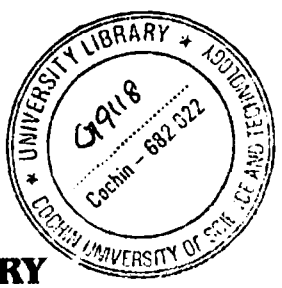
CHARACTERISATION AND DISTRIBUTION OF AMINO ACIDS IN THE MANGROVE SEDIMENTS OF KOCHI

A Thesis Submitted to the Cochin University of Science and Technology in Partial Fulfilment of the Requirements for the Degree of



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ENVIRONMENTAL CHEMISTRY

Under the Faculty of Marine Sciences

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Certificate

This is to certify that the thesis titled "Characterisation and Distribution of Amino Acids in the Mangrove Sediments of Kochi" is an authentic record of the research work carried out by Smt. Zeena P. Ravi, under my supervision and guidance in the Department of Chemical Oceanography, School of Marine Sciences, Cochin University of Science and Technology, in partial fulfilment of the requirements for the Ph.D . degree of Cochin University of Science and Technology and no part thereof has been presented before for any other degree in any University.

Kochi -16

May, 2005

Dr. N. Chandramohanakumar

(Supervising Guide)

DECLARATION

I hereby declare that this thesis entitled "Characterisation and distribution of amino acids in the mangrove sediments of Kochi" is an authentic record of the research carried out by me under the supervision of Dr. N. Chandramohanakumar, Professor, Department of Chemical Oceanography, School of Marine Sciences, Cochin University of Science and Technology, and that no part of it has previously formed the basis of award of any degree, diploma, associateship, fellowship or any other similar title or recognition in any University.

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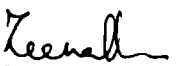

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If there are no mangrove forests, then the sea will have no meaning. It is like *having a tree with no roots, for the mangroves are the roots of the sea....*

– Fisherman on the coast of the Andaman Sea, Trang Province, Southern Thailand

Preface

Mangroves occur in dense, brackish swamps along coastal and tidally influenced shorelines. Leaf litter, which includes leaves, twigs, seeds, flowers and small branches, is the major nutrient source to consumers in mangrove systems. Once fallen, leaves and twigs decompose rapidly and as the decomposition progresses nitrogen, protein, and caloric content within the leaves increase. Areas experiencing high tidal flushing rates, or which are flooded frequently, have faster rates of decomposition than other areas. To study the past history of the ecosystem, it is important to study the sediment there, as the sediment act as a sink and a source of materials. Studies on the core of the sediment provide a historical record of both natural and man-induced accumulation of various chemical compounds.

Large quantity of organic matter composed of carbohydrates, proteins, amino acids, pigments, lipids and phenolic substances are present in mangroves. The organic matter content of sediment is determined by various sources and the rates at which these are degraded by biological and chemical processes. Proteins are generally the largest components of organic nitrogen compounds. Plants and animal residues are the major source of proteins in sediments. Microorganisms utilise proteins since they are easily hydrolysable compounds and produce amino acids. A major chemical process in the early stage of protein diagenesis is this degradation to free amino acids through various polypeptides. The individual amino acids and their ratios are significant indicators of depositional environment and changes in source materials that could be responsible for anomalies found in sediments.

The title of my thesis is "Characterisation and Distribution of Amino Acids in the Mangrove Sediments of Kochi." For the study, sediment samples were collected from two mangroves in Kochi area. Station I is

Mangalavanam, which is surrounded by brackish waters can be considered as a closed system with minimum human intervention. There is one outlet in the form of a canal opening to backwaters. Avicennia, Rhizophora and Acanthus are the three main mangrove plant species seen here. Station II is Vypeen, which is a semi-enclosed system lie adjacent to the brackish waters. Vypeen is an island closer to the sea than the other station. Collections of both water and surface sediments were made for a period of one year and sediment-cores during the months of April, July and December.

The thesis is divided into five Chapters. The first chapter gives an introduction on mangrove ecosystem, the general hydrography, sedimentary organic matter and amino acids.

The second chapter gives a description of the study area, sampling protocols for water, sediment and leaf samples and the various analytical methods employed in the estimation. Besides this, the hydrographical characteristics and the sedimentary characteristics of the study area are also given in this chapter.

In the third chapter, the seasonal and vertical distribution of various organic compounds like organic carbon, nitrogen, carbohydrates, proteins and amino acids in the sediment are discussed.

The fourth chapter gives the characterisation and vertical distribution of each amino acid in the sediment and leaves of three common mangrove species in the study area. High Performance Liquid Chromatography is used for this study.

In the fifth chapter, Principal Component Analysis of the various amino acids and the bio-geo-chemicals present in the sediment is discussed. The identification of sources and fate of these compounds along with bioavailability could be well established by this statistical tool.

A brief summary of the work done is given at the end of the thesis and the references at the end of each chapter.

CONTENTS

List of Abbreviations Used

Vyp	-	Vypeen
Mngl	-	Mangalavanam
FAA	-	Free Amino Acids
TAA	-	Total Amino Acids
SOM	-	Sedimentary Organic Matter
SOC	-	Sedimentary Organic Carbon
SON	-	Sedimentary Organic Nitrogen
MCHO	-	Mono Carbohydrates
TCHO	-	Total Carbohydrates
PCHO	-	Poly Carbohydrates
Premon	-	Pre monsoon
Postmon	-	Post monsoon
Mon	-	Monsoon

Chapter 1

INTRODUCTION

1.1 Mangrove Ecosystem

1.2 Organic matter

1.3 Different Organic Compounds

Aquatic ecosystems are responsible for a major share of the planet's biotic productivity. These ecosystems can be divided into open sea, coastal zone, lakes and reservoirs, rivers and streams and fresh water wetlands. Of these, the coastal zone includes estuaries, tidal wetlands, and coral reefs. In estuaries and along coastlines, tidal movements of waters can create tidal wetlands like marshes or mangroves. Mangrove forests belong to the major ecosystems of the biosphere, and about 60-75% of tropical coasts are fringed by this highly productive ecosystem.

1.1 Mangrove Ecosystem

Mangroves form a unique association of plants dominated by the mangrove forest as the primary producers interacting with associated fauna and the physical environment. Mangroves are important as stabilizers of sediments, in some areas creating new areas of land over long period of time. Mangroves accumulate sediment and consequently many pollutants toxins washed into it are retained there in the soil and plants. The sediment accumulated in the mangroves, traps the pollutants from the overlying water and thus purifies the water (Machado *et al*, 2004). The sediments in mangroves are more anoxic than usual soil. This means that they have less oxygen and will be darker and stronger smelling. The prolonged presence of water and the lack of oxygen cause chemical changes that eventually affect the dark color of the soil (Murray *et al.*, 2002). The sediments are made of sand, silt, clay, and elements such as iron and manganese.

Mangrove ecosystems have extremely high natural productivity in terms of plant growth and all the associated organisms. Much of this productivity translates into useful products for people in the form of wood, fish and crustaceans and various other ecological and economic benefits.

Mangrove productivity is important because it has direct impact on the health and function of the marine food chain (Saenger *et al.*, 1983). The role of mangrove trees as primary producers in the inshore areas is substantial. Mangroves may enhance adult fish biomass by enriching the primary production in the ecosystem by the addition of nutrients to it and these mangroves act as nurseries that provide the juveniles a refuge from predators and provide them plentiful food (Mumby *et al*, 2004). The productivity of the mangrove ecosystem is high, and a substantial fraction of this represents energy that is available for secondary production by animals and decomposers, or for export from the ecosystem.

Up to half of the world mangrove swamps have disappeared in the last 20-30 years because of the development of tourist resorts, transport infra structure and commercial prawn fishing. Instead of protecting this vital ecosystem that nature provides against wind and wave, they had been foolishly degraded or removed for unsustainable developments.

1.1.1 Different Types of Mangrove Forests

Gilmore and Snedaker (1993) described 5 distinct types of mangrove forests based on water level, wave energy, and pore water salinity. These are 1) mangrove fringe forests, 2) overwash mangrove islands, 3) riverine mangrove forests, 4) basin mangrove forests, and 5) dwarf mangrove forests. Riverine forests grow as tall flood plain forests along flowing tidal rivers and creeks. Overwash forests are islands frequently flooded by tides. Fringing forests are found as a relatively thin fringe of mangroves along waterways. Basin mangrove forests occur in inland depressions, which are irregularly flushed by tides. Because of irregular tidal action in these forests, hypersaline conditions are likely to occur periodically and this may severely limit growth, or induce mortality in mangroves. Dwarf mangrove forests occur in areas where nutrients, freshwater, and inundation by tides are all limited. Any mangrove species can be dwarfed, with trees generally limited in height to approximately 1 meter or less. Despite their small size

and relatively low area to biomass ratios, dwarf mangroves typically have higher leaf litter production rates.

1.1.2 Factors affecting the growth of Mangroves

Mangroves depend on many factors like Climatic or environmental factors like temperature, rainfall, humidity, wind, edaphic and geomorphologic factors, geological factors and biological factors. Tidal fluctuations have a great influence on the mangrove distribution. Changes in sea level resulted in changes in coastal levels and thus distribution of mangroves, as the mangroves grow in the tidal or intertidal coastal zone. Geological factors that affect the growth of mangroves include changes in altitude between sea and land, sea land fluctuation, changes in tidal range, compactness in the sediment, soil erosion, deposition of silt etc.

1.1.3 Geographical Distribution of Mangroves

- *Mangroves of the world*

According to the report of the World Resources Institute, mangroves resources are available in 117 countries covering an area of 190000 km2 occupying about one-quarter of the world's coastal line. Countries like Indonesia, Nigeria and Australia have the largest mangrove areas. Mangroves can be divided into New World group and Old World group mangroves. The New World group includes north, central and southern America and Western Africa. In the Old World group mangroves are confined to the Persian Gulf, Madagascar, Indo-Malaysian and Australian regions. India, Pakistan, Bangladesh, Myanmar, Indonesia, Papua New Guinea and Northern Australia represent the Indo Malaysian group. Sixty-five species found in the old world group are not found in the new group and ten dominant species in the new world group are not found in the old world group (Upadhyay *et al.*, 2002). The largest mangrove area occurs in Indonesia (30%) followed by Nigeria (10%), Australia (8%) and Mexico

(7%). India contributes approximately 3% to the world mangrove area. The Indian coastline can be divided into the east and west coasts and island chains. The east coast covers the maritime states like Tamil Nadu, Andhra Pradesh, Orissa, West Bengal and Andaman-Nicobar Islands. The West coast extends from Kerala, Karnataka, Goa, Maharashtra, and Gujarat and also includes the coral atolls of Lakshadweep Islands. The total mangrove area along the Indian coast is estimated to be approximately 700,000 ha.

➢ *Mangroves of India*

The Indian coastal zone is a dynamic area with many cyclic and random processes owing to a variety of resources and habitats. India has a coastline of 6,000 km with many sprawling and still growing coastal sites. The coastal region is thus a place of hectic human activity, followed by intense urbanization, resulting in human interference of rapid development. The coastal ecosystems are now highly disturbed and very much threatened, encountering problems like pollution, siltation, and erosion, flooding saltwater intrusion, storm surges and other activities due to ever expanding human settlements. The total area of mangroves in India is approximately 6740 sq km., of this, about 57% of mangroves are found on the east coast, 23% on the west coast and the remaining 20% on the Andaman & Nicobar Islands.

The mangrove ecosystem of the East coast of India are mostly deltaic type and distributed in 5 major deltas as well as estuarine mouths of 4 states viz. Tamil Nadu, Andhra Pradesh, Orissa and West Bengal. The coastline of Tamil Nadu extends about 950 km. Mahanadi mangroves are present near the mid region of Orissa coast. The east coast of India is endowed with the world's largest mangrove forest with Gangetic Sunderbans, 60% of which lies in Bangladesh and 40% in India. The total land area of the Indian Sunderbans mangrove forest at present is about 2300 km2.

Gujarat is the north-western state of India and the total length of the coastline, facing the Arabian Sea is about 1600 km. The total length of the

Maharashtra coast is estimated about 720 km and the mangrove area is only 148.4 km2. Goa coastal region is situated in the Central-West Coast of India, facing the Arabian Sea and extended North to South. The total length of the coast line of Goa is approximately 120 km. Karnataka state coastline is about 320 km long and the mangroves in Karnataka are of fringing type, found in the intertidal regions along the estuaries, backwaters, islands and other protected areas.

The Indian mangroves comprise approximately 59 species in 41 genera and 29 families. There are about 25 mangrove species, which have restricted distribution along the east coast and are not found on the west coast. Similarly, there are eight species of mangroves like *Sonneratia caseolaris, Suaeda fruticosa, Urochondra setulosa* etc., which have been reported only from the west coast. There are approximately 16 mangrove species reported from the Gujarat coast, while Maharashtra has about 20 species, Goa 14 species and Karnataka 10.

➢ *Mangroves of Kerala*

Coastal plains and seas include the most taxonomically rich and productive ecosystems on the earth. Backwaters are an attractive, economically valuable feature of Kerala. These include lakes and ocean in lets which stretch irregularly along the Kerala coast. The biggest among these backwaters is the Vembanad Lake, with an area of 200 sq km, which opens out into the Arabian Sea at Cochin port, which is at the tip of the northern part of the Vembanad Lake. Cochin backwaters are widely regarded as one of the polluted estuaries in India as it receives contaminated freshwater inputs and discharges of effluents and partially treated sewage from many points throughout its tidally mixed zone.

The length of the Kerala coast is about 560 km, extending from north to south with parallel to the 'Western Ghat'. It is reported that 17 true mangrove species occur in the State (Unni and Kumar, 1997). Mangrove

area in Kerala is estimated to be 17 km2 in 1992 and of these 36% are in degrading or degraded condition (Basha, 1992). In Kerala, Mangroves are distributed in the northern part of Kochi port and Vypeen, Mahe to Dharmadom coastal belt, Ashramom, Paathiramanal, Mangalavanam and in several other small bits. There are hardly three to four species of mangrove, which are rarely found along the Kerala coast. The dominant mangrove species recorded in Kerala are *Avicennia marina*, *Rhizophora mucronata*, *Acanthus ilicifolius*, *Excoecaria agallocha*, *Acrostichum aureum and Cerebra manghas*. The higher population density in the Kerala coast has resulted tremendous pressure on the natural ecosystem. For urbanization, construction of harbors, ports, prawn farming, coconut plantation and rice-fish culture vast mangrove lands were cleared or reclaimed. .

Near Cochin Estuary mangrove patches are now mainly found in Mangalavanam, Panangad, Thripunithura, Kumbalam, Nettur, Panambukad, Puthuvype, Vypeen, Mulavukad, Kumbalangi, Kannamaly and Chellanam. Mangalavanam has a core area of 3.44 hectares of mangroves. It is also a bird sanctuary situated right in the heart of Kochi city. It is the home of many exotic and rare varieties of migratory birds. Here the mangroves are facing the growing threat of oil pollution. With the rich mangroves depleting fast, the number of migratory birds and also the shrimp population had come down considerably. At Kannamaly and Kumbalangi, mangroves are found in a stretch of around 8 hectares each. Panambukad and Puthuvype have a mangrove cover of around 10 hectares (Suma and Joy, 2003).

1.1.4 Significance of Mangroves

Mangroves play an important role in the biogeochemical cycles of coastal and marine ecosystems in the tropics (Dittmar and Lara, 2001). They form extensive and productive forests in the sheltered coastlines and a reservoir of plants and animals associated together over a long evolutionary time. They control floods, erosion, and sedimentation, improve water quality, recharge the water supply, and provide recreational opportunities.

They form natural barriers against sea intrusion and they are important land builders. They break up large storm and strong tidal currents, protects seacoasts from erosion, influence deposition of mud and silt by filtering sediments and toxic wastes originating from land

Many aquatic species, though not permanent mangrove inhabitants, make use of mangrove areas for foraging, roosting, breeding, and other activities. Mangrove canopies and aerial roots offer a wealth of habitat opportunities to many species of estuarine invertebrates. Mollusks, segmented worms, shrimp, insects, crabs, and lobsters all utilize mangrove prop roots as habitat for at least part of their life cycles. Additionally, mangrove roots are particularly suitable for juvenile fishes. Comparatively more fishes were sampled from mangrove areas than from adjacent sea grass beds (Thayer *et al.*, 1987). Mangroves may enhance adult fish biomass by enriching the primary production in the ecosystem by the addition of nutrients to it and these mangroves act as nurseries that provide the juveniles a refuge from predators and provide them plentiful food (Mumby *et al.*, 2004). They provide resting and nesting place for many birds. Mangroves are one of the most productive natural ecosystems and form an important part of the coastal and estuarine ecosystems and are nursery ground for many organisms.

1.2 Organic Matter

Mangroves are high organic matter producing ecosystems, which is the habitat of a many marine species. The high nutrient demand to maintain this productivity is met by external supply from runoff, rivers and tides and by intensive internal recycling through microbial and benthic activity (Jennerjahn and Ittekkot, 2002). Dissolved organic matter (DOM) enters the water that comes into the mangal at high tide. This promotes the growth of bacteria and other microorganisms in the water, as well as some algae, which support the suspension-feeding components of the food web. DOM is

also a major export from the mangrove ecosystem, where it is incorporated into the food webs of adjacent areas. Energy is also exported from the mangal into adjacent ecosystems as DOM, as well as in the form of planktonic organisms supported by DOM, in the currents that flow through the forest. Sedimentary organic matter (SOM) is significant since it exerts very strong control over the nature and changes occurring in sediments subsequent to deposition. Only a very small portion of dissolved organic matter escapes remineralisation during sinking and gets incorporated into sediments. Peptides, carbohydrates and other organic compounds of high molecular weight are adsorbed to metal oxides and mineral particles within the water column, which protects them against degradation, thus leading to an enrichment of compounds with higher molecular weight on the sediment surface (Kappler *et al.,* 2001).

Large quantities of OM composed of variety of organic compounds like carbohydrates, proteins, amino acids, pigments, lipids and phenolic substances are present in mangroves. A large component of the soft, grey mud found in mangroves is sediment that form when freshwater meets seawater at a river mouth. These particles tend to be fine and closely packed and there is little air among them. Thus mangrove mud tends to be soft and anaerobic (contains little or no oxygen), rich in detritus, on which some special bacteria that can breathe both with and without oxygen thrive. At first, these bacteria use up all the oxygen, and then start to use sulphur, releasing hydrogen sulphide as a by-product. The release of hydrogen sulphide turns the mud black and produces the smell of rotten eggs. These bacteria are eaten by other small creatures thus sparking off food chains in the mangroves. Thus we can say that black, stinky sediment is an indication of life in mangroves.

Organic matter has a high affinity for fine-grained sediment that accumulates in mangroves since it adsorbs onto mineral surfaces. As a consequence of efficient particle trapping, salt-marsh sediments are usually comprised of organic-rich and relatively impermeable clay. Sandy

sediments are relatively poor in organic matter preservation (Suthhof *et al.*, 2000). The finer particles may provide increased surface area per unit weight for adsorption of organic matter. So organic matter concentrations increase with decreasing grain size (Hedges and Keil, 1995; Nair *et al.*, 1993; Nandan *et al.*, 1996). It is also found that total SOC content increased with precipitation and clay content and decreased with temperature (Jackson and Jobbagy, 2000).

SOM has to be regarded as the residue of organic life and this becomes more important and more abundant with the development and diversification of life. The preservation of OM is almost exclusively restricted to sediments. The sources and burial processes of OM in marine sediment are not well understood, yet they're important if we are to have a better understanding of the global C cycle. Large quantities of OM composed of variety of organic compounds are present in mangrove sediments. Both natural and anthropogenic material accumulates simultaneously in sediments and it is difficult to identify the proportion of each source. The rate of loading of these materials depends on the different chemical and physical properties of the sediment (Soto and Paez, 2001). The main sources are decayed matter from plants, zooplankton, phytoplankton and higher plants. Particles from the euphotic zone sink to the sediment-water interface, where benthic organisms rapidly degrade the labile organic compounds present in the settled materials. The survival of these compounds in sediments depends mainly on their chemical stability (Premuzic *et al.*, 1982).

In an aquatic ecosystem, biological productivity depends on the production of phytoplankton and algae, which are major primary producers. But in the case of mangrove ecosystem, in addition to the occurrence of these primary producers, the accumulation of primary productive elements of mangrove flora itself in the form of detritus is an additional major support to the biological production (Rajendran and Kathiresan, 1999). The formation of detritus and release of nutrients in the mangrove areas directly

increase the benthic primary production and thereafter the secondary production in a large scale.

Mangrove detritus are not just limited to leaf materials. They also include twig, stem, prop roots, flower etc. (Wafar *et al.,* 1997). They can be classified into refractory and labile groups. Refractory detritus constituting humic acids, tannin and lignin represents the class of organic matter that are resistant to microbial attack and consequently decomposed at a relatively slow rate and labile detritus that constitutes proteins amino acids and carbohydrates can be easily consumed by bacteria and decomposed at a faster rate. Microbial degradation rates are dependent upon organic matter composition, as well as on molecular structure. Thus the presence of highly refractory organic compounds might significantly slow down their decomposition (Fabiano and Danovaro, 1998) and get preserved in the sediment (Henrichs, 1992).

Tidal rhythms operating in the coastal area of mangrove environment export the detritus, organic residues and nutrients to the adjacent waters and soil. It has been found that mangrove litters, flushed by tidal action represent the major component of organic matter export. The export of detritus and faunal biomass from mangroves has been considered as an important support for offshore biological production and has been widely used as an argument for mangrove conservation. Twilley (1992) estimated that 83% of the total allochthonous organic matter input to the estuarine environments was accounted for by mangrove forests. He also estimated that these forests accounted for approximately 18% of the total (allochthonous + autochthonous) organic carbon available for secondary productivity in the adjacent estuary. The efflux of detritus and nutrients in mangroves were supposed to enrich primary production in neighbouring ecosystems and thus mangrove nurseries provide plentiful food that increases the survivorship of fish- juveniles. This fact is supported by the abundance of various types of fishes in creeks and water masses lying adjacent to mangrove forests (Mumby *et al.,* 2004). Primary production exists in the form of microalgae

on the sediment surface and roots. The animals living there feed on the organic matter in the sediment. But benthic microalgal production in mangrove forests is often low due to light limitation and/or inhibition by soluble tannins (Alongi 1994) produced by certain species of plant leaves like Rhizophora mangle (Lacerda *et al.*, 1995).

The most extensive degradation of organic matter in aquatic environments takes place in the sediments (den Heyer and Kalff, 1998). From the surface water the organic matter gets vertically transported to the sediment surface and there it gets significant modification due to the activities of living organisms as a result of which the more labile components are preferentially lost. Organic material that which has not been degraded in the water column, underlie several degradation processes, chemical and physical reactions in the sediment. The amount of organic matter found in sediment is a function of the amount of various sources reaching the sediment surface and the rates at which different types of organic matter are degraded by microbial processes during burial. Many factors affect the degradability of organic matter in sediment. Resuspension is a factor that affects the degradation. Relatively labile organic matter can escape degradation if adsorbed within the sediment pores.

The decomposition of organic matter is variously referred to as oxidation, metabolism, degradation and mineralisation. Availability of oxygen is an important factor that determines the decomposition of organic matter (Bastviken *et al.*, 2001). For relatively fresh organic matter there won't be much difference between oxic and anoxic degradation (Suthhof *et al.*, 2000). Usually anaerobic respiration and fermentation processes are responsible for the degradation and mineralisation of organic matter (Kappler *et al.*, 2001; Holmer *et al.*, 2002). But if dissolved oxygen is present in the water column, organic matter is preferentially decomposed by oxygen-consuming bacteria. The concentration of dissolved oxygen is usually lowered when organic matter is degraded by aerobic bacteria. This will lead to the development of anoxic & hypoxic conditions. In many cases,

anoxia and hypoxia result from eutrophication and reflect the underlying problem of excessive nutrient loads. Eutrophication is caused by excessive nutrient loads and results in an increase in the rate of organic matter production in an ecosystem, and therefore of particulate organic matter supplied to bottom sediments (Nixon, 1995).

Organic matter is first oxidised by molecular oxygen, and the products of the reaction are carbon dioxide and recycled nutrients (the reaction is the reverse of photosynthesis). Oxygen is consumed within a few millimetres, and anaerobic respiration and fermentation processes are responsible for the degradation and mineralisation of organic matter (Kappler *et al.*, 2001; Holmer *et al.*, 2002). Harvey *et al.* (1995) and Sun *et al.* (1997) supported the view that oxic degradation is faster than anoxic. But, Gong and Hollander (1997) and Lee (1992) reported that the difference between oxic and anoxic decomposition rates is almost nil. These contradictory findings resulted in a debate regarding oxic and anoxic degradation in marine environments (Hedges and Keil, 1995). Anyhow, the OM in the surface was found to be decayed at a faster rate than those buried under due to the anaerobic conditions prevailing there (Albright, 1976). The thermal stability of the organic matter in the sediment increased from the surface layer (0-2 cm), which corresponds to the layer of microbial oxygen and nitrate reduction to the deeper sediment zone, whereas the amount of organic matter decreased with depth. This indicates a clear shift from the freshly deposited organic matter on the sediment surface to more humified material with increasing distance from the sediment surface (Kappler *et al.*, 2001).

Organic matter accumulates in the mangrove from both land and marine deposits as well as from recycled leaf litter. The rates of leaf litter fall and exchange with the coastal ocean may vary regionally. Robertson and Daniel (1989) and Lacerda (1992) reported 50% of the global rate of leaf litter fall is exported to the coastal zone, 25% recycled inside the mangroves and the remaining 25% accumulating in mangrove sediments. Micheli (1993) reported that 20-70% of litter in mangrove forests is

recycled within the forest by crabs, which remove the litter to burrows or consume it directly from the forest floor (Twilley *et al.,* 1997; Lee 1998, Robertson and Daniel 1989).

Many investigators have studied litter fall and litter decomposition in Indian mangroves. The overall biological production in mangrove areas is highly correlated to the detritus loading and their transportation through tidal waters. So litter fall is a valuable indicator of high productivity in mangrove ecosystem and its input of materials and energy into subtidal systems (Wafar *et al.*, 1997). Once the leaves fall, they begin to be degraded by a number of bacterial, fungal and meiofaunal organisms. Bacterial biomass predominates throughout decomposition of mangrove litters followed by fungi (Blum *et al.*, 1988) and some organisms feed directly on mangrove detritus.

In mangroves the decomposition was slower for leaves buried in the sediment than in the surface (Holmer and Olsen, 2002). But most carbon is exported from mangrove systems as leaves (Jennerjahn and Ittekkot, 2002). The extent to which the OM is preserved in sediments depends largely on the rate of deposition of total sediment components. Usually the concentration of organic matter is high at the surface of the sediment and its concentration decreases with depth. The organic matter undergoes diagenesis through various chemical or biochemical changes, like decarboxylation, deamination, demethylation, cyclisation, aromatisation etc. The preservation of OM is almost exclusively restricted to sediments.

The different types of organic matter found in sediments are humic acids, fulvic acid, amino acid, fatty acids, lipids, lignins, proteins, carbohydrates, purines, pyrimidines, hydrocarbons, steroids, chlorophyll, pheophytin etc. All these are present at different concentration at different areas. The amount and quality of the material depends on different factors, beginning with the season and ending with grain size of the sediment.

Almost all organic matter preservation occurs in coastal marine sediments, where a variety of factors might affect burial efficiencies (Hedges and Keil, 1995). The organic matter from the surface water gets vertically transported to the surface sediments and there it gets significant modification due to the activities of living organisms. The amount of organic matter found in sediment is a function of the amount of various sources reaching the sediment surface and the rates at which different types of organic matter are degraded by microbial processes during burial. Many factors affect the degradability of organic matter in sediment. Resuspension is a factor in the degradation of organic matter. Relatively labile organic matter can escape degradation if adsorbed within sediment pores. The extent to which the OM is preserved in sediments depends largely on the rate of deposition of total sediment components.

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Sediment studies can provide information about the role of sediments as a reservoir and a source of nutrients like C, N and P, which are liberated back to water through remineralisation and sediment water exchange processes. Sediments play a very important role in aquatic systems. Investigations on the organic matter in the sediments indicate the extent of biological activity and indirectly the fertility of overlying seawater as well as the status of pollution of the waters (Alagarsamy, 1991).

1.3 Different organic compounds

Large quantities of OM composed of variety of organic compounds like carbohydrates, proteins, amino acids, pigments, lipids, phenolic substances are present in mangroves. The main sources are decayed matter from plants, zooplankton, phytoplankton and higher plants.

1.3.1 Organic Carbon

In the biosphere, carbon is present as the building block of the plants and animals in the form of variety of carbon compounds such as carbohydrates, proteins and amino acids. Carbon enters the biological system either through geological process (weathering of carbon-bearing minerals such as limestone (CaCO3) and /or chemical process directly from the atmosphere (CO2) by photosynthesis. When the organism (including plant) dies out, the carbon is released back either directly to the atmosphere as CO2 or is mineralised as coal, limestone etc. So that it is returned to the lithosphere. Thus the carbon cycle is complete.

Wetlands are of great ecological importance, for instance by constituting unique habitats, but also by storing huge amounts of organic carbon and by contributing the largest source in the atmospheric methane budget thus affecting global climate. Dissolved organic carbon is the largest organic carbon pool in the marine environment and it plays a central role in the marine biogeochemistry (Cosovic *et al.*, 2000). Besides the organic matter input, the biogeochemistry of wetland soils is largely controlled by the availability of O_2. Wetland soils in general are characterized by a dominance of anaerobic processes in the bulk soil, while aerobic processes are restricted to thin oxic layers. These layers are formed at the very surface of the soil in contact with the floodwater (11) or around the roots of wetland plants. The anaerobic mangrove sediments produce favourable conditions for the preservation of organic carbon (Matsui, 1998).

Primary production by phytoplankton in surface waters is a major source of labile organic carbon to coastal sediment. High sedimentation and carbon accumulation rates are commonly reported features of mangrove ecosystems (Jennerjahn and Ittekkot, 2002). Particles from the euphotic zone sink to the sediment-water interface, where benthic organisms rapidly degrade the labile organic compounds present in the settled materials. The rate and extent of OM degradation significantly affect the chemistry of marine sediments (Berner, 1980). Pigments contribute only a small fraction of total C and N in marine particulates, but their unique source in surface waters makes them useful indicators of diagenesis. Plant functional types significantly affect the vertical distribution of SOC. Globally, the relative distribution of SOC with depth had a slightly stronger association with vegetation than with climate (Jobbagy and Jackson, 2000).

Most carbon is exported from mangrove systems as leaves. The mangrove carbon exported to the coastal zone forms a minor food source for higher organisms and its accumulation in sediments is mostly restricted to the vicinity of its source. The high rates of carbon production and accumulation in mangroves result in the increased fertility of adjacent coastal waters. These are mainly achieved by high biological activity inside the mangroves and the permanent recycling and exchange of nutrients between mangroves and coastal waters (Jennerjahn and Ittekkot, 2002).

1.3.2 Organic Nitrogen

Nitrogen is an essential nutrient for plants and animals. Nitrates in the soil result from natural biological processes associated with the decomposition of plant residues and organic matter. Nitrates can also come from animal manure and nitrogen fertilizers. In comparison with seawater, nutrients are consistently higher in the mangrove habitat. Partially treated sewage and farm drainage canals are proposed to form additional sources of nutrients (Al-Sayed *et al.*, 2004). Nitrogen is one of the important nutrients, the cycling of which highly influences the phytoplankton growth and

thereby the net primary production. It exists in water both in dissolved and particulate forms.

Leaf litter falling to the sediment bed represents a heterogeneous mixture of organic and inorganic molecules that are recycled through both anaerobic metabolic processes. DIN comprises NO_2^-+NO_3^++NH_4^+ and dissolved organic nitrogen is found in a wide range of complex chemical forms such as amino acids, proteins, urea and humic acids. Most of the nitrogen containing compounds are known to be highly sensitive to microbial degradation, and are expected to be rapidly mineralized or re-utilized for biological production. Some of them escapes mineralisation and gets incorporated into the refractory pool of the sediment and gets isolated from the overall nitrogen cycle. Approximately 90 % of the total N in sediments is incorporated into the organic fraction. The nitrogenous compounds are released during the degradation of organic matter.

Seitzinger (1988) reported denitrification as to be an important sink for biologically available nitrogen in coastal areas. In the surface sediments the organic matter remineralisation produces ammonium, a portion of which is converted to nitrate in presence of oxygen (Kemp *et al.*, 1990), which in turn denitrified to nitrogen (Howarth *et al.*, 1988) at the sediment water interface. The anthropogenic nutrient load has increased the primary production in coastal waters, thereby increasing the mineralisation in the sediment.

Biological nitrification-denitrification reaction is important as a nitrogen removal mechanism in fresh water marshes (Reddy *et al.*, 1989; Lindau and De laune, 1991), and in estuarine sediments (Jenkins and Kemp, 1984). It has been suggested that the denitrification in mangrove sediment, together with the assimilation of N by plants, might improve water quality in eutrophicated river (Nedwell, 1975). Evidence suggests that mangrove forests are generally nutrient limited with N (Onuf *et al.*, 1977; Boto and Wellington 1984). N was also considered a limiting factor for microbial

activity in the mangrove swamps (Kristensen *et al.*, 1992). On the other hand, natural and artificial wetlands have been used to control and remove N in contaminated wastewater discharges (Brodrick *et al.*, 1988). The fate of mineral forms of N in soil is determined to some extent by non-biological reactions involving NH_4^+, NH_3 and NO_2

1.3.3 Carbohydrates

These are the most abundant class of organic compounds produced in the biosphere. These are polyhydroxy aldehydes or ketones or compounds that can be hydrolysed to these compounds. Generally they are linked together into polymers and there are several important polymeric sugars that decompose and enter into aquatic system. These are susceptible to degradation, both chemical and biochemical and are important sources of monosaccharides and polysaccharides in aquatic environment.

