INTER-VARIABILITY OF PHOSPHORUS SPECIATION IN SELECTED MANGROVE ECOSYSTEMS AROUND GREATER COCHIN

A Thesis Submitted to the
COCHIN UNIVERSITY OF SCIENCE AND TECHNOLOGY
in Partial Fulfilment of the
Requirements for the Degree Of

Doctor Of Philosophy
In
Environmental Chemistry
Under The Faculty Of Marine Sciences

By

SHALY JOHN

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

MARCH 2003

Certificate

*This is to certify that this thesis is an authentic record of the research work carried out by **Ms. Shaly John**, 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 requirement for the degree of Philosophiae Doctor of the Cochin University of Science and Technology.*

Prof. Dr. Jacob Chacko
Supervising Teacher.

Cochin – 16
March 2003.

CONTENTS

Chapter 1

INTRODUCTION

Mangroves are the characteristic littoral plant formations of tropical and subtropical sheltered coastlines and are at the interface between the land and the sea. The importance of mangroves stems from their pivotal role in both terrestrial and aquatic production, and by the many amenities provided within and beyond its boundaries. Although these ecosystems are economically extremely valuable, they are under increasing threat of being wiped out by rapid human encroachment and environmental pollution. Thus an understanding of these ecosystems is vital to their survival. The classic work of Heald (1969) and Odum (1970) on mangrove productivity in Florida have attracted wide attention to the general significance of mangrove communities in the coastal zone. Mangrove forest areas and their associated food chain and nutrient cycles are often closely linked to those in adjacent coastal waters (Alongi *et al.*, 1993; Alongi, 1996). The trees can be regarded as links between the terrestrial and marine ecosystem (Chale, 1993), and mangrove ecosystems are open with exchange of nutrients, detritus and sediment facilitated by tidal flushing (Woodroffe, 1985; Lee, 1995). The habitat receives nutrient and organic detritus from land and from fresh water streams (Morell and Corredor, 1993) and nutrients are effectively recycled within the ecosystem. The extent to which the mangrove systems exchange dissolved and particulate nutrients with adjacent waters depends on several factors including geomorphology, tidal regime and climate (Alongi, 1996). Mangroves are considered to play an important role in controlling coastal hydrodynamics and sediment movements (Boto, 1992; Eong, 1993).

A mangrove is a tree, shrub, palm or ground fern, generally exceeding one half meter in height, and which normally grows above mean sea level in the intertidal zone of marine coastal environments, or estuarine margins. Of late, the terms 'mangroves' or 'mangal' are being synonymously used to refer to the mangrove habitat although the former is far more popular. Mangroves are a diverse group of predominantly tropical trees and shrubs growing in the marine intertidal zone, sheltered coastlines, mudflats and river banks in many parts of the world, belong to a variety of plant families. Here they are subject to both short term rhythms of tides and seasons, as well as to longer-term changes of climate and sea level. As a group, they share several highly specialized and collectively well-known adaptations, notably exposed breathing roots and support roots, salt excreting leaves, and viviparous water – dispersed propagules. However, as individuals, these characteristics are not shared equally by all species. It is believed that the variation at particular sites influences both the types of mangroves that can become established and survive (Karim, 1991), and their morphology (Soto and Corrales, 1987: Duke, 1990). Hence, the type and condition of mangroves at particular sites reflect the physical conditions of those sites. The common characteristic they all possess is tolerance to salt and brackish waters. Furthermore, different taxa have different mechanisms for coping with high salt concentrations, and not all have salt - excreting gland on their leaves. Others exclude salt at the roots, although this creates xeric conditions for the plant. Another group also allows low concentrations of salt into their sap, but this is neutralized by its transfer into senescent leaves or by storing it in their bark or wood. Mangroves also need to cope with growth in water-saturated, often anaerobic, substrates. Some of these latter characteristics are shared with freshwater swamp trees. This lack of gaseous exchange in substrate requires them to have special breathing structures on the exposed roots and/or trunk. These may be quite different, depending on the taxon. Some species like *Rhizophora* have aerial prop roots bending down either from the trunk or branches, high above the substratum. Others have shallow, subsurface cable roots with series of vertical, stem like breathing roots, called pnuematophores. By contrast in certain mangroves, there are no elaborate physical structures, instead numerous air breathing lenticels are often present on the trunk. Other essential attributes in this water-saturated environment are structures to support the above groundmass of the trees. This is very important to larger individuals, which commonly attains a height of about ~40 meters height. Where roots are unable to penetrate more than a metre or so because of the anaerobic condition, lateral support structures are essential. In these cases, the root structures, contribute a great deal. However other support structures like trunk buttresses are also common in mangrove plants.

1.1 GLOBAL DISTRIBUTION OF MANGROVES

Mangroves are distributed according to three important scales, namely their coastal range, their location within an estuary, and their position along the intertidal profile. On the global scale, mangrove plants are found throughout tropical regions of the world. The mangrove species, the most tropical, shallow marine coastal habitats, are divided into two global hemispheres, the Atlantic East Pacific (AEP) often referred to as the New World, and the Indo West Pacific (IWP), or Old World. These more or less equal portions of the earth also have equivalent aerial extent of mangrove forests (Saenger *et al.*, 1983). The AEP has fewer species and fewer additional genera. The most diverse flora is seen in the IWP. The dominanent world mangrove zones are restricted to the Indo-West Pacific region of the Old World. The most important world mangroves are distributed in South-East Asia, North-East Australia and South- East Africa and extend mainly within the tropics and subtropics between latitude 32°00'N and 33°00'S and longitude 30°E and 165 °E. In the New World zone, the mangroves are distributed in North America at Lousiana, Pacific coast of North-West Mexico, Bermuda Islands and Pacific coast of South America.

1.2 DISTRIBUTION OF MANGROVES IN INDIA

The Sunderban mangroves of Ganga delta form the largest belt covering about 4200km^2 area intersected by criss-crossing rivers and estuaries. These mangroves present complex ecological conditions due to their vastness in extent and ramification of the riverine system leading to the several islands. The diversity of habitats resulted in zonation and development of different associations. Physiogonomically also these mangroves are highly variable, depending upon the dominant species which may be *Excoecaria agallocha, Avcennia officinalis, Sonneratia apetala or Ceriops decandra*. Each of these gregarious species may constitute a pure formation. Besides these, *Bruguiera gymnorrhiza, Xylocarpus granatum, X. moluccenis, Aegiceras corniculatum, Phoenix paludosa and Rhizophora mucornata* are also observed (Dagar, 2000).

The glory of Sunderban mangroves is, however, disappearing rapidly due to increasing biotic pressure. Many species which once dominated the mangrove stands have rare or all together are absent. Some of them have been listed as endangered (Nasker and Guha Bakshi, 1987) include *Heritiera fomes, Ceriops decandra, C. tagal, Rhizophora apiculata, R.mucronata, and Kandelia candal. Heritiera fomes* which had been a common dweller of the Sunderbans delta region is now very occasionally found in the tidal swamps. It has been exploited indiscriminately for its timber value.

The Mahanadi mangroves covering an area of about 200km^2 are in a degraded state due to conversion for agriculture and development of port facilities at Paradweep. Dense forest are seen in Bhatarkanika estuarine mud flats and deltaic creeks between the rivers Devi and Dharma. *Phoenix paludosa and Aegialitis rotundifolia* occur more towards estuarine conditions. *Rhizophora mucronata, Avecennia alba, Avecennia officinalis, Sonneratia alba, Ceriops decandra, Ceriops tagal, Bruguiera gymnorrhiza, B.parviflora, B.cylindrical, Xylocarpus granatum and Kandelia candal* grow luxuriantly in the tidal zone. *Acanthus ilicifolius* is found in elevated fringe areas. But most of the areas particularly away from the river remain highly degraded.

The mangroves of Godavari and Krishna estuaries depend on the frequency and amount of flooding of the river and configuration of the coast. During the hot season, salinity increases considerably and only certain taxa such as *Avecennia, Excoecaria* and *Sonneratia* with wide ecological amplitude exist. *Ceriops decandra, Rhizophora mucronata, Rhizophora mucronata, and R.apiculata* can be found frequently nearer to lagoons but are rare elsewhere. *Scyphiphora hydrophyllacea* once reported to be widely distributed, is found in new patches.

The mangroves of Cauvery deltaic system are discontinuous. The Pichavaram mangrove area (southeast India) support about 1100 ha, of which 50% is covered by forest, 40% by water-ways and the remaining filled by sand flats and mud flats (Krishnamurthy and Jayaseelan, 1983). The mangals of Pichavaram show a marked zonation where *Avecennia marina* forms pure stands and *Rhizophora apiculata and R. mucronata* grow well along the channel and creeks. These are mixed with *Bruguiera cylindrical, Ceriops decandra, and Sonneratia apetala*. Other species in this region included *Lumnitzera racemosa, Aegiceras corniculatum and Excoecaria agallocha*. The fresh water zone is generally dominated by *Acanthus ilicifolius, Avcennia marina* is found more towards the marine zone and *A. officinalis* towards freshwater zone influenced by Coleroon estuarine water.

Mangroves of Karnataka coast are highly degraded. These are formed on shallow coastal waters, estuaries or lagoons. *Avcennia officinalis, A. marina, Excoecaria agallocha,Acanthus ilicifolius, Rhizophora mucronata, Ceriops tagal, Sonneratia caseolaris, Kandelia candal, and Heritiera littoralis* are frequent species forming pure or mixed association.

The mangroves of Goa region cover about 200km^2 consisting of seven estuaries of which Zuari, Mandovi, and the Cambarjua canal connecting them with harbour cover about 75% mangrove area. *Avcennia officinalis, Rhizophora mucronata,Sonneratia alba,* are the prominent species which are associated with *R.apiculata, S. Caseolaris, Kandelia candal, Bruguiera gymnorrhiza, B.parviflora, Aegiceras corniculatum, Excoecaria agallocha, and Acanthus ilicifolius.* These stands are not rich in their biodiversity due to excessive biotic pressure but during recent times attempts have been made to regenerate mangrove stands by planting the trees artificially (Dagar, 2000)

The mangroves of Maharashtra coast are under tremendous biotic pressure at almost all sites. Many species which were reported as common have become rare or all together absent on many of these sites. At many localities bushes of *Avcennia marina* are most prominent showing the capacity of tolerance to biotic pressure. All along Gujarat coast *Rhizophoraceae* element is very rare. Species of *Avcennia* form gregarious but stunted stands. (Dagar,2000)

The Andaman and Nicobar Islands harbour some of the best developed mangroves which are comparatively less disturbed. There is a distinct zonation pattern. *Rhizophora mucronata* and *Rhizophora.stylosa,* are the prominent towards sea where others cannot stand. Species of *Bruguiera, Sonneratia, Aegiceras, Xylocarpus, Aegiceras, Avcennia, Ceriops, and Scyphiphora* are common in the middle zone while species of *Excoecaria, Lumnitzera, Cynomitra, and Heritiera are* common towards land. *Nypa fruticans, Acanthus spp, and Phoenix paludosa* are common along creeks. The distribution of *Acanthus ebractatus, A.volubilis, Lumnitzera littorea, Bruguiera sexangula, Rhizophora stylosa and R.lamarckii* is interesting in these islands as these are not frequent elsewhere. In recent years due to developmental activities these stands are also under high biotic pressure and many species are becoming rare.

Besides the over exploitation of these resources there are other reasons also which are responsible for the dwindling of mangrove ecosystems. Khushoo (1986) has stated that role of pollutants is very discriminatal for the deterioration of these coastal vegetation in Bombay, Madras, Ernakulam to Trivandrum, Andhra Pradesh, Karnataka and Orissa.

1.3 DISTRIBUTION OF MANGROVES IN KERALA

Kerala once supported about 700km^2 mangroves along its coast (Ramachandran *et al.*, 1986) and what is seen now are only relics of the great past. The increasing pressure on the coastal area as the population density increases initiates a radical transformation of the natural environment. Early development of the state was mainly through sea trade in the past and more recent changes in agricultural and industrial sectors resulted in consumption of large extents of mangrove vegetation. Moreover, the ecological significance of this unique ecosystem was not at all understood. By the time the ecological importance are realized, the mangroves had dwindled from 700km^2 to about 17km$^{2.}$

The entry of tidal waters regularly from the sea, the enrichment of 30 estuaries and backwaters with the regular supply of fresh water flowing from the 44 perennial rivers create a peculiar ecological environment leading to the development of a unique mangrove vegetation on the fringes of the backwaters, estuaries, and creeks. The important species found are *Acanthus ilicifolius, Acrostichum aureum, Avcennia marina, Avcennia officinalis, Bruguiera gymnorrhiza, B.parviflora, Ceriops tagal, Derris trifoliate, Excocaria indica, Kandelia candal, Lumnitzera racemosa, Rhizophora mucronata, R. apiculata and Sonneratia casealaris.*

The district wise distribution of mangroves is given in a table below (Chand Basha, 1991)

District	*Mangrove area (approximate ha)*
Thiruvanathapuram	23
Kollam	58
Alappuzha	90
Kottayam	80
Ernakulam	260
Thrissur	21
Malappuram	12
Kozhikode	293
Kannur	755
Kasarkode	79
Total	1671

Patches of varying extent exist along the sides of the railway line especially in the Trivandrum-Quilon, Ernakulam- Alleppy and Thanur-Kasargode sectors. In most places the vegetation is in a very narrow linear strip. Bigger bits are available in some parts especially on the sides of the line from Mahe to Dharmadom, Pazhayangadi, Ezhimala, Payyannur, Edakkad and so on. These are comparatively bigger patches, and support fairly good and developed mangrove vegetation. The Quilon strip has a length of 0.75km and a varying width of 1-10metres from the water front. The total extent of this may be around 2ha. Kumarakom which is declared as a bird sanctuary supports a narrow belt of approximately one-kilometer long mangrove vegetation along the fringe of Vembanad lake varying in width from 10-20m. This area comes approximately to 4ha including vacant marshy patches.

The Vypeen area in Ernakulam district, support about 10ha of mangroves. These forms a part of the naturally accreted area called Puthuvypu at the southern tip of Vypen Island located on the North- Western bank of Cochin bar-mouth.In Kerala some of the mangrove vegetation are under the forest department. In Ernakulam district the land called "Mangala Vanam" also support a good amount of mangrove vegetation.

1.4 ECONOMIC IMPORTANCE

The viability of an ecosystem can be judged from its diversity of species which indicate the survival value of the community. A rich gene pool means a higher adaptation potential. It leads to increased stability in an ecosystem. In mangrove ecosystem there is large accumulation of plant debris. To a wide range of animals, the litter is valuable feed either as such or after microbial degradation. Many of them make use of mangrove communities as habitat, nursery ground and source of food. The debris also serves as breeding ground for the juveniles of many types of fish, crustaceans and other fauna. Mangrove roots and branches serve as a good shelter for large number of organisms including many beautiful mosses, lichens, algae, fungi, bacteria, ciliates, nematodes and amphipods which colonize and form food for many kinds of fish. Many of the fish species utilize the mangrove water as good nursery and breeding ground. Thus mangrove ecosystems not only provide fuel wood and charcoal, timber and construction material, pulp, tannin, food and beverages, honey, fodder, medicine, and stabilization of the coast, but also sustain diverse communities of flora by providing them with habitat, energy and nutrition. In the mangrove ecosystems, phytoplanktons and zooplanktons become supplementary source of nutrition to the small fish and other aquatic life. The fish culture ponds may be created in cleared portions or behind the mangrove without further denudation of mangroves. Low lying marshy areas connected with the sea offer good scope brackish water fish and prawn culture. Mullets grow well in mangrove waters. The prominent commercial mollusks, the black lip pearl oyster and green mussel culture offer good scope in intact mangrove areas.

1.5 MANGROVES AND NUTRIENT ELEMENTS

Carbon, nitrogen and phosphorus are the most significant micronutrients in aquatic ecosystems. In the aquatic environment, the nutrients are distributed between the water and the sediment interface in both dissolved and particulate forms. Bioavailable nutrients are taken up and metabolized by aquatic organisms in the lifecycles. In a specific aquatic ecosystem, nutrient dynamics partition the elements carbon, nitrogen, and phosphorus among water, sediment and biota to attain a natural balance. This balance may change as nutrients are introduced from agricultural, industrial and urban sources.

Sediment particles in lakes and rivers are constantly resuspended and redeposited, depending on environmental conditions. The nutrient content in particles is important in their transport from bottom sediments to the overlying water. The knowledge of their concentrations is used to understand their movement within the aquatic ecosystem, particularly at the sediment water interface.

Mangrove forests are best developed on tropical shorelines where there is an extensive intertidal zone, with an abundant supply of fine grained sediment (Walsh,1974). While mangroves are generally associated with low-energy, muddy shorelines, particularly tropical deltas, they can grow on a wide variety of substrates, including sand, volcanic lava or carbonate sediments.

