (Joseph and Chandrika, 2000).

For all the environmental compartments studied here an increase in concentration is observed downstream which shows that majority of organics originated in the upstream area are carried downstream and precipitated in the estuarine stations in the downstream end. Mixing of river water of high ionic strength and estuarine water of high ionic strength is known to result in precipitation of organics (Burton and Liss, 1976). Though, station 1, was riverine in nature, the concentrations reported here was slightly higher than the other riverine stations. The low content noticed in the other riverine region may be a result of frequent dredging of river sand and the influence of grain size (sandy nature).

Statistical Approach

Abbreviations

NS	:	Not Significant
dof		degrees of freedom
MSS		Mean Sum of Squares
(P<0.05)		calculated F is significant at 5% level
(P<0. 01)		calculated F is significant at 1% level
(P<0.001)		calculated F is significant at 0.1% level
MDS		Multidimensional scaling

Table 6.5 Distribution of dissolved tannin and lignin

station	mean	std	CV%	station	Mean	std	CV%
S1	0.993	0.301	30.27	S5	0.545	0.162	29.69
B1	1.023	0.091	8.91	B5	0.606	0.162	31.66
S2	0.157	0.101	64.22	S6	0.919	0.272	29.63
B2	0.157	0.101	64.22	B6	0.911	0.319	35.01
S3	0.236	0.172	73.15	S7	0.840	0.229	27.29
B3	0.236	0.172	73.15	B7	0.839	0.223	26.60
S4	0.475	0.118	24.91	S8	1.195	0.265	22.17
B4	0.553	0.184	33.24	B8	1.182	0.269	22.78

Distribution of dissolved Tannin and Lignin (Table 6.5), averaged over seasons, showed a range of 0.157 (station 2) to 1.195 (station 8) at surface with a seasonal variation of 22.17% (station 8) to 73.15% (station 3). Tannin and Lignin at bottom depicted a pattern similar to that observed at surface with a highest value of 1.182 at station 8 and least value of 0.157 at station 2 along a seasonal variation range of 8.91% (station B1) to 73.15% (station B3) with an increasing trend both for seasonal average as well as seasonal variation.

3 way ANOVA (Table 6.6) carried out showed only high station wise ($F_{(7,35)}$=205.52, $p<0.001$) and seasonal ($F_{(5,35)}$=82.83, $p<0.001$) with high interaction between stations and seasons ($F_{(356,35)}$=2.23, $p<0.05$).

Table 6.6 3 way ANOVA for comparing dissolved tannin and lignin with respect to station, surface and bottom and seasons

Source	SS	dof	MSS	F ratio	Remarks
Stations (A)	11.4716	7	1.6388	205.5179	(P<0.001)
Sur/Bot (B)	0.00799942	1	0.007999	1.00317	NS
Seasons (C)	3.30234	5	0.66047	82.8262	(P<0.001)
AB interaction		7	0.003530	0.4427	NS
BCinteraction		5	0.011282	1.41487	NS
ACinteraction		35	0.017803	2.23265	(P<0.05)
Error	0.279095	35	0.007974		
Total	60.0470	95			

Dendrogram drawn, grouped July and September in one cluster, which are the periods of lower values at stations 1 to 3, both at surface and bottom and grouped January, November, May and March together which are the periods of flourishing values of Tannin and Lignin at stations 1 to 8 (Figures 5.42 a and b).