Carbohydrates represent a group of compounds including simple sugars or monosaccharides, oligo and polysaccharides. Carbohydrates give an idea of the concentration of readily assimilable organic matter in the sediment and together with amino acids, they constitute about 40 to 80% of organic matter in marine organisms, suspended particles, sediment particles, dissolved organic matter and marine sediments of marine environments (Parsons *et al.*, 1984, Lee & Wakeham, 1987; Cowie & Hedges, 1992, Hernes *et al.*, 1996; Horsfall & Wolf, 1997). Given their ubiquity and abundance, carbohydrates are potentially powerful tools in elucidating the sources, processes, and pathways of biologically important organic materials in natural environments (Cowie and Hedges, 1984).

Carbohydrates are considered as primary products of photosynthesis (Liebezeit and Behrends, 1999). Both plankton and bacteria are characterized by high relative abundances of carbohydrates (Cowie and Hedges, 1984). These labile organic compounds can undergo chemical and biochemical degradation and influence various biogeochemical processes

occurring in the environment. Their high concentration in sediment may be due to the influence exerted on the composition of organic matter by bottom fauna, capable of resynthesising it from non-carbohydrate components of organic matter during the course of their vital activity. They form the main component of the sedimentary organic carbon. Their positive correlation to organic carbon is an evidence for their common source of origin in sediment (Bhosle *et al.,* 1978). They are typically labile relative to bulk C and N and account for a considerable portion of the particulate and dissolved OC and N recycled in both the water and sediments (Henrich & Farrington, 1987; Burdige & Martens, 1988).

The main source of carbohydrates is dead remains of plants in the form of monosaccharides and polysaccharides and organic acids rich in carbohydrates. The sediments also contain carbohydrates including amino sugars, uronic acids, hexoses, pentoses, cellulose and its derivatives. These are continuously used up by organisms in sediments and released carbohydrates represent an important food source for heterotrophs (Ittekkot *et al.,* 1984). In addition to sediments, algae and plants are important contributors to carbohydrates.

1.3.4 Proteins

Proteins occupy the central portion in the architecture and functioning of living organic matter. They are quantitatively the main material of animal tissues and are widely distributed in the sediments in different forms like plants, animal tissues and microbial population. They are generally the largest components of organic nitrogen compounds (Parsons *et al.*, 1977), in combination with carbon, hydrogen, and oxygen. Some also contain sulfur, phosphorus, or other basic elements also. The properties of each protein differ from one another in the total number and the type of amino acid in each of them, and the arrangement of the amino acids relative to each other.

Proteins are generally the largest components of organic nitrogen compounds (Parsons *et al.*, 1977). They occupy a central portion in the architecture and functioning of living organic matter. They are quantitatively the main material of animal tissues and are widely distributed in the sediments. Plants, animal residues and microbial population are the major source of proteins in sediments. Proteins are preferentially utilized since they are easily hydrolysable compounds. A vast group of microorganisms attack proteins and organic compounds to produce amino acids. All proteins contain carbon, hydrogen, oxygen, nitrogen and some contain even sulphur.

Adsorption of organic N compounds by clay minerals protects the molecule from decomposition. Complexes formed between organic N compounds and polyvalent cations, such as Fe, are biologically stable. Some of the organic N occurs in small pores or voids and is physically inaccessible to microorganisms. Microbial communities in shallow marine sediments play a key role in the oxidation of complex organic compounds and regeneration of nutrients essential for sustaining primary production in the overlying water column (Herbert, 1999). The fundamental significance and interdependence of these processes is well exemplified by the biogeochemical cycling of carbon and nitrogen. Since these elements are key constituents of all living matter it is perhaps not surprising that the impact of carbon and nitrogen availability on primary production and mineralisation of organic matter has been the subject of intensive study. Proteins serve as important substrates for bacterial growth, for the most part being rapidly recycled in the marine water column (Nguyen and Harvey, 1997).

Proteins have been considered very labile and unlikely to survive as high molecular mass components during early diagenesis. Dipeptides are found to be one of the major products as well as free amino acids during the earliest stage of protein degradation in sediments (Ogasawara, *et al.*, 2001). But recent works revealed that high molecular mass proteinaceous material comprised a significant fraction of the nitrogen in some sediment.

1.3.5 Amino acids

General formula shows a distinctive side group (R) together with two functional groups (amino and carboxyl), and a H atom all bound to a carbon called the alpha-carbon from organic chemistry nomenclature. When placed in solution at pH 7, the amino group and carboxyl groups are both ionoised. The state of ionisation varies with pH. In acid solution there are plenty protons about, and the carboxyl group is not ionised. In alkaline solution less protons are present, so the amino group not ionised, but the carboxyl group is ionised. All twenty amino acids are essential to life, but only nine amino acids are dietary essential. The body can form the other eleven amino acids from the dietary essential amino acids. The dietary essential amino acids are histidine, isoleucine, leucine, lysine, methionine, phenylalanine, threonine, tryptophan and valine. Arginine, ornithine, cysteine, taurine and tyrosine are classified as non-essential amino acids. Both the essential and non-essential amino acids are reassembled as hormones, enzymes, neurotransmitters (chemical messengers), antibodies and nutrient carriers. Glutamic acid is involved in the metabolism of sugars and fats, as well as being important for brain function, synthesis of DNA, glutathione and other amino acids. It also helps in removing excess ammonia from the body. Glycine is a natural antacid and sweetener that is involved in the synthesis of DNA, phospholipids and collagen, which also helps spare glucose for energy by improving glycogen storage. (Lehninger et al., 1993). Amino acids are categorised in 4 groups depending on chemical properties provided by the R side-chain. The groups are: non-polar (8 amino acids), polar uncharged (7), polar acidic (2), polar basic (3).

Non-polar amino acids: Alanine, Valine, Leucine, Isoleucine, Proline, Phenylalanine, Tryptophan, Methionine. These are hydrophobic amino acids, which do not interact with water since they have no polar groups.

Polar uncharged amino acids: Glycine, Serine, Cysteine, Asparagine, Glutamine, Tyrosine, Threonine. These amino acids are relatively

hydrophilic (water loving) because they possess polar functional groups in side chains i.e. oxygens and nitrogens, which can participate in hydrogen bonding with water so capable of interacting with water. The hydrophobic amino acids tend to repel the aqueous environment and, therefore, reside predominantly in the interior of proteins. This class of amino acids does not ionize nor participate in the formation of H-bonds. The hydrophilic amino acids tend to interact with the aqeuous environment, are often involved in the formation of H-bonds and are predominantly found on the exterior surfaces proteins or in the reactive centers of enzymes.

Polar basic (+ve charged) amino acids: Lysine, Arginine, Histidine. Lysine and Arginine have functional groups that are +vely charged at pH 7.

Polar acidic (-ve charged) amino acids: Aspartic acid and Glutamic acid. Both Aspartic acid and Glutamic acid have additional carboxyl groups in the side chains, which are fully ionised at pH 7. Consequently these amino acids are charged and very polar so tend to be located on the surface of proteins where they can form H-bonds with water molecules.

A protein is a polypeptide chain and the sequence of amino acids and the nature of the side chains determine how proteins fold, and this in turn determines the role and function of proteins. The properties of each protein are dictated by the precise sequence of amino acids in it. Although dipeptides are the smallest peptides consisting of only two amino acids, 400 dipeptides are theoretically possible for protein amino acids (Ogasawara, *et al.*, 2001). Though peptides are believed to be important intermediates in the degradation process, their presence in sediments has been suggested generally by the analyses of amino acids released by acid hydrolysis. Free and combined amino acids can be an important nitrogen source for some plants and soil nitrogen may play an important role in plant nutrition and ecosystem function (Yu, *et al.*, 2002). Nitrogen-rich compounds of OM such as amino acids are generally degraded faster than nitrogen-poor compounds like lipids.

Natural waters contain a wide range of free amino acids (FAA) and hydrolysable combined amino acids, which constitute the most important fraction of the dissolved organic nitrogen matter. They can be found in natural waters as excretion products of living organisms and as hydrolysis products of polypeptides. FAA can be formed in natural waters by the reaction of ammonia obtained during the biological fixation process of elemental nitrogen with naturally occurring carboxylic acids, in presence of NADPH (De Stefano *et al.*, 2002). In phytoplankton, most of the organic matter is made up of amino acids, carbohydrates and lipids and hence amino acids are abundant in waters with high productivity (Mulholland, 2002).

Amino acids that are important for many chemical and biochemical processes exist in different forms in the sediment. Presence and absence of different amino acids in an ecosystem indicate specific reactions taking place in that system. Free amino acids are generally present in very low concentrations in sediment and they almost disappear below 10 cm of the core. But combined amino acids present bound to sediment can be released into solution by acid hydrolysis and they are present in higher concentration than free amino acids.

The distribution of amino acids in many types of sediment is pretty similar. Coastal sediments can contain different types of amino acids like aspartic acid, glutamic acid, serine, glycine, threonine, alanine, lysine, leucine, valine, arginine, histidine, proline, tyrosine, phenylalanine etc. The study of amino acids helps to give an insight into various sources of amino acids and their depositional environments along with the degradation status of various amino acids.

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Chapter 2

MATERIALS AND METHODS

A brief description of the location of the sampling sites and an outline of the methods employed are given in this chapter. Besides, the general hydrography and grain size character of the sediment of the sampling sites form part of this chapter.

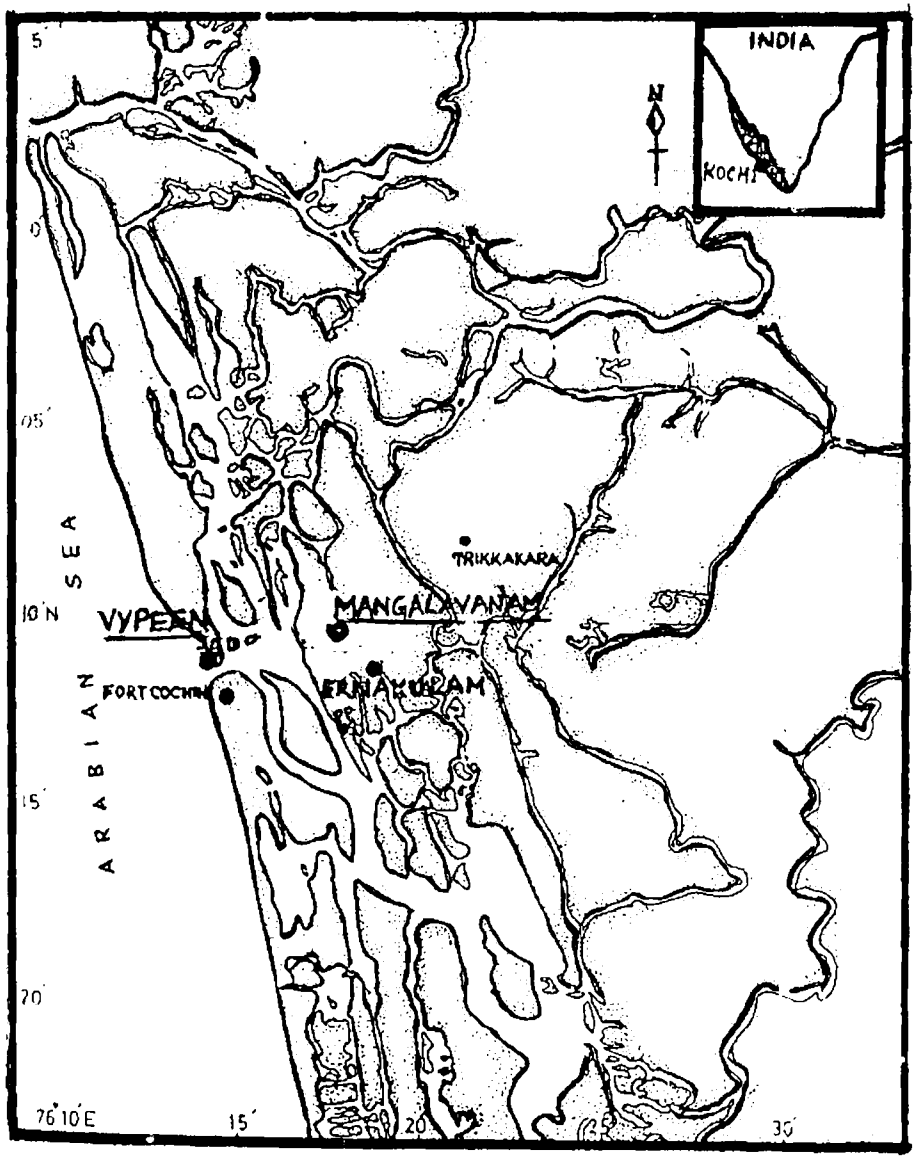
2.1 Description of the Study Area

Two different mangrove ecosystems in Cochin estuary, Mangalavanam and Vypeen are chosen for the study. Kochi has a moderate climate as it is situated very close to the sea. It gets heavy rains during June-August. The climatic condition available at Cochin identifies three seasons viz Monsoon, Post Monsoon and Premonsoon. The premonsoon coincides with summer and in summer the temperature rises to a maximum of 35°C. The monsoon starting from end of May up to October, Post monsoon from October to January and the premonsoon from February to the beginning of May.

The maximum rainfall usually occurs during the monsoon period i.e. from June to September. The annual rainfall in the region varies between 2500 mm and 3500mm. The maximum wind speed observed was of the order of 112 KMPH from WSW (west-south-west) direction. The wind speed and wind direction is determined by the season and by the daily temperature differences between land and sea. Temperature at Cochin varies from about 22 degrees to 31 degrees C. There are not much distinct seasonal variations in the temperature, which is more or less uniform throughout the year. However, highest temperatures tend to occur in the months of March to May. The humidity is high all through the year. It ranges from approximately 75% in the morning during winter months to approximately 90% in the monsoon period. Vegetation of the area is dominated by

mangrove species Avicennia marina, Rhizophora mucronata and Acanthus ilicifolius.

2.1.1. Map of Kochi showing the Study Sites



➢ ***Mangalavanam***

Mangalavanam is situated right in the heart of Kochi city at 9°59' N latitude and 76°11' E longitudes. The total area is 3.44 ha. The northern and eastern portion of the area is bordered by Bharath Petroleum Company, South by Ernakulam Railway goods station, west by Salim Ali road 16 and Central Marine Fisheries Research Institute. It is almost a closed system surrounded by brackish waters connected with a canal to the Cochin backwaters. This forest is bounded with thick mangrove vegetation. These thick forests here attract many exotic and rare varieties of migratory birds that find shelter during their breeding season. Many species of fishes, shrimp, insects, crabs and prawns come here for breeding and other activities. The main species of mangrove plants found here are Avicennia, Acanthus and Rhizophora species. The area is well protected from natural predators and not many similar communal roosting sites are available to birds in a crowded city like Ernakulam. Apart from the much needed breeding and roosting site for birds, the rare and threatened mangrove vegetation is preserved here. But the mangroves here are facing the growing threat of oil pollution and are depleting fast. As a result the number of migratory birds and aquatic animals has also decreased over the years (Suma and Joy, 2003).

➢ ***Vypeen***

Vypeen Island is situated at 9°58' N latitude and 79°17' E longitudes. Mangroves here are the largest single stretch of mangroves found in Kerala, comprising about 101 hectares of area. It is a semi-closed system, which is lying closer to the Arabian Sea than the other station. The Pokkali fields (rice fields) here have been affected due to the destruction of mangrove forests. The more economical benefits from fish culture forced the people here to convert the rice fields to prawn farms (Suma and Joy, 2003). Though large areas have been converted to fish farms, thick patches of mangroves can be still seen in different parts of this island. The main mangrove plants found here are Avicennia, Acanthus and Rhizophora species.

Mangalavanam

Vypeen

2.2 Sampling and Storage

Surface water and sediment samples from both stations were collected from February 2001 to January 2002. The core sediments from both stations were collected on April, August and December 2002 representing the three seasons of the year. Surface water samples were collected using clean plastic buckets and stored in clean plastic bottles and surface sediment samples using a clean plastic spatula and stored in polythene covers. The sediment cores upto a depth of 30 cm were collected using a PVC corer of 7cm internal diameter. The core tubes were pushed into the sediment, sealed with rubber stoppers, and dug out of the sediment. At each station three cores each at a distance of 1m apart were collected. These cores were cut with a plastic knife into 5cm pieces from the surface to the bottom immediately after return to the laboratory, removed the plant remains, cleaned and kept frozen at –5 °C in polythene bags till further analysis. A portion of the sediments in each depth was kept as such separately in plastic bags for texture analysis. Another portion was dried, powdered and kept airtight in plastic containers for the analysis of organic carbon, organic nitrogen, proteins, amino acids and carbohydrates. The leaves of three common species of mangrove plants found at both stations also were collected, dried in shade, powdered and kept airtight in plastic containers. The plastic containers used for the storage of all the samples were soaked in 1: 1 nitric acid and washed thoroughly with water and finally rinsed with distilled water.

2.3. Analytical Methods

2.3.1.Hydrographical Parameters

The physico-chemical parameters like pH, temperature, salinity, alkalinity and Dissolved Oxygen were noted. Salinity was measured argentometrically on the same day of collection by modified Mohr-Knudsen method (Muller, 1999). The D.O was determined by Winkler's method

(Hansen, 1999). Alkalinity was determined by Koroleff method using Bromothymol blue as indicator (Anderson et al., 1999).

2.3.2. Sediment Characteristics

Sediments play a very important role in aquatic systems, since it indicates the extent of biological activity and indirectly the fertility of overlying water as well as the status of pollution of the waters (Alagarsamy, 1991). The mangrove sediment geochemistry is greatly influenced by the hydrology there. Low pH, low O_2 content and clayey nature of the sediment favours the accumulation of organic matter in mangroves. The organic matter from the water column gets vertically transported to the surface sediments and there it gets significant modification due to the activities of living organisms. The sediment is waterlogged and oxygen deficient will be darker and stronger smelling. Dissolved oxygen concentrations are usually lowered when aerobic bacteria degrade organic matter, and anoxic and hypoxic conditions may develop under stratified conditions.

Mangrove roots and burrowing organisms contribute to the diagenetic character of the sediment by bringing the organic rich deeper soil to the surface and allowing air to penetrate to deeper parts. Organic matter has a high affinity for fine-grained sediment because it adsorbs onto mineral surfaces. Mangrove sediments are usually comprised of organic-rich and relatively impermeable clay. The finer clay particles may provide increased surface area per unit weight for adsorption of OM. So organic matter concentrations increase with decreasing grain size (Hedges and Keil, 1995).

Generally organic rich sediments are deposited in areas where organic productivity is high and oxygen supply is low (Reghunath and Murthy, 1996). Monsoon season is marked by heavy rain and flood, river discharge etc. and it is therefore not favourable for the accumulation of organic matter. Pre-monsoon season is most favourable for organic matter accumulation (Nandan and Aziz, 1996). Mangroves accumulate sediment and

consequently many pollutants and toxins washed into the mangrove are retained there in the soil and plants. Input of wastes also results in organic matter enrichment. The sedimentary organic matter of mangrove swamps is dominantly derived from the decay of higher plant tissues mediated by microbial activity. The amount of organic matter found in sediment is a function of the amount of various sources reaching the sediment surface and the rates at which different types of organic matter are degraded by microbial processes during burial. Large quantities of OM composed of variety of organic compounds like carbohydrates, proteins, amino acids, pigments, lipids and phenolic substances are present in mangroves. The main sources of organic matter are decayed matter from plants, zooplankton, phytoplankton and higher plants.

2.3.2.1 Grain size Analysis

Textural analysis of the sediment was done based on Stoke's law using the method of Krumbein and Pettijohn (1938). About 40 g of the sample was treated with 10-20ml 1 to 4 N HCl and washed with distilled water to remove all the carbonates. Then the sample was treated with 30% H_2O_2 (20-50 ml) little by little to remove the organic matter. Finally excess H_2O_2 was boiled off and sediment washed and dried at 60°C. The dried sample was powdered and 10 to15 g taken and added 20 ml dispersant or calgon solution (50g Sodium hexa metaphosphate dissolved in 1 litre distilled water, 20 ml dispersant solution ≡1g dispersant in 1 litre solution). Kept overnight after the addition of the dispersant and then filtered through a sieve such that particles < 62 μm (silt and clay) passes through the mesh and collected in a 1 litre measuring jar. Sand particles (> 63μm) remained in the mesh are washed with water carefully and the washings were collected in a pre-weighed petri-dish and dried. The petri dish plus dried sand was weighed and from this mass of the sand and its percentage can be calculated. The mixture of silt and clay collected in the measuring jar was stirred well to ensure even distribution of the sediment throughout the jar. At 20 seconds, after stirring was stopped, withdraw 20 ml of the sample from 20

cm depth of the measuring jar with a pipette. This was transferred to a previously weighed petri-dish, dried at 60°C, cooled to room temperature and weighed. This contained both silt and clay. Stirred the sample in the measuring jar and allowed it to settle for 3 hours and 27 minutes. After 3 hours and 27 minutes, pipette out 20 ml of the sample at 5 cm depth and transferred it to a previously weighed petri-dish, dried at 60°C, cooled in a desiccator and weighed. After subtracting the weight of dispersant from these weights, the percentage of sand, silt and clay was calculated.

2.3.2.2 Exchangeable Nitrite, Nitrate and Ammonia

Exchangeable ammonium, nitrite, and nitrate were estimated by extracting the samples with 2 N KCl solution for 2 h by using a mechanical shaker (Keeney and Nelson, 1982) for all three compounds. Ammonia was quantified spectrophotometrically at 630 nm by the indophenol-blue method and nitrate was determined by reduction to nitrite via a copperized cadmium column. This nitrite was then determined by diazotizing with sulfanilamide followed by coupling with N-(1-naphthyl)ethlyenediaminie dihydrochloride. The absorbance of the dye produced was measured at 540 nm. Nitrite is determined in the same manner with the cadmium column off-line.

2.3.2.3 Elemental Analysis

The analysis of organic carbon, organic nitrogen, organic sulphur and hydrogen of sediment and dried leaves were performed on German made ELEMENTAR Vario EL III CHNS-O analyzer by dynamic flashes combustion, their absorption and description techniques (Agemian, 1997).

2.3.2.4 Biochemical Analysis

- *Carbohydrates*

Carbohydrates were estimated by phenol-sulphuric acid method (Dubois et al, 1956). Total carbohydrates from the sediments were leached by hydrolysis of about 20 mg sample with IN H_2SO_4 at 100°C for 1 hr.

cm depth of the measuring jar with a pipette. This was transferred to a previously weighed petri-dish, dried at 60°C, cooled to room temperature and weighed. This contained both silt and clay. Stirred the sample in the measuring jar and allowed it to settle for 3 hours and 27 minutes. After 3 hours and 27 minutes, pipette out 20 ml of the sample at 5 cm depth and transferred it to a previously weighed petri-dish, dried at 60°C, cooled in a desiccator and weighed. After subtracting the weight of dispersant from these weights, the percentage of sand, silt and clay was calculated.

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2.3.2.4 Biochemical Analysis

➢ *Carbohydrates*

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Cooled the aliquots at room temperature and filtered. To 1ml of the aliquots added 1ml of 5% phenol and 5ml concentrated Sulphuric acid. Cooled the test tubes and measured absorbance at 490 nm using a UV-Visible Spectrophotometer (Genesys 10 UV). Blank and standards of D-glucose were also treated similarly. Monosaccharides were analyzed by extracting a known weight of sediment with distilled water and 1 ml of the extract was analysed as before. Polysaccharides were estimated by subtracting mono carbohydrates from total carbohydrates (Burney and Sieburth, 1977)

➢ *Protein*

Protein content was analysed by the method suggested by Herbert *et al.*, (1971). About 20 mg of sediment samples were homogenized in 5ml IN NaOH at 80°C for 30 minutes to dissolve the protein. Cooled, centrifuged and to 1ml extract taken in clean test tubes added 5 ml Cu-reagent (prepared by mixing 2 ml 2% $CuSO_4.5\ H_2O$, 2 ml 4 % Sodium Potassium tartarate and 96 ml 3 % Na_2CO_3 in 0.I.N NaOH) followed by 0.5 ml. Folin-Ciocalteau reagent after 10 minutes. Appropriate blank and standards of Bovine Albumin are similarly treated. After 40 minutes the samples are analysed spectrophotometrically at 750 nm.

➢ *Amino acids*

a) Free Amino Acids (FAA)

FAA was determined by fluorescence method (Parsons et al., 1984) using o-phthalaldehyde and 2-mercaptoethanol, which produces highly fluorescent compound when reacted with primary amines. About 20 mg dried sediment samples was extracted with a definite volume of milliQ water and centrifuged. The centrifugates were collected and 1 ml treated with 5 ml *ortho*- Phthalaldehyde reagent (1 ml of 2-Mercaptothanol added to 400ml borate buffer, to which 20 ml 10% OPA in 95% ethanol was added and kept for 1 hour) and the fluorescence of the solution was analysed using a Spectrofluorimeter (Model No. Hitachi F-3010) at an excitation wavelength

340 nm and emission wavelength 450 nm. The conc. of FAA determined from the measured absorbance after applying suitable blank correction. The standards of glycine were treated similarly.

b) Total Hydrolysable Amino Acids (THAA)

Analysis of THAA was carried out by the method adopted by Tsugita et al (1987). About 20 mg of air-dried sediment samples were weighed in clean pre-weighed small boiling tubes. Each tube was inserted in 10 ml Screw-capped vials in which1 ml of a mixture of 7 mol/L HCl, 10% trifluroacetic acid and 0.1% phenol were added. After flushing for about 2 minutes with high purity N_2 the vials were tightly closed. Vapour hydrolysis was carried out at 156°C for 23 minutes. After cooling, the vials were opened and the tubes taken out, cooled and dried under a stream of N2 gas to remove any acid present and extracted using milliQ water. The extractions were analysed using a spectroflurimeter, using OPA reagent. A portion of the extractions were taken to HPLC. Fluorescent amino acids derivatives were prepared by reacting the hydrolysate with OPA reagent and these derivatives were then separated by reverse phase HPLC with detection of the individual amino acid peaks by flurimeter at excitation wavelength 340 nm and emission wavelength 452 nm. Solvent gradients were formed using acetate/borate buffer and methanol in the ration 60:40. Separations were then carried out on a Cosmosil C_{18} column 150 mm X 4.6 mm, internal diameter 5 micron particles size. Best separation of upto 13 amino acids was obtained with a flow rate of 1 ml/ minute. The identification of individual amino acids in the samples was determined by comparing the retention times of peaks in samples with those in standard solution. All glasswares used in this procedure were cleaned by soaking in 10% HCl for at least 1hr and rinsing with warm tap water and again two times with milliQ water, dried in oven at 150°C for 2 hrs. The concentrations of combined amino acids were obtained by subtracting the concentrations of free amino acids from that of the total hydrolysable amino acids.

2.4. Results of Hydrographical Parameters

2.4.1. pH

Many of the life processes are dependant on pH of the surrounding medium, which in turn depends on photosynthetic activity, rainfall, and discharge of effluents and nature of organic materials. The state of ionisation varies with pH. In acid solution there are plenty protons about, and the carboxyl group is not ionised. In alkaline solution less protons are present, so the amino group not ionised, but the carboxyl group is ionised. Monitoring of pH is therefore essential for checking water quality.

The monthly variation of pH in both the stations is shown in *Table: 2.1.* Spatially there was no marked variation in pH throughout the year. In Mangalavanam, pH was observed maximum during pre-monsoon and minimum during post-monsoon. In Vypeen also the same trend was observed.

Months	Mngl	Vypeen
Feb-01	7.65	7.9
Mar-01	7.4	7.8
Apr-01	7.95	7.9
May-01	7.6	7.85
June-01	7.55	7.8
July-01	7.8	7.8
Sept-01	7.9	7.95
Oct-01	7.5	7.9
Nov-01	6.91	7.01
Jan-02	6.93	7.36

Table: 2.1. Spatial and Monthly Variation of pH

The highest value of pH, 7.95 at Mangalavanam in April and at Vypeen in September may be due to the high photosynthetic activity of algae. Premonsoon season favours primary production and during the process of photosynthesis CO2 is reduced to carbohydrates leading to an increase in the pH value, hence the high pH value (7.95 at Mangalavanam and 7.9 at Vypeen in April).

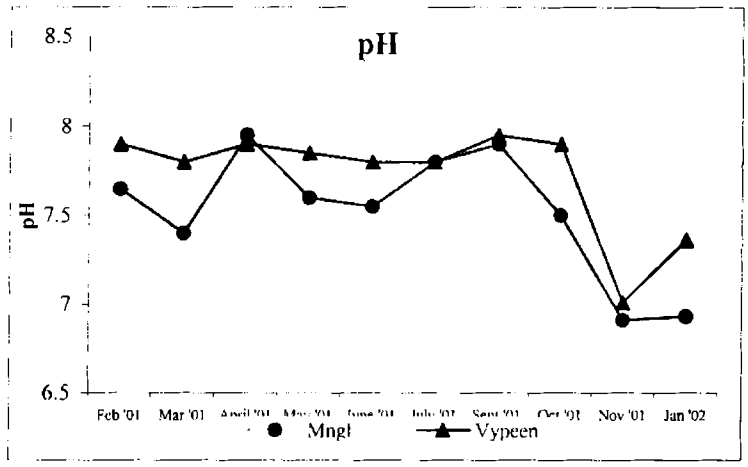

Fig: 2.1. Monthly variation of pH at Mangalavanam and Vypeen

During monsoon addition of freshwater slightly lowered the pH values at both stations *(Fig: 2.1.)*. The reduction in pH observed at both stations during post monsoon season may be due to the effect of precipitation. Moreover the decomposition of organic matter led to an increase in CO_2, which depressed the pH value. In mangroves, generally low pH was observed due to microbial degradation of OM, which depletes oxygen and enhances the bacterial sulphate reduction to take place leading to the formation of H_2S (Berner, 1983), supported by the pronounced odour of H_2S due to the anoxic nature of the sediment. Thus pH is highly influenced by dissolved oxygen. Other factors that determine pH are bacterial activity, water turbulence, chemicals in the run-off constituents, sewage outflow and anthropogenic activities.

2.4.2. Salinity

Mangroves being the inhabitants of the saline areas salinity play a vital role in this ecosystem since it gives an idea about the dissolved solids in water. This parameter therefore provides information on freshwater runoff and upstream tidal penetration of seawater into mangroves. Mangroves are unique amongst land plants in their ability to tolerate a wide range of salinities.

Months	Mngl	Vypeen
Feb-01	19.6	28.7
Mar-01	17.97	31.9
Apr-01	14.8	28.7
May-01	3.5	4.8
June-01	3.2	2.1
July-01	2.3	3.2
Sept-01	9.63	17.24
Oct-01	3.21	3.19
Nov-01	25.67	18.5
Jan-02	26.96	24.5

Table: 2.2. Spatial and Monthly Variation of Salinity

In Mangalavanam, the salinity varied from 2.3 ppt in July to 26.96 ppt in January and in Vypeen, a minimum of 2.1ppt was observed in June and a maximum of 31.9 ppt in March *(Table: 2.2.)*. The low values during monsoon may be due to the dilution effect by high fresh water input into the estuary and rainfall. During summer, seawater penetration into the estuary and low discharge of freshwater resulted in high salinity. The sharp variation in salinity seasonally was observed in earlier studies also (Joseph and Chandrika, 2000).

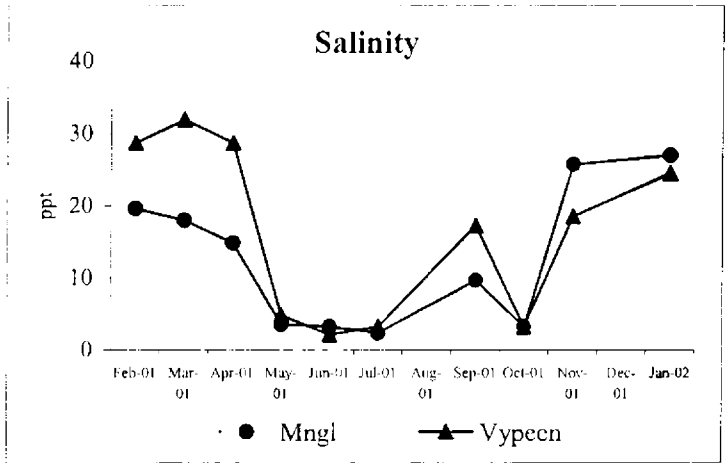

Fig: 2.2. Monthly variation of salinity at Mangalavanam and Vypeen

Salinities at both stations were found to be lowest during monsoon season (Fig: 2.2.). This may be mainly due to fresh water input due to rainfall. The increase in salinity during premonsoon seasons was mainly due to the evaporation, which was higher at Vypeen, which is an open system than at Mangalavanam, which is a closed system.

2.4.3. Dissolved Oxygen

Dissolved oxygen (D. O) is another important parameter for assessing water quality. It is important since the existing of aquatic life is linked with availability of oxygen for their survival. Oxygen solubility varies inversely with salinity, water temperature and atmospheric and hydrostatic pressure. DO concentrations naturally vary over a twenty-four hour period due to high tide and low tide. The seasonal variations of D.O are given in *Table: 2.3.*

Months	Mngl	Vypeen
Feb-01	2.80	1.80
Mar-01	4.70	4.30
Apr-01	0.88	3.72
May-01	0	1.06
June-01	3.85	4.84
July-01	4.25	4.26
Sept-01	5.42	3.25
Oct-01	2.74	2.28
Nov-01	1.37	4.10
Jan-02	3	2.4

Table: 2.3. Spatial and Monthly Variation of Dissolved Oxygen (ml/l)

In March a comparatively high value of D.O was observed at both stations, followed by a sharp decrease upto May. Warm temperature during pre monsoon season favors productivity and photosynthesis. The high D.O in March may be due this high productivity, which removed CO_2 and released Oxygen to the water.

In both stations minimum dissolved oxygen was observed during the month of May. This may be due to the maximum consumption of oxygen for the decay of organic matter produced after the decay of the bloom of phytoplankton produced in March. Oxygen is taken up for the decomposition of OM, leading to a sharp decrease in DO. At Mangalavanam, even zero value for D.O was observed giving rise to reducing conditions. This arises due to the combined effect of low solubility of oxygen due to high salinity and temperature and also due to the utilization of oxygen for organic matter decomposition.