A comprehensive understanding of nutrient behavior in aquatic ecosystems requires their study in both the water and sediments. Bonanni *et al.* (1992) showed that sediments play an important role in the accumulation and regeneration of nutrients. Organic matter produced by phytoplankton in eutrophic shallow lakes settles to the sediment and decompose by aerobic and anaerobic processes, during which different carbon, nitrogen and phosphorus compounds are produced (Anderson and Jensen,1992). Further more, decomposing organic matter affects changes in oxygen concentration and redox potentials which in turn affects nitrogen and phosphorus release from sediments to the overlying water. In order to obtain a complete picture of the effects of flooded soils on plant productivity, relatively long term studies on nutrient status, redox potential, pH, soil mineralogy, and salinity changes must be made. The redox potential is a convenient measure of the extent to which the soil is in a reducing or anaerobic stage. The large positive values of redox potential indicate a well oxidized or aerated stage. As the oxygen supply is limited, it is rapidly consumed by bacterial respiration. It was found that this process takes place at an Eh range of +350 to +380mV. When all the oxygen is consumed the conversion of Mn^{+4} to Mn^{+2} and NO_3 to N_2 takes place. When Mn^{+2} and NO_3 are completely consumed, then Fe^{+3} is reduced to Fe^{+2} and so on until the soil eventually reaches a highly anaerobic state where the reduction of dioxide to methane takes place. The rate at which all these processes depends upon the time of flooding and organic carbon present in the soil.

The ecological significance of carbon as a nutrient is manifested through its organic forms. The concentration of total organic carbon is often used in correlation with other elements. For example carbon to nitrogen and carbon to phosphorus ratio is used to characterize the association of nitrogen and phosphorus in organic matter. Nitrogen species include organic nitrogen, ammonia nitrogen, nitrate and nitrite nitrogen. Biological activities in living dead tissues produces reduced forms of organic nitrogen ranging from simple amines to complex proteins. Ammonia is the most common form of inorganic nitrogen, and is the product of decomposition of organic matter. Bacterial oxidation in the nitrification cycle produces nitrite and nitrate. Phosphorus species in the environment include organic phosphorus compounds, inorganic phosphates, and mineralized inorganic complexes with iron, calcium and aluminium. Phosphorus precipitates to form low solubility compounds and metallic complexes, and is relatively immobile compared to carbon and nitrogen. The natural abundance of nutrients of interest is carbon, nitrogen and phosphorus. Due to this sequence, phosphorus is often considered to be the limiting nutrient in the ecological cycle.

Sediments receive a mixture of labile and refractory organic and inorganic phosphorus compounds from the overlying water and the surrounding landmasses. Some of these compounds behave as inert material and are simply buried in their orginal form. Others decompose or dissolve and simply release the phosphate to the sediment pore water. The regenerated phosphate may be released to the overlying water, reprecipitated within the sediment as an authigenic phase or adsorbed by other constituents of the sediment. Adsorption on metal oxides in the sediment has been identified as one of the principal reactions involving phosphate. (Lijklema 1976; Krom and Berner 1981:Frolich 1988). Mangrove soils are expected to contain a high proportion of organic phosphorus compounds due to their generally high organic matter content (Boto, 1988). Boto has pointed out that much of this organic phosphorus is in the phytate form and bound to humic compounds, and has been found in lake sediments, and is not probably not available for microbial and mangrove plant nutrition. The inorganic phosphate represents the largest potential pool of plant available, soluble reactive phosphorus. Most of the inorganic phosphorus in mangrove sediments is either bound in the form of Ca, Fe, and Al phosphates or as soluble reactive phosphorus adsorbed onto, or incorporated into hydrated Fe and Al sesquioxides. Total organic P concentrations, proportionally greater in surface sediments, reflect the influence of roots, whereas the inorganic fractions mainly Fe bound phosphorus, proportionally and in real terms increase gradually with depth reflecting the influence of increasing anoxia particularly below the root layer.

Every organism participates to some extent in the phosphorus cycle by virtue of its need to assimilate organic and/or inorganic phosphorus for growth and maintenance, and by excreting phosphorus containing byproducts. Bacteria, algae and higher plants, including mangroves, take up dissolved orthophosphate; and organic phosphates are either taken up directly or first hydrolysed by extracellular alkaline phosphates. Organic phosphorus may be very resistant to hydrolysis and not readily assimilable to organisms. Orthophosphate is coupled to ADP to form ATP in cells, and is essential for energy transfer and phosphorylations, and for synthesis of nucleic acids, phospholipids and phosphoproteins (Ingraham *et al.*, 1983). In comparison with release rate of phosphorus from mineral phosphates a refractory organic material, the turnover time for P uptake, utilization and excretion by living organisms is very short, on the order of minutes to tens of hours, depending on the rate of biological activity and the amount of available phosphorus. Once P is taken up and used in cells as phosphate, it is eventually liberated via excretion or through mineralisation of detritus as phosphte. This means that all organisms have evolved efficient uptake mechanisms for a very small and virtually constant proportion of the earth's P in a very competitive cycle, and P on a localized level may limit growth of biomass. Local P cycle can be very efficient in tropical mangroves, where it has been estimated that up to 88% of the forest P pool is retained within the sysem (Boto and Bunt, 1982). The cycling of phosphorus through mangrove food web is presumably similar to that in other aquatic systems. At the base of pelagic and benthic food webs, a 'microbial loop'exists in which interactions among bacteria, microalgae and nanoprotozoans and larger protests facilitates net release of phosphorus into the water column and pore water.

An increasing number of studies have investigated the influence of mangrove forest on coastal nutrient cycles and food chain and found that the actual amount of dissolved and particulate matter exchanged depends on the factors such as aerial extend of the forest, tidal amplitude and seasonality. Tropical mangrove forests, on average, appear to export particulate nutrients and to import some dissolved species, depending upon season, tidal amplitude and geomorphology. (Alongi *et al.*, 1993).

1.6 SCOPE OF THE STUDY

Tropical mangrove systems in Australia and southeast Asia face continuing degradation from human activities. These include indirect effects from nutrient and toxic pollution associated with development and aquaculture (Kaly *et al.*, 1997). Scientific investigations on mangrove systems are particularly significant allows the Kerala coastline, as the economy of this state largely depends on its coastal fisheries. In the coastal areas especially near mangrove forests, prawn culture farms are established, which produce effluents with organic and inorganic pollutants. These pollutants damage the ecology of the system. Cutting of trees for fuel and over grazing by cattle has led to soil erosion and stunted growth of the plants in this area. Although extensive areas of mangrove woodland were found along the banks of Cochin estuary most of these have now disappeared. Study sites represent some of the few remaining areas of mangroves. It is evident that the remaining mangroves are important breeding and feeding areas for the local commercial fish and prawn stocks.

Basha, (1991) reported on the mangrove vegetation of Kerala coast in its present condition, and also gave a historical background to make the reason clear for the dwindling of the mangrove forest to the present stage of discontinuous and isolated bits. Three mangrove ecosystems of Kerala, namely Veli, Quilon and Kumarakom were compared with respect to the species distribution and the hydrographical characteristics by Thomas and Fernandez (1993). The different factors, that are responsible for the colonization of the predominant vegetation, *Acanthus ilicifolius,* in mangrove areas of Cochin, were investigated by Muraleedharan and Rajagopalan (1993). About thirty three species of polycheaetes were identified in mangrove regions of Cochin (Kumar and Antony, 1994). The texture of Tellichery mangrove sediments was found as silty sand due to the prevalent high energy zone (Raghunadh *et al.*, 1995). A pollution survey was carried out by assessing the heavy metal (Fe, Mn, Cu, Zn, Pb, Co) concentration in mangrove flora and sediments (Thomas and Fernandez, 1997). A critique on the occurrence and distribution of macro-zoobenthos in an aquaculture pond suggested a better scope for aquaculture in brackish water pond lined with mangroves in the margin (Kumar, 1998). The importance of mangroves to the estuarine ecosystem in general and for the propagation of marine shrimps in particular is emphasized in a report of Achuthankutty and Sreepada (1998). A statistically significant correlation was found between sediment size in the distribution pattern of organic carbon (TOC) and total phosphorus (TP) in mangrove sediments at Veli, Kochi and Kannur (Badarudeen *et al.*, 1998a). Investigations on inorganic nutrient levels of interstitial waters in a mangrove forest of Cochin, revealed that dissolved phosphate, ammonium and silicate were several times higher in interstitial waters than in overlying waters (Bava and Seralathan, 1998). A comparison of the distribution of sodium and potassium in sediments of Veli, Kochi, and Kannur mangroves exposed the enrichment of potassium over sodium in sediments of Kannur mangroves (Badaruddin *et al.*, 1998b). Subramanian (2000) reported that Cochin backwaters had many pockets of mangrove habitats with the same species diversity as any other mangrove ecosystems.

Perusal of literature, on the mangrove ecosystems of Kerala revealed that most of the investigations concentrated on the physical and biological characteristics. Biologists often view mangrove forests as highly productive sources of organic matter, from which there is a net outwelling of energy supporting complex estuarine and near shore food webs. Geologists, on the other hand, view mangrove shore lines as sediment sinks, characterized by long-term import of sediment, as indicated by the substantial accumulation of recent sediments which underline mangrove forests and adjacent coastal planes. However chemists attempt to find exact processes by which the mangrove acts as a source or sink of organic and inorganic nutrients.

Until now, no rigorous reports exist on chemical investigations on the nitrogen and phosphorus dynamics in mangrove fringed creek waters and sediments of Cochin. Although there are several studies on the distribution and speciation of nutrients in Cochin estuary, the information regarding the same lacking at the mangrove areas of Cochin estuary. Therefore an attempt has been made to investigate nutrient distribution of selected mangrove systems of the Greater Cochin area. The main objectives of the study undertaken were,

- to determine seasonal trends of dissolved inorganic nitrogen and phosphorus in selected mangrove fringed creeks around Greater Cochin area and the main parameters affecting their variability.
- to attempt a comparison of nutrient concentration among Stations and between seasons.
- to determine the distribution of different forms of phosphorus in surface waters of mangrove-fringed creeks.
- to characterise the sediments of these creeks by monitoring properties like grain-size, moisture percentage, pH, and also the nutrient status by measuring the three important nutrient element, carbon, nitrogen and phosphorus.
- to explore the vertical distribution patterns of C, N and P in sediment cores so as to generate information on aspects that influence the sediment nutrient profile.
- to study the fractionation of phosphorus, in mangrove core sediments and to explore the impact of environmental factors on their distribution.

Clearly, a whole set of processes like mineralogical diagenesis, biotic and abiotic redox processes, biological assimilation enzymatic and non-enzymatic hydrolysis reaction etc. are operating in the sediments at any one time (Hakanson and Jansson, 1983) and the dominant process will depend, in part, upon the phosphorus species present. Therefore, knowledge of phosphorus speciation should allow for an understanding of the mechanisms for phosphorus release or assimilation by sediments.

REFERENCES

Achuthankutty, C.T. & Sreepada, R.A. 1998 Brackish water shrimp farming: Possible impacts on estuarine ecosystems. In *Advances in aquatic biology and fisheries: Prof. N. Balakrishnan Nair, felicitation volume* (Natarajan, P., ed). University of Kerala, India. pp. 175-189.

Alongi. D.M. 1996. The dynamic of benthic nutrient pools and fluxes in tropical mangrove forest. *Journal of Marine Research* **54**, 123-148.

Alongi, D.M., Christoffersen, P. & Tirendi, F. 1993 The influence of forest type on microbial nutrient relationships in tropical mangrove sediments. *Journal of Experimental Marine Biology and Ecology* **171**, 201-223.

Anderson, F.O. & Jensen, H.S. 1992 Regeneration of inorganic phosphorus and nitrogen from seston in a freshwater sediment. *Hydrobiologia* **228**, 71.

Badarudeen, A., Padmalal, D. & Sajan, K. 1998a. Organic carbon and total phosphorus in the sediments of some selected mangrove ecosystems of Kerala. *Journal of Geological society of India* **51**, 679-684.

Badaruddin, A., Sakkir, S. & Sajan, K. 1998b Distribution of Na and K in the sediments of Veli, Kochi and Kannur mangroves. *Indian Journal of Marine Science* **27**, 253-255.

Basha, S.C. 1991 Distribution of Mangroves in Kerala. *Indian Forester* **117**, 439-448.

Bava, K.A. & Seralathan, P. 1998 Interstitial water and hydrochemistry of a mangrove forest and adjoining water system, south west coast of India. *Environmental Geology* **38**, 47-52.

Bonanni, P., Caprioli, R., Ghiara, E., Mignuzzi, C., Orlandi, C., Paganin, G. & Monti, A. 1992 Sediment interstitial water chemistry of the Orbetello lagoon (Grosseto, Italy): nutrient diffusion across the water sediment interface. *Hydrobiologia* **235**, 553.

Boto, K.G. 1988. The phosphorus cycle. In *Mangrove Microbiology* (Agate, A.D., Subramanian, C.V. & Vannucci, M., eds). UNDP/UNESCO Regional Project (RAS/86/1988), New Delhi, pp. 85-100

Boto, 1992 Nutrients and mangroves. In *Pollution in tropical aquatic systems* (Connell, D.W., Hawker D.W., eds). CRC press, Boca Raton, Fl, pp. 129-145.

Boto, K.G., Bunt, J.S. 1982 Carbon export from mangroves. In *The cycling of carbon, nitrogen, sulphur and phosphorus in terrestrial and aquatic ecosystems* (Galbally, I.E. & Freney, J.R., eds). Australian Academy of Sciences, Canberra, pp. 105-110.

Boto, K.G. & Wellington, J.T. 1988 Seasonal variations in concentrations and fluxes of dissolved organic and inorganic materials in a tropical, tidally dominated mangrove water- way. *Marine Ecology Progress Series* **50**, 151-160.

Chale, F.M.M. 1993 Degradation of mangrove leaf litter under aerobic conditions. *Hydrobiologia* **257**, 177-183.

Dagar, J.C. 2000 Biodiversity of saline habitats. In *Environment biodiversity and conservation* (Khan, M.A. ed.) APH Publishing Corporation, Ansari Road, Darya Ganj, pp. 135-170.

Duke, N.C. 1990 Morphological variation in the mangrove genus *Avicennia* in Australia: systematic and ecological considerations. *Australian Systematic Botany* **3**, 221-239

Eong, C.J. 1993 Mangroves- a carbon source and sink. *Chemosphere* **27**, 1097-1107.

Froelich, P.N. 1988 Kinetic control of dissolved phosphate in natural rivers and estuaries: A primer on the phosphate buffer mechanism. *Limnology and Oceanography* **33**, 649-668.

Hakanson, L. & Jansson, M. 1983 Principles of Lake Sedimentology. Springer-Verlag, Berlin, 316 pp.

* Heald, E.J. 1969 The production of organic detritus in a south Florida estuary. *Ph.D. Dissertation, University of Miami.*

Ingraham, J. L., Maaloe, O. & Neidhardt, F. C. 1983 Growth of the Bacterial cell, Sinauer, Sunderland, 435 pp.

Kaly, U.L., Eugelink, G. & Robertson, A.I. 1997 Soil conditions in damaged North Queensland mangroves. *Estuaries* **20**, 291-300.

Karim, A. 1991 Environmental factors and the distribution of mangroves in Sunderbans with special reference to *Heritiera fomes Buch.-Ham.* Ph.D Thesis, Botany Department, University of Calcutta, 230 pp.

Khushoo, T.N. 1986 Presedential address of 63rd session of Indian Science Congress Association, New Delhi.

Krishnamurthy, K. & Jayaseelan, M.J. 1983 The Pichavaram (India) mangrove ecosystems. *International Journal of Ecology and Environment Science* **9**, 79-85.

Krom, M.D., Berner, R.A. 1981 The diagenesis of phosphorus in a near shore marine sediment. *Geochimica et Cosmochimica Acta* **45**, 207-216.

Kumar, R.S. 1998 A critique on the occurrence and distribution of macrozoobenthos in a traditional prawn field and adjacent mangroves in Cochin backwaters. *Journal of Marine Biology Association of India* **40**, 11-15.

Kumar, R.S. & Antony, A.1994 Impact of environmental parameters on polychaetous annelids in the mangrove swamps of Cochin, south west coast of India. *Indian Journal of Marine Science* **23**, 137-142.

Lee, S.Y. 1995 Mangrove outwelling: a review. *Hydrobiologia* **295**, 203-212.

*Lijklema, L. 1976. The role of iron in the exchange of phosphate between water and sediments in interactions between sediments and fresh water. *Symp.Proc.Junk.* pp. 313-317.

Morell, J.M. & Corredor, J.E.1993 Sediment nitrogen trapping in a mangrove lagoon. *Estuarine, coastal and shelf science* **37**, 203-212.

Muraleedharan, C.M. & Rajagopalan, M.S. 1993 Colonization of the mangrove *Acanthus illicifolius* the sea accreted regions near Cochin. *Mariculture Research Under the Post Graduate Programme in Mariculture -Part - 2*

(Rengarajan, K., Noble, A., Prathibha, Kripa, V., Sridhar, N, Zakhriah, M., eds). Cochin, India, **53**, 39-47.

Nasker, K.R. & Guha Baskhi, D.N. 1987 *Mangrove swamps of the Sunderbans*, Naya Prakash, Calcutta.

*Odum, W.E. 1970 Pathways of energy flow in a South Florida estuary. *Ph.D. Dissertation, University of Miami.*

Raghunadh, K., Sushadevi, K.P. & Sajan, K.P. 1995 Texture of Tellichery mangrove sediments, south west coast of India. *Indian Journal of Marine Science* **24**, 91-93.