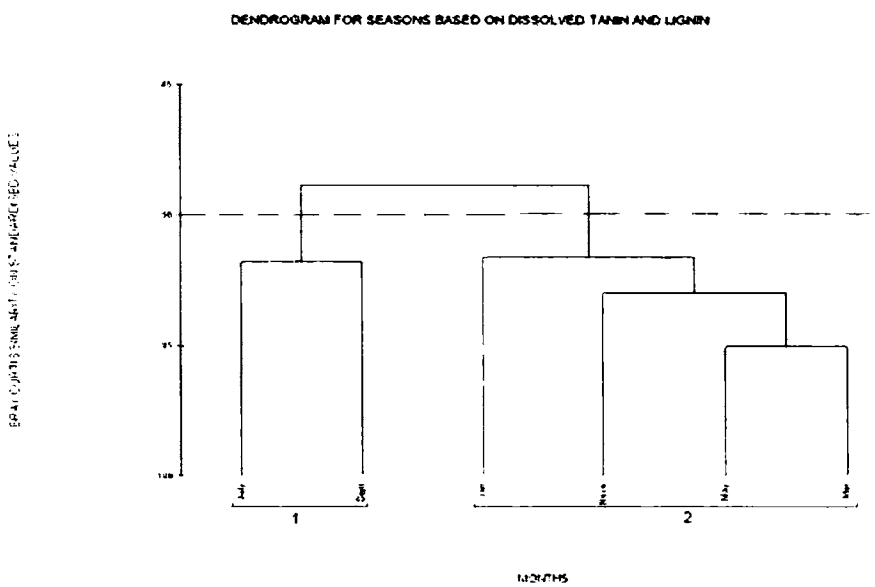

Figure 6.42 a. Dendrogram for seasons based on dissolved tannin and lignin

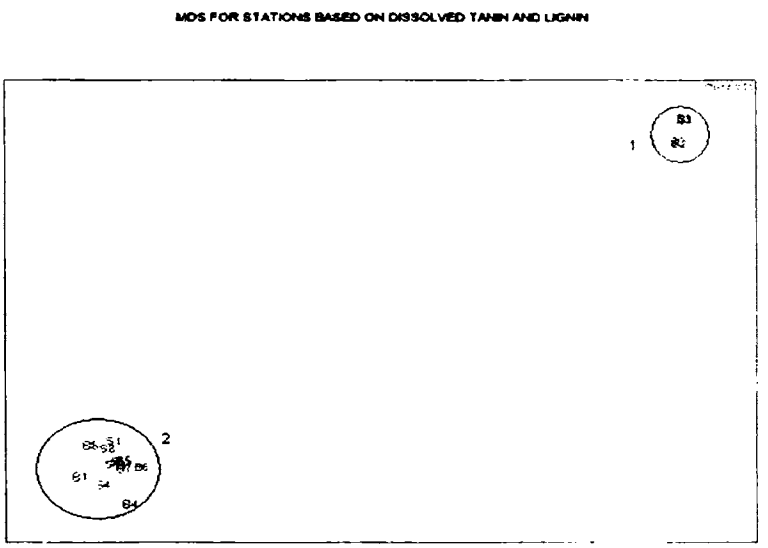

Figure 6.42 b. MDS for stations based on dissolved tannin and lignin

Trellis diagram depicted the significant difference between station 1 and station 2-5 ($t(10) \geq 3.169$, $p<0.01$) and station 2 and 3 with station 4- 8 ($t(10) \geq 3.169$, $p<0.01$) and also station 4 and 5 with stations 6 to station 8 ($t(10) \geq 1.812$, $p<0.10$) (Table 6.7).

Table 6.7 Trellis diagram for students t test to compare between stations based on dissolved tannin and lignin (• Not significant; • Significant at 10% level; • Significant at 5% level; • Significant at 1% level)

	S1	B1	S2	B2	S3	B3	S4	B4	S5	B5	S6	B6	S7	B7	S8	B8
S1		0.21	5.89	5.89	4.89	4.89	3.59	2.8	2.94	2.43	0.41	0.42	0.91	0.92	1.13	1.05
B1	•		14.2	14.2	9.03	9.03	8.21	5.14	5.76	4.39	0.81	0.76	1.66	1.71	1.37	1.25
S2	•	•		0	0.87	0.87	4.56	4.21	4.54	4.62	5.86	5.04	6.09	6.22	8.18	7.96
B2	•	•	•		0.87	0.87	4.56	4.21	4.54	4.62	5.86	5.04	6.09	6.22	8.18	7.96
S3	•	•	•	•		0	2.56	2.81	2.93	3.21	4.74	4.16	4.71	4.78	6.79	6.62
B3	•	•	•	•	•		2.56	2.81	2.93	3.21	4.74	4.16	4.71	4.78	6.79	6.62
S4	•	•	•	•	•	•		0.8	0.78	1.3	3.35	2.87	3.16	3.22	5.55	5.38
B4	•	•	•	•	•	•	•		0.07	0.45	2.5	2.18	2.19	2.21	4.46	4.32
S5	•	•	•	•	•	•	•	•		0.54	2.64	2.29	2.35	2.38	4.68	4.53
B5	•	•	•	•	•	•	•	•	•		2.1	1.84	1.75	1.77	4.03	3.89
S6	•	•	•	•	•	•	•	•	•	•		0.04	0.5	0.51	1.63	1.53
B6	•	•	•	•	•	•	•	•	•	•	•		0.41	0.42	1.53	1.45
S7	•	•	•	•	•	•	•	•	•	•	•	•		0.01	2.27	2.16
B7	•	•	•	•	•	•	•	•	•	•	•	•	•		2.30	2.19
S8	•	•	•	•	•	•	•	•	•	•	•	•	•	•		0.08
B8	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	

Table 6.8 Distribution of particulate tannin and lignin

station	mean	std	CV%	station	Mean	std	CV%
S1	0.401	0.186	46.29	S5	0.063	0.025	40.55
B1	0.443	0.187	42.25	B5	0.083	0.045	54.67
S2	0.057	0.019	33.49	S6	0.136	0.093	68.20
B2	0.057	0.019	33.49	B6	0.136	0.108	69.25
S3	0.054	0.024	44.82	S7	0.332	0.176	52.94
B3	0.054	0.024	44.82	B7	0.353	0.199	56.23
S4	0.071	0.034	47.91	S8	0.521	0.138	26.56
B4	0.078	0.035	44.42	B8	0.545	0.147	26.96