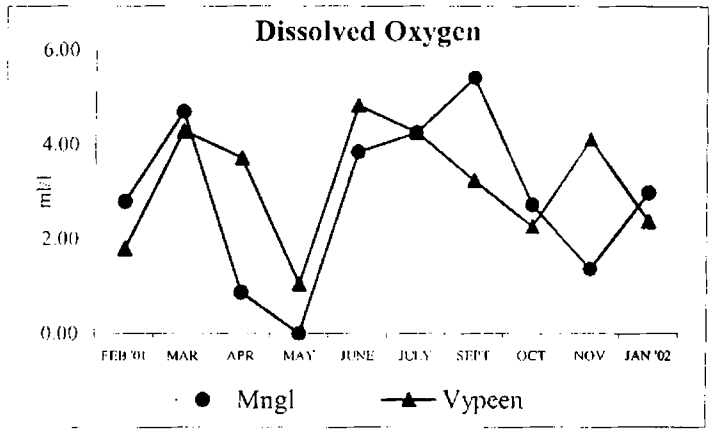

Fig: 2.3. Monthly variation of D.O at Mangalavanam and Vypeen

During monsoon, the solubility of oxygen is high and this leads to high D.O values (Nayar, 1992). Oxygen has limited solubility in water, usually ranging from 6 to 14 mg L^{-1} Freshwater input increased productivity and increased the levels of D.O due to the release of high amounts of oxygen after photosynthesis. Post monsoon showed the low D.O values (*Fig: 2.3.)* due to the low primary production or high rate of decomposition of organic matter supplied to the system.

2.4.4. Alkalinity

Alkalinity is a measure of the capacity of water to neutralize acids. Aquatic systems with high pH values have high alkalinities and vice versa. The pH and alkalinity of waters draining a forest are controlled by a number of factors like supply of strong acid anions (i.e., SAA like SO_4 +NO_3 + Cl +F) and strong base cations (i.e., SBC like Ca+ K+ Mg+ Na) from the atmosphere; chemical weathering and net ion exchange; and production of the weak acid anions (WAA) from H_2CO_3 and dissolved organic acids (Norton et al, 2001). The major ions representing alkalinity are bicarbonates. Abundance of organic matter, temperature and partial pressure of carbon dioxide are some factors affecting alkalinity. Increase in pH and D.O results in increase in alkalinity also. The study of complex mechanisms

involved in the biogeochemical cycles in mangroves requires a constant monitoring of alkalinity of the medium.

Months	Mngl	Vypeen
Feb-01	3.74	3.64
Mar-01	2.44	2.04
Apr-01	3.36	2.21
May-01	2.74	2.38
June-01	2.36	1.28
July-01	2.24	1.36
Sept-01	1.04	1.72
Oct-01	1.2	0.2
Nov-01	0.88	1.56
Jan-02	1.76	2.16

Table: 2.4. Spatial and Monthly Variation of Alkalinity

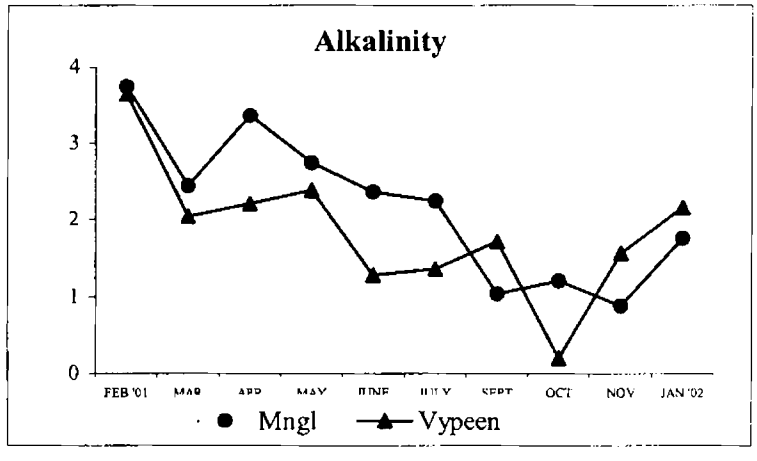

Fig: 2.4. Monthly Spatial variation of Alkalinity

At Mangalavanam, the highest alkalinity 3.74 was observed in February and the lowest alkalinity 0.88 in November and at station 2, the

highest alkalinity 3.64 was observed in February and the lowest 0.2 in October *(Table: 2.4.)*. At both stations, a general decrease in the alkalinity values was observed from premonsoon to post monsoon months *(Fig:*

2.5. Grain size character of sediment

The organic matter content of the sediments is mainly controlled by the nature of the sediment. The sediment at Vypeen was found to be more clayey than that at Mangalavanam. In sediment core, high clay content was observed in deeper layers. The textural studies of the sediment at both stations revealed Vypeen to be more clayey when compared to Mangalavanam (*Table.2.5.*). The percentage of clay was found to be more at Vypeen (~30-40%) than at Mangalavanam (~10-20%). At Mangalavanam, the sand percentage was approximately between 70 and 80%, whereas at Vypeen, it is very much low (~10-25%) *(Table: 2.5.)*.

Mngl	**Pre-monsoon**			**Monsoon**			**Post-monsoon**		
Depth [cm]	Sand	Silt	Clay	Sand	Silt	Clay	Sand	Silt	Clay
0-5	70.5	14.6	14.9	63.7	18.7	17.6	78.0	8.5	13.5
5-10	67.7	12.8	19.5	58.1	20.0	21.9	77.5	7.6	14.9
10-15	66.9	11.2	21.9	63.6	17.9	18.5	74.4	3.5	22.1
15-20	70.2	14.6	15.2	68.1	17.5	14.4	84.6	4.8	10.6
20-25	71.1	14.8	14.1	69.5	16.4	14.1	69.2	10.6	20.2
25-30	73.8	11.8	14.4	69.1	15.7	15.2	74.8	4.6	20.6
Vypeen	**Pre-monsoon**			**Monsoon**			**Post-monsoon**		
Depth [cm]	Sand	Silt	Clay	Sand	Silt	Clay	Sand	Silt	Clay
0-5	23.5	45.7	30.8	10.3	51.5	38.2	14.5	51.1	34.4
5-10	22.1	46.7	31.2	9.6	48.3	42.1	16.8	49.9	33.3
10-15	20.5	45.9	33.6	9.7	50.2	40.1	10.1	59.8	30.1
15-20	22.7	49.1	28.2	11.1	51.1	37.8	12.4	56.6	31.0
20-25	20. 5	45.8	33.7	10.5	51.8	37.7	18.9	42.1	39.0
25-30	20.1	46.5	33.4				17.7	46.8	35.5

Table: 2.5. Distribution of sand, silt and clay (%) in the sediment core

Clay and silt together can be considered as finer fraction with size approximately 63 microns and less and sand as particles with size greater than 63 microns. The preservation of organic matter is almost exclusively restricted to sediments. The texture of the sediment plays a very important role in binding the organic matter. Organic matter has a high affinity for fine-grained sediment that accumulates in mangroves as it adsorbs onto mineral surfaces. The finer particles may provide increased surface area per unit weight for adsorption of organic matter (Sunil Kumar, 1996). So organic matter concentrations increase with decreasing grain size. Sandy sediments are relatively poor in organic matter preservation (Suthhof et al., 2000).

2.6. Statistical Analysis

Correlation analysis was carried out to find out the inter-relation among different parameters and the correlation coefficients are given in each chapter. Factor analysis of individual amino acids and different organic parameters was carried out using SPSS 7, version 2.4 (1995-1998 ACD systems Ltd) and considering factors which have eigen values more than 1 (or eigen values with % variance more than 1), the effective contribution of different environmental processes towards different parameters is discussed in Chapter 5.

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Chapter 3

SEDIMENTARY ORGANIC MATTER

Sedimentary organic matter (SOM) has to be regarded as the residue of organic life and this becomes more important and more abundant with the development and diversification of life. Large quantities of OM composed of variety of organic compounds are present in mangrove sediments. The sources and burial processes of OM in marine sediment are not well understood, yet they're important if we are to have a better understanding of the global C cycle. Both natural and anthropogenic material accumulates simultaneously in sediments and it is difficult to identify the proportion of each source. The rate of loading of these materials depends on the different chemical and physical properties of the sediment. The main sources are decayed matter from plants, zooplankton, phytoplankton and higher plants. Particles from the euphotic zone sink to the sediment-water interface, where benthic organisms rapidly degrade the labile organic compounds present in the settled materials. The survival of these compounds in sediments depends mainly on their chemical stability (Premuzic e*t al,* 1982).

The preservation of organic matter occurs mainly in coastal marine sediments, where a variety of factors might affect its burial efficiencies (Hedges and Keil, 1995). Fine sediments accumulate in mangroves and salt marshes and organic matter has a high affinity for fine-grained sediment because it adsorbs onto mineral surfaces. Organic matter shows a clear positive correlation with the clay contents of the sediments. As a consequence of efficient particle trapping, marsh sediments are usually comprised of organic-rich and relatively impermeable clay. Sandy soils are well aerated and tend to have low soil moisture content, which are environmental conditions favour for low organic matter content. Thus these sediments are relatively poor in organic matter preservation (Suthhof *et al.,* 2000). The finer particles may provide increased surface area per unit weight for adsorption of organic matter. So organic matter concentrations

increase with decreasing grain size (Hedges and Keil, 1995; Nair *et al,* 1993; Sunilkumar, 1996). It is also found that total SOC content increased with precipitation and clay content and decreased with temperature (Jobbagy and Jackson, 2000). The finer textured soils typically show a larger initial flush of microbial activity that is followed by greater incorporation and stabilization of organic matter in the soil than found in coarser textured soils. Preservation of organic carbon in the sediment depends not only on the grain size, but also on the type of organic matter (de Haas *et al.,* 1997). Generally, OM increases with silt percentage and clay percentage.

Organic nitrogen, which forms a significant fraction of sedimentary organic matter, is closely related to biological productivity. Among the most common contributors of organic nitrogen, like terrigenous, macro algal and planktonic sources, macro algal nitrogen was observed the most important contributor to the nitrogen pool, in estuarine sediments (Mayer *et al,* 1988). Nitrogen is efficiently retained in mangrove sediments by the action of microbial biomass. Woitchik *et. al.* (1994), reported nitrogen fixation activities as one of the causes for the excess of nitrogen found in mangrove sediments of Gazi Bay. Once fallen, leaves and twigs decompose rapidly and proceeds faster under saline conditions than under fresh water conditions. Though the fallen litter had very little nitrogen, as the decay proceeds nitrogen, protein, and caloric content within the leaves were found to increase (Wafar *et al,* 1997).

Organic matter has a high affinity for fine-grained sediment and much of the nutrients are trapped in the sediment either by roots of the mangrove trees or by adsorption within the clayey sediments (Twilley *et al.,* 1986). Generally a positive correlation exists between total nitrogen and percentage of clay (Knicker *et al.,* 1996). Processes that govern the transport and deposition of fine sediment therefore control the accumulation of organic matter in coastal areas. Tide-dominated mangroves and salt marshes thus

form the main traps for fine sediments where organic matter is accumulated to a greater extent.

The knowledge of biogeochemical processes is important for the understanding of an ecosystem. Mangroves are considered both as highly productive systems that export organic matter and traps for sediment and organic matter (Woodroffe, 1992). Sediments play a very important role in aquatic systems and the studies on sediments can provide information about their role as a reservoir and a source of nutrients and the sediment water exchange processes. Benthic organisms depend on the SOM as food source, therefore it is important quantify and qualify the organic material. Investigations on the organic matter in the sediments can give evidence to the extent of biological activity and indirectly the fertility of overlying water as well as the status of pollution of the overlaying water. The identification of sources of organic matter in mangrove sediments help to study their effects on the carbon and nitrogen dynamics of these ecosystems.

3.1. Elemental Composition

3.1.1. Organic Carbon

Mangroves appear to be net source of organic carbon and the sediments in these systems are efficient sink for organic carbon (Matsui, 1998; Gonneea *et al*, 2004). Due to the high biological activity in the mangrove sediment and the permanent recycling and exchange of nutrients between mangroves and coastal waters, high rate of carbon is produced and accumulated in the mangrove sediments. Mangrove losses occur through respiration, herbivory, litterfall, and woodfall. These losses contribute to pools of both organic and inorganic carbon. The export of these nutrients from here increased the fertility of adjacent coastal waters (Jennerjahn and Ittekkot, 2002). The textures, vegetation, degree of oxidation and primary production favour the production of organic matter in a system.

Generally, due to the high availability of organic carbon, the rate of consumption of O_2 in mangrove forest is high. The organic matter is degradable under oxic to suboxic conditions. The first stage of decomposition in mangroves involves the leaching of soluble materials (mostly carbohydrate). These compounds are, as a result of their dissolved state, readily available for uptake by bacteria. Degradation takes place both under aerobic and anaerobic conditions. Anaerobic bacteria cannot decompose certain class of organic compounds. Mangrove ecosystems showed analogous patterns of variability in the sources of organic carbon in surface sediments (Middelburg *et al.,* 1997).

The sedimentary organic matter depends on factors like algal mats, roots, tidal fluctuations, rate of change in decomposition and the maturity of the forest. In older forest SOM will be high (Marchand *et al,* 2003). The concentration of organic carbon varies temporarily and spatially since they are regulated by so many factors like forest type, climate, sediment texture, sedimentation rates, tidal effects, oxygen availability, rate of primary production, and biological activity.

- *Materials and Methods*

Details of the method of analysis are given in Chapter 2.

- *Results and Discussions*

The results obtained for the monthly distribution of the sedimentary organic carbon in the present study are given in the *Table A.1.*

The highest concentration of organic carbon (53.57 mg/g) at Mangalavanam was found in September '01 and the lowest (17.677 mg/g) in May '01. At Vypeen, the highest concentration (43.305 mg/g) was observed in October '01 and the lowest (25.77 mg/g) in February '01. The monthly variation in the concentration of SOC is given in Fig: 3. 1.

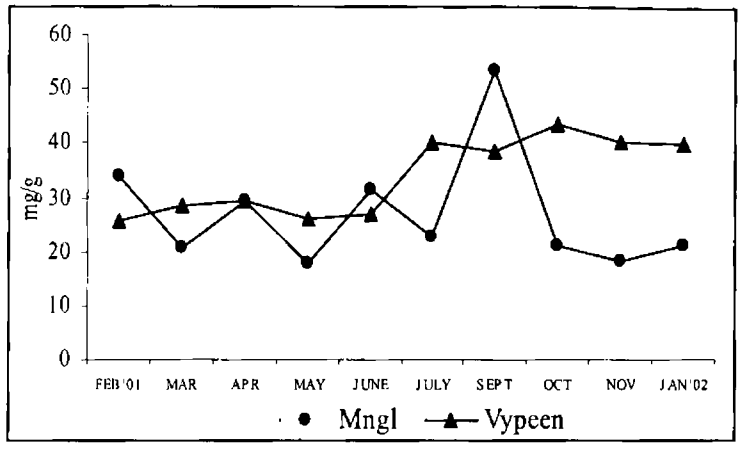

*Fig: 3. 1. **Monthly Variation of Organic carbon in the Surface sediments (mg/g)***

The seasonal concentrations of organic carbon down the core are given in the *Table A.2.* The highest value at Vypeen (35.36 mg/g) was observed during post-monsoon at 20-25 cm depth and the lowest (27.2 mg/g) during pre-monsoon at 15-20 cm depth. At Mangalavanam, the highest value was found to be 61.54 mg/g at the sub surface during monsoon and the lowest, 7.27 mg/g at 25-30 cm depth during pre-monsoon season. Here, a regular decrease in SOC concentration down core was observed during pre monsoon season only, whereas at Vypeen, no such significant variation was observed during any of the three seasons.

The leaves of three common plant species in the study area were also checked (*Table A.3*). At both stations, *Acanthus sp*ecies was found to have the lowest concentration of organic carbon (~ 32 - 35 mg/g) and *Avicennia species, the highest (~ 37- 38 mg/g). Rhizophora species* was found to have organic carbon concentration ranging between 33- 38 mg/g. In general, concentration of organic carbon was found to be higher at Vypeen than that at Mangalavanam. TOC concentrations are bulk sedimentary parameters that represent the organic matter fraction that has survived degradation during sinking. This depends on primary production and subsequent exposure to degradation, the origin of organic matter, delivery routes, depositional processes, and consequent degrees of preservation.

The monthly observations were converted to seasonal averages to identify the behavioral character of this parameter. At Mangalavanam, when seasonal mean was taken, the highest value of SOC (35.972 mg/g) was observed during monsoon season (*Table: 3.1*). This may be due to the deposition of terrestrial organic matter from the land run-off during heavy rainfall, in addition to the usual input of organic matter due to leaf litter. At Vypeen, the highest organic carbon concentration (41.02 mg/g) was observed during post monsoon season and the lowest (27.45 mg/g) during pre monsoon season. The values obtained during pre monsoon and monsoon showed no marked spatial variation. But during post monsoon significant difference was observed between both stations.

Season	Mngl	Vyp
Premon	25.47	27.453
Mon	35.972	35.19
Postmon	20.23	41.02

Table: 3.1. Organic carbon (mg/g)-Seasonal average of the monthly data

When annual mean was observed Vypeen showed higher organic carbon concentration (33.8 mg/g) than Mangalavanam (27.0 mg/g). Generally organic rich sediments are deposited in areas where organic productivity is high and oxygen supply is low (Nandan and Aziz, 1996).

Both Mangalavanam and Vypeen experience high rainfall during monsoon season. Mangalavanam is connected to Cochin estuary by means of a canal and the tidal effect is limited to the discharge through the canal only. Microbial degradation of the high load of organic matter mainly leaf litter and bird excretions at Mangalavanam results in the depletion of oxygen from the system, especially during pre monsoon period, which results in the development of a reducing condition there. Mangalavanam sediments are anoxic with the characteristic smell of hydrogen sulphide. The amount and distribution of organic carbon in mangrove sediments depends largely on the tidal effects (Dittmar and Lara, 2001) and biological factors

like consumption, removal, and degradation processes (Basak *et al,* 1996). Areas like Vypeen, which are flooded frequently, have faster rates of decomposition and export than other areas.

Leaves are one of the major sources of organic carbon in mangrove sediments. Mangalavanam is a forest area where leaf litter forms one of the major sources of the organic carbon in the system. The difference in carbon concentrations between the two stations may be due to the difference in the carbon content of the plants distributed in the two stations.

Valiela (1983) reported that salt marshes that are exposed to natural or man-made nitrogen enrichments have different production rates, standing stock, species composition and quality of plant biomass. Wafar *et al* (1997) reported that leaf litter is one of the major contributors of organic carbon in the mangrove sediments. Litterfall was found to be maximum during post monsoon and pre monsoon seasons and minimum during monsoon. But in the present study maximum concentration of organic carbon was observed during monsoon season indicating the possibility of lateral addition from the surrounding environment since the system is a semi open one. Moreover, during monsoon, the sediment will be having more clay when compared to other seasons and consequently more organic matter will be trapped in it. The texture of the sediment plays a major role in the preservation of organic matter.

In Vypeen the tidal effect will be there always without any seasonal difference, since this site is in the banks of the estuary and Vypeen had more clay content than Mangalavanam. The average organic carbon values reported in Avicennia (32.2 – 41.9 %) and Rhizophora species (38.9 – 45.9 %) were in agreement with the values obtained for the same plant species (~ *37- 38 % and* 33- 38 % respectively) in these two study areas. The concentration of organic carbon observed in the present study is in line with the earlier reports *(Table. 3.2)*

1.	Mangrove sediments, Kochi	0.95- 4.18%	Imelda Joseph and Chandrika, 2000
2.	Mangrove sediments of Gundu Island, Elamkulam and Maradu, at Kochi	0.5- 0.7% (Gundu island) 1.5- 2.2% (Elamkulam) 0.7- 2.4% (Maradu)	Sunil Kumar, 1995
3.	Cochin mangrove sediments	5.2- 48.9 mg/g	Badarudeen, 1997
4.	Vypeen Mangrove sediments	64- 79.4 mg/g	Badarudeen, 1997
5.	Coringa Mangrove sediments India	0.6- 31.7 %	Bouillon *et al*, 2003
6.	Goa mangrove sediments	1.7- 54 mg/g	Jagtap, 1987
7.	Sunderban Mangrove Sediments, Bangladesh	12.2- 15.1 mg/g	Hoq et al, 2002
8.	Itacuruca mangrove sediments, Brazil	3.4 %	Jennerjahn and Ittekkot, 2002
9.	Coastal Sediments, Visakhapatnam	4.22 %	Sarma and Rao, 1988
10.	Present study a) Mangalavanam mangrove sediments b) Vypeen mangrove sediments	 17-53 mg/g 25-43 mg/g	

Table: 3.2. Sedimentary Organic Carbon values reported in earlier studies.

When vertical variations of organic carbon at two stations are considered, at Mangalavanam, most changes were seen upto 15cm depth

(Fig. 3. 2). Oxygen is consumed within a few millimeters of the sediment and hence most of the bacterial activity occurs in the upper sediment layers (Hedges *et al.* 1999). At Vypeen, there was only a slight variation in the concentration down the sediment core. A slight increase with depth in the organic carbon concentrations in the first few centimeters of the core may be due to the development of radial cable root system of particularly Avicennia plants (Marchand *et al*, 2003). They also reported that decomposition would be accelerated in sediments where there is oxygenation due to roots and crab-bioturbation. In such cases decay processes are thought to be suboxic induced by biological processes and vertical variations in the core will be more pronounced and sharp. Such observations were reported in earlier studies also (Twilley *et al.*, 1992 and Lallier-Verges *et al.*, 1998).

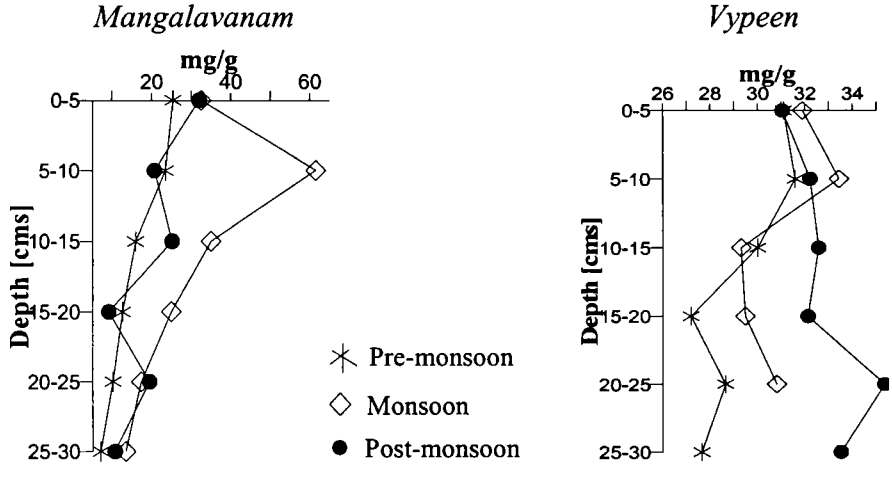

Fig: 3. 2. Distribution of Organic Carbon (mg/g) in the sediment core

Organic matter has a high affinity for fine-grained sediment because it adsorbs onto mineral surfaces. As a consequence of efficient particle trapping, marsh sediments are usually comprised of organic-rich and relatively impermeable clay. Suthhof *et al.*, (2000) reported that sediments, which have comparatively more sand content, are relatively poor in organic matter preservation. Sandy soils are well aerated and tend to have low soil moisture content, which are environmental conditions favor for low organic

matter content. Silt and clay-sized fractions are responsible for the greatest changes occurring for most of the organic matter present in the system.

The finer textured soils typically show a larger initial flush of microbial activity that is followed by greater incorporation and stabilization of organic matter in the soil than found in coarser textured soils. The finer particles may provide increased surface area per unit weight for adsorption of organic matter. So organic matter concentrations increase with decreasing grain size (Hedges and Keil, 1995) and decreased with temperature (Jobbagy and Jackson, 2000). Significant correlation between organic carbon and finer fractions of the sediment (silt+clay) has been reported earlier in the mangrove sediments of Kochi (Sunilkumar, 1996) and also in sediments of Bengal basin (Datta *et al.*, 1999). In the present study, Mangalavanam was found to have lesser clay content than Vypeen and significant positive correlations were observed between the finer fraction of the sediment and organic carbon at both stations.

The preservation of organic matter occurs mainly in coastal marine sediments, where a variety of factors might affect its burial efficiencies (Hedges and Keil, 1995). Preservation depends not only on the grain size, but also on the type of organic matter (de Haas et al., 1997). Owen and Lee (2004) reported that human intervention could alter the type of organic matter added to the system and thereby alter the nutrient availability in that system. Sunilkumar (1996) reported that inconsistent pattern concomitant with the inconsistent concentration in accumulation of organic carbon in the sediment with regard to vertical as well as horizontal distribution was discernible in the tidal area of mangrove swamps near Cochin estuary.

3.1.2. Organic Nitrogen

The total nitrogen in the present study is considered to be constituted more or less by organic nitrogen as the amount of inorganic nitrogen (easily exchangeable or labile) was observed to be significantly low *(Table: 3.3)*.

According to de Lange (1992), mineralogy determines the exchangeable nitrogen content of sediment with less organic matter and the organic matter determines the exchangeable nitrogen content of sediment with comparatively higher organic matter.

	Mangalavanam			Vypeen		
	Pre-mon	**Monsoon**	**Post-mon**	**Pre-mon**	**Monsoon**	**Post-mon**
Ammonia	0.06238	0.31790	0.04343	0.01276	0.05004	0.01273
Nitrite	0.00003	0.00047	0.00027	0.00019	0.0001	0.00018
Nitrate	0.00238	0.00121	0.00270	0.00108	0.00071	0.00077

Table: 3.3. Seasonal distribution of inorganic nitrogen fractions (mg/g) in the surface at both stations

➢ *Materials and Methods*

Details of the method of analysis are given in Chapter 2.

➢ *Results and Discussions*

At Mangalavanam the lowest SON concentration (1.12 mg/g) was observed during November and the highest (4.65 mg/g) in September. At Vypeen the lowest value (1.930 mg/g) was in the month of May and the highest (3.949 mg/g) in the month of July (Table: A.4).

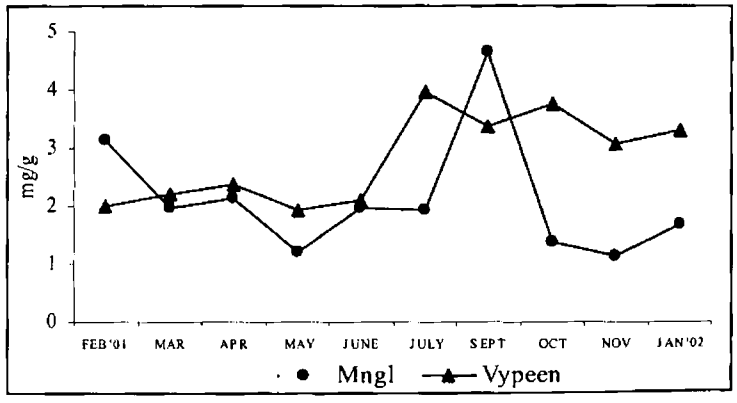

Fig: 3. 3. Monthly Variation of Organic Nitrogen (mg/g) in the Surface sediments

The concentration of organic nitrogen was found to be almost a constant at Mangalavanam throughout the year except a sharp increase in September, whereas, at Vypeen the concentration was increasing from pre monsoon to post monsoon months (Fig. 3. 3). The trend of the concentrations observed for organic nitrogen was similar to those observed for organic carbon.

The concentration of organic nitrogen down the core is given in the *Table: A.5.* At Mangalavanam, during pre monsoon and monsoon seasons the highest values of SON were observed at the sub surface (1.53 and 4.42 mg/g respectively) and the lowest at 25-30 cm depth (0.4 and 0.84 respectively). During post monsoon season, the highest concentration of SON was observed at the surface (2.09 mg/g) and the lowest (0.5 mg/g) at 15-20 cm depth. The concentration of SON at Vypeen did not show much vertical variation during the three seasons. The highest value during pre monsoon season (3.03 mg/g) was observed at the sub surface and the lowest (2.3 mg/g) at 25-30 cm depth. During monsoon, the highest concentration of organic nitrogen (3.03 mg/g) was observed at the sub surface and the lowest (2.5 mg/g) at 10-15 cm depth. During post monsoon season, SON was observed almost constant at all depths. There was almost a regular decrease in OC concentration down core at Mangalavanam, whereas at Vypeen, no such significant variation was observed.

The total nitrogen in the leaves of three common plant species in the study areas was given in ***Table A.3.*** At Mangalavanam, *Acanthus sp*ecies was found to have the lowest concentration of nitrogen (*1.74* mg/g) and *Rhizophora species, the highest (~ 2.3 mg/g). Avicennia species* was found to have a concentration of 2 mg/g approximately. At Vypeen, Rhizophora species was found to have the lowest concentration of nitrogen (1.18 mg/g), whereas Avicennia has the highest (1.78 mg/g). In general, concentration of nitrogen in all the three species was found to be higher at Mangalavanam than that at Vypeen. This is almost opposite to that observed for organic carbon.

Season	Mngl	Vyp
Premon	2.118	2.131
Mon	2.847	3.144
Post mon	1.404	3.374

Table: 9. Seasonal average of organic nitrogen (mg/g)

From the values of seasonal mean of sedimentary organic nitrogen (SON), the maximum concentration was observed during monsoon season at both stations *(Table: 3.4).* This high nitrogen concentration may be a result of the high terrestrial input due to heavy rainfall and land run-off during this season. Similar observations in SOC were made at Mangalavanam Besides this, the droppings, eggshells and dead remains of the birds, especially during the months of April to August add on to the concentration of nitrogen at Mangalavanam. Vypeen is an area that experiences regular tidal flushing and hence has faster rates of addition and export than that at Mangalavanam. Also at Vypeen human intervention is more and Owen and Lee (2004) had reported in their studies that human intervention could alter the type of organic matter added to the system and thereby alter the nutrient availability in that system. Moreover if the sediment is of clayey nature organic matter will be more firmly bound to the sediment, increasing the chances of preservation. This is more evident from the significant positive correlation of finer fraction of the sediment with nitrogen. The observed concentration of organic nitrogen in the present study was found to be in comparable limits with the reported values for other mangrove sediments *(Table: 3.5)*

No.	Study Area	Reported Value	Reference
1.	Itacuruca mangrove sediments, Brazil	0.16-0.18% (under Rhizophora plants) 0.35- 0.2% (under Avicennia plants)	Lacerda *et al,* 1995
2.	Mangrove sediments, continental margin of eastern Brazil	0.42%	Jennerjahn and Ittekkot, 1997
3.	Coastal Sediments, Visakhapatanam	0.60 %	Sarma and Rao, 1988
4.	Goa mangrove sediments	1.7- 19.3 mg/g	Jagtap, 1987
5.	Goa mangrove leaves	0.66- 1.15%	Wafar *et al*, 1997
6.	Mangrove plants, Haad Chao mai National Park, Thailand	1.1- 3.3%	Kuramoto and Mingawa, 2001
7.	Present study (a) Mangalavanam mangrove sediments (b) Vypeen mangrove sediments	1.1 – 4.6 mg/g 1.9 – 3.9 mg/g	

Table: 3.5. Sedimentary Organic nitrogen values reported in earlier studies.

The concentrations of SON at both stations are affected by the contributions from bacteria and plants. Leaves were reported to be the major contributors for litter. Litter fall was found to be the maximum during post monsoon and pre monsoon seasons, and minimum during monsoon (Wafar *et al*, 1997). The nitrogen content of *Avicennia* and Rhizophora species (1.78 and 2.06 mg/g respectively) were found to be in agreement with the earlier observed values of 1.4–16.6 mg/g for *Avicennia* species and 3.0–21.8 mg/g for Rhizophora species (Wafar *et al.*, 1997). It was also reported earlier that the presence of bacteria and other microorganisms in the

mangrove leaf litter increases the rate of decomposition of the leaves especially during pre monsoon period rather than monsoon (Bouillon et al, 2003). The time taken for decomposition of the leaves fallen in the forest is different for different plant species. The thinner leaves of *Avicennia were found to* decompose at a faster rate than those of *Rhizophora species* (Wafar *et al*, 1997).

Usually the sediment contains nitrogen in very low concentrations. The low nitrogen content in the leaf litter may be a reason for this. Typical salt marsh plants have low nitrogen content and after litter fall, leaching removes nitrogen from them. Rao *et al* (1994) reported that before litter fall about 64% of the nitrogen is resorbed by the plants itself, as a result the sediment receives litter that is strongly depleted in nitrogen. But the concentration of nitrogen within the leaves increases as the decay proceeds, resulting in increasing the nitrogen content of the sediment.

The seasonal down core variation of SON is given in the Fig: 3. 4. In general the cores showed a downward decrease in SON concentration. Sunil Kumar (2002) studied the vertical distribution of polychaete in the sediments of Cochin mangroves upto 15 cm depth. He reported a substantial difference in the percentage composition of fauna with respect to the depth of the sediment core and reported that the top 0-5 cm mangrove substratum showed the maximum composition of organisms in all tidal regions due to the maximum food availability there and in deeper sediments a definite decrease in abundance and species composition was found. Therefore in mangrove sediments the decomposition and the mixing of detritus produced will be more pronounced in the topsoil than the deeper soil. The down-core organic C and N accumulations and C/N ratios can alter the nature of organic matter present in the sediment (Teranes and Bernasconi, 2000).