Ramachandran, K.K., Mohanan, C.N., Balasubramaniam, G., Johnson K. and Jessy T. 1986 The mangrove ecosystems of Kerala its mapping, inventory and some environmental aspects. *Progress report. November 1985 to November 1986. State Committee on Science, Technology and Environment*, Trivandrum.

Ramachandran, K.K. & Mohanan, C.N. 1987 Perspectives in management of mangroves of Kerala with special reference to Kumarakom mangroves: a bird sanctuary. *Proceedings of the National seminar on estuarine management, June, 1987*, Trivandrum. pp 252-257.

Saenger, P. Hegerl, E.J. & Davy, J.D.S. 1983. Global Status of Mangrove Ecosystems. *The Environmentalist* **3**,1-88.

*Soto, R. & Corrales, L. F. 1987 Variacon de algunas charcterristica foliares de Avicennia germinas (L.) L. en un gradiente climatico y salinidad. *Revista de Biologia Tropical* **35**, 245-256.

Subramanian, V. 2000 Impact of socio-economic development on the mangrove ecosystems of Cochin in Kerala. In *Environmental Problems of Coastal Areas in India* (Sharma, V.K., ed). New Delhi, India Bookwell Publishers pp. 191-200.

Thomas, G. & Fernandez, T.V. 1993 A comparative study on the hydrography and species composition in three mangrove ecosystems of Kerala, south India. *Journal of Ecobiology* **5**, 181-188.

Thomas, G. & Fernandez, T.V. 1997 Incidence of heavy metals in mangrove flora and sediments in Kerala, India. *Hydrobiologia* **352**, 77-87.

Valiela, I. 1984 Marine Ecological Processes, Springer Verlag, New York, 546 pp.

Walsh, G.E. 1974 Mangroves: a review. In *Ecology of Halophytes* (Reimold, R.J. & Queen, W.H., eds). Academic Press, New York, pp. 51-174.

Woodroffe, C.D. 1985 Studies of a mangrove basin, Tuff Carter, New Zealand. III. The flux of organic and inorganic particulate matter. *Estuarine, coastal shelf science* **20**, 447-462.

Chapter 2

MATERIALS AND METHODS

2.1 DESCRIPTION OF THE STUDY AREA

The areas of investigation were the mangrove-fringed canals in the Cochin backwaters, a major estuary on the south west coast of India. Cochin backwaters situated at the tip of the northern Vembanad lake is a tropical positive estuarine system extending between 9° 40' and 10° 12N' and 76° 10' and 76° 30É with its northern boundary at Azhikode and southern boundary at Thanneermukkam bund. The lake has a length of 80 km and the width varies from 500m and 4000 m. Water from two major rivers viz., Periyar and Muvattupuzha drain into this estuary, whereas Thannermukkam bund regulates the flow from four rivers namely Meenachil, Manimala, Achenkovil and Pamba. During south-west monsoon, the estuary is virtually converted into a freshwater basin even in areas around barmouth where saltwater penetration occurs below 5 m depth only. The two mangrove locations on Vypeen island which were sampled experience only a weak tidal flow. The narrow creeks had with obstructions that restricted the free flow of water. Semidiurnal tidal range of Cochin estuary has been reported to be 1m. No perceptible tidal range was observed in the two selected mangrove locations in Vypeen island.

Around Cochin, good mangrove formation are seen in areas like Vypeen, Kannamali, Maradu, Elamkulam and Vallarpadam. Small patches and isolated strands are seen at Kumbalam, Nettoor, Panangad, and Kundannur. Most extensive and highly developed mangroves are found on Vypeen island. Among the flora *Rhizophora mucornata* is the most dominant species, followed by *Avcennia officinalis* and *Avcennia ilicifolius. Rhizophora mucornata* is the largest species which grows up to nine metre height. The exact nature of early mangrove vegetation on the banks of Vembanad lake is not fully known. This is because the vegetation has undergone considerable disturbances during the last few years due to human interferences. They have been destroyed and used for fuel, and the land has been used for paddy cultivation, prawn culture, coconut plantation and other purposes. The destruction of mangrove plants leads to soil erosion and silting in Cochin backwaters. When accretion along the coast takes place, colonization by mangroves is rapid. In places devoid of human interferences were not affected, colonization of mangrove takes place along some stretches of Cochin backwaters.

Three important mangrove locations around Greater Cochin were sampled (Fig.2.1). Station 1 is situated between latitudes 9°59' North and longitude 76°14' East and is located at Murikkumpadam in Vypeen island. In Vypeen, the areas bordering the canals are densely populated. Station 1 located near the terminus of a 5-7 feet wide canal. It is about 1km distant from the adjoining estuarine water body. It is characterized by a community of dwellings and therefore prone to sewage inputs. Tidal amplitudes do not vary more than a feet. Along the water course a few bushy clumps of *Acanthus ilicifolious* and few relic stands of *Avcennia* could also be seen. *Rhizophora* existed as isolated individuals. No submerged floras were noticed at any part of the year.

Station 2 is situated between latitudes 9° 58' and North longitude 76°11' East and is located at Puthuvypu on the southern tip of the Vypeen Island located on the North Western Bank of Cochin bar mouth. This Station represents a carefully preserved mangrove habitat inside the premises of Kerala Agricultural University campus. The mangrove vegetation consisted primarily of *Avcennia* species which is growing gregariously on the Western side with *Rhizophora spp.*and *Bruguiera spp.* constituting occasional growth. Effective area under mangrove vegetation is about 10 ha.

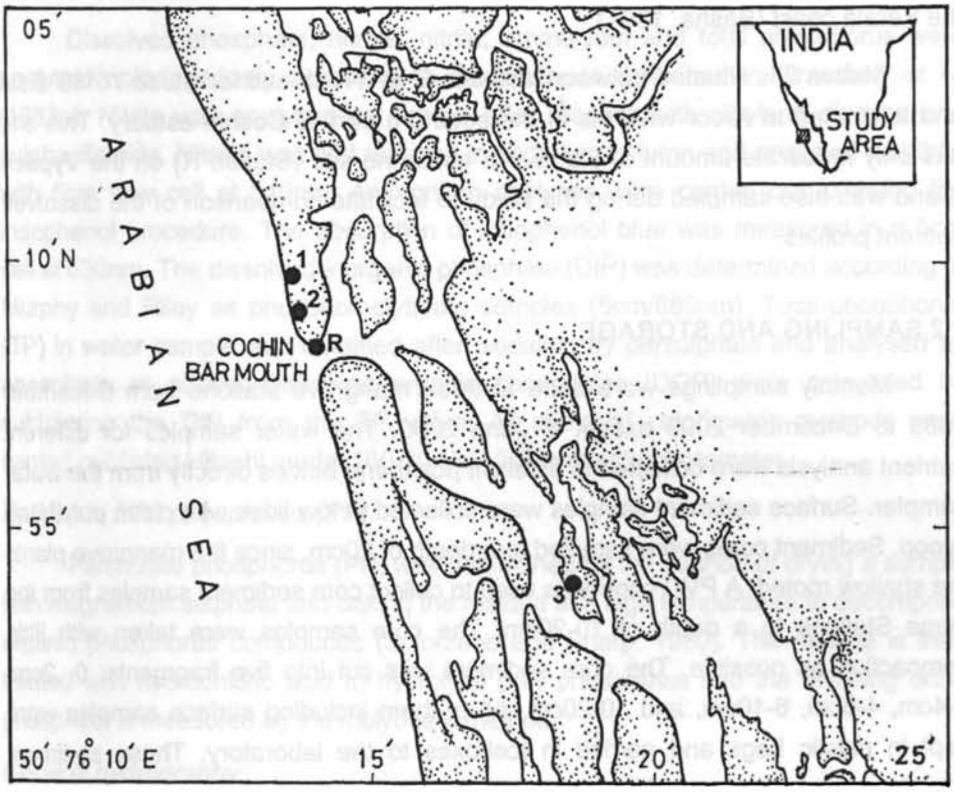


Fig. 2.1 Map of Cochin estuary showing location of sampling sites

The sampling site was located at the terminus of the canal, which extend for about 1.5km from open waters into the Kerala Agricultural University campus. An extent of 10 ha of land supporting mangroves in patches exists at Puthuvypu. This forms part of Vypeen Island having 300 ha in extent. The entire area of 101 ha is marshy containing natural basins; sand pits, crevices and canals support good mangrove vegetation. This area is being used by the university for research in the field of brackish water fish farming. The land is regularly inundated by the tidal rhythm of Cochin bar mouth and the tidal waters bring in lot of fish seed of commercially important species like *Mughil cephalus, Chanos, Lates calcarifer, Eleutheronema tetradactylum,* and prawns such as *Penaeus indicus and Penaeus mondon* (Purushan, 1989). Since there is not much destruction from outside the succession of mangrove vegetation is progressing unhindered. There is even some trial of artificial regeneration of *Rhizophora spp.*and *Bruguiera spp.*in order to speed up the growth of mangroves. This is the biggest mangrove area available in the Kerala coast (Basha, 1991).

Station 3 is situated between latitudes 9°54' North and longitude 76°18' East and is located at Aroor which is in the southern part of Cochin estuary. This site has only moderate amount of plants. An estuarine site (Station R) on the Vypeen Island was also sampled during the study to facilitate comparison of the dissolved nutrient profiles.

2.2 SAMPLING AND STORAGE

Monthly samplings were done at three mangrove stations from December 1999 to December 2000 except in June 2000. The water samples for different nutrient analysis were collected in different polythene bottles directly from the water sampler. Surface sediment samples were collected at low tides with clean polythene scoop. Sediment cores were sampled to a depth of 20cm, since the mangrove plants are shallow rooted. A PVC corer was used to collect core sediment samples from the same Stations to a depth of 10-20cm. The core samples were taken with little compaction as possible. The core sediment was cut into five fragments: 0- 2cm, 2-4cm, 4-6cm, 6-10cm, and 10-20cm. All of them including surface samples were kept in plastic bags and carried in iceboxes to the laboratory. These sediment samples were homogenized and kept deep frozen until analysis.

The dissolved ammonium analyses were done without delay. 50ml of the water samples were preserved by adding 2ml of phenol reagent in the same vessel in which the analyses were carried out. Nitrite analyses were also done within a day. The water samples for analysis of dissolved phosphate were filtered using 0.45µm-poresize glassfibre filter paper (Whatman GF/F) and stored frozen till analyses. The filter papers were stored for the analysis of total particulate phosphorus. The water samples of total phosphorus, nitrate, nitrite etc were kept without filtration.

2.3 ANALYTICAL PROCEDURE

All glass wares used in the analysis were washed, soaked in dilute hydrochloric acid and rinsed with distilled water. All reagents used were of analytical grade, reagents and standard solutions were prepared with Milli-Q water.

Dissolved nutrients

Dissolved phosphate, nitrate, nitrite, ammonium and total phosphorus were analysed colorimetrically according to the methods described in Grasshoff *et al.* (1983a). Nitrite was analysed as azodye after reaction with ethylene diamine and sulphanilamide. Nitrate was first reduced in cadmium column and analysed as nitrite with 5cm flow cell at 540nm. Ammonium analyses were carried out following the indophenol procedure. The absorption of indophenol blue was measured in a 5cm cell at 630nm. The dissolved inorganic phosphate (DIP) was determined according to Murphy and Riley as phosphomolybdate complex (5cm/880nm). Total phosphorus (TP) in water sample was obtained after oxidation by persulphate and analysed as phosphate as above. Dissolved organic phosphates (DOP) were calculated by subtracting the DIP from the TP value. All standard colorimetric methods were carried out using Hitachi model 160-20 UV-Visible spectrophotometer.

Paticulate total phosphorus (PP)

Particulate phosphorus (PP) was determined by the method of drying a sample with magnesium sulphate and baking the residue at a high temperature to decompose organic phosphorus compounds (Solorzano and Sharp, 1980). The residue is then treated with hydrochloric acid to hydrolyze poly phosphates and the resulting ortho phosphate is measured by the molybdate method.

General hydrography

Water samples were analysed for general hydrographic parameters like salinity and dissolved oxygen, following the standard methods (Grasshoff *et al.*, 1983b, 1983c). pH was measured using a portable pH meter and temperature by a sensitive thermometer.

Total suspended solids (TSS)

A known volume of water was filtered through a Whatman GF/F 25mm filter paper held in a filter holder. All filter papers were pre ashed (450°C for 4 hours), pre weighed and held in separate numbered petri dishes. The filter papers containing suspended matter were dried at 59°C in an oven for 24 hours.

Particulate organic Carbon (POC)

POC was determined by the wet digestion of the filter paper containing particulate matter, using acid dichromate followed by titration to determine the concentration of carbon (Parson *et al.*, 1984).

Moisture percentage in sediments

Moisture content was estimated by drying approximately 10g of homogenized wet sediment sample in an oven at 90°C for 48 hours. The difference in weights gave the percentage of moisture in the sediment samples.

Total Organic Carbon in sediment

The organic carbon content in the sediment was estimated by the dichromate method (Walkley and Black, 1934) as modified by El Wakeel and Riley (1957).

Total Nitrogen in sediment

Total nitrogen was measured by Kjeldahl method (De Lange *et al.*, 1992). About 1gm finely ground air-dried sediment samples were digested with 6ml of concentrated sulphuric acid and catalyst (Mix katalyser, Merck). When the colour of the solution changes to white greenish it was centrifuged and the clear centrifugates and washings were transferred to a sample holder connected to the steam distillation unit. The ammonia was distilled into 1% boric acid after adding 25ml of 10 N KOH. The distilled ammonium was determined by back titration with 0.1N hydrochloric acid. The total nitrogen (TN) concentrations were determined from the equivalents of ammonia obtained in boric acid.

Exchangeable ammonium and nitrate in sediments

Exchangeable ammonium and nitrate are defined as the amount of ammonium and nitrate extracted by a 2N KCl solution. Analyses of exchangeable inorganic nitrogen (ammonium and nitrate) were carried out on wet sediment sample. The extraction of the exchangeable fraction of inorganic nitrogen including ammonium, and nitrate were done using a solution of 2N KCl (Agemian, 1997). This method involves the shaking of a wet sediment sample in a centrifuge tube with 2N solution of KCl at room temperature for an hour. A portion of the centrifugate was analyzed for ammonium, colorimetrically, using the indophenol blue method, in which it reacts with phenate in the presence of hypochlorite and nitroprusside as catalyst. Another portion was analyzed for nitrate by reduction to nitrite by the method of spongy cadmium (Jones, 1984). The nitrite was determined colorimetrically by reacting with sulphanilamide under acidic conditions to form a diazo compound that couples with N-1 (Naphthyl)–ethylene diamine dihydrochloride to form reddish purple azodye .

Grain size analysis

Texture analysis was carried out by sieving and pipette analysis. A known weight of wet sediment was dispersed overnight in .025N sodium hexameta phosphate (Calgon) solution. The sand fraction was separated from the dispersed sediments by wet sieving using a 230 mesh (63µm) ASTM sieve (Carvar, 1971). The filtrate containing silt and clay fraction was subjected to pipette analysis (Krumbein and Pettijohn 1938; Lewis 1984).

Total iron in sediments

The oven dried sediment samples were ground in an agate mortar and 0.5g aliquots were weighed into beakers for estimation of total metal. Each sample was carefully digested with 10 ml of an acid solution ($HClO_4$, HNO_3 and HCl in the ratio 1:1:3) at 90°C until complete digestion and evaporated to incipient dryness. After cooling, the sides of the beaker were rinsed with Milli-Q water, centrifuged and the centifugate made up to 50 ml. Metal concentrations in the solution were determined by atomic absorption spectrophotometry (Perkin-Elmer 3110 AAS), calibrated using secondary standard solutions prepared by appropriate dilution of $1000 mgL^{-1}$ standard solutions (Merck). Analytical blanks were prepared using the same procedures and reagents.

Chemical fractionation of phosphorus

Phosphorus fractionation was performed by sequential extraction with chelating compounds (Golterman, 1996). This procedure was slightly modified in accordance with validation of different fractionation procedures by Pardo *et al.* (1998). The different fractions extracted were water exchangeable inorganic phosphate (W-IP), water exchangeable organic phosphate (W-OP), iron bound inorganic phosphate (Fe-IP), iron bound organic phosphate (Fe-OP), calcium bound inorganic phosphate (Ca-IP), calcium bound organic phosphate (Ca-OP), acid soluble organic phosphate (Ac-OP), alkali exchangeable organic phosphate (Alk-OP) and residual organic phosphate (ROP). The extractions were carried out according to the scheme depicted in Fig. 2.2. All organic phosphates were obtained as the difference of total phosphate (TP) and dissolved inorganic phosphate (DIP) in the extract.