Particulate tannin and Lignin (Table 6.8) observed at station, surface and bottom, averaged over seasons depicted a distribution with range, 0.057 (station 2 to 0.521 (station 8) and with a seasonal dispersion of values, range, 26.56% (station 8) to 68.20% (station 6) at surface. At bottom the corresponding values are 0.057 (station 2) to 0.545 (station 8) with values 26.96% (station 8) to 69.25% (station 6).

3 way ANNOVA (Table 6.9) carried out for various comparative purposes, showed high station wise differences ($F_{(7,35)}$=1688.62, $p<0.0001$) surface and bottom differences ($F_{(1,35)}$=19.47, $p<0.001$) and seasonal differences ($F_{(5,35)}$=19.47, $p<0.001$) with high station-surface/bottom interaction ($F_{(97,35)}$=13.28, $p<0.001$) and station-season interaction ($F_{(35,35)}$=10.67, $p<0.001$) as indicated by high values at bottom, at stations 4 to 8 and lower values during July and September at all stations.

Table 6.9 3 way ANOVA for comparing particulate tannin and lignin with respect to station, surface and bottom and seasons

Source	SS	dof	MSS	F ratio	Remarks
Stations (A)	3.0711	7	0.43873	1688.9171	0.01%
Sur/Bot (B)	0.006884	1	0.006884	32.9199	0.1%
Seasons (C)	0.74549	5	0.149098	19.4719	0.1%
AB interaction		7	0.000590393	13.2768	0.1%
BC interaction		5	0.00041151	1.18178	NS
AC interaction		35	0.014025	10.6607	0.1%
Error	0.00909185	35	0.00025977		
Total	8.6753	95			

Dendrogram for season grouped the 6 months into 2 clusters: 1. July and September, periods of lower particulate Tanin and Lignin 2. January, November, May and March, periods of comparatively higher values of Tanin and Lignin (Figure 6.43).

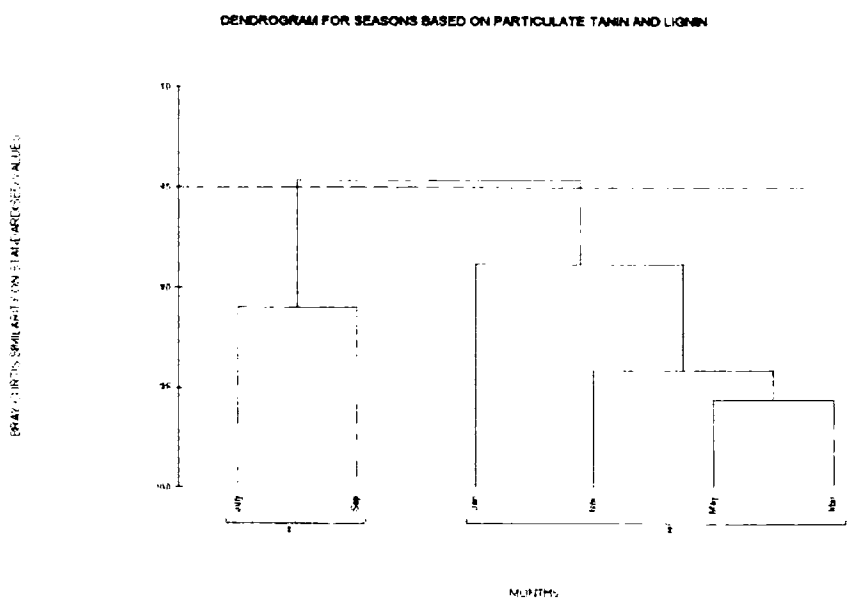

Figure 6.43 Dendrogram for seasons based on dissolved tannin and lignin

Trellis diagram presented the significant differences between station 1 and station 2 to 6 ($t(10)>3.169$, $p<0.90$) and also between station 2 to 6 and stations 7 and 8 ($t(10) \geq 3.169$, $p<0.01$) (Table 6.10).