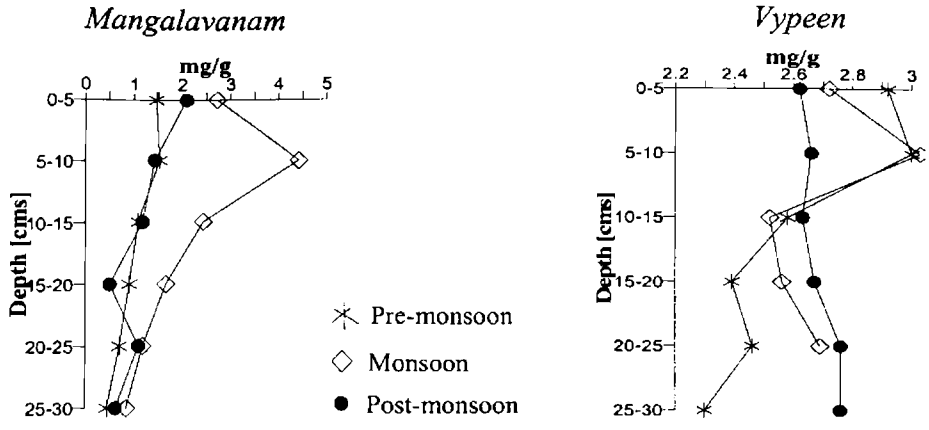

Fig: 3. 4. Distribution of Organic Nitrogen (mg/g) in the sediment core

3.1.3. Carbon: Nitrogen Ratio

The monthly data of the C/N ratios of the surface sediments are given in the *Table A.6.* The ratio seemed to be ranging between 10.67 and 15.39 at Mangalavanam and 10.15 and 13.5 at Vypeen. There was not much monthly variation in the ratio at both stations (Fig: 3. 5).

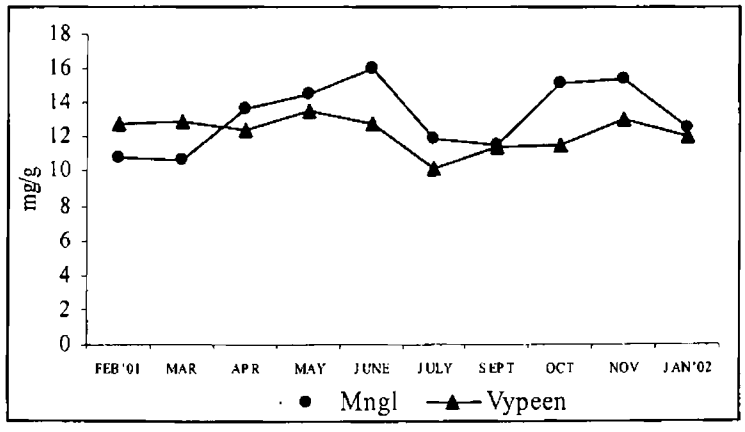

Fig: 3. 5. Monthly Variation of C/N in the Surface sediments

The vertical variations of C/N ratios at both stations are given in the *Table A.7.* At Mangalavanam, irregular variations in the ratio were observed

down the core, whereas at Vypeen, the ratio seemed to be a constant except during pre monsoon season when a slight increase was observed. The highest C/N ratio, 21.39 were observed at 10-15 cm depth and 12.8 at 20-25 cm depth at Mangalavanam and Vypeen respectively during post monsoon season. The values showed marked spatial variations during all seasons. The C/N ratios at Mangalavanam in all depths (11- 21) were comparatively higher than those at Vypeen (10-13).

The C/N ratios in mangrove sediments help to determine the availability of different sources of carbon and nitrogen in this system. C/N elemental ratios are utilized to trace the three sources, mangroves, sea grasses and phytoplankton, contributing to sedimentary organic matter, where, all the three contribute to organic carbon burial. The C/N ratios, which are highly variable, help to distinguish between algal and land-plant origins of sedimentary organic matter. Sediment low in organic carbon reflects allochthonous sources and C/N ratios of such sediments are usually much lower than sediments rich in mangrove litter. Seasonally slight variations were observed at both stations (Table: 3.6). The difference in C/N ratios between the two stations can be due to many factors.

Season	Mngl	Vyp
Premon	12.40	12.90
Mon	13.12	11.45
Post mon	14.36	12.21

Table: 3.6. Spatial and seasonal variation of C/N at both stations.

In 2000, Strauss and Lamberti reported that the microbial activity in stream sediments could be increased by the addition of organic carbon. But when carbon was added C/N ratio became high, heterotrophic bacteria outcompeted nitrifying bacteria for available ammonium, thereby reducing the nitrification rates. Bacterial activity thus proves to be an important factor controlling the mineralization of organic matter and the retention of nitrogen within the coastal sediments. Such mineralisation of organic matter is very

effectively taking place in mangrove sediments due to the abundant microbial population (Nedwell *et al.*, 1994; Stanley *et al.*, 1987).

Nitrogenous components of biological origin are more effectively recycled than other forms of organic matter when it undergoes degradation. This results in retaining a greater proportion of carbon content in it thereby enhancing the C/N ratio (Bouillon *et al.*, 2003). During senescence of the leaves, i.e. before litterfall, about 64 % of the nitrogen is resorbed by the mangroves (Rao *et al.*, 1994). Consequently, the sediment receives mangrove material that is strongly depleted in nitrogen with respect to fresh mangroves leaves. The absence of cellulose in algae and its abundance in vascular plants resulted in a high difference in their C/N ratio. Holmboe *et al* (2001) reported high C/N values for Bangrong mangrove sediment due to the higher content of structural carbohydrates (e.g. cellulose) in and lower nutrient release from the sedimentary organic matter.

The C/N ratios of the leaves of three most commonly occurring plant species were also calculated from the corresponding carbon and nitrogen concentrations *(Table: A.3)*. The ratio was observed higher at Vypeen than at Mangalavanam for all the species. Several authors have mentioned that organic matter should have a C/N ratio lower than 17 to be of nutritional use to invertebrates. Mangrove leaf litter is of little nutritional value due to its high C/N ratios even after considerable degradation (Lee, 1997). However, leaves, which make up the major portion of detritus exported from mangroves, have a C/N ratio of between 20 and 95 (Jennerjahn and Ittekkot 1997). The decomposition rate of different plant leaves was different. Under similar conditions, the decomposition rate of leaves was greater for red (Rhizophora species) mangroves, than that for black mangroves (Avicennia species) (Wafar *et al*, 1997). They reported that during the course of decomposition of leaves, the concentrations of carbon decreased, but that of nitrogen increased, as a result the C/N ratio decreased.

In spite of the high C/N ratios for plant species comparatively lower C/N ratios were observed for the sediments at Vypeen than that at Mangalavanam (Fig: 3. 6). This may be due to the high nitrogen values that arise from the higher rate of degradation of organic matter at this station. Similar results were earlier reported in the sediments of the lower Mississippi delta (Paramasivam and Breitenbeck, 1994) and in Bengal basin (Datta *et al.*, 1999). But comparing the C/N ratio of the mangrove plants and sediment, it can be seen that there is a considerable fall in the ratio in the sediment sector, especially at Vypeen.

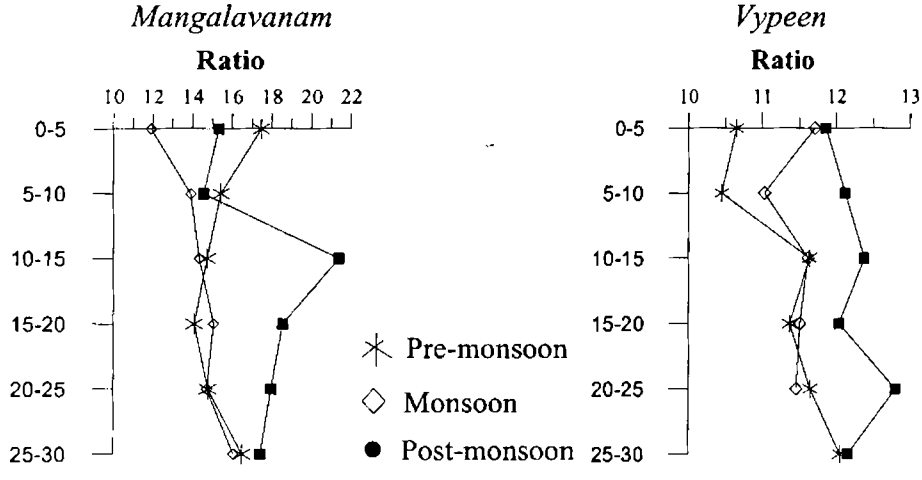

Fig: 3. 6. Distribution of C/N Ratio in the sediment core

Generally a low C/N is indicative of aquatic origin and a high, terrestrial. The analysis of actual concentration of C/N indicated a significant lateral addition of organic matter at Vypeen from the surroundings. This observation along with the C/N ratio is clearly indicative of a different mechanism in the dynamics of organic matter. The earlier works have suggested a preferential removal of organic carbon during decomposition of the mangrove litter retaining the nitrogen thereby decreasing C/N substantially (Paramasivam and Breitenbeck, 1994). The

litterfall and the C/N is in good agreement with the earlier explanation viz. C/N of sediment is significantly lower than the C/N of plants. But the major difference between Mangalavanam and Vypeen is that Vypeen being more open to the estuary than Mangalavanam, the possibility of exchange of organic matter with the estuary is high. Such an exchange will have in low C/N organic matter of estuary to the system and thereby considerably decreasing the C/N of the system.

The decrease in C/N ratio was attributed to colonization by bacteria, which incorporated nitrogen from the overlying water column or from the indigenous particulate organic nitrogen pool in the sediments (Holmer and Olsen, 2002). The decreasing C/N ratio with decreasing size fraction indicates that the intensity of microbially mediated decomposition processes decrease from sand to clay. This may also account for the low C/N ratio at Vypeen.

The change in the ratio can also be due to the difference in grain size distribution of the sediment. Since clay can hold more organic mater due to its greater surface area (Rasheed *et al*, 2003), the difference in grain size can alter the C/N ratio. Bouillon *et al.*, (2003) reported high C/N ratios between 17 and 25 in sediments of mangrove vegetation. Some organic carbon-rich sediment has also been shown to display high C/N ratios upto 43 (Lallier-Verges *et al.*, 1998). Algae typically have atomic C/N values between 6 and 8 (Marchand *et al.*, 2003) and vascular land plants have C/N values of 20 and greater (Meyers, 1994 and Prahl et al., 1994). Preferential loss of nitrogen-rich proteinaceous matter also elevates the C/N ratio of algal organic matter. Mangrove sediment from Coringa area in Godavari Delta was shown to have C/N ratios of on average 8–10 indicated that phytoplankton is the major source of this organic matter (Dehairs *et al.*, 2000). Normally, the C/N ratio of marine organic material is in the range of 6-7 and that of terrigenous organic matter is >20 (Emerson and Hedges, 1988).

The high C/N ratios (>7) are indicative of a certain amount of terrestrial material in the organic carbon fraction. Therefore these ratios are valuable for identifying terrestrial input to the study area. C/N values of similar studies are given in *Table: 3. 7.*

No.	Study Area	Reported Value	Reference
1.	Bangrong mangroves.	30	Holmboe *et al*, 2001
2.	Mangrove fringed coastal sediments, French Guiana.	6- 8	Marchand *et al*, 2003
3.	Coringa Mangrove sediments, India	7- 27.3	Bouillon *et al*, 2003
4.	Itacuruca mangroves, Brazil	16.9	Jennerjahn and Ittekkot, 2002
5.	Goa mangrove sediments	7.22- 13.44	Jagtap, 1987
6.	Paraiba do Sul mangroves, Brazil.	11.7	Jennerjahn and Ittekkot, 1997
7.	Vembanad Lake sediments, India	1- 21.8	Verma and Subramanian, 2002
8.	Mangrove plants, Haad Chao mai National Park, Thailand	16.6- 49.7	Kuramoto and Mingawa, 2001
9.	Mangrove leaves, Gazi Bay	27- 32 (Avicennia marina) 43 to 78 (Rhizophora mucronata	Hemminga et al, 1994
10.	Present study a) Mangalavanam mangrove sediments b) Vypeen mangrove sediments	10.67- 15.97 10.15- 13.5	

Table: 3.7. Sedimentary C/N ratios reported in earlier studies and the present study.

3.1.4. Hydrogen and Sulphur

➢ *Materials and Methods*

Details of the method of analysis are given in Chapter 2.

➢ *Results and Discussions*

The observed monthly concentrations of hydrogen and organic sulphur are given in appendix A.9 and A.10 and in Fig. 3.7 and Fig 3.8 respectively.

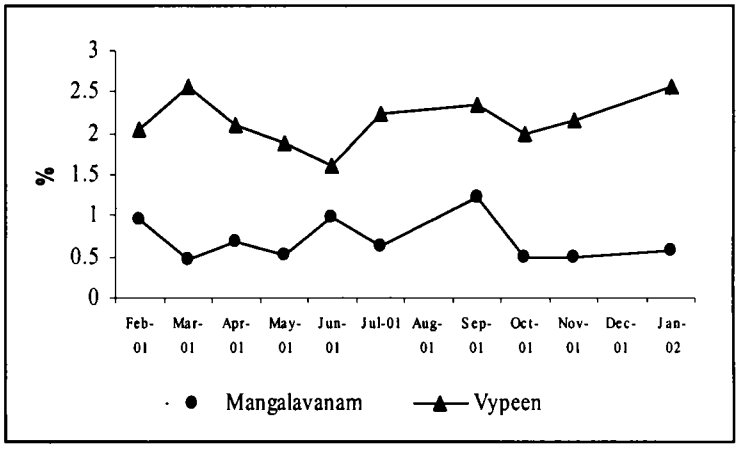

Fig: 3. 7. Monthly Variation of Hydrogen (%) in the Surface sediments

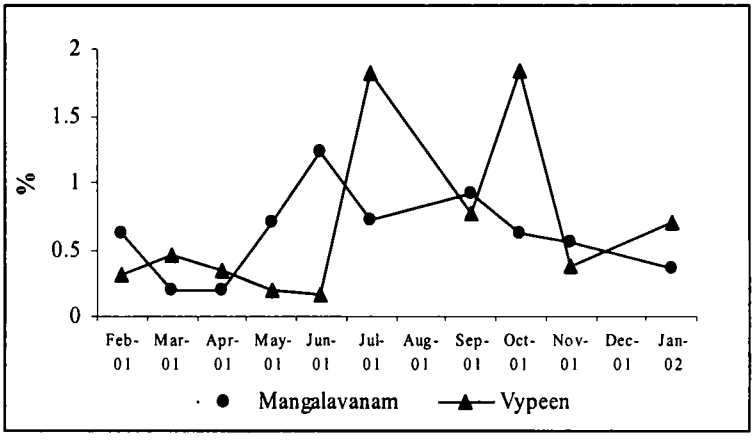

Fig: 3. 8. Monthly Variation of Sulphur (%) in the Surface sediments

The behaviour of these two elements was found to be in line with that of carbon and nitrogen. No specific comments are given here, as generally, one expects the processes of addition and removal in these cases as one and the same as that of carbon and nitrogen. In sediment core also, the trend is similar to that of carbon and nitrogen (Fig. 3.9 and Fig. 3.10).

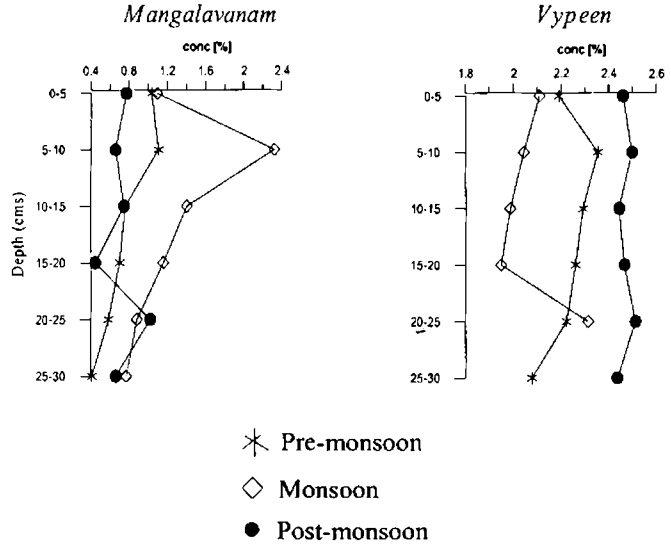

Fig: 3. 9. Distribution of Hydrogen (%) in the sediment core

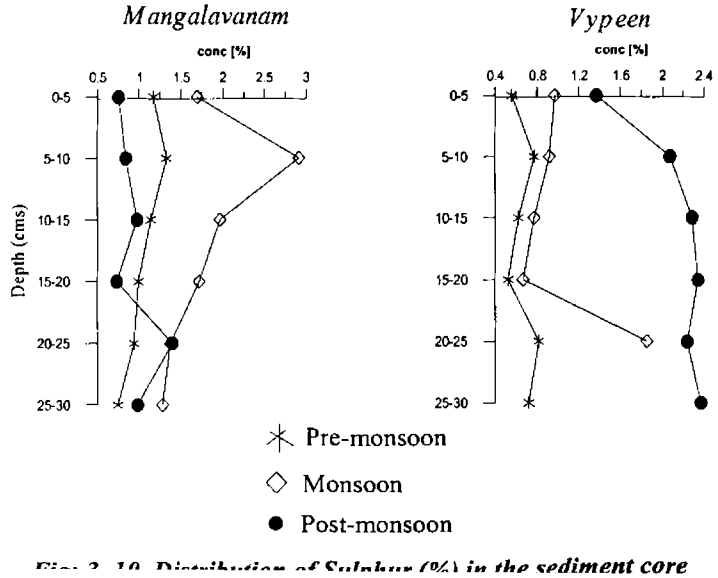

Fig: 3. 10. Distribution of Sulphur (%) in the sediment core

3.2. Bioorganics

Organic matter that is transported through the water column in the form of aggregates attached to the sinking particles (Ransom *et al.*, 1998), is labile and provides sites for active mineralization by heterotrophic bacteria (Alldredge *et al.*, 1993). These aggregates undergo several chemical and physical processes and ultimately get buried in the sediments (Ransom *et al.*, 1998). During these processes OM is continuously mineralized and altered and become less labile down core. Microbial communities in shallow marine sediments play a key role in the oxidation and degradation of complex organic compounds in the overlying water column (Herbert, 1999) and a significant portion ranging 10-60% escapes degradation and reach the sediment surface where it is subjected to further chemical and biological transformations. Thus, according to Soetaert *et al.*, (1998), sedimentary OM can be classified into non-degradable, rapidly degradable and slowly degradable fractions.

The first stage of decomposition involves leaching of soluble materials (mostly carbohydrates). These compounds are readily available for the bacterial uptake owing to their dissolved nature. Generally total carbohydrates are composed of monosacharides, polysaccharides, acid polysaccharides (such as uronic acids), amino sugars and other alcoholic sugars. Polysaccharides are common structural and storage compounds in both marine and terrestrial organisms and represent the major form of photosynthetically assimilated carbon in the biosphere (Cowie and Hedges, 1984). Polysaccharides in the sediment are converted to monosaccharides and oligosaccharides and released into overlying water. These are flushed away during monsoon season into the estuary.

Proteins are considered labile and their most part is rapidly degraded chemically and biologically in the marine water column itself (Nguyen and Harvey, 1997). In sediments, polymeric compounds like proteins are degraded at a slower rate than their monomeric counterparts like amino

acids, carbohydrates and fatty acids. Due to ageing proteins become more and more resistant to degradation by microorganisms (Keil and Kirchmann 1994). The other factors that are believed to protect organic matter from its enzymatic decomposition are 1) chemical resistance of organic substances, either due to their humification or due to the lack of oxygen necessary for their complete degradation. So the decomposition rate of organic matter in deeper sediments will be very low and 2) physical resistance due to the sorption of organic substances to the mineral surfaces (Boetius *et al*, 1999).

Complexes formed between organic N compounds and polyvalent cations, such as Fe, are biologically stable. Some of the organic N occurs in small pores or voids and is physically inaccessible to microorganisms. Thus peptides, carbohydrate and other high mol wt compounds that is adsorbed to metal oxides and clay mineral particles within the water column are resistant to microbial degradation and gets preserved in the surface sediments (Sugai and Henrichs, 1992; Mayer 1994; Kappler *et al*, 2001). Recent reports give evidence to the fact that the high molecular mass proteinaceous material observed in algae, detritus and sediments in aquatic environments are resistant to degradation and get preserved in the sediments (Nguyen and Harvey, 2001).

Amino acids, the building blocks of proteins and major components of organic matter in the aquatic environment (Parsons *et al.*, 1977). Amino acids are the most labile class of biochemicals (Henrichs and Farrington, 1987) and are a critical substrate for microbial growth in marine environments (van Mooy and Keil, 2002). These nitrogen-rich compounds compose the bulk of organic matter that may be characterized at the molecular level in marine sediments (Wakeham *et al.* 1997). The amount and composition of proteinaceous matter has been found to provide information on sources and transformation processes (Haake *et al.*, 1992). Due to high respiration activity, oxygen penetrates only the upper few mm and anaerobic activities become responsible for the degradation and transformation below this depth, where a vast group of microorganisms

attack proteins since they are easily hydrolysable compounds and produce amino acids. Thus free amino acids may originate in soils from: i) leaching of biological tissues (plant, animal and microbial remains), ii) release during the conversion of protein N to NH 3 (proteins peptides amino acids NH_3) by heterotrophic organisms, and iii) plant root/microbial excretion. Once amino acids are released in soils, many factors affect their abundance, including synthesis and destruction by biota, adsorption by clay minerals and reactions with quinines and reducing sugars (Stevenson 1994).

The relative molecular distribution of amino acids changes as the microbial degradation of organic matter proceeds, and this observation has been used to assess the extent of degradation of sedimentary organic matter (Dauwe *et al.* 1999). Thus the study of amino acids in sediments may provide additional insight regarding the availability of organic matter for microbial degradation.

Studies on the distribution of carbohydrates, proteins and amino acids provide useful information on the nature, source, diagenetic changes and decomposition of organic matter and therefore useful to study cycling of organic matter during its transport to greater depths (Cowie and Hedges, 1992; Hernes *et al.*, 1996).

3.2.1 Materials and Methods

Details of the method of analysis are given in Chapter 2.

3.2.2 Results

- *Carbohydrates*

The monthly distribution of different forms of carbohydrates in the surface sediments is given in the *Table: A.12.* There is no significant monthly variation for MCHO (Fig: 3. 11) between both stations, but comparatively lesser TCHO (Fig: 3. 12) were observed at Mangalavanam.

At Mangalavanam, the highest concentration of MCHO (0.979 mg/g) was found to be in June and lowest (0.177 mg/g) during April and TCHO and PCHO highest during September (19.34 and 18.9 mg/g respectively) and the lowest (4.684 and 4.481 mg/g respectively) during February. At Vypeen, the highest value for MCHO (1.089 mg/g) was observed in July and the lowest (0.096 mg/g) during January; the highest TCHO and PCHO values in July (23.36 and 22.27 mg/g respectively) and the lowest) in February (9.305 and 9.14 mg/g respectively. At both stations the values of mono carbohydrates (MCHO) were found to be comparatively very low during all seasons.

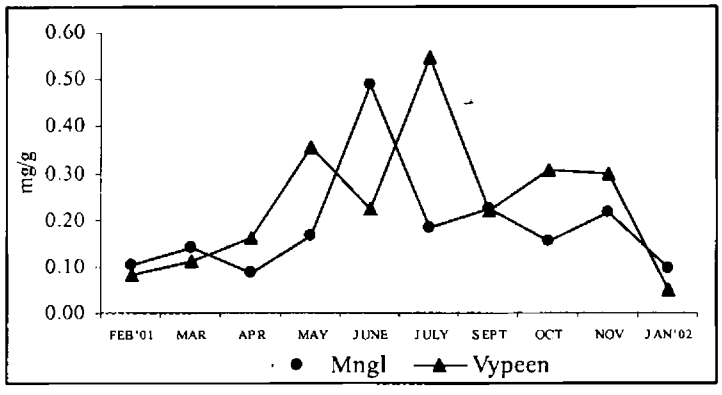

Fig: 11. Monthly variations of MCHO (mg/g) at both stations

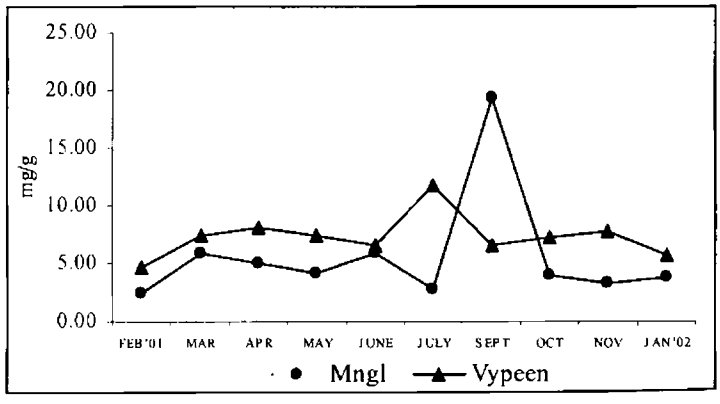

Fig: 12. Monthly variations of TCHO (mg/g) at both stations

The vertical distribution of MCHO, TCHO and PCHO in sediment upto 30 cm depth in Mangalavanam and Vypeen are shown in the *Tables A.13, A.14 and A.15* respectively. At both stations the concentrations of MCHO, TCHO and PCHO were found to be the highest (12.08, 17.8 and 10.77 mg/g at Mangalavanam and 12.8, 13.14 and 14.33 mg/g at Vypeen) at the sub surface (5-10 cm depth) during all the seasons. The highest TCHO and PCHO were observed in post monsoon season and the lowest in pre monsoon season.

➢ *Proteins*

Like carbohydrates, the concentration of protein also did not show much monthly variation between the two stations (Fig: 3. 13). In the present study, concentration of protein was found to be higher at Mangalavanam (17.94 mg/g) in September and lower at Vypeen (1.36 mg/g) in March *(Table: A.16).* The vertical variation showed the highest concentration during monsoon at both stations *(Table: A.17).* At Vypeen, no marked down core variation was observed, indicating more preserved nature of the organic matter.

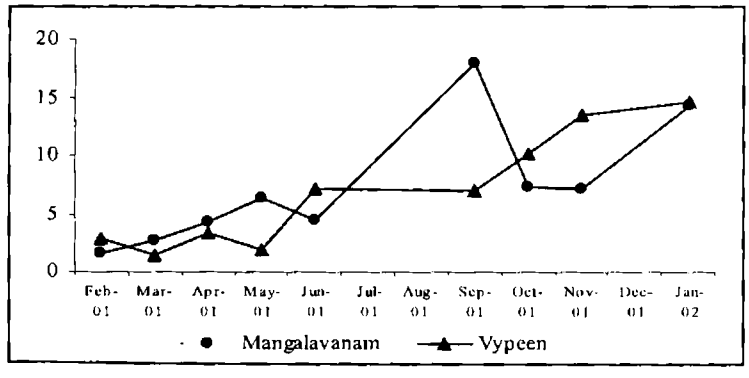

Fig: 3. 13. Monthly Variation of Protein (mg/g) in the Surface sediments

The quantity of protein delivered to sediments via the watercolumn depends little on the redox conditions of the watercolumn; anoxic and oxic watercolumns both deliver the same relative quantity and quality of proteins

to sediments, and its fate is to be essentially completely remineralized. Most organic matter present in sediments is found in the form of aggregates that are surrounded by clay plates. There is a positive correlation between the proportion of clay-to-organic in the aggregates and the degradation state of the organic matter. Proteins in clay-rich aggregates are more fragmented and partially degraded than those in organic-rich aggregates. Most proteins identified in sediments are derived from bacteria, not from phytoplankton, and the predominant forms are those that are typically present in the cell walls of proteobacteria.

➢ *Free Amino Acids*

Comparatively higher concentrations of free amino acids (FAA) were observed at Mangalavanam than that at Vypeen. Monthly variations at both stations are given in the Fig. 3. 14. The maximum concentration of 1.6 mg/g was found in March '01 at Mangalavanam and 0.6 mg/g in January '02 at Vypeen, whereas the minimum was observed in November '01 (0.26 mg/g) and February '01 (0.29 mg/g) at Mangalavanam and Vypeen respectively *(Table: A.18).*

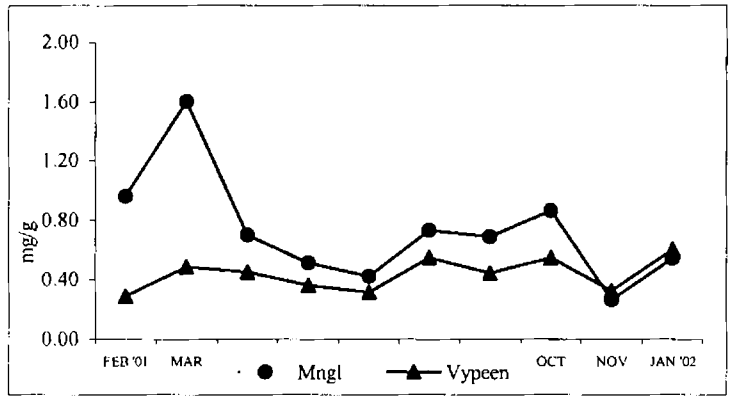

Fig: 3. 14. Monthly variations of FAA (mg/g) at both stations

When vertical variations are considered *(Table: A.19),* the highest FAA concentration was observed at the surface during monsoon season at

both stations (2.29 and 1.03 mg/g at Mangalavanam and Vypeen respectively). At Mangalavanam, the lowest concentration was observed during pre monsoon season and at Vypeen, during post monsoon season.

3.2.3 Discussions

➢ *Carbohydrates*

The seasonal average of the concentration of SMCHO, STCHO and SPCHO in the surface sediments at two stations were given in *Table 3.8.* At both stations, the concentrations were found to be the highest during monsoon. A similar trend in the lowest values was observed at both stations. Only slight seasonal variations were observed for MCHO, TCHO, and PCHO at both stations. The concentration was found to be slightly lower at Mangalavanam than that at Vypeen and this was in accordance with the values found for carbon at both stations.

Season	Mangalavanam			Vypeen		
	MCHO	TCHO	PCHO	MCHO	TCHO	PCHO
Pre mon	0.249	8.703	8.454	0.354	13.870	13.516
Mon	0.597	12.203	11.606	0.660	16.502	15.842
Post mon	0.308	7.438	7.130	0.434	13.780	13.346

Table: 3.8. Seasonal average of Carbohydrates in the surface sediments (mg/g)

Considering the vertical distribution patterns, concentrations of MCHO, TCHO and PCHO were found to be decreasing down the core almost regularly (Fig: 3. 15, Fig: 3. 16 and Fig: 3. 17 respectively). Pre monsoon and monsoon seasons marked the higher concentrations at both stations except TCHO variation at Vypeen, which was observed higher in monsoon and post monsoon seasons. Sub surface maxima were observed in monsoon season at Mangalavanam for all fractions during monsoon season.

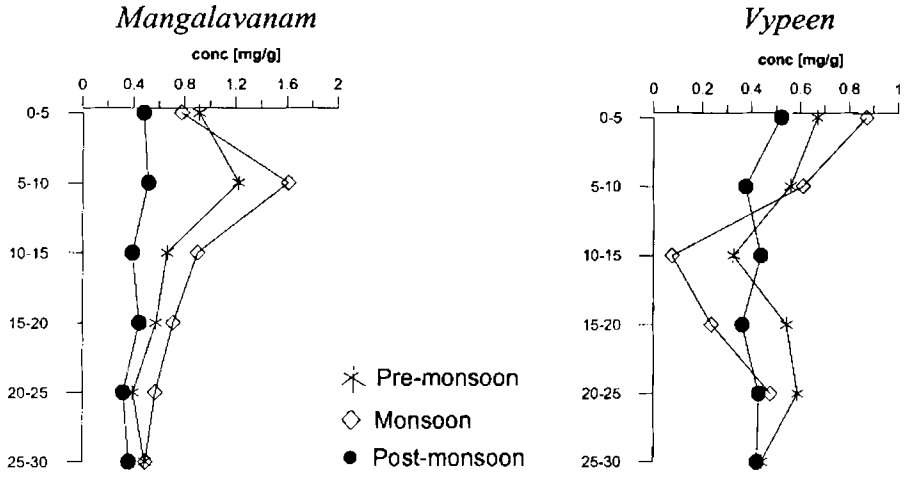

Fig: 3. 15. Distribution of Mono Carbohydrates in the sediment core (mg/g)

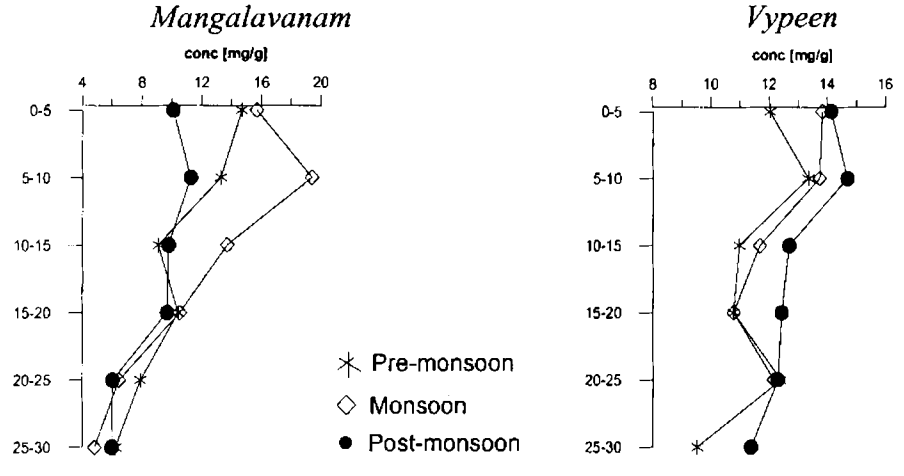

Fig: 3. 16. Distribution of Total Carbohydrates in the sediment core (mg/g)

The first stage of decomposition in mangroves involves the leaching of carbohydrate making them readily available for uptake by bacteria. The microbial conversion of organic matter and preferential decomposition of other easily oxidisable organic matter seemed to increase in the concentration of carbohydrates in the system (Lacerda *et al,* 1995).