Phosphorus Extraction Scheme

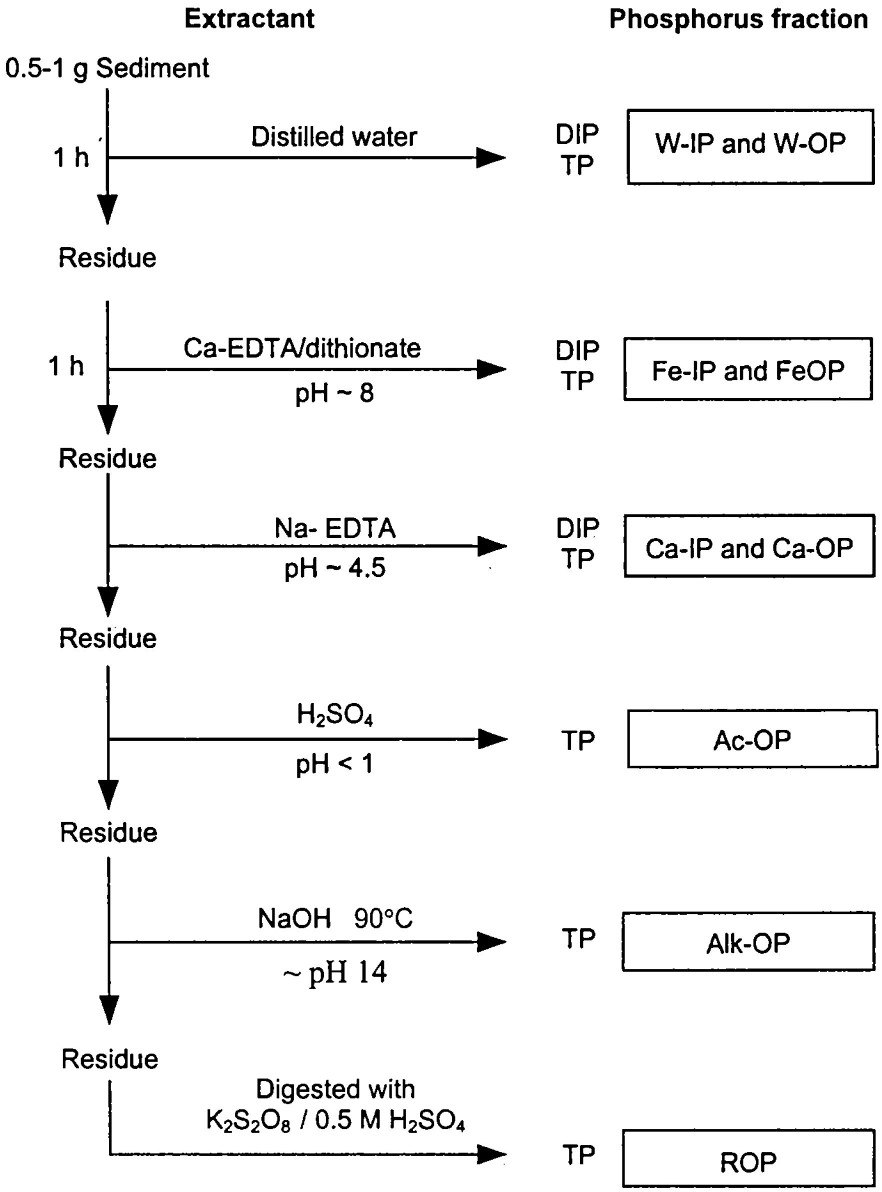


Fig. 2.2 Phosphorus fractionation scheme illustrating the sequential extractions

Data analysis

Monthly variations of dissolved nutrients and general hydrographic parameters are presented with a view to find the variations of these parameters within the Stations. Spatial variations are discussed mainly using seasonal distributions which are presented in tables and graphs. The three seasons categorized in this study are pre-monsoon (Feb-May), monsoon (June-Sept) and post-monsoon (Oct-Jan) unless otherwise specified. Correlation analysis was carried out to find the influence of various hydrographic parameters on the distribution of dissolved nutrient concentrations (Snedecor and Kocharan, 1962). Comparison of dissolved nutrients among stations and seasons was carried out using two-way analysis of variance (ANOVA). The nutrient profile of surface and core sediments are illustrated as annual mean variations as well as seasonal variations. The annual mean variations of each parameter was used to compare the spatial variation, while seasonal variations are depicted in a view to identify within the system variations. Comparison of nutrient concentrations between stations, seasons and sediment depth were carried out using three-way anlysis of variance. ANOVAs were followed by a least significant difference test (LSD) if a significant temporal or spatial effect was found. All statistical analyses were conducted as described by Freud and Wilson (1992).

REFERENCES

Agemian, H. 1997 Determination of nutrients in aquatic sediments. In *Manual of physico-chemical analysis of aquatic sediments* (Murroch, A., Azcue, J.M. & Mudroch, P., eds). CRC Lewis publishers, London.

Basha, S.C. 1991 Distribution of Mangroves in Kerala. *Indian Forester* **117**, 439-448.

*Carvar, R.E. (Ed) 1971 In *Procedures in sedimentary petrology.* Wiley-Interscience, New York, 427-428.

De Lange, G.J. 1992 Distribution of exchangeable, fixed, organic and total nitrogen in interbedded turbiditic / pelagic sediments of the Madeira Abyssal Plain, eastern North Atlantic. *Marine Geology* **109**, 95-114.

*El Wakeel, S. K., Riley, J. P. 1957 The determination of Organic Carbon in marine muds. *J. Con. Int. Pour. Expior. Mer.,* **22** 180-183.

Freund, R.J. and Wilson, W.J. (Eds) 1993 The Analysis of Variance. In *Statistical methods* Academic Press, INC.pp. 203-260.

Golterman, H.L. 1996 Fractionation of sediment phosphate with chelating compounds: a simplification, and comparison with other methods. *Hydrobiologia* **335**, 87-95.

Grasshoff, K., Ehrhardt, M. & Kremling, K. (Eds) 1983a Determination of nutrients. In *Methods of sea water analysis*. Verlag Chemie, Weinheim, 125-187.

Grasshoff, K., Ehrhardt, M. & Kremling, K. (Eds) 1983b Determination of Salinity. In *Methods of sea water analysis*. Verlag Chemie, Weinheim, 31-58.

Grasshoff, K., Ehrhardt, M. & Kremling, K. (Eds) 1983c Determination of oxygen. In *Methods of sea water analysis*. Verlag Chemie, Weinheim, 61-72.

Jones, M.N. 1984 Nitrate reduction by shaking with cadmium. *Water Research* **18**, 643-646.

Krumbein, W. C., Pettijohn, F. J. (Eds) 1938 In *Manual of sedimentary petrography.* Appleton Century Crafts Inc., NewYork, 1-549.

Lewis, D.W. (Ed) 1984 In *Practical Sedimentology* Hutchinson Ross, Stroudsburg, Pensylvania, 1-229.

Pardo, P., Lopez-Sanchez, J. F., Rauret, G. 1998 Characterisation, validation and composition of three methods for the extraction of phosphate from sediments. *Analytica Chimica Acta* **376**, 183-195.

Parsons, D.W., Maita, Y. and Lalli, C.M. 1984 A manual of chemical and biological methods for sea water analysis, Pergamon Press. 173p

Purushan, K.S. 1991 Prospects of fish production from mangrove ecosystems. *Fishing Chymes* **June**, 24-26.

Snedecor, G.W. & Cocharan, W.G. (Eds) 1962. Statistical methods, Oxford and IBH Publishing Company, Culcutta. pp. 339

Solorzano, L. & Sharp, J.H. 1980 Determination of total dissolved phosphorus and particulate phosphorus in natural waters. *Limnology and Oceanography* **25**, 754-758.

* Not referred in original

Chapter 3

DISTRIBUTION OF NITROGEN AND PHOSPHORUS IN THE WATER COLUMN

3.1 INTRODUCTION

Nutrients in biological system

A nutrient element is defined as one that is involved functionally in the processes of living organisms (Parsons, 1975). Traditionally, the term has been applied almost exclusively to phosphate, nitrate, and silicate. Phosphorus one of the important nutrient, brought into the aquatic system through weathering of minerals. Phosphorus inputs can increase the biological productivity of surface waters. The mean phosphorus content of sea water has been estimated as 2 $\mu molL^{-1}$ (Grasshoeff *et al.*, 1983). Primary production appears to be phosphorus limited in many tropical estuarine and coastal systems. Very high nutrient level may build up in esturies and land locked bodies of water as a result of discharge of sewage and of effluents containing detergents rich in polyphosphates. Increased inputs of nitrogen and phosphorus usually result in higher primary production that can cause eutrophication problems. Advanced eutrophication of surface water leads to problems with its use for fisheries, recreation, industry or drinking because of the increased growth of undesirable algae and aquatic weeds and oxygen shortages caused by their senescence and decomposition. Several outbursts of phytoplankton, were reported around Indian coast which often reached bloom proportion (Qasim, 1972).

Nitrogen is brought to the aquatic system, from fluvial and atmospheric sources, by diffusion from sediments and in situ nitrogen fixation. Ammonia, nitrite and nitrate are the three principal dissolved inorganic forms of nitrogen in coastal systems with nitrate occurring in highest concentration. Nitrite occurs in aquatic system as an intermediate compound in the microbial reduction of nitrate or in the oxidation of ammonia. It also comes into the water when phytoplanktons are fed luxuriantly by nitrate and phosphate. The natural level of nitrite in seawater is very low <0.1μmolL^{-1}. But where anoxic condition occurs a high nitrite concentration may occur >2 μmolL^{-1} together with low levels of dissolved oxygen as given by Grasshoeff *et al.* (1983). High nitrite values may also indicate polluted waters in estuaries. Nitrate is considered to be the thermodynamically stable product of inorganic nitrogen in the presence of oxygen in seawater. In many sea areas nitrate is considered to be the micronutrient controlling primary production in the euphotic surface layer. The concentration of nitrate in these layers is governed by the advective transport of nitrate into surface layers, microbial oxidation of ammonia and the uptake by primary producers. If light penetration into the water is sufficient, the uptake rate is much faster than the processes transporting nitrate into the surface layers. Therefore, the nitrate concentration in most ocean surface waters is close to zero.

The amount of ammonium (NH_4^+) rarely exceeds 5 μmolL^{-1} in oxygenated unpolluted water. But in anoxic deep stagnant water, such as in the Black sea, the amount of ammonium-N can be as high as 100 μmolL^{-1}. Since acid-base pair, NH_4^+ -NH_3 has a pKa of about 9.3, the ammonium ion is the dominant species in natural waters with a pH of 8.2 or less. It is the NH_3 form that is toxic to fish and other marine organisms and not the NH_4^+ ion. The concentration of ammonium in the aquatic system shows considerable variations and can change rapidly. Ammonium is found to be the abundant form in surface layers after a period of productivity when the phytoplankton blooms were removed the greater part of nitrate and phosphate. In the assimilation processes of phytoplankton ammonia is preferentially used for synthesizing protein. When nitrate is incorporated it must first reduced to ammonia before it can be transferred into aminoacid compounds. The organic nitrogen compounds resulting from decaying organisms and those excreted by plants and animals are rapidly broken down to ammonia by various species of proteolytic bacteria. When organisms sink below euphotic zone, they decompose as a result of oxidative bacterial action releasing nitrate and phosphate. As the water approaches anoxic condition, bacteria use the nitrate ions to continue the oxidation process. This denitrification leads to the production of molecular nitrogen and ammonia. Interaction between nitrate and ammonia produces more nitrogen gas. At the onset of sulphate reduction, ammonia and hydrogen sulphide are often produced, some times in high concentration.

There are a variety of forms of phosphorus in seawater; this includes dissolved inorganic phosphate (predominantly orthophosphate ions) organic phosphates and particulate phosphorus. Phosphate is also released back into the water column during the oxidative destruction of organic tissues. Most of the regeneration of phosphorus probably takes place via bacterial decomposition, which leads to the formation of orthophosphates, although chemical decomposition may occur. The dissolved organic nitrogen and dissolved organic phosphorus also constitute important sources of nitrogen and phosphorus in the water column. The total dissolved organic nitrogen and dissolved organic phosphorus concentration are frequently several times higher than dissolved inorganic concentrations, especially in marine waters (Wells *et al.*, 1991). These nutrients are constantly removed from solution by organisms, mainly phytoplankton, during primary production in the euphotic zone.

The phytoplankton are autotrophs, important members include diatoms, cocolithophores, silicoflagellates and dinoflagellates, all of which are eukaryotes. The only major group of autotrophic prokaryotes is the cyanobacteria. They are unique because they can fix gaseous nitrogen, whereas other phytoplankton can utilize only already fixed forms of nitrogen. The photo- autotrophic biomas is the most important primary source of organic carbon in the aquatic system, and primary production is the initial stage in the marine food production. This subsequently involves a number of trophic levels in which herbivorous zooplankton consumes the phytoplankton during secondary production, which in turn is fed upon by carnivorous zooplankton and fish species.

The process of photosynthesis, in which organic compounds are synthesized from inorganic constituents present in seawater during the growth of phytoplankton, is usually termed as primary production. Primary production controls are, light availability, nutrient availability and zooplankton grazing. The limiting factors for primary production are therefore the critical minimum of these factors. However the concept of limiting nutrient strictly refers only to new production, because productivity can be maintained in the presence of low nutrient concentration by recycling. Nitrate has usually been considered to be the most important limiting nutrient for primary production in the marine environment. In certain oceanic region phosphate can act as limiting nutrient for phytoplankton growth.

Nutrients in mangrove ecosystem

The waters of mangrove swamp ingress and egress with the tides with an overall and gradual progressive displacement towards the sea. This process of ebb and flood gives the waters a long residence in the swamp, the duration of which varies with tidal amplitude, coastal profile and amount of land runoff. Sea water brings with it nutrients of a different kind than those usually dissolved in land run-off thus input supplement each other: Nutrients are usually not a limiting factor to productivity in mangrove waters. The waters that flow out of the mangroves have characteristics peculiar to them, acquired during their long residence in the swamps. They contain a large amount of dissolved organic matter in the form of nutrient salts, like nitrates, nitrites, and phosphates also silicates. Mangrove ecosystem produces large amount of litter in the form of falling leaves, branches and other debris. Decomposition of the litter contributes to the production of dissolved organic matter and the recycling of nutrients both in the forest and in adjacent habitats. The organic detritus and nutrients potentially enrich the coastal waters and ultimately, support fishery resources. The contribution of mangroves could be particularly important in clear tropical waters where nutrient concentrations are normally low.

The importance of mangroves in sustaining productivity in tropical ecosystem, was established by coupling of mangrove forest and aquatic primary productivity (Rivera-Monroy, *et al.*, 1998) and opined that the surface mangrove water could potentially stimulate aquatic primary productivity throughout the year. In many tropical mangrove systems complex organic compounds are quantitatively released during decomposition of mangrove leaf litter. Approximately 30-50% of the organic matters in mangrove leaves are leachable water-soluble compounds such as tannins and sugars (Cundell *et al.*, 1979). High concentration of dissolved organic material exported from mangrove ecosystems may be a key factor supporting phytoplankton growth. Twilley (1985) showed leaching of dissolved organic carbon from mangrove leaf litter provided dissolved organic carbon to the surface of the basin forest and later exported during rainfall.

The mangrove fringe forest in a lagoon was shown to be an area of active nutrient transformation (Rivera-Monroy *et al.*, 1995). An export of the dissolved inorganic nitrogen from the creek water was found, it was transformed to organic nitrogen and the forest supplied particulate nitrogen mostly to the creek. Thus, the fringe mangrove forest in Estero Pargo (Mexico) acts as a sink of inorganic nitrogen and as a source of dissolved and particulate nitrogen. Export of nitrogen from the forest coincides with the high net aquatic primary production rates obtained for the same months in Estero Pargo indicating a direct potential relationship. The uptake of inorganic nitrogen from tidal waters within mangrove ecosystem does not necessarily represent a nitrogen sink via denitrification, but retention of nitrogen in mangrove sediments (Rivera-Monroy and Twilley, 1996). In Matang Mangrove estuary (Malaysia) the spring tide concentration of ammonium, silicate and phosphate concentration were higher than those in the neap tide which suggest that these nutrients are flushed from the mangrove area by the inundation and tidal mixing of spring tide (Tanaka and Choo, 2000). Nutrient concentration in creek water were found higher than those of estuarine water, indicating the nutrient outwelling from the mangrove swamp and ammonium regeneration from mangrove litter in the creek sediments by the same authors. Matang mangrove forest is a Riverine Forest type mangrove (Wolanski *et al.*, 1992). The eastern Brazilian shelf is bordered by small river mangrove systems. An important fraction of DOP and DON present in adjacent waters are supplied by river-mangrove systems (Ovalle *et al.*, 1999). A comparison of the mangrove waters of the United Arab Emirates and the nearby creek waters, showed a higher nitrogen: phosphorus: silicon ratio in mangrove creek water (Shriadah, 2000). Strong outwelling of nutrients and organic matter was measured and found in Braganca (North Brazil), exceeding that of other mangroves in the world (Dittmar and Lara, 2001). In a study which compares the benthic nutrient pools and rates of dissolved nutrient exchange between the forest floor and tidal waters in Hinchinbrook island in Queensland, Australia found that a large proportion of nutrients are tied up in below- ground biomass, the dissolved nutrient pools and flux are closely linked to plant assimilation mechanism and to mineralisation processes by microbes. These nutrient cycling process are highly dynamic and leading to net import of dissolved nitrogen, phosphorus and silicon to the extent that mangrove forests are a finely balanced and highly efficient sink for dissolved nutrients in this tropical ecosystem (Alongi, 1996).