Table 6.10 Trellis diagram for students t test to compare between stations based on particulate tannin and lignin (• Not significant; • Significant at 10% level; • Significant at 5% level; • Significant at 1% level)

	S1	B1	S2	B2	S3	B3	S4	B4	S5	B5	S6	B6	S7	B7	S8	B8
S1		0.35	4.12	4.11	4.15	4.15	3.91	3.82	4.04	3.72	2.86	2.36	0.6	0.39	1.15	1.35
B1	•		4.58	4.58	4.61	4.61	4.37	4.29	4.5	4.18	3.29	2.97	0.96	0.73	0.75	0.96
S2	•	•		0	0.27	0.27	0.77	1.17	0.36	1.16	1.86	2.01	3.47	3.32	7.42	7.36
B2	•	•	•		0.26	0.27	0.77	1.17	0.36	1.16	1.86	2.01	3.47	3.32	7.42	7.36
S3	•	•	•	•		0	0.92	1.3	0.57	1.28	1.92	2.07	3.51	3.35	7.44	7.38
B3	•	•	•	•	•		0.92	1.3	0.57	1.28	1.92	2.07	3.51	3.35	7.44	7.38
S4	•	•	•	•	•	•		0.34	0.44	0.48	1.47	1.68	3.26	3.13	7.06	7.03
B4	•	•	•	•	•	•	•		0.81	0.19	1.3	1.53	3.17	3.05	6.94	6.91
S5	•	•	•	•	•	•	•	•		0.88	1.71	1.88	3.39	3.25	7.29	7.24
B5	•	•	•	•	•	•	•	•	•		1.15	1.39	3.07	2.97	6.72	6.72
S6	•	•	•	•	•	•	•	•	•	•		0.32	2.21	2.22	5.17	5.27
B6	•	•	•	•	•	•	•	•	•	•	•		1.91	1.95	4.67	4.77
S7	•	•	•	•	•	•	•	•	•	•	•	•		0.18	1.88	2.08
B7	•	•	•	•	•	•	•	•	•	•	•	•	•		1.54	1.73
S8	•	•	•	•	•	•	•	•	•	•	•	•	•	•		0.27
B8	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	

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SUMMARY

Environmental biogeochemistry is a dynamic subject, because it is greatly concerned with chemical transformations especially those that are catalysed by living organisms. This thesis focuses attention on the role of biogeoorganics in modifying the ecological and environmental condition as well as the status of the sediments with their minute variability subjected to various physicochemical processes.

The investigations reported herein pertain to the studies conducted on the dissolved, particulate and sedimentary environments of Chalakudy river between 2005 and 2006. The study has incorporated the general hydrographic parameters like temperature, pH, salinity, dissolved oxygen and chemical oxygen demand for water samples and sediment organic carbon, moisture content, CHN and grainsize for sediments. Quantitative evaluation of proteins, carbohydrates and tannin and lignin were discussed in detail.

High values of salinity were registered only at the estuarine stations. Textural studies based on sand, silt and clay ratios of sediments indicated that sand was predominant in the riverine region and clay or silt in the estuarine region. The decreasing trend was observed in grain size due to the transport of sediment from riverine to estuarine region. The important factors affecting the general hydrography of estuarine stations are rainfall, freshwater inflow and intrusion of seawater through the river mouth.

Organic matter comes from a once-living organism, is capable of decay or the product of decay or is composed of organic compounds. The definition of organic matter varies upon the subject it is being used for. Measurements of organic matter generally quantify only organic compounds or carbon, and so are only an approximation of the level of once-living or decomposed matter. Proteins are organic compounds made of amino acids arranged in a linear chain. Carbohydrates included polyhydroxylated aliphatic compounds ranging in size from monomers to large biopolymers. Tannin and lignins are high molecular weight polycyclic aromatic compounds widely distributed throughout the plant kingdom. Waterfall stations exhibited the lowest carbohydrates and proteins and tannin and lignin. The concentrations were highest at the dam and estuarine end. Protein, carbohydrates and tannin and lignin contents of waterfall regions were lower than other six stations which was due to low organic matter and high sandy nature of the sediments. High flowing nature of the river at these sites restricted the accumulation of organic carbons and were washed away with every incoming water. The maximum value was obtained at the Azhikodu estuary. Presence of high organic carbon and clay contents increased the amount of carbohydrates, proteins and tannin and lignin at reservoir and the riverine stations. These components could be strongly adsorbed onto particulate matter and clay minerals and the sediments of these stations contained much of the adsorbed proteins and those were not readily desorbed. The high values of these organic components in the estuarine region could also be attributed to anthropogenic input, high rate

of sedimentation, productivity and death and decay of aquatic organisms and floating plants.

All parameters were analyzed for comparing between surface and bottom and among stations in the dissolved, particulate and sedimentary environment and statistical approach was done as applicable to each of the parameters using 3 way ANOVA. Advantage of the 3 way ANOVA over the 2 way ANOVA is that we get the interaction between the 3 factors, taken two at a time in the former case. Pair wise comparison carried out using students 't' test gave significant results.

The studies of biogeoorganics revealed that the organic matter is mostly of terrestrial origin and make profound influence in the biogeochemical processes and there is every scope for effective management of the Chalakudy river- estuarine system.