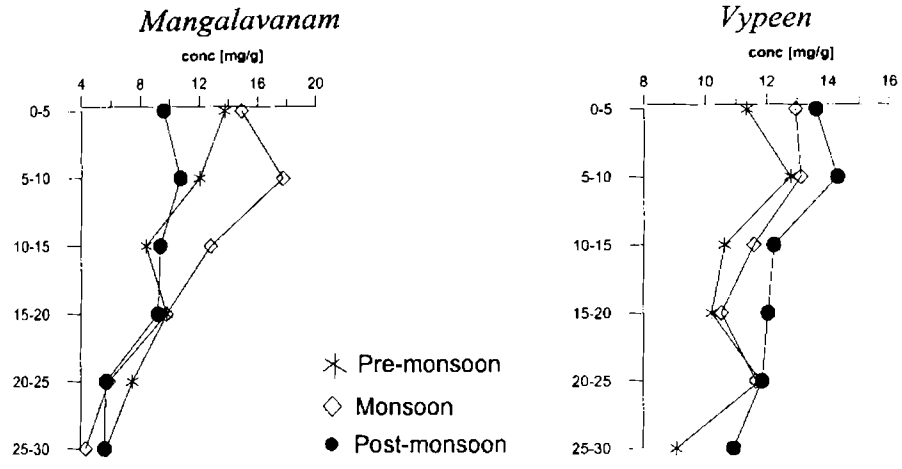

Fig:3. 17. Distribution of Poly Carbohydrates in the sediment core (mg/g)

Moreover, the biomass of burrowing organisms were found to be high at both atations and in many previous studies it is reported that decomposition will be accelerated in sediments where there is oxygenation due to high bioturbation (Gong and Ong, 1990; Marchand et al., 2003). Results obtained for similar studies are given in Table: 3.9.

No.	Study Area	Reported Value	Reference
1.	Mangrove sediment core, South-eastern Brazil.	1.41- 3.83 mg/g (under Avicennia plants) 2.4- 2.5 mg/g (under Rhizophora plants)	Lacerda *et al*, 1995
2.	Coastal Sediments, Visakhapatnam.	1.09 mg/g	Sarma and Rao, 1988
3.	Dabob Bay sediment core, Washington.	13.9-10.8 % (0-30 cm depth)	Cowie and Hedges, 1984
4.	Eastern north Sea Sediment core.	0.11- 7.74 mg/g (0-15 cm depth)	Dauwe and Middelburg, 1998

5.	Sediment core from Continental margin off southern New England.	10.73- 1.18 µM/g (0- 30 cm depth)	Steinberg *et al.*, 1987
6.	Ebro delta sediments, Spain	0.05- 1.37 %	Gonzalez *et al*, 1983
7.	Marsala lagoon sediments, Italy.	0.09- 0.58 mg/g	Pusceddu *et al.*, 2003
8.	Present study a) Mangalavanam mangrove sediments b) Vypeen mangrove sediments	 7.4- 12.2 mg/g (surface sediment) 19.4- 4.8 mg/g (0- 30 cm depth) in sediment core. 14- 16.5 mg/g (surface sediment) 14.7- 9.5 mg/g (0- 30 cm depth) in sediment core.	

Table: 3.9. Sedimentary carbohydrate values reported in earlier studies and the present study.

➢ *Proteins*

The average seasonal variation showed the highest protein concentration during monsoon at Mangalavanam (11.21 mg/g) and (12.76 mg/g) during post monsoon season at Vypeen. In mangroves, the tidal flushing takes away the organic matter, restricting the accumulation of protein. Comparatively higher concentration of protein during monsoon season at Mangalavanam *(Table. 3.10)* may be due to the high organic load and less tidal influence, which helps the adsorption of proteins in the sediment.

Season	Mngl	Vyp
Premon	3.71	2.38
Mon	11.21	6.99
Postmon	9.6	12.76

Table: 3.10. Seasonal average of Protein (mg/g) in the surface sediments

At both stations, the concentrations of protein seemed to decrease down the core *(Fig: 3.18)*. At Vypeen protein seemed to be in a more preserved condition than that at Mangalavanam. Adsorption of organic matter into the clay minerals also accounts for the high protein content in the sediment, where much of the adsorbed protein was not readily desorbed (Ding and Henrichs, 2002) and they are resistant to degradation or only partially degraded (Keil and Fogel, 2001). Adsorption of organic matter to marine sediment particles can decrease its availability to microbial degradation (Sugai and Henrichs, 1992; Mayer, 1994; Hedges and Keil, 1995).

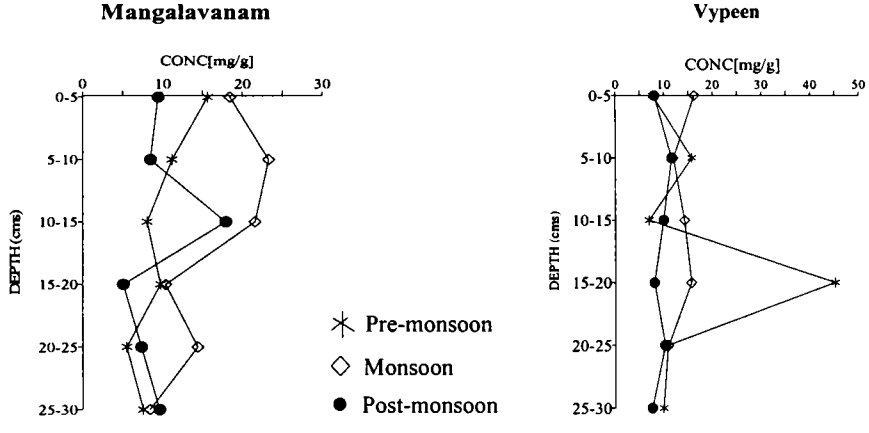

Fig: 3. 18. Distribution of Proteins in the sediment core (mg/g)

Ding and Henrichs (2002) reported that the weakly adsorbed proteins were preferentially consumed by microorganisms compared with strongly adsorbed proteins in the sediments. The presence of microbes and polychaete fauna in the sediments can also affect the concentration of sedimentary proteins. Abundance of polychaete fauna in the sediment of

Kochi mangroves during premonsoon and post monsoon seasons have been reported earlier (Sunil Kumar and Antony, 1994; Sunil Kumar 2002).

Season	Mngl	Vyp
Premon	0.42629	0.171593
Mon	0.918627	0.423585
Postmon	1.29067	0.92598

Table: 3.11. Seasonal average of Protein: Carbohydrate ratio

In the present study, seasonal variation in protein: carbohydrate ratio in both surface *(Table: 3.11)* and core sediments *(Table: 3.12)* were found to be higher at Mangalavanam than at Vypeen and the ratio was <1 during all the seasons at Vypeen.

Depth	Mangalavanam			Vypeen		
	Pre-mon	Monsoon	Post-mon	Pre-mon	Monsoon	Post-mon
0-5	1.06	1.17	0.93	0.64	1.18	0.57
5-10	0.84	1.20	0.75	1.18	0.87	0.79
10-15	0.89	1.57	1.83	0.63	1.22	0.78
15-20	0.93	0.98	0.52	0.00	1.45	0.64
20-25	0.70	2.23	1.22	0.87	0.90	0.83
25-30	1.22	1.73	1.60	1.04		0.66

Table: 3.12. Distribution of Protein: Carbohydrate ratio in the sediment core at both stations

Generally in all lagoon sediments, carbohydrates is found to dominate the organic matter pool and this result in a protein to carbohydrate ratio that is always < 1 (Danovaro, 1996), especially in oligotropic environments, where proteins reach very low concentrations (Danovaro *et al*, 1993). The low value of this ratio is also indicative of the presence of aged organic matter in the system (Pusceddu *et al.*, 2000), since proteins are easily mobilized than carbohydrates. The sedimentary protein values obtained in some previous studies are given in the *Table: 3.13.*

No.	Study Area	Reported Value	Reference
1.	Marsala Lagoon Sediments.	0.09- 0.58 mg/g	Pusceddu *et al.*, 2003
2.	Mangrove sediments, Kochi, Kerala	0.31- 45.07 mg/g (Mangalavanam) 0.87- 21.45 mg/g (Vypeen)	Geetha, 2002
2.	Mangrove sediments, Vypeen, Kochi, Kerala	9.55 mg/g	Rini, 2002
3.	Present study a) Mangalavanam mangrove sediments b) Vypeen mangrove sediments	3.71- 11.21 mg/g (surface sediment) 23.3- 5.0 mg/g (0-30 cm depth) in sediment core. 2.38- 12.76 mg/g (surface sediment) 16.3- 7.0 mg/g (0- 30 cm depth) in sediment core.	

Table: 3.13. Sedimentary protein values reported in earlier studies and the present study.

➢ *Free Amino Acids*

At Mangalavanam, the concentration of FAA was found to be the maximum during pre monsoon season (0.944 mg/g) and at Vypeen the highest concentration of 0.49 mg/g was observed during post monsoon season *(Table: 3.14).*

Season	Mngl	Vyp
Premon	0.944	0.398
Mon	0.614	0.437
Postmon	0.556	0.491

Table: 3.14. Seasonal average of FAA mg/g

At both stations, free amino acids (FAA) were found to be in very low concentrations. The distribution of FAA at Vypeen did not vary much seasonally because of the increased rate of consumption and degradation of amino acids by higher benthic activity during all seasons. But in the case of Mangalavanam the pre monsoon season presented a significantly high concentration of FAA. One speciality of Mangalavanam is that it hosts a large variety of migratory birds especially during May and July every year and nesting of different species of birds was observed from February to July (Jayson, 2001). A substantial contribution of nitrogen in the form of uric acids and purines is evidenced in earlier works (Janat, 2002). The structural elucidation of humic acids has suggested high nitrogen content with uric acid like structures. Thus the increased FAA can be due to the excretions from birds also.

Generally, FAA was found to be in lesser amounts in natural aquatic environments (Lee and Bada, 1977), suggesting that organic matter sustained proteolytic attack by organisms in the sediment (van Mooy and Keil, 2002). The combined amino acid pools were found to meet the bacterial requirements for protein metabolism in a better way than the FAA pool (Hollibaugh and Azam, 1983; Kirchman and Hodson, 1984). Free amino acids are formed from the excretions of living organisms and also by the reaction of ammonia obtained during the biological fixation process of elemental nitrogen, with some naturally occurring carboxylic acids (De Stefano *et al.*, 2002). The concentrations of ammonia formed at both stations were found to be the highest during monsoon season *(Table: 3.3)*. This may be a reason for the observed high values of FAA in the surface sediments during monsoon season.

Major contributors of amino acids to the mangrove systems are leaves, in addition to land run-off and in situ production (Chen *et al.*, 2004). Marine invertebrates also have a large pool of free amino acids in their tissues (Pruski *et al*, 2000). In the systems of concern, i.e., Mangalavanam and Vypeen, the land addition is generally restricted to monsoon. In several studies, plants

were found to be the major contributors of amino acids in mangroves and salt marshes (Woodroffe, 1985). Comparatively higher plant biomass accounts for the higher concentrations of amino acids observed at Mangalavanam. In (1975) de la Cruz and Poe studied the amino acid content in live, dead plants and detritus of some marsh plants and found that generally live plants have the highest concentration of amino acids, but in some species detritus was found to have the highest concentration of amino acid. This increase in amino acid concentration from dead plants to detritus was probably due to the biochemical changes occurring to the dead plants during decomposition. The rapid loss of organic matter from leaf litter is mainly due to the leaching of water-soluble organic compounds (Twilley, 1985), which are subsequently converted into microbial biomass (Benner *et al.*, 1986).

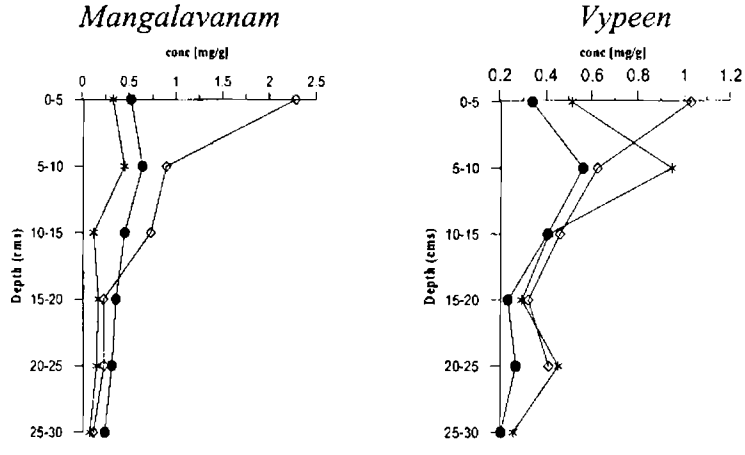

Fig: 3. 19. Distribution of FAA in the sediment core at both stations

In the sediment core, FAA at both stations was observed high at the surface during monsoon and at subsurface during the other two seasons *(Fig: 3. 19),* and the concentrations of FAA were found to decrease in the sediment core at both stations almost regularly during all the seasons. A possible explanation is that the highly productive bacterial populations in the upper sediment layers use all of the amino acids, since dissolved free amino acids provide a moderate percentage of bacterial carbon and nitrogen

requirements (Jorgensen, 1986). At both stations, FAA was observed highest during monsoon and the lowest during pre monsoon season. Microbial hydrolysis of peptides and protein is thought to be the major source of free amino acids and this was found to be more intense during post monsoon and pre monsoon, when microbial activity was triggered by an increase in temperature and by higher deposition of organic matter to sediments, and minimal in rainy season (Pantoja and Lee, 1999).

The observation of FAA more at sub surface than that at the surface especially during pre and post monsoon seasons may also be due to the dissolution of the soluble amino acids into the overlying water during the pre and post monsoon seasons. A similar trend in concentration of amino acids was observed in marine anoxic sediments of Cape Lookout Bight, North Carolina (Henrichs and Farrington, 1987, Burdige and Martens, 1988). They reported that the concentrations of FAA were found the highest in surface sediment and decreased to very low values at depths > 20 cm. A review of similar works in various places is given in the *Table: 3. 15.*

Concentrations and composition of FAA were found to differ significantly between sediments and overlying tidal waters. The levels of amino acids in surface sediments were found always at least one order of magnitude higher than in the overlying water and had a marked difference in composition (Stanley *et al.*, 1987). Flux chamber experiments done in Chunda bay and Hinchinbrook Island suggest that surface sediment bacterial populations are capable of utilizing all of the amino acid flux to the sediment-water interface in tropical mangroves (Stanley *et al.*, 1987). In contrast, the concentration at the surface was found to be higher at both stations during monsoon because of several reasons like the high terrestrial addition to the system and clay particles form slurry with this organic matter and like sand this is not transported easily by physical forces, resulting in a higher concentration organic matter in the surface. This is supported by the observation of high clay and less sand content at both stations during

No.	Study Area	FAA	Authors
1.	Pore water from mangrove sediments, Hinchinbrook Island.	169- 268 ng/ml (percolated water 0-5 cm depth) 323- 1175 ng/ml (squeezed water from 0-5 cm depth)	Stanley *et al.*, 1987.
2.	Pore water, Kysing Fjord, Denmark	~850 ng/ml	Jorgensen, 1980
3.	Pore water, Georgia Salt Marsh, U.S.A	~ 670 ng/ml (Spartina site) ~ 100 ng/ml (Mud flat)	Gardner and Hanson, 1979.
4.	Lakes in Central Jutland.	190- 1963 nM (Hylke Lake) 1000- 3672 nM (Almind Lake)	Jorgensen, 1987.
5.	Frederiksborg Slotsso Lake, Northern Zealand	78- 377 nM	Jorgensen, 1987.
6.	Present study a) Mangalavanam mangrove sediments b) Vypeen mangrove sediments	0.56- 0.94 mg/g (surface sediment) 2.3- 0.09 mg/g in sediment core. 0.4- 0.5 mg/g (surface sediment) 1.03- 0.21 mg/g in sediment core.	

Table: 3.15. Sedimentary FAA values reported in earlier studies and the present study.

Amino acids associated with refractory pool of bacterial cell walls could account for approximately one-third of the total hydrolysable amino acids in the deeper sediments (Grutters *et al.*, 2002). According to Burdige and Martens (1988) the decrease of THAA concs. with depth may be due to the utilization

of labile amino acids as carbon substrates in microbially mediated reactions such as fermentation, sulphate reduction and methanogenesis.

In addition to labile amino acids, refractory amino acids are also present, but the degradation of labile ones takes place at a faster rate than refractory ones. Alldredge *et al.*, (1993) have reported earlier that the refractory nature of organic matter will increase down core due to the changes occurring to it before getting buried into the sediments. There are several sources of free amino acids in an aquatic ecosystem. FAA can originate from dead bacteria present in the pore water or can leak out from the pore water by diffusion.

There are several studies that reported close similarity between the amino acids found in the pore waters and those found within the intracellular pool of number marine bacteria (Stanley and Brown, 1976; Makenson and Hastings, 1979). Some researchers reported that amino acids are unlikely to be derived from the breakdown of microbial cell walls because these contain D-isomers, particularly of glutamic acid (Stanley and Brown, 1976), that were not detected in the pore waters in their study.

3.3. Correlation Analysis

In the surface sediments, SOC and SON are significantly correlated with each other at both stations (Table: 3. 16, Table: 3.17). SOC has significant positive correlation with TCHO and PCHO also at Mangalavanam, but not at Vypeen. MCHO did not show significant correlation with TCHO at Mangalavanam, whereas at Vypeen, a significant correlation of MCHO with TCHO was observed. TCHO and protein also showed high positive correlation with each other at Mangalavanam, but not at Vypeen. Both SOC and SON showed very good correlation with FAA at Vypeen, but not at Mangalavanam. In addition to this, at Vypeen, SOC showed significant correlation with protein also.

Parameters	Mangalavanam		Vypeen	
	Mean	Std. Deviation	Mean	Std. Deviation
SOC	27.05	10.89	33.85	7.006
SON	2.123	1.056	2.808	0.763
MCHO	0.371	0.234	0.470	0.297
TCHO	9.373	4.244	14.63	3.722
PROTEIN	6.604	5.619	6.180	5.163
FAA	0.727	0.370	0.439	0.109

Parameters	SOC	SON	MCHO	TCHO	PROTEIN	FAA
SOC	1.000					
SON	0.960**	1.000				
MCHO	0.221	0.021	1.000			
TCHO	0.723**	0.643*	0.336	1.000		
PROTEIN	0.457	0.404	-0.013	0.614*	1.000	
FAA	0.006	0.196	-0.378	0.094	-0.314	1.000

**Correlation is significant at the 0.01 level

* Correlation is significant at the 0.05 level

Table: 3: 16. Pearson Correlation between different organic compounds in surface sediments at Mangalavanam (n=10)

Parameters	SOC	SON	MCHO	TCHO	PROTEIN	FAA
SOC	1.000					
SON	0.959**	1.000				
MCHO	0.338	0.454	1.000			
TCHO	0.316	0.456	0.827**	1.000		
PROTEIN	0.582*	0.370	-0.284	-0.396	1.000	
FAA	0.635*	0.701	0.087	0.349	0.154	1.000

**Correlation is significant at the 0.01 level

* Correlation is significant at the 0.05 level

Table: 3: 17. Pearson Correlation between different organic compounds in surface sediments at Vypeen (n=10)

Like surface sediments, significant positive correlation was observed between SOC and SON at both stations for core sediments also. This excellent correlation existing between SOC and SON suggests that the concentration of SON may be regulated by organic sources (Datta *et al,* 1999). SOC also showed significant correlation with carbohydrates, proteins, FAA and finer fraction of the sediment at Mangalavanam. At Vypeen, SOC has significant positive correlation with TCHO and PCHO only. This suggests that the carbohydrates are enriched with organic carbon. SON is significantly correlated with other organic parameters like protein and FAA and also with finer fraction of the sediment. But at Vypeen, SON has significant positive correlation with FAA only and not with protein. When organic matter is bound to finer sediments they will be less available to microbial degradation or subjected to selective degradation (Hedges and Keil, 1995). This is evident from the correlation coefficients obtained different organic parameters and texture at Mangalavanam.

Several researchers have reported that clayey sediments can hold more organic matter than sandy sediments and organic matter concentrations increase with decreasing grain size (Sunilkumar, 1996; Hedges and Keil, 1995; Nair *et al,* 1993; Bordovskiy, 1965). Significant positive correlation was obtained between carbohydrates and finer fraction of the sediment at Mangalavanam, which is indicative of the effective binding nature of fine textured sediment with organic matter. The protein content distribution in the bed sediments seems to be correlated with the distribution of the grain size class <1 mm. The low protein concentrations found on the sediment grains >1 mm were probably due to the low colonization and activity of decomposers (Spacil & Rulik, 1998). Further, FAA and protein also are significantly correlated with each other at Mangalavanam, but no such correlation was seen at Vypeen. At Mangalavanam, protein showed significant positive correlation with free amino acids (FAA) indicating that protein comprise major part of free amino acid pool, but such correlations was not observed in the case of Vypeen. At Mangalavanam, FAA showed positive correlation with both SOC and SON whereas, at Vypeen FAA

showed positive correlation with SON only MCHO, TCHO and PCHO have good correlation at Mangalavanam, but not at Vypeen. Like that in surface sediments, carbohydrates are positively correlated with proteins in core sediments also at Mangalavanam, but such correlation was not observed at Vypeen. From the above study, it is evident that at Mangalavanam, the source of carbohydrates and proteins are the same, but at Vypeen, they have different source. But SOC and SON have the same origin at both stations. This is clear from the positive correlations seen between them for surface and core sediments at both stations.

Parameters	Mangalavanam		Vypeen	
	Mean	Std. Deviation	Mean	Std. Deviation
SOC	22.108	12.927	31.064	2.163
SON	1.461	0.975	2.663	0.198
MCHO	0.661	0.332	0.469	0.178
TCHO	10.303	3.897	12.299	1.371
PROTEIN	11.784	5.451	12.979	8.824
FAA	0.467	0.507	0.457	0.231
SAND	70.600	6.077	15.941	5.154
SILT+CLAY	29.400	6.077	84.059	5.154

MNGL	SOC	SON	MCHO	TCHO	PROTEIN	FAA	SAND	SILT +CLAY
SOC	1.000							
SON	0.979**	1.000						
MCHO	0.772**	0.788**	1.000					
TCHO	0.818**	0.835**	0.834**	1.000				
PROTEIN	0.812**	0.790**	0.659**	0.718**	1.000			
FAA	0.545**	0.638**	0.341	0.628**	0.563**	1.000		
SAND	-0.617**	-0.667**	-0.688**	-0.495*	-0.651**	-0.364	1.000	
SILT+ CLAY	0.617**	0.667**	0.688**	0.495*	0.651**	0.364	-1.000	1.000

**Correlation is significant at the 0.01 level.

* Correlation is significant at the 0.05 level.

Table: 3:18 Pearson Correlation between different organic parameters in the core sediments at Mangalavanam (n=18)

VYPEEN	SOC	SON	MCHO	TCHO	PROTEIN	FAA	SAND	SILT+ CLAY
SOC	1.000							
SON	0.729**	1.000						
MCHO	0.145	0.364	1.000					
TCHO	0.557**	0.568**	0.386	1.000				
PROTEIN	-0.470*	-0.300	0.127	-0.203	1.000			
FAA	0.133	0.498*	0.555**	0.564**	0.058	1.000		
SAND	-0.263	-0.083	0.200	-0.298	0.202	-0.092	1.000	
SILT+CLAY	0.263	0.083	-0.200	0.298	-0.202	0.092	-1.000	1.000

**Correlation is significant at the 0.01 level.

* Correlation is significant at the 0.05 level.

Table: 3: 19. Pearson Correlation between different organic parameters in the core sediments at Vypeen (n=17)

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Chapter 4

CHARACTERISATION AND DISTRIBUTION OF AMINO ACIDS

4.1. Results

4.2. Discussion

4.3. Correlation Analysis

Amino acids represent one of the more labile classes of organic matter in marine sediments, which are the structural components of proteins and constitute the largest reservoir of organic nitrogen in most organisms. Organic matter in marine environments is derived from both allochthonous and autochthonous sources. Detailed source apportionment is difficult using bulk chemical characterization owing to the contribution of organic matter from multiple sources. Chemical characterization of individual organic compounds, however, can yield detailed information on organic matter sources in complex ecosystems. The distribution and abundance of amino acids have been used to assess diagenetic status of organic matter and their isotopic compositions have been linked to organic matter source identification (Hage *et al.*, 2003)

Sediments contain a mixture of proteins and amino acid degradation products (Nunn and Keil, 2004) and mangrove sediments can be considered as large reservoirs of amino acids. In order to assess survival conditions of organisms of mangroves, it is important to understand stability of amino acids in the sediments. Plant remains and other debris contribute nitrogen N in the form of amino acids. Amino acids exist in soil in several different forms, like free amino acids in the sediment micropores, as amino acids, peptides or proteins bound to clay minerals, as amino acids, peptides or proteins bound to humic colloids, as mucoproteins or as a muramic acid. Amino acids, being readily decomposed by microorganisms, have only an ephemeral existence in soil. Thus the amounts present in the soil solution at any one time represent a balance between synthesis and destruction by microorganisms. Because free and combined amino acids can be an important nitrogen source for some plants, soil DON may play an important role in plant nutrition and ecosystem function. Most of the DON was found in the hydrophobic fraction, which suggests the presence of protein/peptide-polyphenol complexes or amino compounds associated with humic substances (Yu *et al.*, 2002).

Amino acids do not comprise the major fraction of the total sedimentary organic matter. They most likely form the principal source of nitrogen for benthic heterotrophs (Cowie & Hedges, 1994; Wakeham *et al.*, 1997; Dauwe and Middleburg, 1998). In marine surface sediments, proteins, peptides, and free amino acids account for 30–40% of the total nitrogen and 10–15% of the total organic carbon (Burdige and Martens, 1988; Cowie and Hedges, 1992). A major chemical process in the early stage of protein digenesis is the degradation to free amino acids through various polypeptides along with the condensation with other organic compounds to form humic substances. Though peptides are believed to be important intermediates in the degradation process, their presence in sediments has been suggested generally by the analyses of amino acids released by acid hydrolysis.

Amino acids derived from different source materials are useful indicators of diagenesis of organic matter and its decomposition gives an important pathway in the recycling of organic carbon and nitrogen (Suthhof *et al.*, 2000). The individual amino acids and their ratios are also significant indicators of depositional environment and changes in source materials that could be responsible for anomalies found in sediments. Hence, amino acid analysis offers more insight into the processes of diagenesis, which changes the nature and characteristics of organic matter upon deposition and decomposition. The down-core analyses will help to determine the extent of organic matter diagenesis in these sediments and help to identify their sources.

4.1. Results

While there are hundreds of amino acids in nature, only 20 are commonly found in proteins. The general structure of amino acids is NH2-CH(R)-COOH. All amino acids have this same structure, but their side chain groups (the R group) may vary in size, shape, charge and

hydrophobicity. The different amino acids detected in Mangalavanam and Vypeen sediments were serine, aspartic acid, glutamic acid, glycine, threonine, alanine, tyrosine, valine, phenyl alanine and tryptophan.

Season	Depth (cms)	Asp	Glu	Ser	Thr	Gly	Tyr	Ala
Pre monsoon	0-5	1.5701	0.6569	94.473	2.9840	0.1762	0.0000	0.1400
	5-10	5.5503	4.3343	76.455	11.103	1.1735	0.0000	1.1610
	10-15	1.2301	0.0739	93.272	0.0000	0.2410	0.5798	0.1106
	15-20	0.9918	0.4817	69.172	27.996	0.2053	0.0248	0.0807
	20-25	1.0627	0.6073	68.748	29.289	0.1841	0.0270	0.0819
Monsoon	0-5	0.3463	0.1128	95.477	0.4990	0.0881	2.6833	0.0000
	5-10	1.7411	0.6536	92.538	2.2671	1.4358	0.2852	0.2423
	15-20	0.3930	0.0000	84.035	0.0000	14.315	1.2570	0.0000
	20-25	0.8030	0.0000	86.393	0.0000	11.439	1.3640	0.0000
Post monsoon	0-5	1.0260	0.2356	88.855	2.2563	6.8059	0.6482	0.1724
	5-10	0.5265	0.0000	89.076	2.0306	7.6108	0.6427	0.1131
	10-15	1.0438	0.3665	90.400	2.9549	4.5926	0.4957	0.1457
	15-20	1.1384	0.3582	90.791	1.6064	5.3112	0.6307	0.1637
	20-25	0.3483	0.0780	93.724	1.1045	4.1870	0.4785	0.0792
	25-30	0.2783	0.0000	96.691	2.6155	0.0000	0.3321	0.0823

Table: 4.1. Seasonal distribution of amino acids (mole %) in the sediment core at Mangalavanam

The concentration (μM) of these amino acids in sediment *(Table: A.20, Table: A.21)* and in leaves *((Table: A.22, Table: A.23)* of three common plant species at Mangalavanam and Vypeen are given in *Appendix.* The relative abundance of various amino acids (or mole %= concentration of individual amino acids in μmoles/ concentration of total amino acids) at Mangalavanam and Vypeen are given in *Table: 4.1. and Table: 4.2* respectively. The relative abundance of individual amino acids in plant leaves at Mangalavanam and Vypeen are given in *Table: 4.3. and Table: 4.4* respectively. As significant concentrations were observed only in the case of

seven amino acids viz Aspartic acid, glutamic acid, serine, threonine, glycine, tyrosine and alanine, the detailed analysis and discussion of the data is restricted to these amino acids only. In the case of Mangalavanam, the core samples representing 25-30 cm depth in the pre monsoon, 10-15 cm and 25-30 cm depths in the monsoon season exhibited abnormal values during analysis and hence these results are not included in the present study.

Season	Depth (cms)	Asp	Glu	Ser	Thr	Gly	Tyr	Ala
Pre monsoon	0-5	1.3521	0.0000	88.296	7.8230	2.0683	0.3023	0.1579
	5-10	1.9891	0.6647	88.677	6.6376	1.7808	0.0000	0.2505
	10-15	0.4890	0.0000	89.658	6.1000	3.6297	0.0000	0.1237
	15-20	0.4609	0.0000	93.793	3.1635	2.4037	0.0000	0.1790
	20-25	0.9487	0.6718	86.106	1.6958	8.2779	2.1902	0.1097
	25-30	1.4334	1.1876	92.581	0.0000	4.0206	0.6321	0.1455
Monsoon	0-5	1.9800	2.1942	89.343	4.0762	1.6023	0.6443	0.1604
	5-10	0.5504	0.3196	90.396	0.0000	6.6074	1.9550	0.1717
	10-15	0.3212	0.3671	62.854	0.0000	11.299	0.0000	0.1568
	15-20	1.6808	1.5724	90.369	2.8485	1.8178	1.1667	0.1708
	20-25	1.4051	1.4243	94.448	1.0319	0.0945	1.4440	0.1519
Post monsoon	0-5	0.9535	1.1072	71.504	2.1099	1.4224	0.9658	0.1039
	5-10	0.8193	0.0000	41.805	0.0000	25.962	19.144	0.1087
	10-15	0.9849	0.8382	86.555	2.6938	3.1615	2.3726	0.1529
	15-20	0.9500	1.1398	92.446	3.6260	1.1008	0.7079	0.0297
	20-25	0.3403	0.2893	90.752	0.0000	8.4489	0.1260	0.0439
	25-30	1.9315	0.0000	44.426	0.0000	52.399	0.9929	0.2501

Table: 4.2. Seasonal distribution of amino acids (mole %) in the sediment core at Vypeen

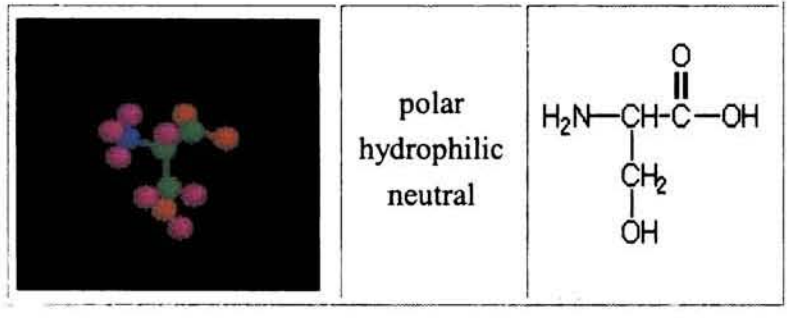
Plant Species	Asp	Glu	Ser	Thr	Gly	Tyr	Ala
Acanthus	1.1180	0.1720	87.645	10.4707	0.1395	0.0443	0.3394
Avicennia	1.8080	0.8790	66.833	9.6687	0.1288	0.3760	0.2545
Rhizophora	2.3750	0.5390	83.475	3.0900	0.0412	0.7071	0.3962

Table: 4.3. Seasonal distribution of amino acids (mole %) in the leaves of three commonly seen plants at Mangalavanam

Plant Species	Asp	Glu	Ser	Thr	Gly	Tyr	Ala
Acanthus	1.5183	0.8499	85.313	10.796	0.1438	0.8578	0.4061
Avicennia	4.4275	-	74.770	9.4253	0.1256	0.8269	0.1935
Rhizophora	1.3863	3.7252	72.213	16.835	0.2243	1.1523	0.3965

Table: 4.4. Seasonal distribution of amino acids (mole %) in the leaves of three commonly seen plants at Vypeen

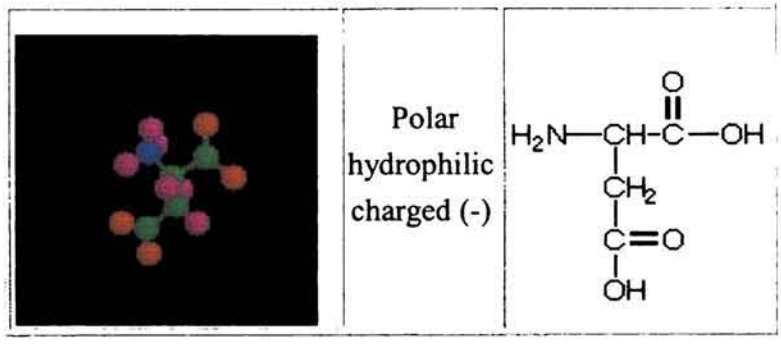
4.1.1. Serine



At Mangalavanam, the relative abundance of serine (mole %) was observed to decrease down the core during pre monsoon and monsoon seasons, but increases down the core during post monsoon season. During pre monsoon season, the highest mole % (94.47) was observed in the surface and the lowest at 20-25 cm depth (68.7); during monsoon the highest (95.5%) was observed at the surface and the lowest (84.04) at 15-20 cm depth and during post monsoon season the highest concentration was observed at 25-30 cm depth (96.7%) and the lowest at the surface 0-5 cm

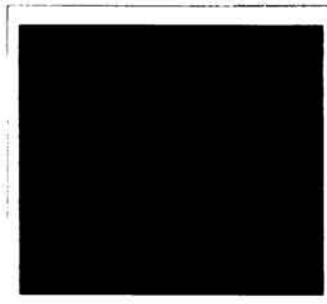
depth (88.85 %) *(Table: 4.1.)*. At Vypeen, in general, the relative abundance of serine was found to increase down the core during all seasons. The mole % was the highest (93.8) at 15-20 cm depth season and the lowest (86.1) at 20-25 cm depth during pre monsoon; the highest (94.5) at 20-25 cm depth season and the lowest (62.8) at 10-15 cm depth during monsoon season and the highest (92.45) at 15-20 cm depth and the lowest (41.8) at the sub surface during post monsoon season *(Table: 4.2.)*.