The works at Pichavaram mangrove area (southeast India), have established their importance in enriching the coastal area (Kathiresan, 2000). The total phosphorus, total nitrogen and ammonia nitrogen concentration in Adayar mangrove waters showed a tidal variation with low values during high tide (Selvam *et al.*, 1994). He also found that along with the phytoplankton the mangrove plant community of the Adayar estuary may also remove large amount of inorganic nutrients which can be exported out of the estuary. The mangroves in West Bengal, Sunderbans, support the growth of rich algal communities, which provide a novel source of nutrients to the whole ecosystem. They remain in the mangrove forest subsystem as an epiphytic assemblage of algae living on the stems, pnuematophores of mangrove trees and on the surface of the sediment as epibenthic form. Besides a good number of algae remain in the water subsystem as phytoplanktors and and play a great role in the total productivity and energy flow in the system. (De *et al.*, 1987). This mangrove ecosystem harbours different types of bacteria in abundance in their vegetations, soil, water, litter etc that plays a key role in the nutrient cycle of the ecosystem (Bhowmick *et al.*, 1985). Nutrient status of the water depends on the availability of silicate (82 μgL^{-1} to 140 μgL^{-1}), phosphate (0.92 μgL^{-1} to 2.3μgL^{-1}) and nitrate (6 μgL^{-1} to 18 μgL^{-1}), which are instrumental for the total biological productivity of the system (De *et al.*, 1987).

The foregoing observations reveal the importance of nutrients in a mangrove ecosystem. Examination of the variations in concentration of nitrogen and phosphorus species in time and space can provide insight into some of the processes controlling the distribution of nitrogen and phosphorus in mangrove creek waters. The survey of general hydrographic parameters of the creek waters provides background information necessary for the study of the processes involved in the cycling of these elements in this ecosystem. Even though considerable work has been done on the distribution of nutrients in mangrove ecosystem of Indian subcontinent there is a paucity of data on the nutrient distribution in the mangrove areas of Greater Cochin.

The environmental parameters recorded may characterise the mangrove ecosystem under observation, and those values were compared with Station R (an estuarine station). The data was analysed using Analysis of Variance technique to find any significant difference between any of these mangrove stations. Two factor ANOVA without replication was used for the purpose. Wherever significance is noted the least significant difference was worked out.

3.2 RESULTS AND DISCUSSION

3.2.1 General hydrography

Salinity

Physical processes control several key biological and chemical processes in the mangroves. The trends and variation in the distribution of salinity indicate the physical processes involved and movement of water masses. The tidal circulation is the dominant cause of water movement in mangrove creek systems. The salinity values have an impact on the distribution of marine and brackish water invertebrates. The fall in salinity causes heavy precipitation, while surface drainage during monsoon interferes with the distribution of marine forms and higher salinity during pre monsoon interferes with the freshwater forms in Sunderbans, West Bengal (Chakraborthy, 1995). The ammonium nitrogen, nitrate nitrogen, and silicate silicon concentrations in mangrove forest of Matang (Malaysia) increased with decreasing salinity, showing fresh water source of these nutrients (Tanaka and Choo, 2000).

Seasonal variations of salinity in surface waters are given in Table 3.1. In mangrove-fringed creek waters, salinity values ranged between 0.96 x 10^{-3} at Station 3 (monsoon) and 31.86 x 10^{-3} at Station 2 (pre-monsoon). While at Station R, salinity values ranged between 0.96 x 10^{-3} (monsoon) and 21.70 x 10^{-3} (pre-monsoon). The annual mean values of salinity, recorded a minimum of 11.28 x 10^{-3} at Station 3 and maximum of 18.41 x 10^{-3} at Station 2. Station R recorded a mean salinity value of 11.26 x 10^{-3}. Monthly variations of salinity (Fig. 3.1) recorded higher values during February, March and April in all mangrove fringed creek waters. However a remarkable increase in salinity values were also observed during May at Station 2 and Station 3. July, August, September and October were characterized by low salinity values at all mangrove-fringed creeks.

Table 3.1 Seasonal variation of salinity ($x10^{-3}$) in surface waters

Stations	Season	Min	Max	Mean
Station 1	Pre-monsoon	10.83	28.57	22.96
	Monsoon	5.10	12.43	7.97
	Post-monsoon	8.11	26.50	18.57
	Annual mean			**16.98**
Station 2	Pre-monsoon	24.67	31.86	28.85
	Monsoon	4.78	12.74	7.75
	Post-monsoon	4.06	24.00	16.45
	Annual mean			**18.41**
Station 3	Pre-monsoon	11.95	19.89	17.31
	Monsoon	0.96	6.37	3.61
	Post - monsoon	1.16	19.00	10.97
	Annual mean			11.28
Station R	Pre-monsoon	7.65	21.70	16.84
	Monsoon	0.96	6.37	3.61
	Post - monsoon	5.50	15.99	11.46
	Annual mean			11.26

Min – minimum, Max – maximum.

The salinity values of surface water exhibited significant spatial variations. Generally higher salinities were observed at Station 1 and Station 2 during all seasons (Fig. 3.2). The salinities recorded during pre-monsoon at Station 1 and Station 2 were remarkably higher than that recorded at Station 3 and at Station R (Table 3.1). Station 1 and Station 2 are located at the head of the respective creeks. Then this upper reaches of mangrove fringed creeks might become completely isolated from the near shore zone during pre-monsoon, due to low fresh water discharge into the creek. This might resulted in the formation of salinity maximum at Station 1 and Station 2. Hence the water in the creek showed salinity greater than that of seawater. This observation is in unison with the finding of Wolanski (1989).

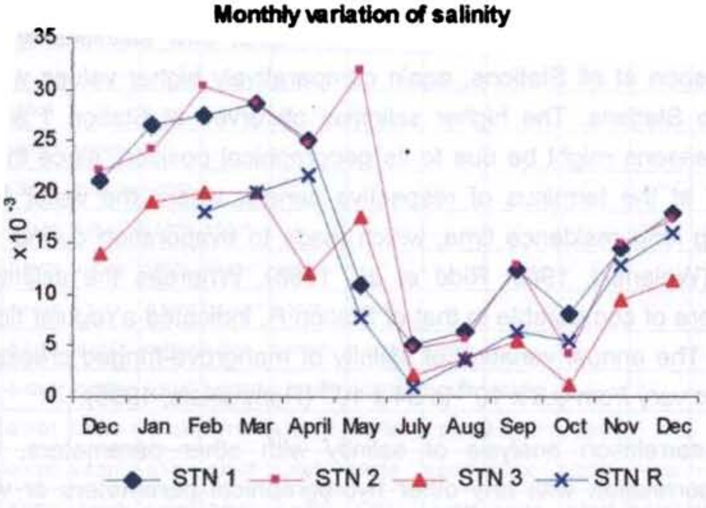


Fig 3.1Monthly variation of salinity in surface waters

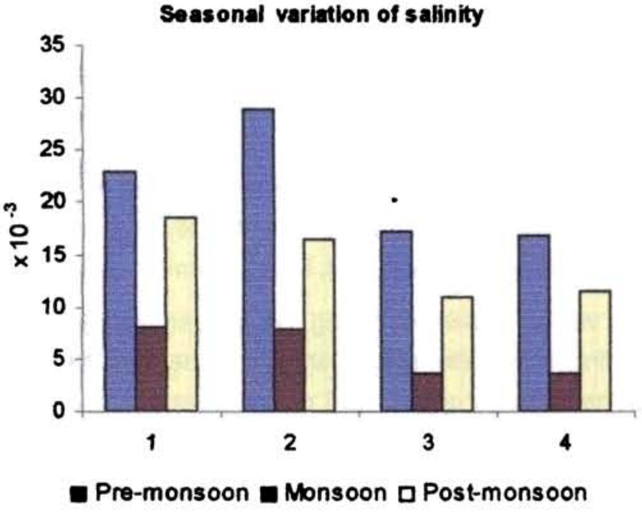


Fig. 3.2 Seasonal mean variation of salinity in surface waters

Seasonal variations of salinity in this estuary are influenced by the increased fresh water discharge during the monsoon rains. Low salinities were recorded during monsoon at all Stations, again comparatively higher values were found at the first two Stations. The higher salinities observed at Station 1 and Station 2 during all seasons might be due to its geographical position, since these stations are located at the terminus of respective canals, where the water in the creek experiencing long residence time, which leads to evaporation during dry weather conditions (Wolanski, 1989; Ridd *et al.*, 1988). Whereas the salinity values at Station 3 were of comparable to that of Station R, indicated a regular tidal influence at this site. The annual variation of salinity of mangrove-fringed creeks at Vypeen was found to vary from 0.8×10^{-3} to 34×10^{-3} (Rathnakala, 1995).

The correlation analysis of salinity with other parameters, showed no significant correlation with any other hydrographical parameters or with nutrient concentrations (Table 3.2a). At Station R, significant positive correlation was found with temperature and total phosphorus concentrations (Table 3.2b).

Two way ANOVA was used to test the significance of months and stations on salinity. The results of ANOVA are given in appendix 1 (App. 1). There is significant difference between stations ($p < 0.001$). The least significant difference (LSD) at 5% level for stations is 3.559. Significantly higher salinities were remained at Station 1 and Station 2 than at Station 3 and Station R may be due to the restricted tidal influence and evaporation. No significant difference was noticed between Station 3 and Station R, while significant difference experienced between months ($p < 0.001$). The LSD at 5% level for months is 3.559. Significantly higher salinity is found in months of March followed by February, April, May, December and January.

The salinity values observed during the present study indicate less tidal inundation at the first two Stations compared with the third Station. Also salinity variation showed the isolation of the head of the creeks (Station 1 and Station 2) during pre-monsoon due to less fresh water discharge. Station 3 found to be an open system, with a tidal impact as at Station R.

Table 3.2a Correlation matrix of general hydrographic parameters and nutrient concentrations at the mangrove fringed stations.

	Salinity	DO	pH	Temp	TSS	POC	DIP	DOP	PP	TP	Nitrite	Nitrate	Ammonium
Salinity	1.0000												
DO	-0.1194	1.0000											
pH	0.1193	0.4517*	1.0000										
Temp	0.3714	0.3477	-0.0271	1.0000									
TSS	0.2633	-0.2505	0.1640	0.0779	1.0000								
POC	0.1951	-0.3170	-0.1396	0.0205	0.4751*	1.0000							
DIP	0.1373	-0.1801	0.3112	-0.1700	0.5408**	0.3722	1.0000						
DOP	0.0318	-0.2193	-0.0055	-0.1631	0.0759	0.4694*	0.1285	1.0000					
PP	0.2052	-0.4001*	-0.0968	-0.0248	0.5079**	0.6884***	0.6338***	0.0352	1.0000				
TP	0.1844	-0.3537	0.1009	-0.1206	0.5710**	0.6624***	0.8768***	0.2395	0.9066***	1.0000			
Nitrite	0.0743	-0.1206	0.0251	-0.1196	-0.0907	0.0985	0.3756	0.0595	0.0358	0.2080	1.0000		
Nitrate	-0.1596	-0.3094	-0.4078*	-0.1062	-0.2550	-0.2706	-0.1654	-0.0700	-0.1902	-0.2049	0.0289	1.0000	
Ammonium	0.0940	-0.4625*	-0.1254	0.0715	0.4425**	0.1225	0.4542*	-0.0532	0.4957**	0.5015**	-0.0891	0.1090	1.0000

Table 3.2b Correlation matrix of hydrographic parameters and nutrient concentrations at Station R.

	Salinity	DO	pH	Temp	TSS	POC	DIP	DOP	PP	TP	Nitrite	Nitrate	Ammonium
Salinity	1.0000												
DO	-0.0695	1.0000											
pH	0.5143	-0.0865	1.0000										
Temp	0.7939*	-0.0290	0.6179*	1.0000									
TSS	0.0441	0.0242	0.4363	0.1478	1.0000								
POC	0.3297	-0.4454	0.5088	0.4456	0.5774	1.0000							
DIP	0.1446	-0.4858	-0.1406	0.3419	0.0326	0.3412	1.0000						
DOP	0.2094	0.3204	-0.0113	-0.0444	-0.2488	-0.2531	-0.3849	1.0000					
PP	0.5235	-0.2576	0.0497	0.4158	0.4372	0.3711	0.2541	-0.0715	1.0000				
TP	0.6124*	-0.2517	0.0206	0.4648	0.2980	0.3261	0.3674	0.1780	0.9355**	1.0000			
Nitrite	0.0205	-0.1243	0.2236	0.0750	0.5856	0.3149	-0.1520	-0.6576*	0.4984	0.1752	1.0000		
Nitrate	-0.3662	-0.0256	-0.5694	-0.1145	-0.0484	-0.2274	0.1832	-0.2530	0.3300	0.2137	0.2025	1.0000	
Ammonium	-0.2271	-0.5082	-0.3814	-0.2839	0.1959	0.2337	0.6852*	-0.0845	0.2072	0.3339	-0.1846	0.0948	1.0000

$p<0.05^{*}$ $p<0.01^{**}$ $p<0.001^{***}$

Dissolved Oxygen (DO)

The degree of horizontal and vertical mixing of water influences the DO concentrations in mangrove waterways. Boto and Bunt (1981) found that DO concentration in mangrove creeks dropped significantly at upstream stations due to phenolic compounds and bacterial population. DO values < 2 ppm were often recorded in blind ending creeks. High concentration of dissolved phenolic compounds leached from mangrove detritus can cause drop in lowering of oxygen concentration as they are oxidized. The larger residence time of water in the upstream sections presumably leads to higher concentration of polyphenolics and thus lower DO concentration.

Seasonal variations of DO are depicted in Table 3.3. At the mangrove locations, DO values ranged between 0.52 mlL^{-1} at Station 2 (monsoon) and 8.93 mlL^{-1} at Station 3 (pre-monsoon). At Station R the DO values vary from 0.22 mlL^{-1} to 6.99 mlL^{-1}. The annual mean DO values showed highest value (3.84 mlL^{-1}) at Station 3 and lowest (2.86 mlL^{-1}) at Station 2.

Monthly variations of DO (Fig. 3.3) showed higher values during July, August and September at all Stations except Station 2. However Station 2 recorded highest value of DO during February, March and July. A high value of DO was also observed during December at Station R (Fig. 3.3).

Table 3.3 Seasonal variation of Dissolved oxygen (mlL^{-1}) in surface waters

Stations	Season	Min	Max	Mean
Station 1	Pre-monsoon	1.64	3.59	2.60
	Monsoon	3.39	6.63	4.76
	Post-monsoon	0.69	4.82	2.36
	Annual mean			3.04
Station 2	Pre-monsoon	3.28	7.56	5.24
	Monsoon	0.52	4.08	2.30
	Post-monsoon	0.71	2.89	1.66
	Annual mean			2.86
Station 3	Pre-monsoon	1.87	8.93	3.79
	Monsoon	3.13	5.02	4.25
	Post - monsoon	1.20	5.47	3.64
	Annual mean			3.84
Station R	Pre-monsoon	2.24	3.74	2.95
	Monsoon	4.08	4.75	4.51
	Post - monsoon	0.22	6.99	3.21
	Annual mean			3.70

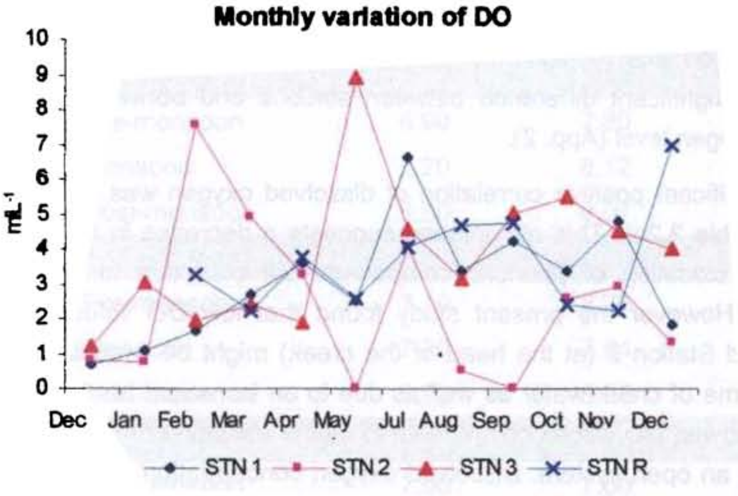


Fig 3.3 Monthly variation of dissolved oxygen in surface waters

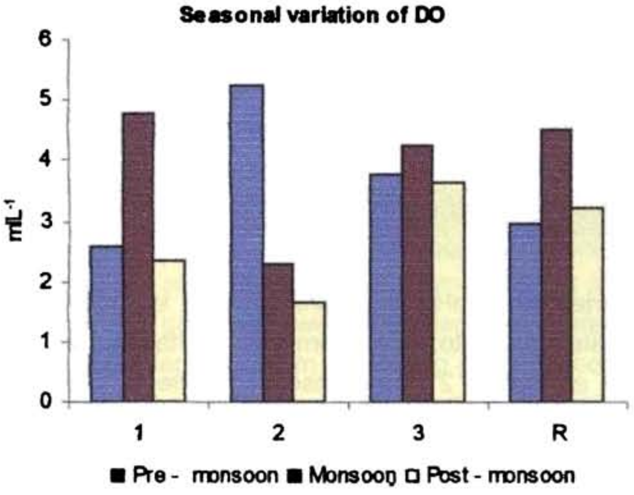


Fig. 3.4 Seasonal mean variation of dissolved oxygen in surface waters

The seasonal variations of DO (Fig. 3.4) recorded comparatively higher DO values at Station 3. Monsoon season was characterized by maximum DO at all Stations except at Station 2. However remarkably high DO value was recorded at Station 2 during pre-monsoon. The earlier studies also reported similar observation (Rathnakala, 1995). Lowest oxygen content was recorded during post monsoon season invariably at all mangrove stations. The low values of DO were found during pre-monsoon at Station R. The lower oxygen concentrations during this period might be due to high microbiological activity (Nair *et al.*, 1988). ANOVA showed no significant difference between stations and between months of the dissolved oxygen level (App. 2).