4.1.2. Aspartic acid

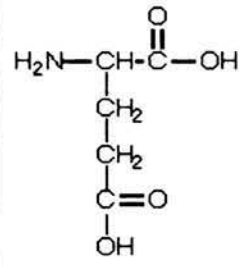


The relative abundance of Aspartic acid at Mangalavanam was found to be the highest (5.56 mole %) and the lowest (0.99 mole %) during pre monsoon season were found to be at the sub surface and 15-20 cm depth respectively. During monsoon season this was found to be 1.74% and 0.34% at the sub surface and surface respectively and during post monsoon season 1.14% and 0.28% at 15-20 cm depth and 25-30 cm of the core respectively. *(Table: 4.1.)*. At Vypeen the relative abundance of Aspartic acid was found to decrease initially and then increase at deeper parts (20-30 cm) of the sediment core. The highest mole % (1.99) and the lowest (0.46) during pre monsoon season were found to be at the sub surface and 15-20 cm depth respectively. During monsoon season this was found to be 1.98% and 0.32% at the surface and 10-15 cm depth and during post monsoon season 1.93% and 0.34% at 25-30 and 20-25 cm of the core respectively *(Table: 4.2.)*.

4.1.3. Glutamic acid

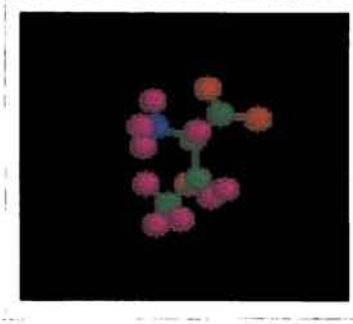


Polar
hydrophilic
charged
(-)

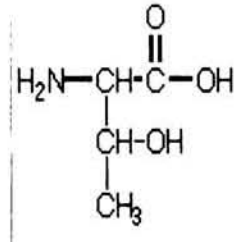


During pre-monsoon, at Mangalavanam, the mole % of Glu was maximum (4.33) at the sub surface and a minimum (0.074) at 10-15 cm depth. During monsoon, Glu was observed only at the surface and sub surface (0.113 and 0.654 respectively). During post-monsoon, a maximum, 0.37 was observed at 10-15 cm and a minimum 0.078 at 20-25 cm depth *(Table: 4.1.)*. The mole % of Glu at Vypeen, during pre-monsoon season, was found to be the maximum at the lowest depth (1.19). It was absent at the surface and between 10-20 cm depth of the sediment core during this season. During monsoon, mole % was maximum (2.19) at the surface and minimum (0.32) at the sub surface. During post-monsoon, the relative abundance was maximum at the surface and minimum at 20-25 cm depth (1.107 and 0.289 respectively). Glu was not detected at the sub surface and at the lowest (25-30 cm) depth of the core *(Table: 4.2.)*.

4.1.4. Threonine

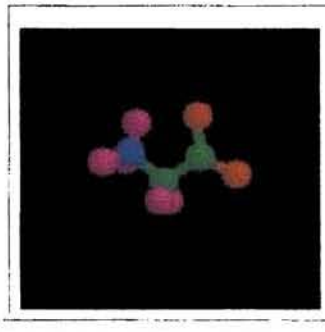


Polar
hydrophilic
neutral

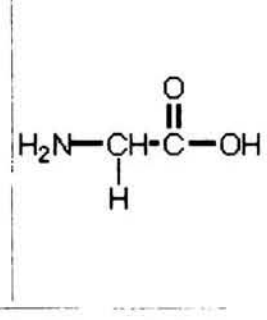


The mole % of Thr was observed the highest at 20-25 cm of the core (29.29%) and the lowest at the surface (2.98%) at Mangalavanam during pre monsoon season. During monsoon season it was absent below 10 cm of the sediment core. Sub surface exhibited higher mole % (2.29) than the surface (0.499). During post monsoon season, the highest mole % was observed at 10-15 cm depth (2.95) and the lowest (1.1) at 20-25 cm depth of the core *(Table: 4.1.)*. The relative abundance of threonine at the surface during all the seasons was found to be almost constant. At Vypeen, during pre monsoon season, the relative abundance of threonine was maximum at the surface (7.8 mole %) and the minimum at the lowest depth (1.69%). During monsoon, Thr was absent between 5-15 cm of the core. A maximum was observed at the surface and the minimum at the lowest depth of the core (4.08 and 1.03 mole % respectively). During post monsoon season, Thr was abundant maximum at 15-20 cm depth (3.63%) and minimum at the surface (2.7%) *(Table: 4.2.)*. Thr was not detected below 20 cm depth of the core during this season.

4.1.5. Glycine



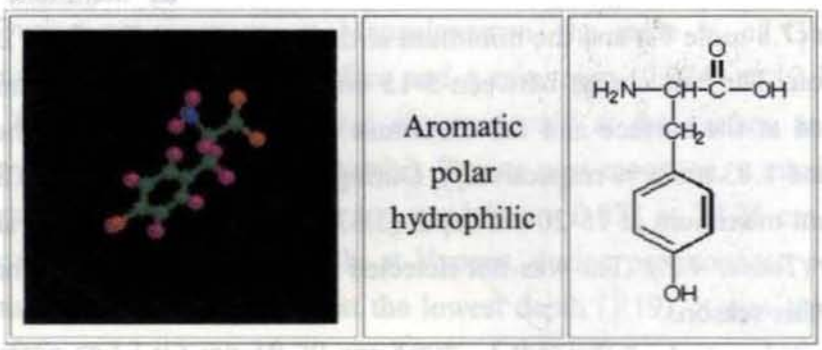
Aliphatic neutral



At Mangalavanam, during pre-monsoon season, the relative abundance of Gly was found to be the highest at the sub surface and the lowest at 0-5 cm and 20-25 cm depths of the core, where a mole % of 1.17 and 0.176 were found. During monsoon glycine was most abundant at 15-20 cm depth (14.32 mole %) and the least 0.088% at the surface. The mole % of glycine during post monsoon season was observed maximum at the surface (7.6%) and minimum at 20-25 cm depth (4.187%) *(Table: 4.1.)*. At

Vypeen, the mole % was found to be maximum at 20-25 cm depth (8.28) and minimum at the sub surface (1.78) during pre monsoon season. During monsoon, the maximum was observed at 10-15 cm depth (11.3 %) and minimum at the lowest depth of 20-25 cm (0.094%). During post monsoon season, 25-30 cm showed the maximum abundance, where a mole% of 52.4% was observed and minimum at 15-20 cm depth, where a mole% of 1.1% was observed *(Table: 4.2.)*.

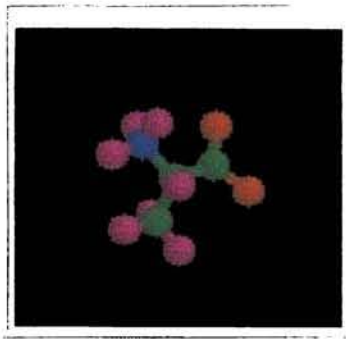
4.1.6. Tyrosine



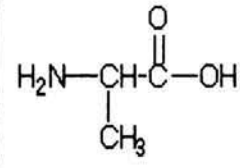
At Mangalavanam, the relative abundance of Tyr was very less at all depths and absent at the surface and sub surface depths. The maximum mole% during pre monsoon season was observed at 10-15 cm depth (0.58%) and minimum at the lowest part of the sediment core (0.025% at 20-25 cm depth). During monsoon, the highest mole% (2.68) was seen at the surface and the lowest (0.285) at the sub surface. During post monsoon, the highest mole% (0.648) was observed at the top 0-5 cm depth and the lowest at the bottom 25-30 cm depth of the core (0.33%) *(Table: 4.1.)*. The mole % of Tyr at Vypeen was very low during pre monsoon period *(Table: 4.2.)*. At 20-25 cm a maximum abundance was observed (2.19 mole %) and minimum abundance was observed at the surface (0.3 mole %). During monsoon season, there was a slight increase in the relative abundance of tyrosine and the highest mole% was detected at the sub surface (1.96 mole %) and the lowest at the surface (0.64 mole %). During post monsoon, tyrosine was

observed at all depths. The highest mole% was observed at the sub surface (19.14 mole %) and the lowest at 20-25 cm depth (0.126 mole %).

4.1.7. Alanine



Aliphatic
hydrophobic
neutral



At Mangalavanam, during pre monsoon season, the maximum mole % was observed at the sub surface (1.16%) and minimum at 15-25 cm depth (0.08 mole %). Alanine was below detectable levels at almost all depths during monsoon season. Only sub surface layer (5-10 cm depth) showed a mole% of 0.24 during this season. During post monsoon season maximum mole% was present at the surface (1.17 mole %) and minimum at 20-30 cm depth (0.079 mole %) *(Table: 4.1.)*. At Vypeen, the relative abundance of alanine during pre monsoon season was the maximum of at the sub surface (0.25 mole %) and minimum 0.110 mole% at 20-25 cm depth. During monsoon, a maximum 0.172 mole % was observed at 10-15 cm depth and minimum 0.152 mole % at 20-25 cm depth. During post monsoon season, Alanine was abundant maximum (0.250 mole %) at the lowest 25-30 cm depth and minimum 0.03 mole % at 20-25 cm depth *(Table: 4.2.)*.

The concentrations of various amino acids in leaves are given in the Table: 4.3 and Table: 4.4. Tryptophan, which was observed in certain depths in the sediment, was totally absent in leaves at both study sites. The graphs obtained for various sediment and leaves samples at both stations by HPLC analysis are given below.

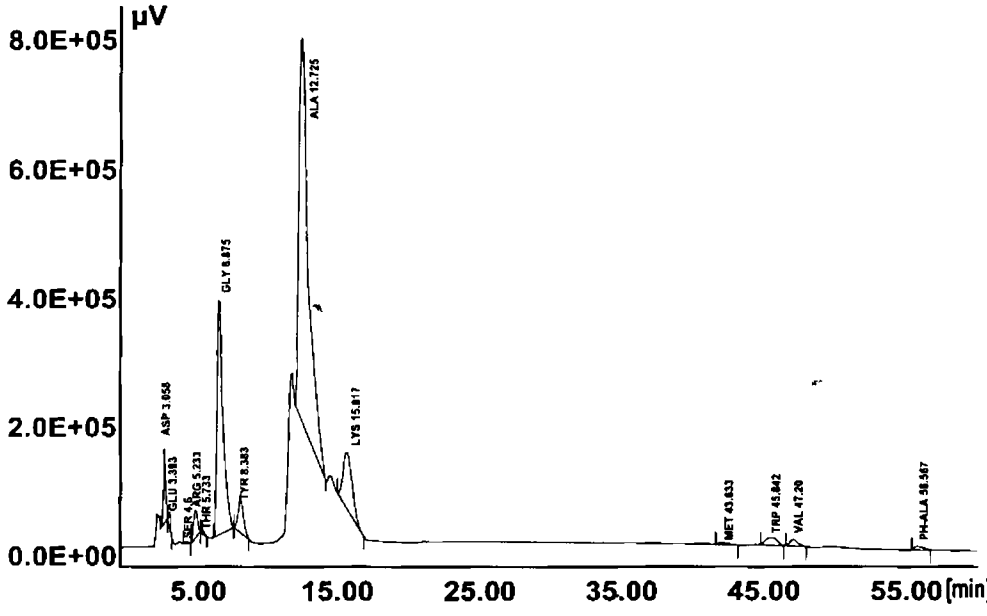


Fig: 4.1. Peaks obtained for Amino acids standards

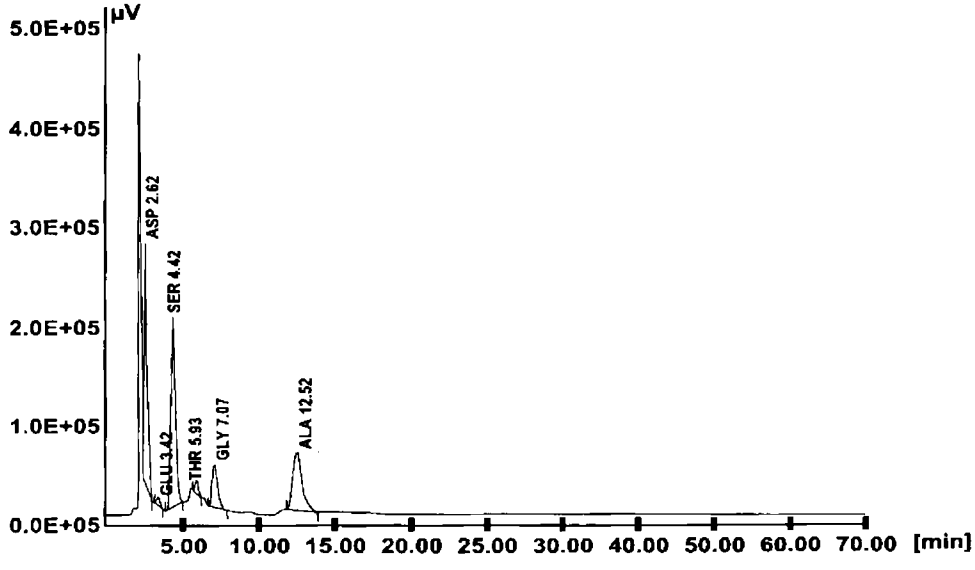


Fig: 4.2. Peaks of Amino acids obtained for the sediment (0-5 cm depth) at Mangalavanam during premonsoon season

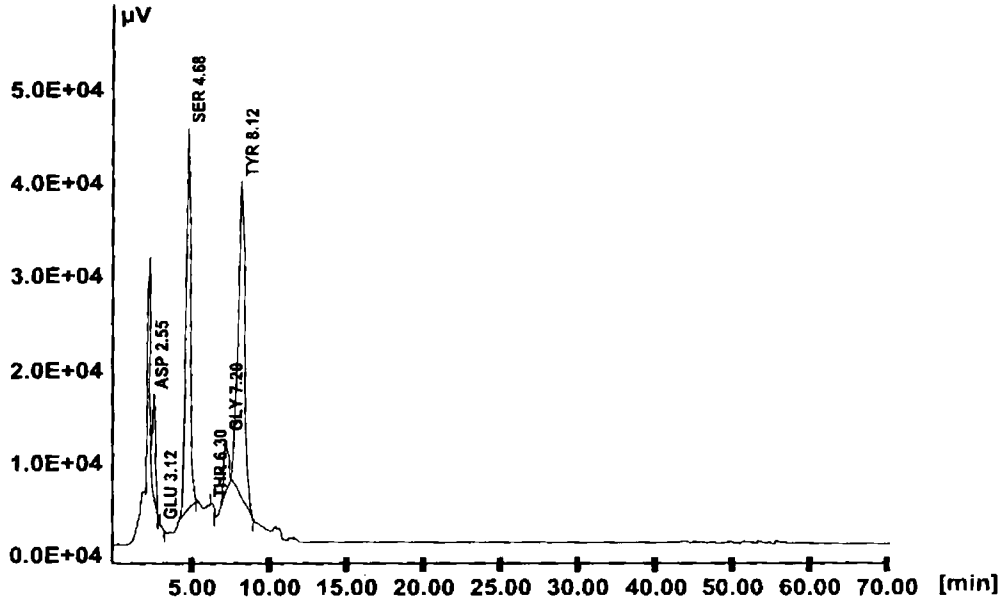


Fig: 4.3. Peaks of Amino acids obtained for the sediment (0-5 cm depth) at Mangalavanam during monsoon season

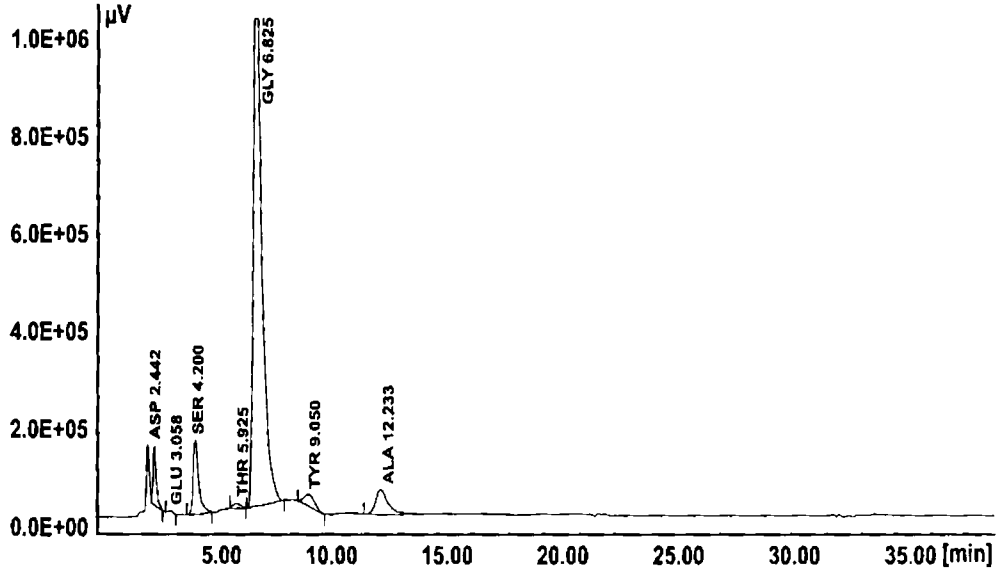


Fig: 4.4. Peaks of Amino acids obtained for the sediment (0-5 cm depth) at Mangalavanam during post monsoon season

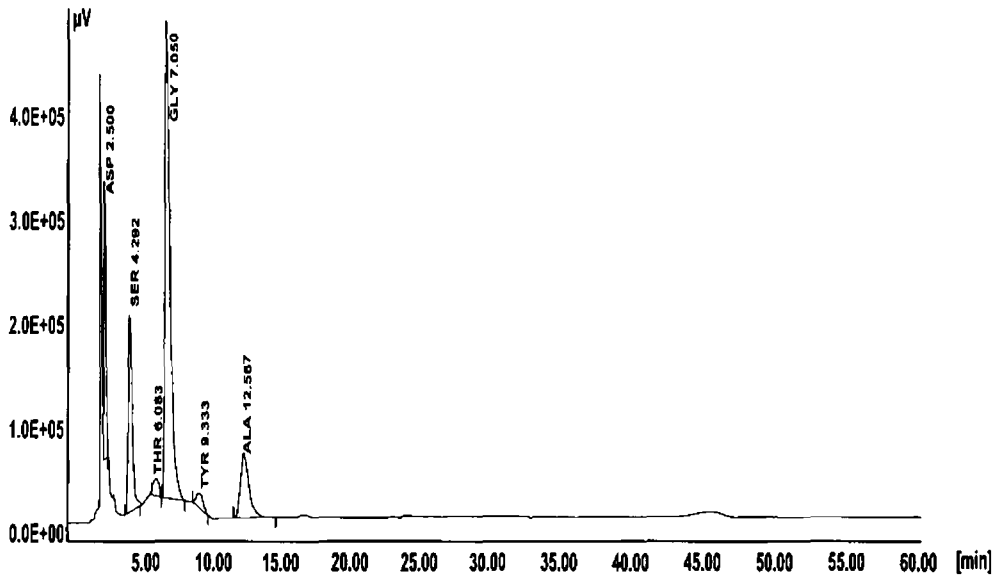


Fig: 4.5. Peaks of Amino acids obtained for the sediment (0-5 cm depth) at Vypeen during premonsoon season

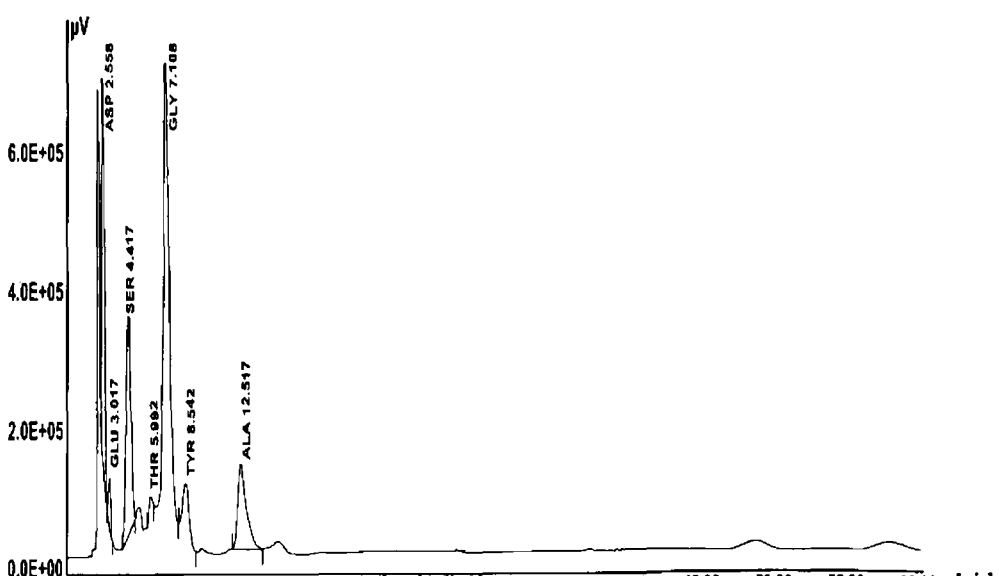


Fig: 4.6. Peaks of Amino acids obtained for the sediment (0-5 cm depth) at Vypeen

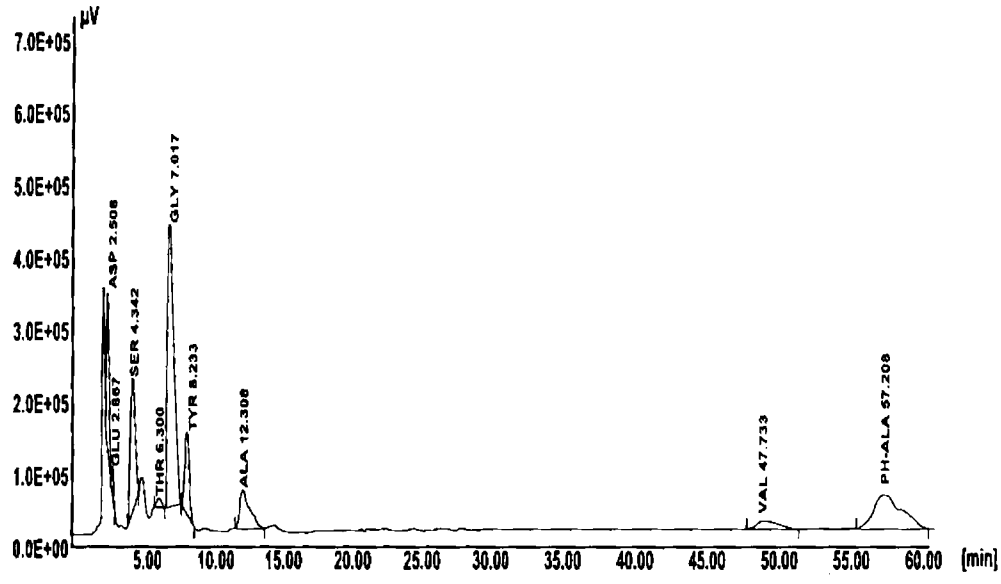


Fig: 4.7. Peaks of Amino acids obtained for the sediment (0-5 cm depth) at Vypeen during post monsoon season

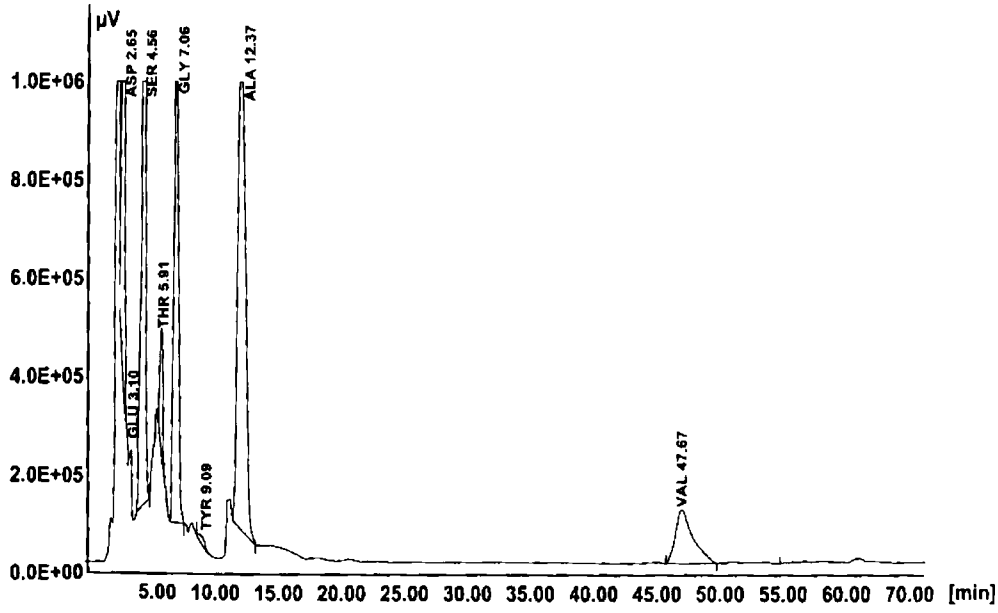


Fig: 4.8. Peaks of Amino acids obtained for the Acanthus plant species at Mangalavanam

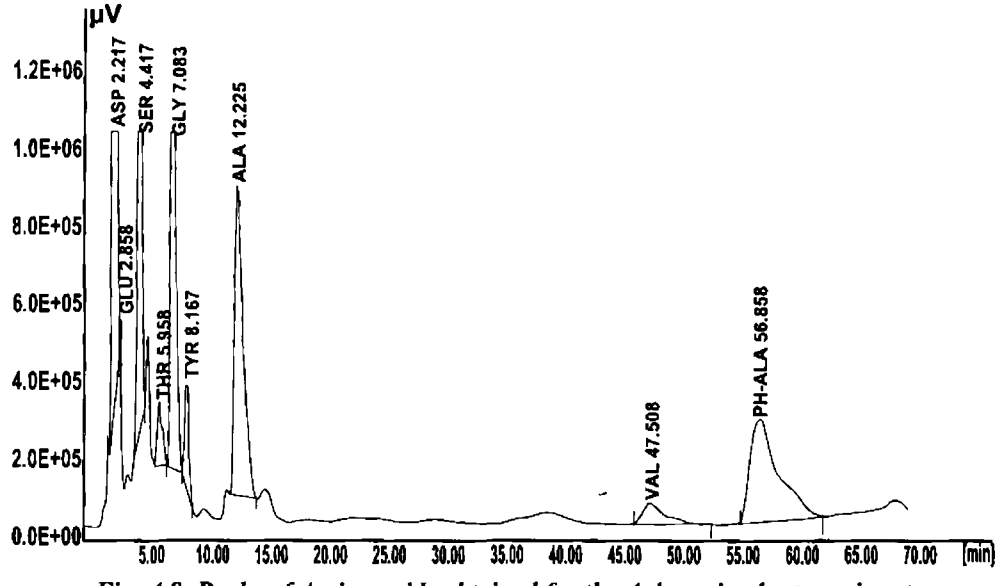


Fig: 4.9. Peaks of Amino acids obtained for the Avicennia plant species at Mangalavanam

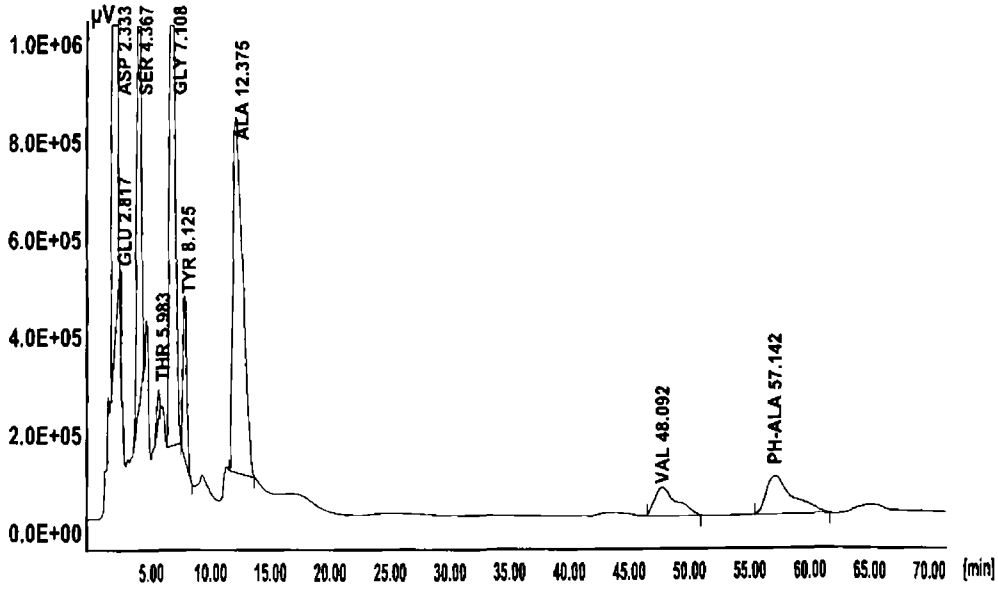


Fig: 4.10. Peaks of Amino acids obtained for the Rhizophora plant species at Mangalavanam

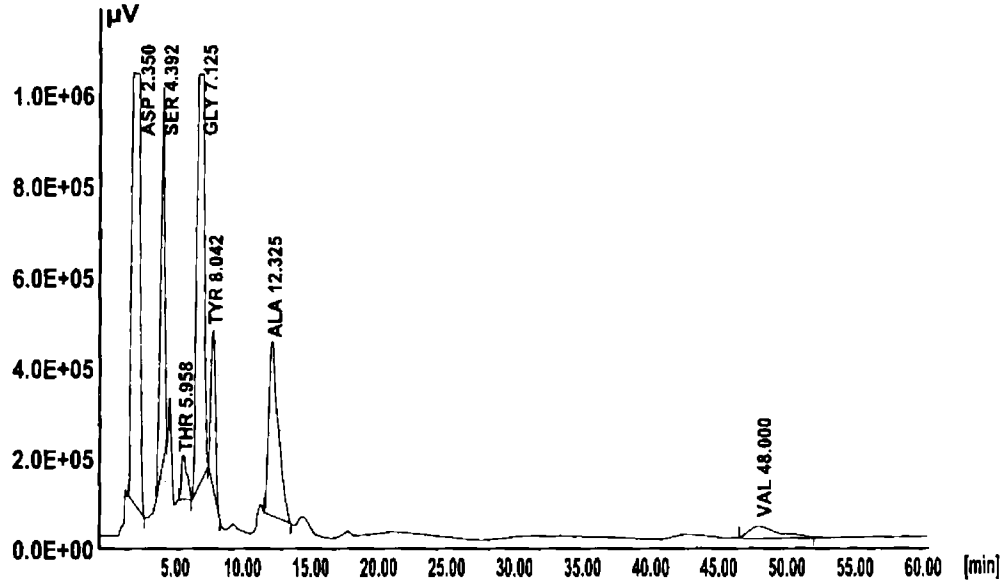


Fig: 4.11. Peaks of Amino acids obtained for the Acanthus plant species at Vypeen

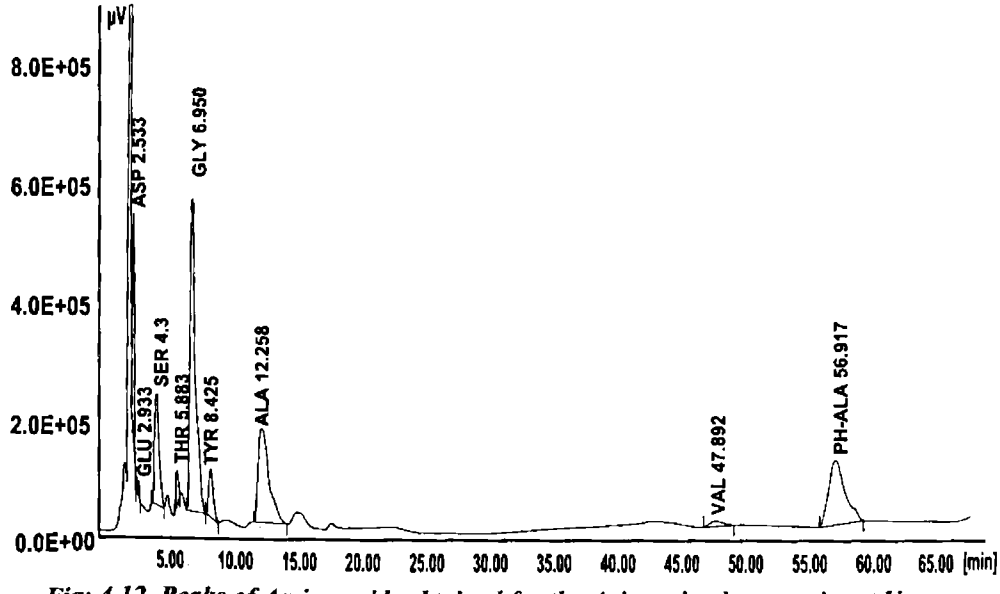


Fig: 4.12. Peaks of Amino acids obtained for the Avicennia plant species at Vypeen

4.2. Discussion

Contributors of amino acids to the mangrove systems are leaves, land run-off and in situ production. In the systems of concern, i.e., Mangalavanam and Vypeen, the land addition is generally restricted to monsoon. Comparison of C/N in chapter 3 has shown that the organic matter in these two stations is more or less mangrove plant origin. The trend of relative abundance of amino acids in the sediment and leaves exhibits close similarity *(Tables: 4.1, 4.2, 4.3 and 4.4)* indicating a major influence of plants in the supply of these compounds to the sediment.

Water is vital for all life and provides a ready source of the hydrogen needed for aerobic photosynthesis. Probably the low water depth has a limiting behaviour on the primary producers. Oxygen is also a limiting factor of primary production. Oxygen is taken up for the decomposition of organic matter present in the system. If there is high organic load oxygen will be depleted from the system giving rise to anoxic conditions, which have a negative effect on the growth of phytoplankton.

Of the twenty-two naturally occurring amino acids, which are reported to have significant concentration in the aquatic system, only ten could give a detectable concentration in these sediments. Serine, threonine, aspartic acid, glutamic acid, glycine, alanine, tyrosine, phenyl alanine, valine and tryptophan were the different amino acids detected. In the case of leaves all the amino acids except tryptophan were detected. The relative abundance of the amino acids in the surface sediments and plants are in the same tune. Of the nine amino acids observed in the plants only six contributed to the major amino acid share, the others being of very low concentration. So is the case with sediments also. The major discussion is also limited to the variation in these seven amino acids namely serine, threonine, aspartic acid, glutamic acid, glycine, alanine and tyrosine.

Of the ten amino acids, which were quantified upon acid hydrolysis, the dominant ones were serine, threonine, aspartic acid, glutamic acid, tyrosine, glycine and Alanine. Several workers reported similar results earlier *(Table: 4.5)*. Tryptophan has been largely ignored by almost all previous studies because acid hydrolysis has been commonly used and tryptophan is destroyed during this process due to its indole side chain. The contributions of tryptophan in the samples were very less (< 1 mole%) and present only at some depths at both stations.

Amino acids like serine, threonine, glycine (Muller *et al.*, 1986) and tryptophan (Wu and Tanoue, 2002) in sediments are enriched in the cell wall protein of the diatoms and hence considered to be selectively preserved by the protein-silica complex of diatom cell walls. The vertical changes in the amino acid mole% appear to change slightly with depth and this may be attributed to the difference in the reactivity of individual amino acids (Cowie and Hedges, 1992), depending on their nitrogen content, chain length and functional groups (Dauwe and Midddleburg, 1998).

The amino acids at Mangalavanam and Vypeen, even though didn't differ much in their composition, differed in their relative abundance at both stations. The different amino acids detected in Mangalavanam and Vypeen sediments were serine, aspartic acid, glutamic acid, glycine, threonine, alanine, tyrosine, valine, phenyl alanine and tryptophan. Almost all the amino acids detected were found to be higher at Vypeen than that at Mangalavanam.

Of the ten amino acids detected, serine was the most abundant amino acid, followed by threonine, glycine, aspartic acid, tyrosine, glutamic acid and alanine. Serine, threonine, glycine, valine and alanine were aliphatic neutral amino acids, whereas, aspartic acid and glutamic acid were aliphatic acidic amino acids. Tyrosine, Tryptophan and Phenyl alanine are aromatic neutral amino acids. The relative abundance of Asp was more than that of glutamic acid at both stations. The relative abundance of aromatic amino

acid, tyrosine was found to be the highest among all aromatic amino acids and it was almost same at both stations.

Acidic amino acids were found to be more than the basic ones. Of the two acidic amino acids, Asp and Glu, aspartic acid was found to be relatively more abundant than glutamic acid. Basic amino acids were not detected in the samples. In the surface, the neutral amino acids glycine and alanine together contributed ~ 2 mole % at both stations and acidic amino acids (Asp+ Glu) contributed ~1 mole% at Managalavanam and ~2 mole% at Vypeen.

The hydroxylic amino acids (Ser+ Thr) contributed the maximum mole% and aromatic amino acids Tyr, Phenyl alanine and Tryptophan together contributed ~1 mole % to the total amino acids. Of these the hydroxyl amino acids contributed the major share of the total amino acids.

Amino acids are generally transported through the water column by large, rapidly sinking aggregates. During this transport nitrogen-rich compounds like amino acids are degraded faster than nitrogen-poor compounds like lipids. Therefore the contribution of amino acids to bulk organic matter decreases with ageing of the organic matter and hence with increasing water depth in the water column (Grutters *et al.*, 2001). Changes occur in the distribution of individual amino acids due to the differences in nutritional value, adsorption capacity, resistance against degradation etc.

The labile amino acids undergo decomposition easily, whereas refractory ones, which remain in the system, are assumed to be either non-reactive or degraded at rates, which are significantly slower than those at which labile amino acids are remineralised. The changes in total amino acid concentrations with depth are assumed to be the result of utilization of labile amino acids in microbially mediated reactions such as fermentation, sulphate reduction and methanogenesis (Burdige and Martens, 1988). Thus amino acids can be used to assess the diagenetic state of organic matter in the

sediments. The concentration of individual amino acids varies due to their selective microbial utilization in the sediments (Burdige and Martens, 1988).

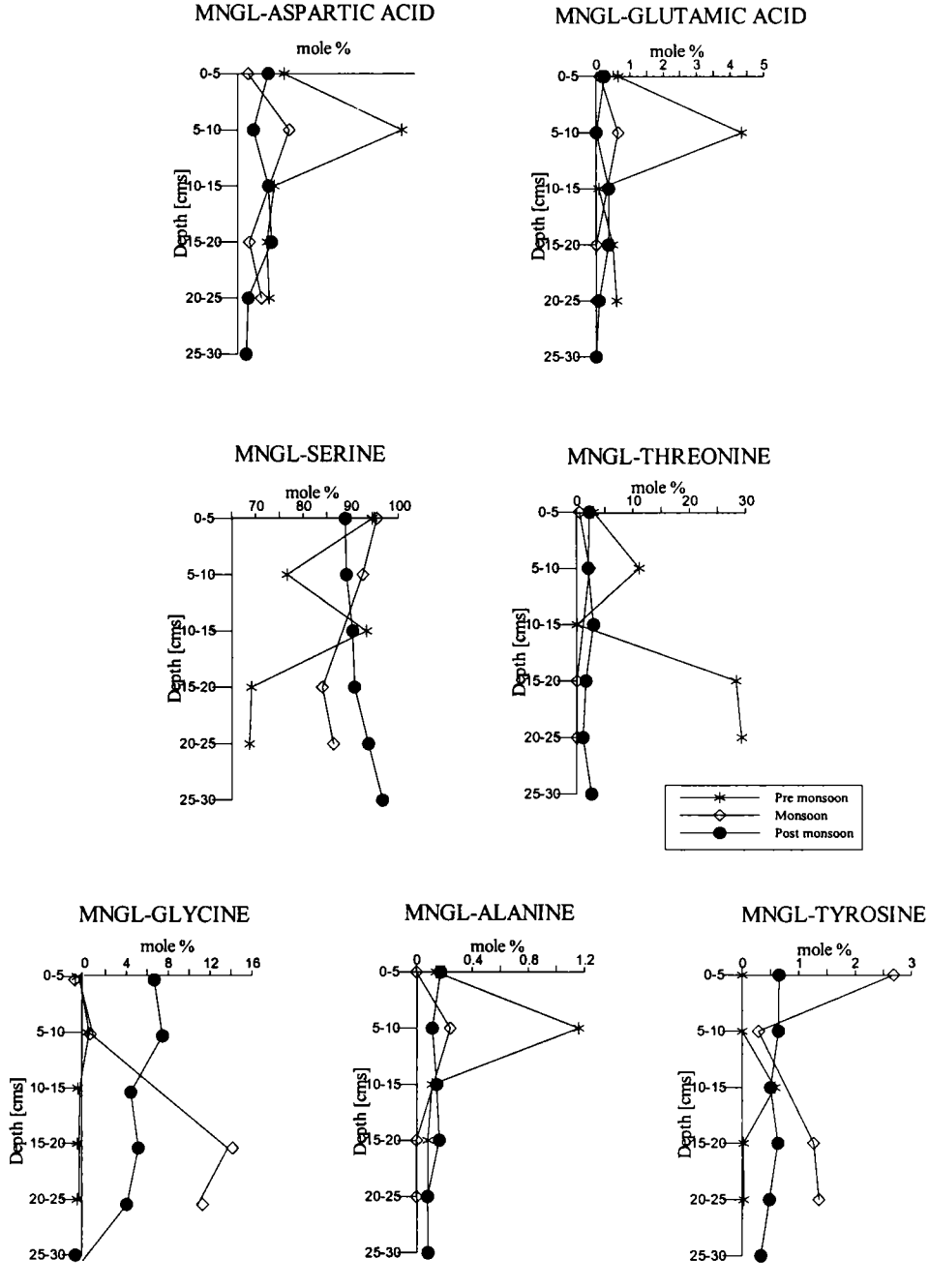


Fig: 4.13. Distribution of amino acids (mole %) in the sediment core at Mangalavanam

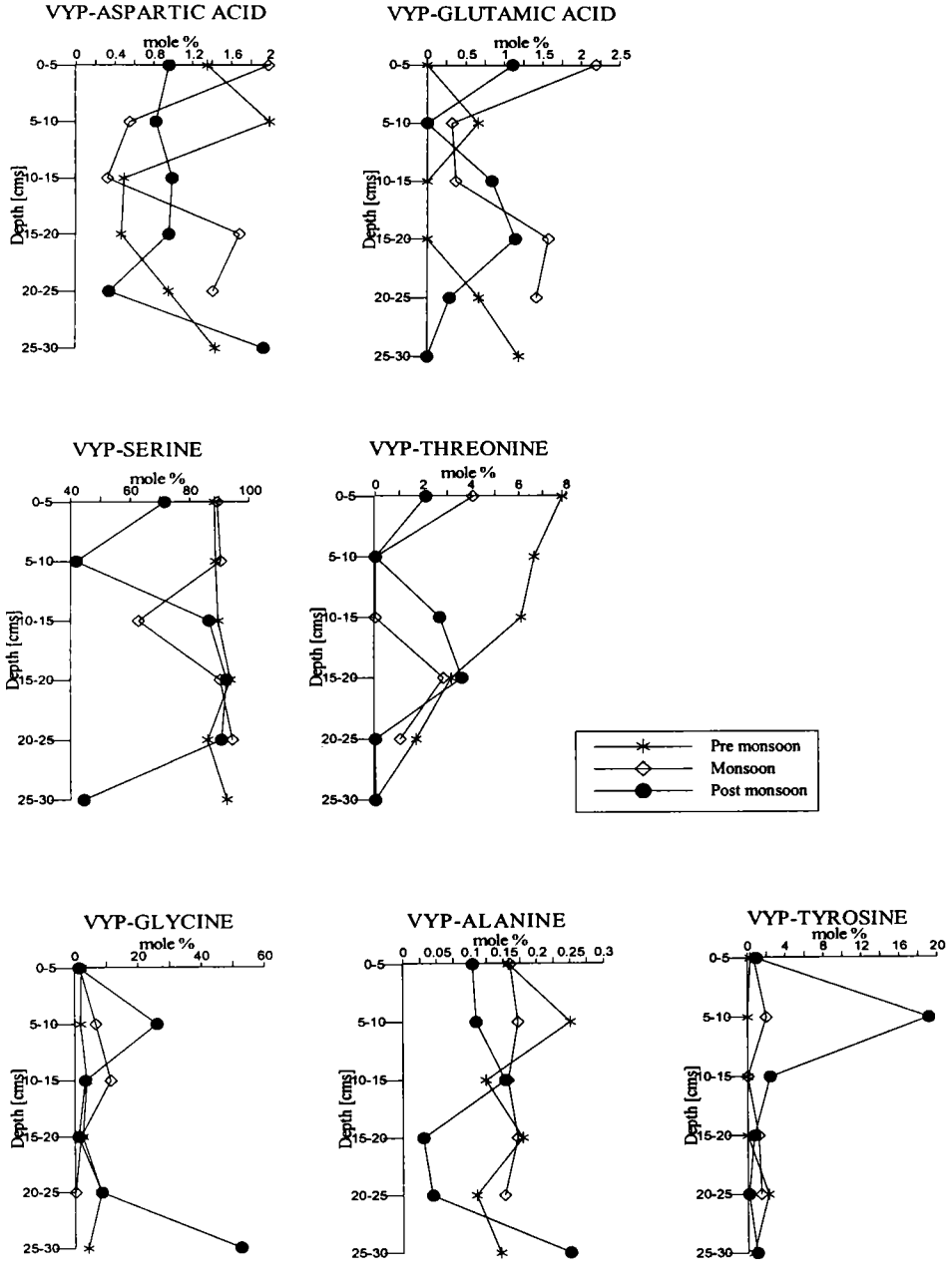


Fig: 4.14. Distribution of amino acids (mole %) in the sediment core at Vypeen

The changes in relative abundance or mole% [percentage of (concentration of individual amino acid/ total amino acids)] of various

amino acids at Mangalavanam and Vypeen are given in *Fig. 4.13 and 4.14* respectively. The values of these ratios at different depths indicate significant variability indicative of the biogeochemical activity. Significant seasonal variability is also observed between the surface ratios and ratios at different depths. Glycine and threonine associated with the diatoms were found more during premonsoon and post monsoon season, due to their high contribution to primary productivity, relatively high sinking rates and stability (Burdige and Martens, 1988). Glutamic acid and tyrosine are cell plasma compounds and they are considered relatively more labile than other amino acids. These two together with aspartic acid are expected to decrease down the sediment core *(Fig.4.13 and 4.14).*

The behavior of amino acid concentrations at the two stations is different. At Mangalavanam, which is a closed system, during pre monsoon season there is very little chance for the organic matter to get flushed away from the system. This suggests a very long residence time for mangrove detritus in anaerobic sediments. Sometimes due to less tidal inundation the sediment surface gets direct contact with atmospheric air leading to aerobic degradation of the organic matter along with the usual anaerobic decomposition. Tidal influence will be comparatively less during post monsoon season. But during monsoon, fresh water abundance in the system due to rainfall and high tidal inflow enable the flushing of the organic matter from the system. Due to this, a reproducibility of the values of amino acid concentrations may not be expected at Mangalavanam. At Vypeen human intervention and aquatic life are more than that at Mangalavanam due to the semi open nature of the system and hence the reactivity here is governed by these factors. During all the seasons tidal flushing will be there at Vypeen since it is lying close to the sea and estuary. More reproducible results, therefore, can be expected here.

Marine sediments contain amino acids such as aspartic acid, glutamic acid, serine, threonine, glycine, alanine, valine, lysine, phenyl alanine, tyrosine, arginine, histidine etc. The most commonly occurring amino acids

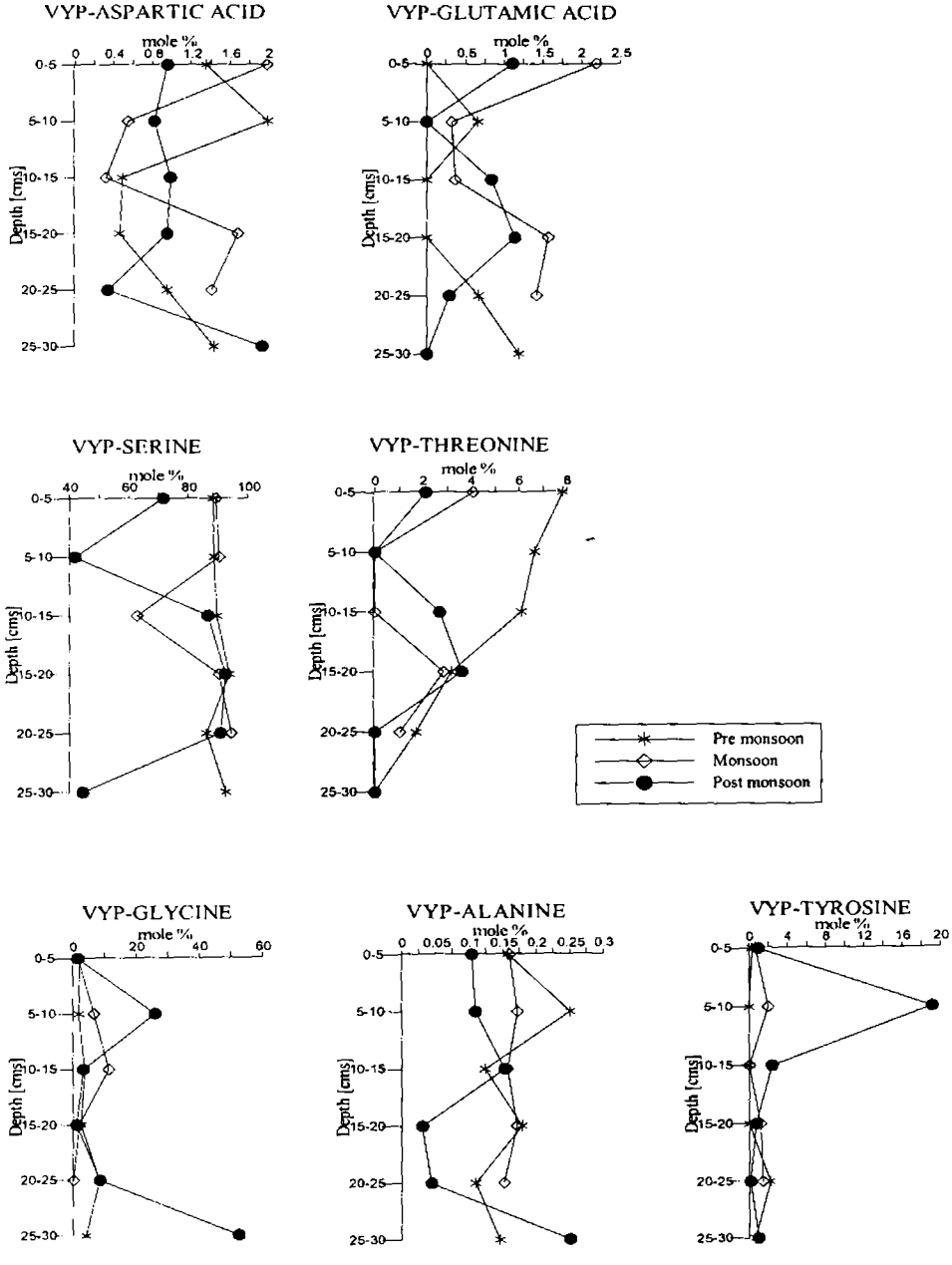


Fig: 4.14. Distribution of amino acids (mole %) in the sediment core at Vypeen

The changes in relative abundance or mole% [percentage of (concentration of individual amino acid/ total amino acid)]

amino acids at Mangalavanam and Vypeen are given in *Fig. 4.13 and 4.14* respectively. The values of these ratios at different depths indicate significant variability indicative of the biogeochemical activity. Significant seasonal variability is also observed between the surface ratios and ratios at different depths. Glycine and threonine associated with the diatoms were found more during premonsoon and post monsoon season, due to their high contribution to primary productivity, relatively high sinking rates and stability (Burdige and Martens, 1988). Glutamic acid and tyrosine are cell plasma compounds and they are considered relatively more labile than other amino acids. These two together with aspartic acid are expected to decrease down the sediment core *(Fig.4.13 and 4.14).*

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Marine sediments contain amino acids such as aspartic acid, glutamic acid, serine, threonine, glycine, alanine, valine, lysine, phenyl alanine,

are aspartic acid and glutamic acid. These two amino acids are eluted first during HPLC analysis and exhibit the highest reproducibility (Kaufman and Manley, 1998). Aspartic acid was found to be abundant in sediments receiving large organic inputs in early studies (Pelet and Debyser, 1977). Glutamic acid was found to be abundant in phytoplankton and marine bacteria (Henrichs and Farrington, 1979). In the present study aspartic acid is more abundant than glutamic acid in almost all depths at both stations *(Table: 4.1 and 4.2).*

Serine, threonine (hydroxy amino acids) and glycine, which constitute the diatom cell walls, were the most abundant amino acids at Mangalavanam and Vypeen (*Table: 4.1 and Table: 4.2* respectively). In several previous studies their concentrations have been found to be higher in reducing sedimentary environments (Gonzalez *et al.*, 1983). These amino acids are found resistant to environmental degradation also (Siezen and Magne, 1978). Hydroxy amino acids were found to be stabilized by their reaction with phenolic compounds giving rise to humic materials (Degens, 1970). The ratio of tyrosine to phenyl alanine (aromatic amino acids) is indicative of their source in the system. This ratio is ~ 0.3 for mangroves, ~1 for sea grasses, ~ 0.6 for brown algae and >1 for macro algae. Jennerjahn and Ittekkot (1997) in their study observed high concentrations of these amino acids in mangrove sediments in Brazilian continental margin.

In general essential amino acids like arginine, methionine and histidine occur only in traces in marine sediments (Dauwe and Middelburg, 1998). Basic amino acids, especially lysine, are more common in offshore sediments due to the more stability in such depositional environments (Degens, 1970). Basic amino acids, aromatic amino acids containing sulphur are labile and are easily lost in sediments during geochemical degradation of sedimentary organic matter. The basic amino acid ornithine exists in sediments where decomposition from plankton material predominates and is formed mainly from the decomposition of arginine. Valine is another geochemically less stable amino acid. Sulphur containing amino acids [illegible]

cystein and methionine are almost absent in marine sediments and even if present, they tend to diasappear during the geochemical degradation of organic matter (Gonzalez *et al.*, 1983).

No.	Area	Order of abundance	Authors
1.	Anoxic and highly reducing sediments, Cape Lookout Bight.	Gly > Asp > Ala > Glu	Burdige and Martens, 1988.
2.	Sediments from Paraiba do Sul mangroves, Brazilian continental margin.	Gly > Glu > Asp > Ala > Thr	Jennerjahn and Ittekkot, 1997.
4.	Surface sediments of an intertidal mudflat, Lowescove, central coastal Maine.	Glu > Ala > Asp > Gly	Mayer *et al.*, 1995
5.	Sediment cores (15 cm depth) from Itacuruca mangrove forests, southeastern Brazil.	Gly > Asp > Glu > Ala > Ser in Rhizophora soils. Asp > Glu > Gly> Val> Thr in avicennia soils.	Lacerda *et al.*, 1995
6.	Sediments from the slope of Brazilian Continental Margin.	Gly > Asp > Glu > Ala	Jennerjahn and Ittekkot, 1999.
11.	Sediment, Equatorial Pacific Ocean.	Asp > Gly > Ala > Glu	Lee *et al.*, 2000
13.	Rhizophora and Avicennia leaves from Paraiba do Sul mangroves, Brazilian Continental Margin.	Glu > Asp > Gly > Leu > Ala in Rhizophora *sp.* Glu > Gly > Asp> Ala in Avicennia *sp.*	Jennerjahn and Ittekkot, 1997.
15.	Sediment cores, Peru	Gly > Asp > Ala > Ser > Glu	Henrichs *et al.*, 1984.

16.	Sediments, Ebro Delta, Spain	Gly > Thr > Glu > Phe > Val	Gonzalez *et al.*, 1983.
17.	Intracellular free amino acids in the leaves and roots of Avicennia in the mangroves of Hinchinbrook island, Queensland, Australia.	Asp, Ser, Ala > Glu, Thr, Asn	Stanley *et al.*, 1987
18.	Surface sediments, Goban Spur continental slope, Northeastern Atlantic.	Gly > Asp > Ala > Glu	Grutters *et al.*, 2001
19.	Estuarine sediment, Pearl River, China.	Gly > Ala > Asp > Glu	Chen *et al.*, 2004
20.	Sediment, Northwest European Continental Margin.	Gly (0.149 mg/g) > Asp (0.139 mg/g) > Ala (0.114 mg/g) > Thr (0.114 mg/g) in Goban Spur area. Asp (.039 mg/g) > Gly (0.035 mg/g) > Glu (.031 mg/g) > Ser (0.029 mg/g) > Ala (0.028 mg/g) in Meriadzek Terrace area.	Boski *et al.*, 1998
21.	Present study a) Mangalavanam mangrove sediments b) Vypeen mangrove sediments	Ser> Thr> Asp> Glu Ser> Thr> Asp> Glu	

Table: 4. 5. Sedimentary Amino acids reported in earlier studies.

4.3. Correlation Analysis

In order to evaluate quantitative similarities and differences in the dynamics of the individual amino acids, a correlation matrix of amino acids was calculated using the data of relative abundance of each amino acid. At Mangalavanam, in all depths aspartic acid, glutamic acid and Alanine showed significant positive correlation to one another (R= 0.971-0.978; $p< 0.001$; n=15) (Table: 4.6) implying that these group of amino acids was subject as a whole to similar mechanisms of biogeochemical alteration in the system. Serine and threonine showed strong negative correlation (R= 0.888; $p< 0.001$; n=15) suggesting their different diagenetic behavior.

At Vypeen significant positive correlation was observed between Aspartic acid and Alanine (R= 0.560, $p< 0.01$, n=17) and between Aspartic acid and glutamic acid (R= 0.513, $p< 0.01$, n=17) (Table: 4.7) suggesting similar diagenetic behaviour in between them, whereas, a negative correlation is observed between glycine and serine (R= 0.835; $p< 0.001$; n=17) and between tyrosine and serine (R= 0.607; $p< 0.01$, n=17), which are indicative of their different diagenetic behaviour.

At Mangalavanam, Thr alone showed significant positive correlation with TAA (0.603, n=15, $p< 0.01$), but at Vypeen Asp, Glu, Ser and Thr showed significant positive correlation (0.549, 0.668, 0.508, 0.524, n=17, $p< 0.01$) and Gly showed significant negative correlation (-0.593, n=17, $p< 0.01$) with TAA.

Sediment characteristics of both Mangalavanam and Vypeen mangroves cannot be compared with other reported observations like that in seawater, estuaries etc. Deep sediments in fact show seasonal variations. Such variations were reported in restricted water bodies also. And so the considerations that we arrive at in these sediments can never been equal to those reported earlier. So specifically written because even the preliminary analysis of the reactivity of sediments by other workers (Nunn and Keil, 2004) earmarks the first few centimeters of the sediment as reactive zones

and rest almost stable or inert. But in the case of estuaries and restricted aquatic systems like mangroves, salt marshes etc it has been shown that sediment is reactive even upto 30 cm depth (Marchand et al., 2003; Gonneea et al., 2004).

MNGL	ASP	GLU	SER	THR	GLY	TYR	ALA	TAA
ASP	1.000							
GLU	0.977**	1.000						
SER	-0.328	-0.402	1.000					
THR	0.196	0.268	-0.879**	1.000				
GLY	-0.263	-0.273	-0.009	-0.405	1.000			
TYR	-0.403	-0.365	0.347	-0.468*	0.332	1.000		
ALA	0.971**	0.978**	-0.277	0.136	-0.234	-0.382	1.000	
TAA	-0.184	-0.202	-0.338	0.603*	-0.396	-0.498	-0.295	1.000

**Correlation is significant at the 0.01 level.

* Correlation is significant at the 0.05 level.

Table: 4.6. Pearson Correlation matrix of individual amino acids in terms of relative abundance (mole %) and TAA in the sediment core at Mangalavanam (n=15).

MNGL	ASP	GLU	SER	THR	GLY	TYR	ALA	TAA
ASP	1.000							
GLU	0.507*	1.000						
SER	-0.197	0.430*	1.000					
THR	0.261	0.008	0.350	1.000				
GLY	0.128	-0.463*	-0.943**	-0.474*	1.000			
TYR	-0.074	-0.230	-0.643**	-0.301	0.403	1.000		
ALA	0.474*	-0.105	-0.275	0.082	0.325	-0.142	1.000	
TAA	0.549*	0.668*	0.508*	0.524*	-0.593*	-0.333	0.017	1.000

**Correlation is significant at the 0.01 level.

* Correlation is significant at the 0.05 level.

Table: 4.7. Pearson Correlation matrix of individual amino acids in terms of relative abundance (mole %) and TAA in the sediment core at Vypeen (n=17).

The distribution character of amino acids, which is available in the sediment both as free and bound to protein exhibited significant variability between depths. The contributors to the concentration of the amino acids in such typical systems are the 1) the microbial decomposition or diagenic transformations of the organic matter, 2) external input (allochthonous) including those from higher plants present in the system itself, 3) adsorption of the individual amino acids to the sediment particles, 4) the influence of the tidal activity including contributions from and to seawater and 5) the uptake and release by the biological activity of the higher organisms.

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Chapter 5

STATISTICAL ANALYSIS

5.1. System Characteristics

5.2. Approach

5.3. Principal Component Analysis

5.4. General Characteristics

5.5. Amino acid Characteristics

5.6. Summary

The high productivity of mangroves and their role as a nursery for a number of fishes are well recognized and mangroves are considered to be one of the major sources of organic matter and biomass of the adjacent water bodies. The evaluation of the contribution can be attempted in many ways. The assessment and classification of organic matter and the mass balance studies to estimate the flow character of water as well as organic matter and nutrients, evaluation of the assessment of the primary productivity and fertility of the system, identification of the contribution towards the promotion of fisheries etc are some of the yardsticks used for characterizing the contributions. It is well agreed that there is a net flow of organic matter to the adjacent water bodies (Woodroffe, 1992; Jennerjahn and Ittekkot, 2002). The geochemical character of the system has also been explored considerably to identify the exact contribution.

Though the attempts in the earlier works were to identify the reactivity of the system, the models opted were not able to provide details of the relation between the different contributing factors. Therefore only the bulk character was proposed there. This study is mainly concentrating on the micro scale analysis to distinguish the role of each of the contributing processes and also the net effect of the different processes on the micro components. The parameter considered was protein and the micro components, amino acids. The observations presented in earlier chapters were subjected to detailed statistical analysis with an intention to identify the character of each of the components in the system. Principal component analysis (PCA) is the statistical tool used here.

The systems studied in this investigation have been subjected to macro and microanalysis for the evaluation of characteristics by many other investigators (Geetha, 2002; Rini, 2002). The mass balance studies

conducted on the particulate organic matter and the geochemistry of the sediment (Geetha, 2002) have indicated that,

1. There is significant contribution of organic matter to the system in the form of lateral addition, which includes the detritus from the mangrove plants and the land run-off.
2. The input from the adjacent water mass contributes only very low percentage of the total particulate organic carbon (POC) reaching the system.
3. A high outflow from the system to the adjacent water mass.
4. The geochemical character of the sediment showed that there is a very high reactivity at the surface 0-5 cm of the sediment. The sediment at depth > 5 cm indicated more or less uniform reactivity and attenuation factor (Factor One-G Model, Berner, 1989).

5.1. System Characteristics

The following processes affect the systems under consideration.

Mangalavanam

Plant detritus, land run-off during monsoon, system productivity (especially benthic), input from estuary, birds contributions, microbial activity (inside the system) and tidal effect affect the fate of organic matter within the system. Mangalavanam is connected to the estuary by means of a canal approximately 200 m long and 3 m wide and water enters the system at the time of high tide and recedes during low tide.

Vypeen

Vypeen is on the banks of the estuary and is mostly affected by the flow of water in addition to the plant detritus, land run-off, human intervention and microbial activity in the system.

5.2. Approach

Changes taking place in aquatic systems with high diagenetic potential are depending on microbes, which play a highly specific and important role in the decomposition of chemical compounds present there. Microbial processes are too selective and different microbes are required for different chemical reactions. If any particular type of microbes are absent in a system, a particular reaction will be hindered or slowed down or even does not take place in that system.

The decomposition of the chemical compounds mainly depends on the type and concentration of the microbes responsible for the decomposition of that particular compound in the system. This makes it clear that the presence of a particular compound in a system is affected by decomposition processes that take place in that system. For example, presence of amino acid is affected by the decomposition of proteins, which is brought about by bacteria. Concentration of different compounds in a system depends on the microbial activity of the system. As a result, certain compounds will be completely removed from the system and certain others will be present in high concentration or in general, it can be said that different compounds will be present at different composition irrespective of its origin.

Through PCA we compare different parameters like carbohydrates, proteins, amino acids etc with environmental parameters like dissolved oxygen, salinity, eh, ph, texture, carbon, nitrogen etc. and help to define the general characteristics of the system. The contribution of different processes to the variance of the parameters was also assessed by PCA and thus it helps to check the correlation between the character of the system and different compounds produced there. But in normal correlation studies, the variation and the magnitude of overall variations are carried out.

When an environment sample is considered concentration of different parameters will be affected by different processes. So it is not necessary that

there should be a significant correlation between different parameters or their variance can sometimes be high. This may be due to the contribution of a number of processes contributing to the basic parameters of the environment like D.O, salinity etc.

5.3. Principal Component Analysis

In a complex environmental system the distribution and actual concentration of a matter will be dependant on a large number of processes, which makes the exact definition of the system very difficult. A definite correlation will be absent in many cases. Such a complex system can be analysed only by taking into consideration the effective contribution of each process towards a particular parameter. This differentiation and identification of the significance of the processes can be done by factor analysis. The available data will be subjected to a multivariant analysis, thereby segregating the contribution of different processes. The different factors will be an index of the magnitude of the processes and the components of the respective factors will be indicating the significance of that process in the variance of the concentration of that particular component.

Here the factor analysis is carried out using SPSS 7, version 2.4 (1995-1998 ACD systems Ltd). Factors which have eigen values with % variance more than 1 are taken for further analysis and the discussion is based on that.

5.4. General Characteristics

Principal component analysis (PCA) has conducted to factorize the contributions of different processes to the effective concentration of amino acids. Based on the percentage of variance four major processes were

identified to have significant contribution to the variance and analysis with respect to the four factors was done.

To identify the character of each factor the general parameters like carbohydrates, protein, total carbon, total nitrogen, TAA and FAA along with the texture were considered in the factor analysis and four significant factors with variance >1 % were obtained. Of these, the first two are most important. As in earlier studies, microbial degradation is the major factor that governs these ecosystems. It has been reported that the first principal component factor (PC_I) from PCA in several organisms and sediments may be an indicator of their degradation (Dauwe and Middelburg, 1998; Dauwe et al, 1999; Amon et al, 2001; Yamashita and Tanoue, 2003), and therefore this component is designated as the degradation index.