A significant positive correlation of dissolved oxygen was found with pH at Station 1(Table 3.2a). This observation suggests a decrease in DO was not only due to the oxidation of phenolic compounds but also due to some microbial processes. However the present study found that low DO values observed at Station 1and Station 2 (at the head of the creek) might be associated with large residence time of creek water as well as due to an increased bacterial population. Station 3 showed DO values comparable to that of estuarine reference Station was found to be an open system. Dissolved oxygen concentration at mangrove waters also negatively correlated with particulate phosphorus concentration and concentrations of ammonium. No significant correlation of DO concentration with any other parameters was noted at Station R (Table 3.2b).

pH

High concentration of dissolved phenolic compounds leached from mangrove detritus, can cause drop in pH. The organic matter accumulating at the sediment also causes low pH values. The higher pH in surface layer may be due to the intense photosynthesis confined to the upper layer.

Seasonal variations of pH values are depicted in Table 3.4. pH values at mangrove creek waters found to varied from 6.80 at Station 1 and Station 3 (post-monsoon) to 8.20 at Station 2 (pre-monsoon). While at Station R, pH varied between 6.94 and 8.40. The lowest and highest values of annual mean of pH values recorded were 7.42 (Station 3) and 7.64 (Station 2) respectively (Table 3.4). Similar to Station 2, a mean pH value of 7.66 recorded at Station R. The monthly variation in pH (Fig. 3.5) recorded higher values during April, May, July, October and November at all stations. At Station 2 higher pH values were observed during February and March.

Table 3.4 Seasonal variation of pH in surface waters

Stations	Season	Min	Max	Mean
Station 1	Pre-monsoon	6.90	7.80	7.20
	Monsoon	7.20	8.12	7.62
	Post-monsoon	6.80	8.07	7.53
	Annual Mean			7.49
Station 2	Pre-monsoon	7.10	8.20	7.90
	Monsoon	7.30	7.64	7.50
	Post-monsoon	6.90	8.07	7.46
	Annual Mean			7.64
Station 3	Pre-monsoon	7.00	7.60	7.33
	Monsoon	7.20	7.68	7.47
	Post - monsoon	7.10	7.93	7.30
	Annual Mean			7.42
Station R	Pre-monsoon	7.30	8.40	7.77
	Monsoon	7.10	8.24	7.58
	Post - monsoon	6.94	8.42	7.55
	Annual Mean			7.66

The high pH values were observed during monsoon at station 1and Station 3, while at Station 2 high pH values were recorded during pre-monsoon season. However Station R recorded maximum pH during pre-monsoon (Fig. 3.6). In the present study the lower pH at all Stations during certain seasons, may be attributed to the high microbial activity in the water column. Increased microbial activity decrease the pH value in surface waters (Ram and Zingde, 2000). pH values at Station 1 and Station 2 showed high variation, which may be attributed to the low pH values observed during pre-monsoon. The pH values in mangrove-fringed creek waters of Cochin estuary were found to vary between 7.5 and 8.7 (Preetha, 1991; Venketesan, 2001).

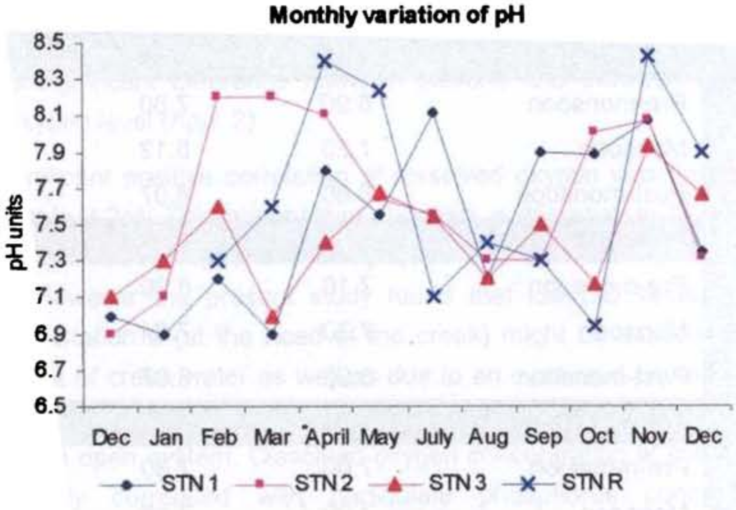


Fig 3.5 Monthly variation of pH in surface waters

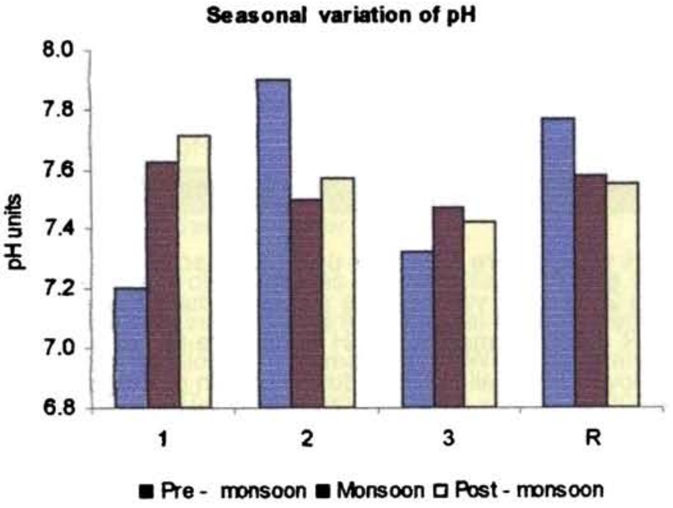


Fig. 3.6 Seasonal mean variation of pH in surface waters

ANOVA showed (App.3) significant difference between months at ($p<0.05$). Significantly higher pH was observed during November followed by October, April and September. There is no significant difference among the other months. The high pH values observed during post-monsoon were attributed to high photosynthetic activity. Which in turn was high during this season due to availability of light and nutrients. No significant difference was observed between stations. Similar observation was reported in another mangrove ecosystem study of Cochin (Rathnakala, 1995). pH values at mangrove creek waters showed a significant negative correlation with concentrations of nitrate-N (Table 3.2).

Temperature

Seasonal variations of temperature are given in Table3.5. At the three mangrove fringed creeks, temperature ranged between 26.5°C at Station 2 (post-monsoon) and 34.0°C at Station 3 (pre-monsoon). At Station R the temperature ranged between 29.50°C (post-monsoon) and 32.0°C (pre-monsoon). The lowest and highest mean values recorded were 29.21°C (Station 1) and 30.13°C (Station 3) respectively. Reference Station recorded an annual mean temperature of 30.55°C. Monthly variations in temperature are depicted in Fig. 3.7. Higher values of temperature were recorded during March, April, May, November and December. However Station 2 recorded higher values also during July and August.

Table 3.5 Seasonal variation of temperature (°C) in surface waters

Stations	Season	Min	Max	Mean
Station 1	Pre-monsoon	29.00	32.00	30.25
	Monsoon	29.00	29.00	29.00
	Post-monsoon	27.00	30.00	28.50
	Annual mean			29.21
Station 2	Pre-monsoon	30.00	32.00	30.63
	Monsoon	29.00	31.00	30.33
	Post-monsoon	26.50	30.00	28.20
	Annual mean			29.54
Station 3	Pre-monsoon	30.00	34.00	31.13
	Monsoon	27.00	30.00	28.67
	Post - monsoon	29.00	31.50	30.20
	Annual mean			30.13
Station R	Pre-monsoon	30.00	32.00	31.00
	Monsoon	30.00	30.00	30.00
	Post - monsoon	29.50	31.00	30.50
	Annual mean			30.55

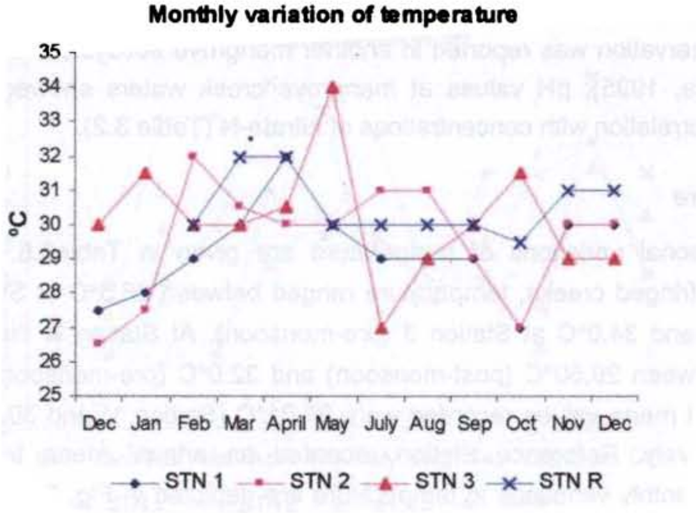


Fig 3.7 Monthly variation of temperature in surface waters

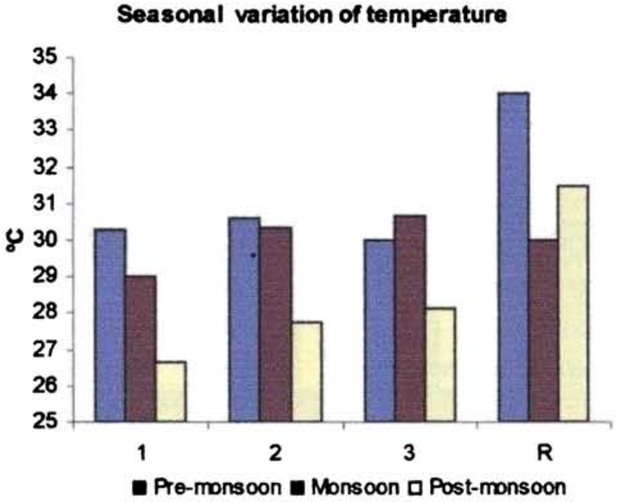


Fig. 3.8 Seasonal mean variation of temperature in surface waters

The mangrove fringed creek waters were found to exhibit minimum temperature during post-monsoon season as against the observation at the reference Station, where minimum temperature recorded during monsoon (Fig. 3.8). It was reported that, the lowest annual temperature of the Cochin backwaters usually occurred during the monsoon season (Ramaraju *et al.*, 1975). Water temperatures were found to vary within normally expected ranges at all the stations. The lowest annual mean value of 29.1 °C recorded at Station 1, 29.5°C at Station 2, and 30.2°C at Station 3. A clear seasonal variation was found at all three stations. As expected, the maximum temperature was recorded during pre-monsoon at all stations.

ANOVA (App. 4) showed no significant variation of temperature between months and between stations and between seasons.

Total Suspended Solids (TSS)

TSS in mangrove waters can be divided into two types. The macroscopic litter and finely divided materials retained on glass fibre filters. The litter from mangrove area was effectively removed from the system via tidal action. The litter lying on the ground at low tide always seems to be effectively removed during each high tide, in areas frequently inundated in Coral Creek, Queensland (Boto and Bunt, 1981; Boto, 1982). Here the effect of grazing and decomposition is minor. But in higher areas, less frequently flooded, the effect of grazing may be considerable and some decomposition may occur before exported. The mangrove detritus was observed floating on the surface of the tidal creek during both the flood and ebb tide in Tuff Crater, Auckland and the concentration of which varied from 8 mgL^{-1} to 92 mgL^{-1} (Woodroffe, 1985).

Seasonal variations of TSS are given in Table 3.6. The TSS values ranged between 4.40mg L^{-1} at Station 3 (pre-monsoon) and 360.00mg L^{-1} at Station 2 (monsoon) at the mangrove creek waters. Similar seasonal variations were observed at Station R, which recorded values varied between 5.43mg L^{-1} (post-monsoon) and 88.41mg L^{-1} (monsoon). Comparatively higher values were recorded during monsoon at all Stations (Fig. 3.10). The highest mean value of TSS was recorded at Station 2 (73.15mg L^{-1}) and lowest value was recorded at Station 1(2.39mgL^{-1}).

TSS concentrations observed in mangrove stations were found to be comparatively higher than at the estuarine reference station (Fig.3.9). Generally higher values were observed during February, April, May and September at the mangrove fringed creek waters. However at Station 2, a high value was also observed during November. At Station R, higher values were recorded during April, May and July.

Table 3.6 Seasonal variation of TSS(mgL^{-1}) in surface waters

Stations	Season	Min	Max	Mean
Station 1	Pre-monsoon	8.16	149.92	54.72
	Monsoon	30.60	179.00	88.36
	Post-monsoon	17.43	57.29	32.61
	Annual mean			52.39
Station 2	Pre-monsoon	7.13	108.82	41.94
	Monsoon	21.56	360.00	135.39
	Post-monsoon	14.31	138.16	72.41
	Annual mean			73.15
Station 3	Pre-monsoon	4.40	76.78	47.63
	Monsoon	50.20	102.60	80.59
	Post - monsoon	20.56	150.13	63.46
	Annual mean			58.98
Station R	Pre-monsoon	23.04	53.20	36.03
	Monsoon	28.40	88.41	54.92
	Post - monsoon	5.43	9.06	7.55
	Annual mean			33.38

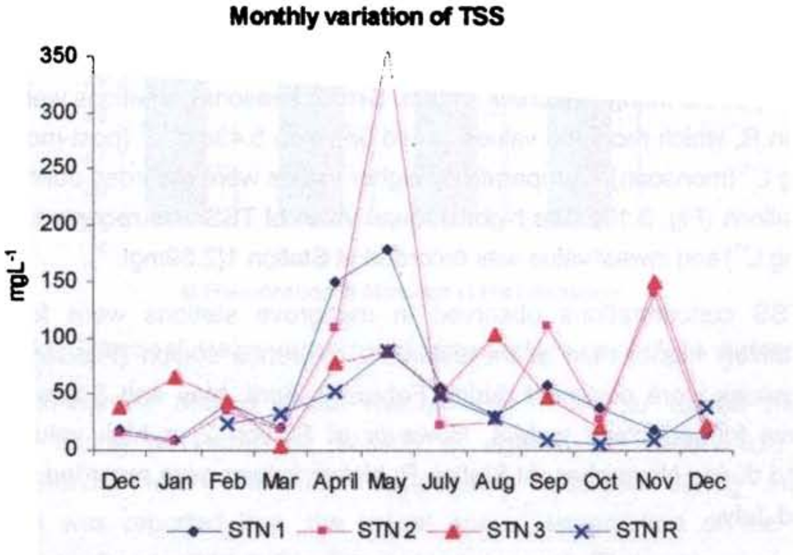


Fig 3.9 Monthly variation of TSS in surface waters

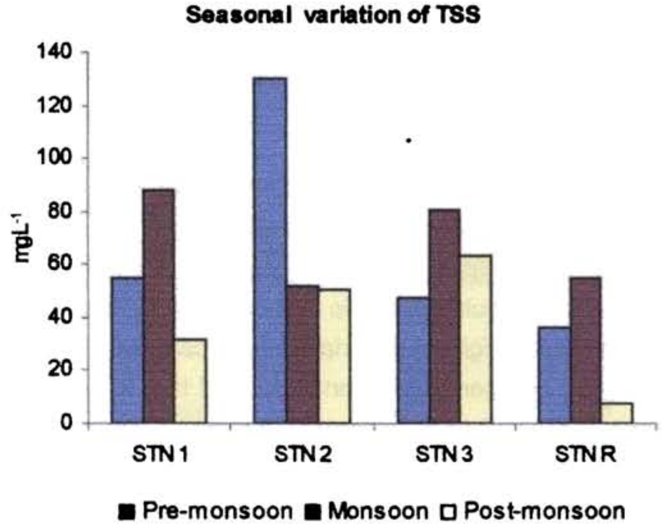


Fig. 3.10 Seasonal mean variation of TSS in surface waters

The mangrove creek waters receive maximum suspended load through river run-off during monsoon season. During the present observation, examination of the residue retained on glass fibre showed that a good deal of suspended solid is fine sediment. Occasionally, small plant debris material was also observed. Therefore the variations in TSS concentrations were associated with the amount of fresh water inundating the respective creeks. However the significantly high TSS concentration during pre-monsoon at Station 2 was associated with the dry conditions. The TSS concentrations in creek waters of Vypeen were found to be vary between 65mgL^{-1} and 96mgL^{-1} (Venkatesan, 2001) during monsoon.

A significant difference in TSS concentration among months ($p< 0.001$) were recorded (App.5). The LSD at 5% level was found to be 73.49mg L^{-1}. Significantly higher values were observed in the month of May, November, September and July. The higher TSS in the month of May, at Station 2 was associated with the dry condition. Suspended sediments associated with river influx and plant litter may contribute to the large amount of TSS at the creek waters under study area. In litter bag experiment, the maximum litter fall recorded during the month of July at Murikkumpadam and Puthuvypu area (Preetha, 1991). ANOVA did not showed any significant difference between stations. At the mangrove creek waters, TSS concentrations showed significant positive correlations with POC, DIP, TP,PP and ammonium concentrations (Table 3.2a).