Components	Initial Eigen values		
	Total	% of Variance	Cumulative %
1	237.642	80.849	80.849
2	41.705	14.189	95.038
3	8.442	2.872	97.910
4	4.866	1.655	99.565

Table: 5.1 Total variance explained for the initial eigen values of the first four components in PCA of various organic parameters at Mangalavanam

From the principal component analysis of various organic parameters at Mangalavanam (Table: 5.1.), the first component (PC_I) from PCA with 81 % variance is microbial degradation and hence this factor represents degradation index. The organic fractions FAA, protein, MCHO, TCHO, C and N have significant contribution in this factor. Lateral addition also plays a major role at these stations and it is found to have a significant effect in the concentration of particulate organic matter (Geetha, 2002) where the texture of the sediment has a significant contribution. Therefore the second factor represents lateral addition index, which exhibits about 14 % variance

at Mangalavanam. Factor 3 represented sedimentary adsorbed or bound compounds (2.87 % of variance) and Factor 4 represented by seawater input or tidal influence indicative (1.6% of variance) are of least significance since their percentage of variance is very less.

Degradation index at Vypeen showed about 75 % variance (Table: 5.2.) and carbon, nitrogen together with total carbohydrates contribute to this factor here. The second factor, which is the lateral addition index exhibited about 12 % variance at Vypeen. Sedimentary adsorbed compounds (Factor 3 represented by 2.87 % of variance) and tidal influence indicative (Factor 4 represented by 1.6% of variance) are of least significance like that at Mangalavanam, since their percentage of variance is very less.

Components	Initial Eigen values		
	Total	% of Variance	Cumulative %
1	55.381	75.160	75.160
2	8.897	12.075	87.235
3	4.811	6.529	93.764
4	3.561	4.833	98.597

Table: 5.2. Total variance explained for the initial eigen values of the first four components in PCA of various organic parameters at Vypeen

5.5. Amino acid characteristics

Amino acids obtained in the microanalysis include those from the hydrolysis of protein and free amino acids available in the system. Free amino acids concentration is more or less governed by microbial action, but not in protein. The concentration of different amino acids in protein depends on

1. Decomposition patterns of protein itself (i.e. which bond is broken and which amino acids are released or which amino acid is totally degraded.

2. Depends on protein source.
3. Amino acids adsorbed to the sediment (the binding capacity of each amino acid depend on the sediment type and system character, i.e., each amino acid have different binding capacity in different sediments.

When amino acid components alone are considered, their distributional characteristics will be primarily governed by microbial activity (Yamashita and Tanoue, 2003). So the principal factor that determines the variance of amino acids is found to be the microbial degradation. When Eigen values greater than 1 are considered we get three factors for each station.

Components	Initial Eigen values		
	Total	% of Variance	Cumulative %
1	0.017	83.59	83.59
2	0.003	13.96	97.55
3	0.000	2.20	99.75

Table: 5.3. Total variance explained for the initial eigen values of the first three components in PCA of the relative abundance of individual amino acids at Mangalavanam

Components	Initial Eigen values		
	Total	% of Variance	Cumulative %
1	0.040	91.85	91.85
2	0.003	6.27	98.11
3	0.001	1.69	99.80

Table: 5.4. Total variance explained for the initial Eigen values of the first three components obtained in PCA of the relative abundance of individual amino acids at Vypeen

It is evident from the PCA of both stations, that the first component, which is the degradative index (PC_1) has ~84 % of variance at Mangalavanam

and ~92 % of variance at Vypeen (*Table: 5.3. and Table: 5.4.).* The second component (PC_{II} or adsorption component) has a significant contribution of about 14 % at Mangalavanam and ~6.5 % at Vypeen. Contributions from this factor to the actual concentration of amino acids will be less (evident from the percentage of variance) especially at Vypeen and the adsorption process in this particular study will have contributions only in the concentration of FAA. FAA has a significant contribution that is evident from the fact that the PC_{II} exhibits 13.96 % of variance at Mangalavanam and ~6 % of variance at Vypeen (*Table: 5.3. and Table: 5.4.).*

Therefore in the principal component analysis of amino acids only one component has to be looked into, i.e. the microbial factor. Thus, consider the potential of the processes, the microbial processes will have the maximum weightage or concentration of individual amino acids is more or less under the influence of probably a single process, i.e. microbial activity, indicated by the magnitude of the percentage of variance. There will be supplementary factors like adsorption, lateral addition etc. but that has only very low significance because the major part of adsorbed amino acids will be forming a part of FAA category.

MNGL	Mean	Std. Deviation	Factor Coefficient		
			PC1	PC2	PC3
ASP	0.0120	0.0128	0.967	-0.138	-0.126
GLU	0.0053	0.0108	0.961	-0.215	-0.127
SER	0.8775	0.0921	-0.221	0.966	-0.134
THR	0.0580	0.0971	0.024	-0.948	-0.316
GLY	0.0385	0.0453	-0.136	0.095	0.985
TYR	0.0063	0.0070	-0.195	0.373	0.308
ALA	0.0017	0.0028	0.966	-0.082	-0.102

Extraction Method: Principal Component Analysis.
Rotation Method: Varimax with Kaiser Normalization.

Table: 5.5. Results of Principal Component Analysis (PCA) based on relative abundance (mole %) of individual amino acids at Mangalavanam sediment core (n=15)

Considering the degradation index, it is evident that at Mangalavanam *(Table: 5.5)*, concentrations of amino acids like aspartic acid, glutamic acid and alanine (factor coefficient values 0.967, 0.961 and 0.966 respectively) are governed by microbial processes, since they come in the first factor.. At Vypeen, mainly glycine (factor coefficient, 0.972) and alanine (factor coefficient, 0.413) have significance in the first component.

The comparatively higher positive values of their factor coefficients indicate their higher or positive contribution towards microbial degradation than the other amino acids. At Vypeen, Serine and glutamic acid (factor coefficient, -0.888 and -0.451 respectively) showed a significant negative factor coefficient value *(Table: 5.6)*, which is indicative of their less microbial degradation.

VYPEEN	Mean	Std. Deviation	Factor Coefficients		
			PC1	PC2	PC3
ASP	0.0112	0.0056	0.229	-0.030	0.462
GLU	0.0072	0.0068	-0.451	-0.098	-0.046
SER	0.8494	0.1489	-0.888	-0.459	0.013
THR	0.0250	0.0254	-0.314	-0.122	0.933
GLY	0.0847	0.1340	0.972	0.170	-0.161
TYR	0.0210	0.0514	0.224	0.965	-0.127
ALA	0.0015	0.0006	0.413	-0.202	0.234

Extraction Method: Principal Component Analysis.
Rotation Method: Varimax with Kaiser Normalization.

Table: 5.6. Results of Principal Component Analysis (PCA) based on relative abundance (mole %) of individual amino acids at Vypeen sediment core (n=17)

The three-dimensional plot of factors 1, 2, 3 of individual amino acids at Mangalavanam and Vypeen are given in *Fig: 5.1* and *Fig: 5.2.* respectively.

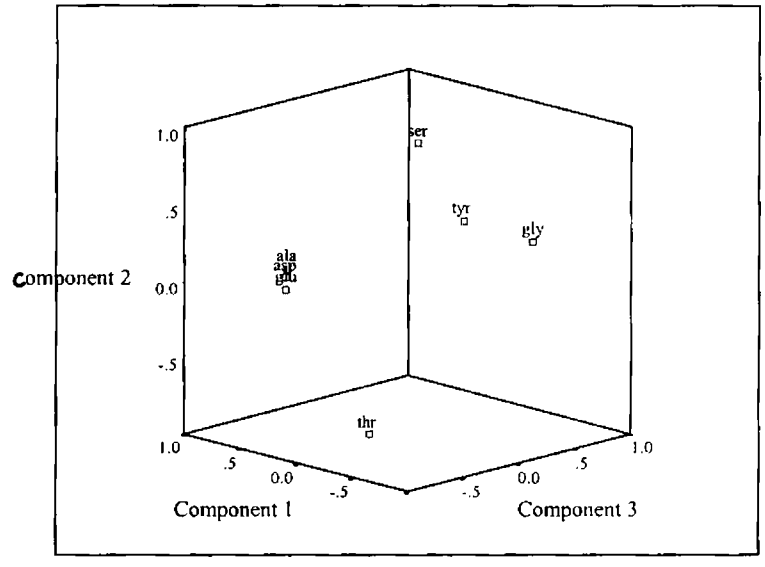

Fig: 5.1. Component plot of factors 1, 2 and 3 of individual amino acids at Mangalavanam

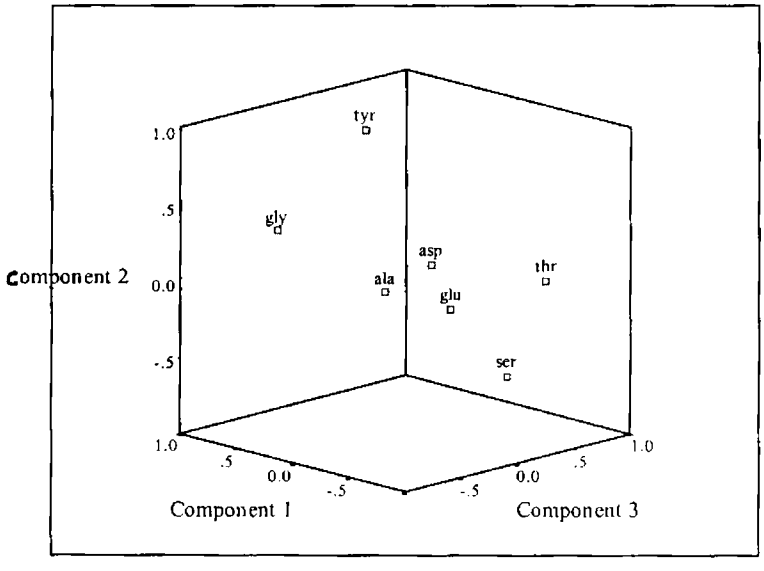

Fig: 5.2. Component plot of factors 1, 2 and 3 of individual amino acids at Vypeen

5.6. Summary

Mangroves are highly productive and naturally the sediments are expected to be enriched with organic matter. Benthic population is considerably high which means that considerable microbial differentiation of organic matter is taking place. The potential of mangroves as a supplier of organic matter can be properly addressed only if we know the compositional character of the supply, especially the beneficial or nutritive part of the supplied organic matter.

The exact character or specificity of the microbial processes and the release of compounds cannot be identified by either checking the contribution character or by conducting selective microbial processes in the laboratory. One of the useful tools in this connection is the statistical factor analysis, which through a multivariance analysis will be able to extract the actual contribution of the different processes.

In the present case, separate factor analysis was carried out with the general parameters like texture, carbon, nitrogen, carbohydrates, protein and amino acids and the individual amino acids to get the general character of the system and the specific distributional character of the amino acids.

Following are the observations:

(1) General characteristics:

Among the general parameters, when eigen values more than one were considered, four factors were obtained, which accounted for around 99.6 % total variance for Mangalavanam and 98.6 % total variance for Vypeen (*Table: 5.1. and Table: 5.2.* respectively). The first factor accounted for ~81 % variance at Mangalavanam. FAA, protein, carbohydrate, carbon and nitrogen are loaded to this factor (*Table: 5.7)*, whereas at Vypeen the first factor accounted for ~75 % variance and carbohydrate, carbon and nitrogen were loaded to it (*Table: 5.8.)*. This explains that microbial degradation mainly governs these two ecosystems. Factor 2 represents lateral addition index, which accounts for about 14 % at Mangalavanam and 12 % at

Vypeen and it is loaded to the finer fraction of the texture at both stations *(Table: 5.7. and Table: 5.8. respectively).* The third factor, which represents adsorption accounts for ~3 % and 7 % at Mangalavanam and Vypeen respectively and the fourth one ~2 % and 5 %, which is indicative of the tidal influence at Mangalavanam and Vypeen respectively (*Table: 5.1. and Table: 5.2.* respectively).

FAA and protein have a significant contribution in factor 3 also in addition to the first factor, which explains the sedimentary adsorbed nature of these compounds at both these ecosystems. TAA has no significant contribution in any of the first three factors, except in the fourth one at both stations (Table: 5.7. and Table: 5.8. respectively) indicating its tidal or seawater influence at both stations.

MNGL	Mean	Std. Deviation	Factor Coefficient			
			PC1	PC2	PC3	PC4
TAA	1.5600	1.0686	0.012	-0.036	0.002	0.318
FAA	0.4973	0.5363	0.478	0.171	0.309	0.158
Protein	11.634	5.2113	0.514	0.337	0.788	-0.029
MCHO	0.6668	0.3544	0.748	0.473	0.129	0.101
TCHO	10.706	3.7586	0.905	0.242	0.202	0.283
Carbon	22.810	13.018	0.837	0.268	0.339	-0.337
Nitrogen	1.5053	0.9905	0.837	0.348	0.271	-0.270
Sand	70.953	6.3492	-0.313	-0.926	-0.188	0.100
Silt+ clay	29.046	6.3492	0.313	0.926	0.188	-0.100

Extraction Method: Principal Component Analysis.
Rotation Method: Varimax with Kaiser Normalization.

Table: 5.7. Results of Principal Component Analysis (PCA) based on relative abundance (mole %) of individual amino acids at Mangalavanam sediment core (n=15)

VYPEEN	Mean	Std. Deviation	Factor Coefficient			
			PC1	PC2	PC3	PC4
TAA	2.8129	2.1600	-0.053	0.097	0.239	0.964
FAA	0.4571	0.2311	0.291	-0.025	0.694	0.317
Protein	10.842	3.0360	0.007	0.280	0.954	0.100
MCHO	0.4691	0.1776	0.288	-0.239	0.086	0.434
TCHO	12.299	1.3709	0.704	0.187	0.208	0.074
Carbon	31.063	2.1629	0.963	0.152	-0.083	-0.077
Nitrogen	2.6629	0.1977	0.785	-0.031	0.152	0.172
Sand	15.941	5.1536	-0.127	-0.983	-0.127	0.029
Silt+ clay	84.058	5.1536	0.127	0.983	0.127	-0.029

Extraction Method: Principal Component Analysis.
Rotation Method: Varimax with Kaiser Normalization.

Table: 5.8. Results of Principal Component Analysis (PCA) based on relative abundance (mole %) of individual amino acids at Vypeen sediment core (n=17)

(2) Amino acid characteristics:

The first factor that accounted for ~84 % variance at Mangalavanam and ~92 % variance at Vypeen represented the microbial degradation index. At Mangalavanam, aspartic acid, glutamic acid and alanine were loaded to this factor *(Table: 5.5.)*, whereas at Vypeen only glycine has a significant contribution to this factor (*Table: 5.6.)*. The second and third factors obtained were less significant (due to low percentage of variance). At Mangalavanam, serine has a significant positive contribution in factor 2 and glycine in factor 3, whereas at Vypeen, tyrosine has a significant positive contribution in factor 2 and threonine in factor 3 *(Table: 5.5. and Table: 5.6. respectively)* indicating the significance of these amino acids in lateral addition and adsorption respectively in addition to microbial degradation.

In general, microbial activity is the major phenomenon that regulates the distributional character of organic matter.

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Summary

Mangroves are important intertidal habitats found in tropical and sub tropical coasts worldwide. They provide breeding, nursery and feeding areas for a great variety of life, including endangered and threatened species. Mangroves also filter upland run off and buffer wave action during intense tropical storms. These ecosystems are very vulnerable to degradation caused by contamination of water and soils, tree falling and dredging for urban and industrial constructions and include different types and intensity of disturbances. Conservation of mangroves is urgently needed for maintaining the faunal diversity associated with it.

Sedimentary organic matter has to be regarded as the residue of organic life and this becomes more important and more abundant with the development and diversification of life. Mangroves appear to be net source of organic carbon and the sediment there, an efficient sink. A variety of organic compounds like proteins, amino acids and carbohydrates are present in mangrove sediments. Proteins and peptides in the surface sediments are further decomposed at sediment-water interface and in deeper sediments into amino acids.

Many of the essential amino acids are not produced within the body of the aquatic organisms or in the system in which they live and the organisms have to depend on externally available sources for these compounds. Mangroves are considered as one of the most productive and fertile aquatic systems. So the fertility of the system depends on the availability of such organic compounds in the system. Mangroves are considered as one of the major nurseries of aquatic life also. The role of amino acid availability for

the fertility of mangroves is yet to be concretized. The attempt that has been made here is to assess the availability of amino acids in mangroves.

Two different mangrove ecosystems in Cochin estuary, Mangalavanam and Vypeen are chosen for the study. Mangalavanam, situated right in the heart of Kochi city is almost a closed system surrounded by brackish waters connected with a canal to the Cochin estuary. Vypeen Island is a semi-enclosed system, which is lying on the banks of the Cochin estuary. The main mangrove plant species found at both stations are same, the Avicennia, Acanthus and Rhizophora species. Vypeen is a waterlogged area whereas water from the estuary enters Mangalavanam only at the time of high tide.

In this study, the biogeochemical compounds like organic carbon, nitrogen and carbohydrates in the surface sediments were slightly higher at Vypeen, whereas, compounds like protein and amino acids were observed to be higher at Mangalavanam. When the vertical distribution is considered, there was a general decrease in the concentration of organic carbon, nitrogen and carbohydrates at Mangalavanam, whereas the concentration remained a constant down the core at Vypeen. Major amino acids identified at both the stations were aspartic acid, glutamic acid, serine, threonine, glycine, alanine and tyrosine. The relative abundance of these amino acids in the sediment core was slightly different at both stations.

From the Principal Component Analysis (PCA), it is understood that the major contributors in the available concentration of organic compounds are bacterial degradation, lateral addition, adsorption and tidal input. In the case of hydrolysable amino acids, PCA indicated only one prominent factor, i.e., the microbial degradation. In the present study, the availability of hydrolysable amino acids in pore water or overlying water is not considered because the storage of the organic compounds in an aquatic system occurs in the sediment and hence the study is limited to the sediment alone. Recent observations have shown that the benthic productivity has a major role in

governing the aquatic life. So sedimentary amino acids has a special significance. The overall performance of the two stations was found to be the same in the case of surface sediments (i.e., the number of amino acids detected, their concentrations, seasonal character of proteins, carbohydrates, carbon, nitrogen etc.). From this it is well understood that in the surface sedimentary environment the geochemical processes at both stations are almost identical, but the vertical distribution pattern differs between the two stations upto 30 cm depth from the surface, indicated more or less a stabilised sediment character at Vypeen, but Mangalavanam indicated a reactive character.

One of the major significance of the study is that it showed the availability of a number of amino acids in substantial concentration in the sediment, which is the media of the benthic activity. For the development of a National Coastal Zone management the data from the all possible aquatic system associated with the coastal waters are essential, especially in defining the fishery potential. Amino acid being the most essential components, where the lateral uptake by the living organisms is expected and established, this work will contribute substantially in overcoming the dearth of data in mangroves.

Further study on the character of microbial action, amino acids in water and their interaction with other organic compounds and their link with primary productivity can lead to the assessment of the exact potential of the system. It is not accomplished in this study, as it is beyond the scope of the present data.

Appendix

Months	Mngl	Vypeen
Feb-01	33.87	25.77
Mar-01	20.88	28.64
Apr-01	29.43	29.34
May-01	17.67	26.05
Jun-01	31.60	27.04
Jul-01	22.74	40.07
Sep-01	53.57	38.45
Oct-01	21.19	43.30
Nov-01	18.25	40.00
Jan-02	21.23	39.75

Table: A.1. Monthly variation of Organic Carbon (mg/g) in Surface Sediments

Depth (cm)	Mngl			Vypeen		
	Pre-mon	Mon	Post-mon	Pre-mon	Mon	Post-mon
0-5	25.4	32.5	32.0	31.1	31.9	31.1
5-10	23.5	61.5	20.7	31.6	33.4	32.2
10-15	16.0	35.0	25.2	30.0	29.3	32.5
15-20	12.6	24.9	9.24	27.2	29.5	32.1
20-25	10.3	17.4	19.5	28.6	30.8	35.3
25-30	7.27	13.5	10.8	27.6		33.5

Table: A.2. Vertical variation of Organic Carbon (mg/g) in the Sediment Core

Stations	Species	C %	N %	C: N	H %	S %
Mngl	Acanthus	32.8	1.74	18.8	7.00	0.45
	Avicennia	38.3	2.06	18.6	6.85	0.71
	Rhizophora	33.8	2.29	14.7	7.28	0.75
Vypeen	Acanthus	35.1	1.51	23.1	7.06	0.47
	Avicennia	37.3	1.78	20.8	7.19	0.30
	Rhizophora	38.3	1.17	32.6	6.83	0.37

Table: A.3. Spatial variation of C, H, N & S (%) in 3 common Plant species

Months	Mngl	Vypeen
Feb-01	3.14	2.01
Mar-01	1.95	2.22
Apr-01	2.15	2.37
May-01	1.22	1.93
Jun-01	1.97	2.12
Jul-01	1.91	3.95
Sep-01	4.64	3.37
Oct-01	1.39	3.75
Nov-01	1.12	3.06
Jan-02	1.69	3.32

Table: A.4. Monthly variation of Organic Nitrogen (mg/g) in Surface Sediments

Depth (cm)	Mngl			Vypeen		
	Pre-mon	Mon	Post-mon	Pre-mon	Mon	Post-mon
0-5	1.46	2.73	2.09	2.92	2.72	2.62
5-10	1.53	4.42	1.43	3.00	3.03	2.66
10-15	1.09	2.44	1.18	2.58	2.52	2.63
15-20	0.90	1.66	0.50	2.39	2.56	2.67
20-25	0.70	1.18	1.09	2.46	2.69	2.76
25-30	0.44	0.84	0.62	2.30		2.76

Table: A.5. Vertical variation of Organic nitrogen (mg/g) in the Sediment Core

Months	Mngl	Vypeen
Feb-01	10.78	12.83
Mar-01	10.67	12.90
Apr-01	13.66	12.39
May-01	14.49	13.50
Jun-01	15.97	12.78
Jul-01	11.87	10.15
Sep-01	11.52	11.42
Oct-01	15.18	11.56
Nov-01	15.39	13.07
Jan-02	12.52	11.99

Table: A.6. Monthly variation of C/N in the Surface Sediments

Depth (cm)	Mngl			Vypeen		
	Pre-mon	Mon	Post-mon	Pre-mon	Mon	Post-mon
0-5	17.46	11.91	15.32	10.65	11.71	11.86
5-10	15.42	13.92	14.56	10.53	11.03	12.12
10-15	14.74	14.36	21.39	11.64	11.62	12.38
15-20	14.10	15.08	18.56	11.37	11.51	12.04
20-25	14.79	14.73	17.97	11.65	11.46	12.80
25-30	16.50	16.06	17.43	12.05	-	12.16

Table: A.7. Variation of C/N ratio in the sediment core

Months	Mngl	Vypeen
Feb-01	0.96	2.04
Mar-01	0.47	2.58
Apr-01	0.69	2.09
May-01	0.52	1.88
Jun-01	0.99	1.60
Jul-01	0.64	2.23
Sep-01	1.22	2.36
Oct-01	0.49	1.98
Nov-01	0.50	2.15
Jan-02	0.57	2.57

Table: A.8. Monthly variation of Hydrogen (%) in Surface Sediments

Months	Mngl	Vypeen
Feb-01	0.62	0.32
Mar-01	0.19	0.46
Apr-01	0.19	0.35
May-01	0.70	0.19
Jun-01	1.22	0.16
Jul-01	0.72	1.82
Sep-01	0.92	0.77
Oct-01	0.62	1.83
Nov-01	0.56	0.38
Jan-02	0.36	0.69

Table: A.9. Monthly variation of Sulphur (%) in Surface Sediments

Depth (cm)	Mngl			Vypeen		
	Premon	Mon	Postmon	Premon	Mon	Postmon
0-5	1.04	1.09	0.78	2.19	2.11	2.46
5-10	1.11	2.32	0.66	2.36	2.04	2.49
10-15	0.76	1.40	0.75	2.29	1.99	2.45
15-20	0.70	1.15	0.45	2.26	1.95	2.47
20-25	0.58	0.88	1.02	2.23	2.32	2.51
25-30	0.41	0.77	0.66	2.08		2.44

Table: A.10. Vertical variation of Hydrogen (%) in the Sediment Core

Depth (cm)	Mngl			Vypeen		
	Premon	Mon	Postmon	Premon	Mon	Postmon
0-5	1.18	1.69	0.75	0.56	0.97	1.37
5-10	1.33	2.91	0.84	0.77	0.92	2.08
10-15	1.14	1.97	0.98	0.63	0.77	2.29
15-20	0.99	1.72	0.73	0.52	0.67	2.35
20-25	0.94	1.38	1.39	0.81	1.86	2.25
25-30	0.75	1.28	0.98	0.72		2.38

Table: A.11. Vertical variation of Sulphur (%) in the Sediment Core

Months	Mngl			Vypeen		
	Mono CHO	Total CHO	Poly CHO	Mono CHO	Total CHO	Poly CHO
Feb-01	0.20	4.68	4.48	0.17	9.31	9.14
Mar-01	0.28	11.6	11.3	0.22	15.0	14.8
Apr-01	0.17	10.2	9.99	0.32	16.2	15.9
May-01	0.33	8.36	8.02	0.71	14.9	14.3
Jun-01	0.98	11.9	10.9	0.45	13.0	12.6
Jul-01	0.36	5.41	5.04	1.09	23.4	22.3
Sep-01	0.45	19.3	18.9	0.44	13.1	12.7
Oct-01	0.31	8.01	7.70	0.61	14.5	13.9
Nov-01	0.43	6.61	6.17	0.59	15.6	15.0
Jan-02	0.19	7.69	7.51	0.09	11.2	11.1

Table: A.12. **Monthly variations of Carbohydrates in the Surface Sediment (mg/g)**

Depth (cm)	Mngl			Vypeen		
	Pre-mon	Mon	Post-mon	Pre-mon	Mon	Post-mon
0-5	0.92	0.77	0.48	0.67	0.87	0.52
5-10	1.23	1.61	0.52	0.56	0.61	0.38
10-15	0.67	0.90	0.39	0.33	0.08	0.44
15-20	0.58	0.71	0.44	0.55	0.24	0.36
20-25	0.40	0.57	0.32	0.59	0.48	0.43
25-30	0.49	0.49	0.36	0.44	-	0.42

Table: A.13. Distribution of MCHO (mg/g) in sediment core

Depth (cm)	Mngl			Vypeen		
	Pre-mon	Mon	Post-mon	Pre-mon	Mon	Post-mon
0-5	14.7	15.7	10.1	12.0	13.8	14.1
5-10	13.3	19.4	11.3	13.4	13.8	14.7
10-15	9.12	13.8	9.81	10.9	11.7	12.7
15-20	10.5	10.7	9.71	10.8	10.8	12.5
20-25	7.92	6.48	6.05	12.4	12.2	12.3
25-30	6.25	4.86	6.01	9.55	-	11.4

Table: A. 14. Distribution of TCHO (mg/g) in sediment core

Depth (cm)	Mngl			Vypeen		
	Pre-mon	Mon	Post-mon	Pre-mon	Mon	Post-mon
0-5	13.8	14.9	9.62	11.4	12.9	13.6
5-10	12.1	17.8	10.8	12.8	13.1	14.3
10-15	8.46	12.9	9.42	10.7	11.6	12.3
15-20	9.87	9.84	9.26	10.2	10.6	12.1
20-25	7.52	5.91	5.73	11.8	11.7	11.9
25-30	5.76	4.36	5.64	9.11	-	10.9

Table: A. 15. Distribution of PCHO (mg/g) in sediment core

Months	Mngl	Vypeen
Feb-01	1.54	2.88
Mar-01	2.72	1.36
Apr-01	4.21	3.39
May-01	6.36	1.88
June-01	4.47	7.07
Sept-01	17.9	6.91
Oct-01	7.29	10.2
Nov-01	7.15	13.5
Jan-02	14.4	14.6

Table: A. 16. Monthly variation of Protein (mg/g) in surface sediments

Depth (cm)	Mngl			Vypeen		
	Pre-mon	Mon	Post-mon	Pre-mon	Mon	Post-mon
0-5	15.7	18.4	9.43	7.71	16.3	8.04
5-10	11.2	23.3	8.48	15.8	11.9	11.6
10-15	8.08	21.6	17.9	6.92	14.2	9.93
15-20	9.73	10.4	5.07	8.87	15.6	8.03
20-25	5.54	14.4	7.35	10.8	10.9	10.2
25-30	7.60	8.42	9.62	9.92		7.57

Table: A. 17. Vertical variation of Protein (mg/g) in the Sediment Core

Months	Mngl	Vypeen
Feb-01	0.96	0.29
Mar-01	1.60	0.49
Apr-01	0.70	0.45
May-01	0.51	0.36
June-01	0.42	0.32
July-01	0.73	0.55
Sept-01	0.69	0.45
Oct-01	0.86	0.55
Nov-01	0.26	0.33
Jan-02	0.54	0.60

Table: A.18. Distribution of Free Amino acids (mg/g) in Surface Sediments

Depth (cm)	Mngl			Vypeen		
	Pre-mon	Mon	Post-mon	Pre-mon	Mon	Post-mon
0-5	0.33	2.29	0.52	0.51	1.03	0.34
5-10	0.45	0.90	0.64	0.95	0.62	0.56
10-15	0.13	0.73	0.46	0.41	0.46	0.41
15-20	0.18	0.23	0.36	0.30	0.33	0.24
20-25	0.16	0.24	0.32	0.46	0.41	0.27
25-30	0.09	0.12	0.25	0.26		0.21

Table: A.19. Distribution of FAA (mg/g) in the sediment core at both stations

Season	Depth (cm)	Asp	Glu	Ser	Thr	Gly	Tyr	Ala	Trp	Val	Ph-ala
Pre mon	0-5	0.525	0.219	31.57	0.997	0.059	0.000	0.047			
	5-10	0.068	0.053	0.937	0.136	0.014	0.000	0.014		0.003	
	10-15	0.145	0.009	10.99	0.000	0.028	0.068	0.013		0.004	0.526
	15-20	0.361	0.1754	25.18	10.19	0.075	0.009	0.029	0.381		
	20-25	0.258	0.147	16.67	7.101	0.045	0.007	0.019			
Mon	0-5	0.022	0.007	6.075	0.032	0.006	0.171	0.000			
	5-10	0.264	0.099	14.02	0.344	0.218	0.043	0.037	0.127		
	15-20	0.027	0.000	5.698	0.000	0.971	0.085	0.000			
	20-25	0.062	0.000	6.627	0.000	0.878	0.105	0.000			
Post mon	0-5	0.007	0.013	0.000	0.000	0.049	0.000	0.000			
	5-10	0.191	0.044	16.57	0.421	1.269	0.121	0.032			
	10-15	0.059	0.000	9.937	0.227	0.849	0.072	0.013			
	15-20	0.159	0.056	13.84	0.452	0.703	0.076	0.022			
	20-25	0.110	0.035	8.791	0.156	0.514	0.061	0.016			
	25-30	0.038	0.009	10.31	0.122	0.461	0.053	0.008			

Table A.21. Seasonal distribution of different amino acids (μM) in the sediment core at Mangalavanam

Season	Depth (cm)	Asp	Glu	Ser	Thr	Gly	Tyr	Ala	Trp	Val	Ph-ala
Pr e mon	0-5	0.395	0.000	25.84	2.290	0.605	0.088	0.046			
	5-10	1.252	0.418	55.83	4.179	1.121	0.000	0.157			
	10-15	0.065	0.000	11.93	0.812	0.483	0.000	0.016			
	15-20	0.112	0.000	22.87	0.771	0.586	0.000	0.043			
	20-25	0.071	0.050	6.521	0.128	0.627	0.165	0.008			
	25-30	0.579	0.480	37.45	0.000	1.626	0.255	0.058			
Mon	0-5	1.192	1.321	53.82	2.455	0.965	0.388	0.096			
	5-10	0.100	0.058	16.52	0.000	1.207	0.357	0.031			
	10-15	0.029	0.033	5.732	0.000	1.030	0.000	0.014			2.280
	15-20	0.613	0.573	32.98	1.039	0.663	0.425	0.062	0.136		
	20-25	0.419	0.424	28.16	0.307	0.028	0.430	0.045			
Post mon	0-5	0.419	0.486	31.43	0.927	0.625	0.424	0.045		0.010	9.587
	5-10	0.017	0.000	0.881	0.000	0.547	0.403	0.002	0.256		
	10-15	0.196	0.167	17.27	0.537	0.631	0.473	0.030	0.647		
	15-20	0.550	0.660	53.55	2.100	0.637	0.410	0.017			
	20-25	0.021	0.018	5.771	0.000	0.537	0.008	0.002			
	25-30	0.017	0.000	0.403	0.000	0.475	0.009	0.002			

Table: A.22. Seasonal distribution of different amino acids (μM)

in the sediment core at Vypeen

Plant Species	Asp	Glu	Ser	Thr	Gly	Tyr	Ala	Val	Ph-ala
Acanthus	0.382	0.059	29.99	3.583	0.048	0.015	0.116	0.024	-
Avicennia	0.805	0.392	29.75	4.304	0.057	0.167	0.113	0.015	8.911
Rhizophora	0.678	0.154	23.82	0.882	0.012	0.202	0.113	0.017	2.658

Table: A.23. Seasonal distribution of different amino acids (μM) in the leaves of three species of plants at Mangalavanam

Plant Species	Asp	Glu	Ser	Thr	Gly	Tyr	Ala	Val	Ph-ala
Acanthus	0.109	0.061	6.116	0.774	0.010	0.062	0.029	0.008	-
Avicennia	1.270	-	21.45	2.704	0.036	0.237	0.056	0.001	2.934
Rhizophora	0.717	1.928	37.37	8.711	0.116	0.596	0.205	0.041	2.063

Table: A.24.Seasonal distribution of different amino acids (μM) in the leaves of three species of plants at Vypeen