Particulate Organic Carbon (POC)

Particulate organic matter is an extremely important part of the marine food chain as it provides food for organisms at several trophic levels. The particulate organic carbon includes chlorophyll, the organic carbon exported from forest and also fine sediment. The particulate organic carbon concentration occurring in the euphotic layer is relatively high and variable and can roughly correlated with phytoplankton activity. It has generally been described that mangrove ecosystems export a large amount of POC to the adjacent coastal waters and the import and export of micro-POC is almost in balance at a mangrove creek in northern Australia (Ayuaki *et al.*, 1998). The POC is derived from two main sources at mangrove ecosystems. They are macro and micro-POC. Macro- POC includes fallen leaves, twigs, propagules and so on. The micro-POC consisted of decaying plankton and mangrove debris. Their behavior is different from that of macro-particulate matter.

Seasonal variations of POC concentrations are given in Table 3.7. At the mangrove fringed creek waters, maximum and minimum concentrations of POC were recorded at Station 2 which vary between 0.27mgL^{-1} (pre-monsoon) and 25.52mgL^{-1} (monsoon). While at Station R, the POC concentration varied from 0.62mgL^{-}1 (post-monsoon) to 12.50mgL^{-1} (pre-monsoon). Comparatively higher values of POC were observed during pre-monsoon and lower values, during monsoon season (Fig. 3.12). The lowest and highest mean values recorded were 5.06mgL^{-1} (Station 3) and 7.15mgL^{-1} (Station 1) respectively. At Station R a mean value of 4.19mgL^{-1} recorded. Monthly variation in POC concentrations (Fig. 3.11) showed a similar pattern both at the mangrove fringed creek waters and at reference Station, except during March and September at Station 2. At all Stations, higher values were recorded during December and May. Other than these, Station 2 recorded a higher value during September and Station R, during March.

Table 3.7 Seasonal variation of POC(mgL^{-1}) in surface waters

Stations	Season	Min	Max	Mean
Station 1	Pre-monsoon	2.39	18.75	9.24
	Monsoon	2.08	18.75	2.85
	Post-monsoon	1.87	23.47	8.06
	Annual mean			7.15
Station 2	Pre-monsoon	0.27	8.45	6.12
	Monsoon	1.67	25.52	5.35
	Post-monsoon	2.08	16.43	12.05
	Annual mean			6.85
Station 3	Pre-monsoon	2.73	8.33	5.29
	Monsoon	1.25	2.08	1.81
	Post - monsoon	1.67	21.12	6.83
	Annual mean			5.06
Station R	Pre-monsoon	1.40	12.50	7.50
	Monsoon	0.83	1.67	1.39
	Post - monsoon	0.62	4.37	2.57
	Annual mean			4.19

High POC values in mangrove waters may be due to mangroves and terrestrial detritus present in the suspended matter. The maximum POC value was obtained during pre-monsoon at Station 1 and at reference station while minimum was observed during monsoon is in agreement with observation of (Rajendran and Kathiresan, 1999) Pichavram mangrove waters. The POC concentration in surface waters of Pichavaram mangrove area (south east India) were found to be 21.3, 33.8, 7.9, and 6µg C l^{-1} in summer, pre monsoon, monsoon and post monsoon. The export of carbon via micro and macro particulate matter amounts to about 11.5 Kg C ha^{-1} day^{-1} in a Northern Australian mangrove system (Boto and Bunt, 1981). A lower mean value of POC recorded at Station R.

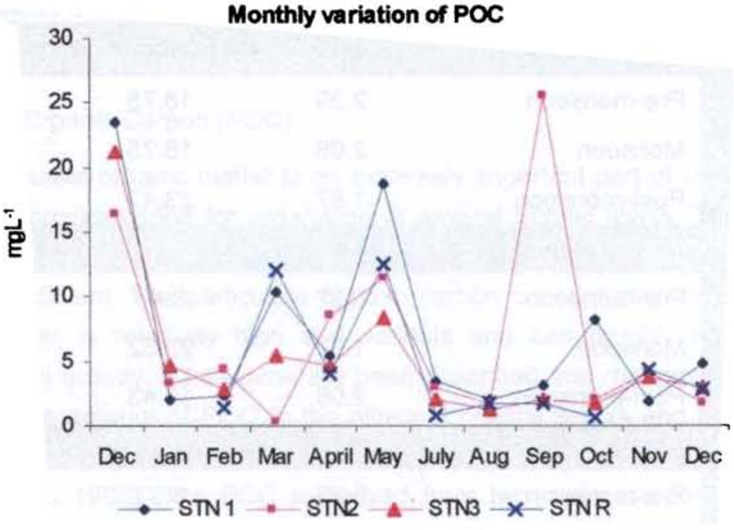


Fig 3.11 Monthly variation of POC in surface waters

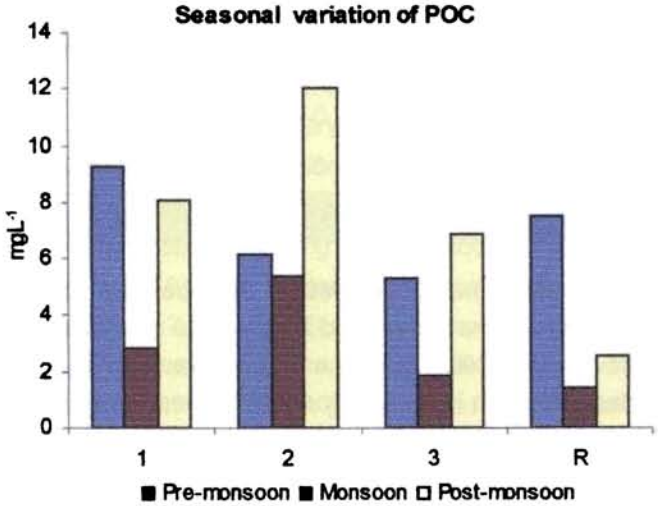


Fig. 3.12 Seasonal mean variation of POC in surface waters

The bacterial density at Station 1 contributed a large amount to the POC concentration at least during pre-monsoon. An elevated POC concentration during post-monsoon at Station 2, might be associated with phytoplankton productivity due to maximum light intensity during this seasons. Waters of mangrove creek are generally turbid because they are shallow regions and subjected to action of tides, and waves (Jagtap, 1987). Hence fine sediment also contributes to the POC concentration. Comparatively higher POC values at Station 2 during monsoon may be associated with the presence of fine sediment along with the particulate matter. Therefore the present observation indicated bacterial density, phytoplankton productivity as well as the presence of fine sediment in particulate matter resulted in an elevated concentration of POC in mangrove creek waters. The correlation analysis showed a significant positive relationship with dissolved organic phosphate and particulate phosphate in mangrove fringed creek waters (Table 3.2a).

The POC concentrations showed a significant difference between months at ($p < 0.05$) (App. 6). The LSD at 5%level was found to be 4.134mgL^{-1}. Significantly higher values were observed in the month of May, followed by March and April. The remarkably high concentration during May was due to dry condition at Station 2.

3.2.2 Distribution of dissolved inorganic forms of nitrogen

The most important dissolved inorganic nitrogen species comprises nitrite, nitrate and ammonia. Concentrations of dissolved inorganic nitrogen species are low in tropical mangrove waters, (within the µmolar range) and are dominated by ammonium with usually low concentration of nitrate and nitrite (Alongi *et al.*, 1992). Variations in concentrations among estuaries and mangrove water ways can be ascribed to differences in the extent of fresh water and ground water input, sun light, oxygen availability and standing stokes and productivity of phytoplankton and bacterio plankton. By virtue of wide range of oxidation states - 3 for ammonia to + 5 for nitrate nitrogen can serve as a reductant or an oxidant in the diagenesis of organic matter in addition to its role as a nutrient in microbial and plant assemblages.

Nitrate nitrogen (nitrate-N)

Seasonal variations in nitrate–N at mangrove fringed creek waters and at Station R, are depicted in Table 3.8. At the mangrove creek waters, nitrate-N concentrations vary between 0.01µmolL^{-1} at Station 2 (pre-monsoon) and 5.18µmolL^{-1} at Station 3 (pre-monsoon). At Station R, nitrate–N concentrations ranged between 1.83µmolL^{-1}(pre-monsoon) and 23.99µmolL^{-1}(monsoon). The annual mean values showed almost similar concentrations of nitrate-N at three mangrove-fringed creeks with a minimum at Station 1 (1.82µmolL^{-1}) and maximum at Station 3 (1.97µmolL^{-1}). However remarkably higher mean concentration of nitrate–N was recorded at Station R (7.74µmolL^{-1}).

Monthly variations of nitrate-N are depicted in Fig. 3.13. Station R recorded higher values during all months, and exceptionally higher value recorded during the month of July. Regarding the mangrove-fringed creeks, the nitrate-N concentrations recorded were comparatively low, however higher values were observed during July.

Table 3.8 Seasonal variation of nitrate-N (µmolL^{-1}) in surface waters

Stations	Season	Min	Max	Mean
Station 1	Pre-monsoon	0.44	3.18	1.68
	Monsoon	0.93	3.98	2.23
	Post-monsoon	0.08	5.02	1.67
	Annual mean			**1.82**
Station 2	Pre-monsoon	1.17	3.43	1.87
	Monsoon	1.28	3.98	2.32
	Post-monsoon	0.01	4.16	1.72
	Annual mean			**1.92**
Station 3	Pre-monsoon	0.49	5.18	3.34
	Monsoon	0.98	4.60	2.39
	Post - monsoon	0.10	3.89	1.70
	Annual mean			**1.97**
Station R	Pre-monsoon	1.83	11.66	6.74
	Monsoon	4.60	23.99	12.85
	Post - monsoon	2.85	7.05	4.48
	Annual mean			**7.74**

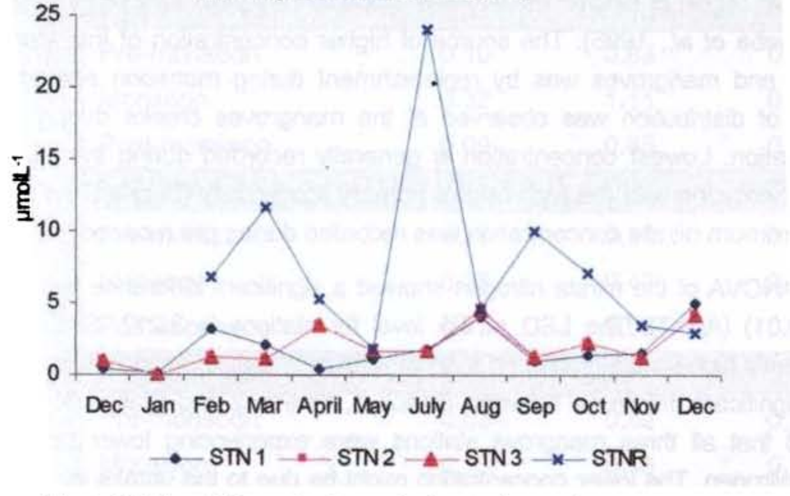


Fig 3.13 Monthly variation of nitrate in surface waters

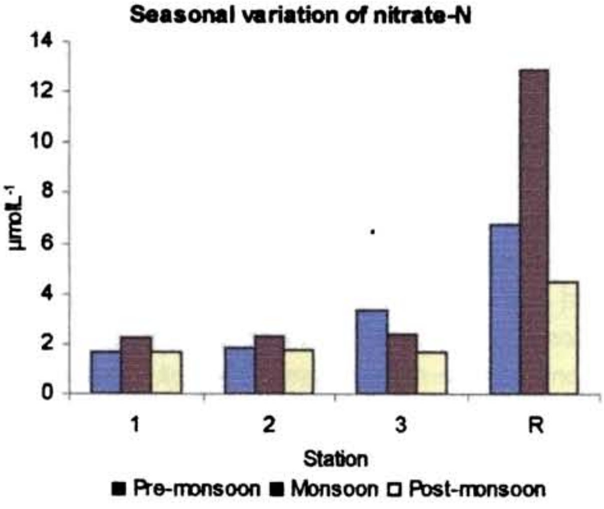


Fig. 3.14 Seasonal mean variation of nitrate in surface waters

Nitrate-N concentrations in surface waters showed seasonal variations at mangrove stations as well as at Station R (Fig. 3.14). The highest values being recorded during monsoon followed by pre-monsoon season. Maximum value of nitrate-N was recorded during monsoon at Station 1 and at Station 2. Minimum value was observed during post monsoon at all stations. A similar trend was reported in

Cochin estuarine waters by Sarala Devi *et al.* (1991). The concentration of nitrate in mangrove region of Cochin estuary was found to vary from 2.72 µmol L^{-1} to 7.41µmol L^{-1} (Sheeba *et al.*, 1996). The source of higher concentration of this element in the estuary and mangroves was by replenishment during monsoon season. A similar pattern of distribution was observed at the mangroves creeks during the present investigation. Lowest concentration is generally recorded during the post monsoon season, coincide with the high rate of primary productivity (Sarala Devi *et al.*, 1991). The maximum nitrate concentration was recorded during pre monsoon at Station 3.

ANOVA of the nitrate nitrogen showed a significant difference between stations at ($p<0.01$) (App.7). The LSD at 5% level for stations is 3.212. Station R showed significantly higher nitrate nitrogen than at Station 1, Station 2 and Station 3. But there is no significant difference between Station 1, Station 2 and Station 3. These results showed that all three mangrove stations were experiencing lower concentration of nitrate nitrogen. The lower concentration might be due to the uptake by plants. Uptake by trees and microorganisms, and by sorption on to the sediment matrix considerably reduces nutrient concentrations in pore water, which can make a mangrove forest to an effective sink for nutrients (Alongi, 1996). Concentrations of nitrate in mangrove creek water were found to be correlated with pH values (Table 3.2a).

Nitrite nitrogen (Nitrite- N)

Nitrite-N concentrations exhibited a similar trend as that of nitrate-N concentrations, with higher values recorded at Station R than the mangrove fringed creek waters. Seasonal variations of nitrite-N are depicted in Table 3.9. Nitrite-N concentration varied between 0.03µmolL^{-1} at Station 3 (pre-monsoon) and 1.11µmolL^{-1} at Station 1 (monsoon) in the mangrove-fringed creeks. However at Station R nitrite-N concentration ranged from 0.39µmolL^{-1} (monsoon) to 1.30µmolL^{-1} (pre-monsoon). The annual mean values of nitrite-N recorded the lowest at Station 3 (0.23µmolL^{-1}) and highest concentration of at Station 1 (0.58µmolL^{-1}). While Station R recorded an annual mean value of 0.82µmolL^{-1}. Temporal variations in nitrite-N concentration are given in Fig. 3.15. Similar to nitrate-N concentrations, relatively higher values were recorded for nitrite-N. The mangrove creek waters showed higher values during July at Station 1, December and August at Station 2 and February at Station 3. Station R showed higher values during March, May, July and September.

Table 3.9 Seasonal variation of nitrite-N (μmolL^{-1}) in surface waters

Stations	Season	Min	Max	Mean
Station 1	Pre-monsoon	0.10	0.83	0.47
	Monsoon	0.32	1.11	0.69
	Post-monsoon	0.09	0.85	0.58
	Annual mean			0.58
Station 2	Pre-monsoon	0.29	0.34	0.31
	Monsoon	0.28	0.42	0.32
	Post-monsoon	0.17	0.63	0.34
	Annual mean			0.33
Station 3	Pre-monsoon	0.03	0.52	0.27
	Monsoon	0.13	0.18	0.16
	Post - monsoon	0.12	0.48	0.24
	Annual mean			0.23
Station R	Pre-monsoon	0.72	1.30	1.09
	Monsoon	0.39	1.18	0.86
	Post - monsoon	0.48	0.54	0.51
	Annual mean			0.82

Nitrite occurs in aquatic system as an intermediate compound in the microbial reduction of nitrate or in the oxidation of ammonia. It also comes into the water when phytoplanktons are fed luxuriantly by nitrate and phosphate. Seasonal variations of nitrite concentrations observed at Station R as well as in mangrove creek waters. A general trend of nitrite nitrogen distribution showed minimum values during pre-monsoon at Station 1 and Station 2 (Fig. 3.16). The maximum value recorded at Station 1 during monsoon may be due to the bacterial activity in surface water. It was found that anoxic conditions results in high nitrite concentration together with low levels of dissolved oxygen (Grasshoeff *et al.*, 1983). The comparatively higher values of nitrite found at Station R, might be due to the impact of industrial effluents in the estuary. Nitrite concentration increases from pre-monsoon to monsoon at Station 1 and Station 2. The maximum concentration was recorded during pre-monsoon at Station 3, gave an indication of enhanced bacterial activity during this season.

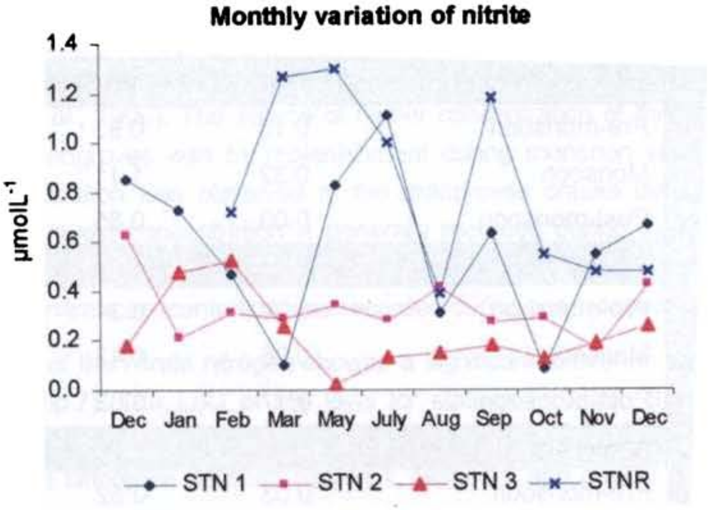


Fig 3.15 Monthly variation of nitrite in surface waters

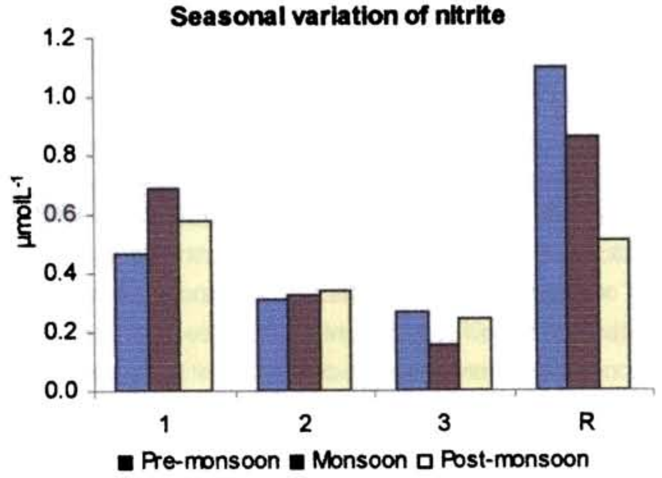


Fig. 3.16 Seasonal mean variation of nitrite in surface waters

ANOVA of the nitrite nitrogen showed a significant difference between stations at ($p<0.01$) (App.8) The LSD at 5% level for stations is 0.2489. Station R showed significantly higher nitrite nitrogen followed by Station 1, while no seasonal variation was observed. No significant correlation was observed with any other

Ammonium Nitrogen (Ammonium-N)

The seasonal variations of ammonium-N are given in Table 3.10. At the mangrove creek waters the ammonium-N concentration ranged between 2.84µmolL^{-1} at Station 1(post-monsoon) and 92.12µmolL^{-1} Station 2 (pre-monsoon). While at Station R ammonium nitrogen varied between 1.69µmolL^{-1} and 24.27µmolL^{-1}. The annual mean values of ammonia-N recorded a minimum of 11.54µmolL^{-1} at Station 3 and a maximum of 32.90µmolL^{-1} at Station 2. Mean concentration of 14.11µmolL^{-1} was recorded at Station R (Table 3.10). Monthly variations of ammonium-N concentration are given in Fig. 3.17. Generally higher ammonium-N concentrations were recorded at Station 1 and Station 2. All mangrove-fringed creek waters showed higher values during the month of August. However several other higher values were also observed at Station 2 during April, May and July. At Station 3, another high value observed during April. Ammonium-N at Station R recorded peaks during August and October.

Table 3.10 Seasonal variation of ammonium (µmolL^{-1}) in surface waters

Stations	Season	Min	Max	Mean
Station 1	Pre-monsoon	9.81	15.80	12.24
	Monsoon	4.81	29.92	13.96
	Post-monsoon	2.84	22.53	12.70
	Annual average			13.28
Station 2	Pre-monsoon	10.40	92.12	46.11
	Monsoon	23.92	70.06	52.70
	Post-monsoon	6.73	27.79	15.81
	Annual average			32.90
Station 3	Pre-monsoon	5.55	23.48	15.29
	Monsoon	10.69	17.32	14.01
	Post - monsoon	4.11	14.32	7.81
	Annual average			11.54
Station R	Pre-monsoon	9.88	20.16	16.60
	Monsoon	1.69	20.96	12.79
	Post - monsoon	5.43	24.27	12.13
	Annual average			14.11

Ammonium was the major dissolved inorganic nitrogen species at three of the mangrove-fringed creeks as well as at the reference station. No significant seasonal pattern of distribution was found at these stations (Fig. 3.18). Ammonium enters the water column mainly by excretion of grazers as well as mineralisation processes. During monsoon maximum concentration of ammonium was observed at Station 1(13.96 µmol L^{-1}). The maximum ammonium concentration was recorded in the month of August at all stations. The high value of ammonium nitrogen during monsoon might be due to the heavy fresh water discharge. The ammonium concentration at Station 3 also attained maximum concentration during pre monsoon (15.09µmol L^{-1}), followed by monsoon and post monsoon.

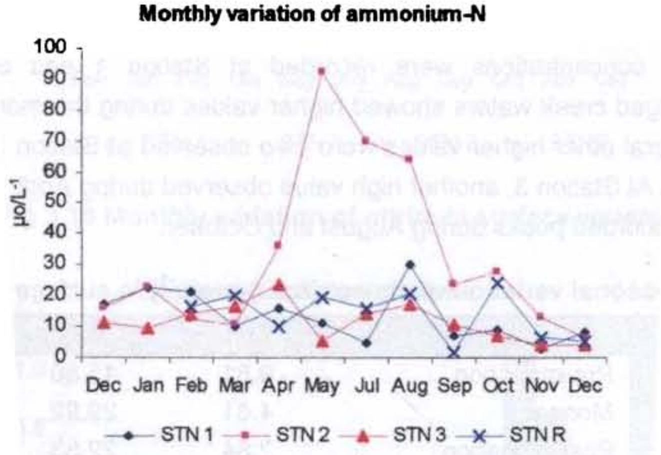


Fig 3.17 Monthly variation of ammonium-N in surface waters

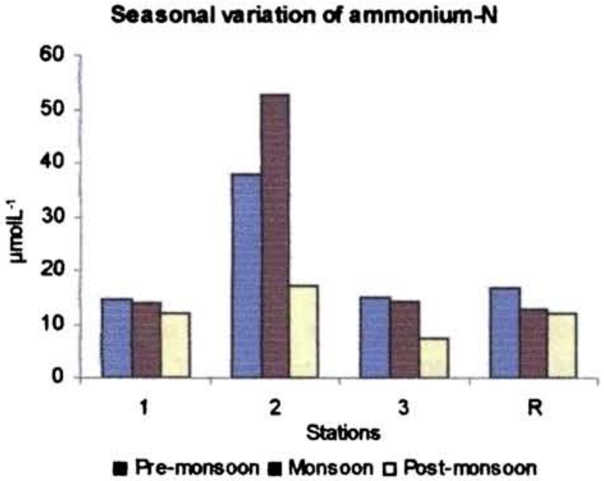


Fig. 3.18 Seasonal mean variation of ammonium-N in surface waters

Remarkably high ammonium-N concentrations were recorded at Station 2 during pre-monsoon and monsoon (Fig. 3.18) may be due to local regeneration. The ammonium concentration at Station 3 also attained maximum concentration during pre monsoon (15.09μmol L^{-1}) followed by monsoon and post monsoon.

The lower value encountered during post-monsoon may be due to utilization by grazers (Nair *et al.*, 1988). Bottom sediments represent important sources of ammonium and phosphate in the water column, especially in summer (Rizzo, 1990). Ammonium immobilization and assimilation were mainly by microbes (bacteria and fungi) and plants, always accompanies and counteracts the mineralisation process. The extent to which these processes balance each other is highly dependent on the C:N ratio of the decomposing organic matter. Substances rich in nitrogen (low C:N) favour net mineralisation, where as those poor in nitrogen (high C:N) favour net immobilization (Boto, 1982). The high concentration of ammonium in dissolved phase in mangrove-fringed waters indicated the net mineralisation of organic matter in this area

ANOVA of the ammonia-N concentrations showed a significant difference between stations at $p<0.01$ (App.9). The LSD at 5% level for stations is 13.695. There is significantly higher concentration of ammonia nitrogen at Station 2. There is no significant difference between Station 1, Station 3 and Station R. The correlation analysis of ammonium with other parameters showed significant positive correlation with TSS, DIP, PP and TP. However the dissolved ammonium also found to be negatively correlated with dissolved oxygen (Table 3.2).

3.2.3 Nitrogen : Phosphorus ratio (N/P)

Measurements of dissolved inorganic nitrogen (DIN, nitrate, nitrite and ammonia) and dissolved inorganic phosphate (DIP, orthophosphate) provide the biologically available forms of nitrogen and phosphorus. The ratio of dissolved inorganic nitrogen and dissolved inorganic phosphate (DIN : DIP) can be used to assess the nutrient status. The Redfield ratio is commonly used to assess the major nutrient demand for production of phytoplankton biomass (Redfield *et al.*, 1963). Redfield found that the proportions of C : N : Si : P in marine particulate matter are 106 : 16 : 16 : 1 (by atoms). Nitrogen and phosphorus are assimilated from seawater in an approximately constant proportion of 16: 1 (by atoms) by phytoplankton as they grow. Thus, N : P ratios > 16 : 1 are considered to reflect an excess of nitrogen, indicating that phosphorus is limiting for algal growth, and ratios < 16 : 1 are considered to reflect an excess of P, indicating that N is limiting. However the outcome of the sewage, rivers, industrial and drainage effluents into the marine ecosystem is likely to influence organic and inorganic nutrient concentration as well as their ratios are consequently affecting the primary production level. It was reported that the large input of organic carbon to the sediments seems to create a reducing environment in a highly productive *Spartina* salt marsh, resulted in removal of nitrate in water column by denitrifying bacteria. At the same time, phosphorus is remobilised in the anoxic pore waters, which may put into the overlying water by diffusion accounted for a low N/P ratio in coastal waters (Nixon, 1980).

Table 3.11 Seasonal variation of N:P ratio in surface waters

Stations	Season	Min	Max	Mean
Station 1	Pre-monsoon	0.51	3.19	1.69
	Monsoon	0.10	0.97	0.45
	Post-monsoon	0.30	3.21	1.68
	Annual mean			**1.38**
Station 2	Pre-monsoon	0.68	1.19	1.00
	Monsoon	0.61	5.76	3.50
	Post-monsoon	0.97	2.50	1.61
	Annual mean			**1.88**
Station 3	Pre-monsoon	1.28	7.21	3.88
	Monsoon	1.28	11.77	7.10
	Post - monsoon	3.78	9.22	6.32
	Annual mean			5.70
Station R	Pre-monsoon	1.93	6.47	4.15
	Monsoon	3.45	9.13	6.00
	Post - monsoon	2.93	4.17	3.40
	Annual mean			4.48

Monthly variations of N/P ratio are given in Fig. 3.19. Station 1 recorded higher ratios during January and February. At Station 2 higher ratio was found during July and August. Station 3 and Station R, showed higher ratio during the month of September. Seasonal variations of N/P ratio are given in Table 3.11. The ratios ranged from 0.10 at Station 1 (monsoon) to 11.77 at Station 3 (monsoon) in mangrove-fringed creeks. At Station R, these ratios ranged between 1.93 and 9.13. The mean annual ratios recorded a minimum ratio of 1.38 (Station 1) and a maximum ratio of 5.70 (Station 3).

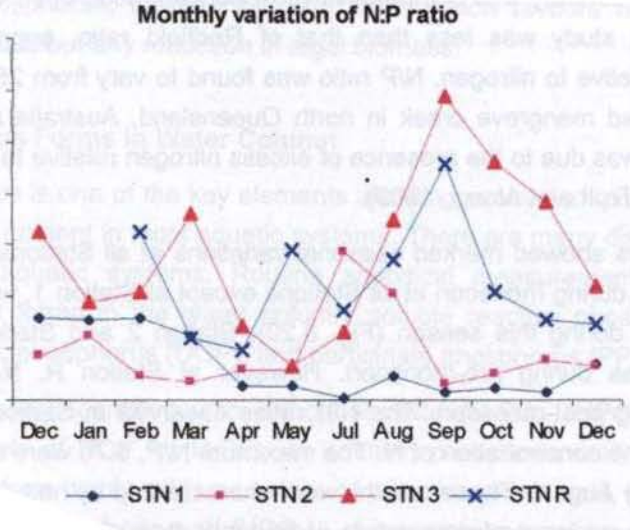


Figure 3.19 Monthly variation of N:P ratio

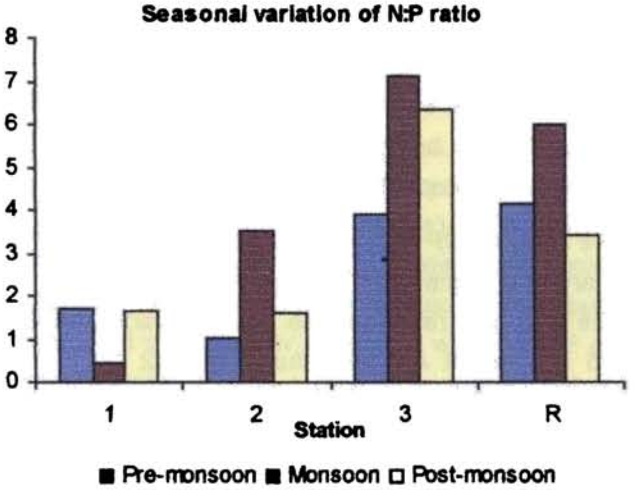


Figure 3.20 Seasonal mean variation of N:P ratio

The N:P ratio at Station 1 was influenced both by the concentrations of nitrogen as well as phosphorus. The minimum N/P recorded during July, characterized with low N and high P. The maximum was observed during December and January with comparatively low concentration of P. The ratio found in the present study was less than that of Redfield ratio, suggesting excess phosphorus relative to nitrogen. N/P ratio was found to vary from 26:1 to 58:1 in a tidally dominated mangrove creek in north Queensland, Australia and concluded that the result was due to the presence of excess nitrogen relative to phosphorus in water column (Trott and Alongi, 1999).

N:P ratios showed marked seasonal variations at all Stations. Higher ratios were observed during monsoon at all Stations except at Station 1, where minimum ratio observed during this season (Fig. 3.20). Station 2 and Station 3 recorded minimum values during pre-monsoon. However at Station R, N/P ratio found minimum during post-monsoon. The N/P ratios observed at Station 2 was found influenced by the concentration of N. The maximum N/P, 5.76 were reached during July followed by August. These months were characterized by heavy monsoon and associated with an input of ammonium compounds through land runoff. N/P ratio varied from 1.28 during May to 11.77 during September at Station 3, the low ratio found during May, may be due to high concentration of phosphorus.

The marine algae are considered to be phosphorus limited when the N/P ratio is >6 and nitrogen limited when the ratio is > 4.5. The two nutrients are near the optimal assimilative proportion in the range 4.5 to 6. According to this observation, it may be concluded that Station 1 and Staion 2 are severely nitrogen limited while this ratio was found as assimilative proportion at Station 3.

A comparative study of N/P ratio in three ecosystems in south India : Ennore creek, Adayar estuary and Pichavaram mangrove waters (Purvaja and Ramesh, 2000) found that the Red field ratio in these syatems varied from 0.96 N: 1 P at Ennore creek, 1.75 N: 1 P at Adayar estuary to 15.2 N: 1 P at Pichavaram mangroves. This observation led them to suggest that Pichavaram mangrove represents a well equilibrated ecosystem with N: P ratio close to steady state values in contrast to anthropogenically altered mangrove ecosystem of Ennore creek and Adayar estuary. It was also reported, at Gorai creek in Mumbai, an anthropogenically influenced creek, the N: P ratios of varied widely from 2.3 to 13.9 (Ram and Zingde, 2000). The coastal waters of eastern Brazilian shelf showed an

N:P ratio of the order of 5:1, and these waters found to be limited of primary production by nitrogen. (Ovalle *et al.*, 1999). The above ratios suggest that the mangrove-fringed creeks of Cochin estuary represent an anthropogenically altered mangrove ecosystem. The reduction of nitrogen input without a proportional reduction in phosphorus, creates low N/P ratio, which favours nitrogen fixing nuisance algae, without any reduction in algal biomass.

3.2.4 Phosphorus Forms In Water Column

Phosphorus is one of the key elements affecting ecosystem productivity and perhaps the key nutrient in most aquatic systems. There are many distinct pools of phosphorus in aquatic systems. Routine analytical measurements commonly distinguish three forms in the water column: soluble reactive phosphorus (DIP) dissolved organic phosphorus (DOP), and particulate phosphorus (PP).

DIP is closely identified with orthophosphate ($H_2PO_4^-$, HPO_4^{2-}) and with negligible amounts of PO_4^{3-} or H_3PO_4. In addition phosphoric acid can undergo condensation to form dipoly acids as anions of pyrophosphoric acid, $H_4P_2O_7$, or as anions of polymetaphosphoric acid $(HPO_3)_n$ - linear polymers, where n is 3-70 per chain. Since polyphosphates are not readily hydrolysed to orthophosphate ions, using the conditions of a standard method. Thus polyphosphates are not separately quantified during the present analysis. Typically the polyphosphate would appear as part of total phosphorus or as organic phosphorus and the amount of polyphosphate could be regarded as a useful index of pollution.

DOP fraction is still poorly characterized, but it is thought to be diverse in terms of structure and size (ranging from simple organic phosphate compounds to macromolecules in the colloidal size range), bioavailibility to aquatic microorganisms (bacteria and algae), and lability towards hydrolysis. Lean (1973) demonstrated that uptake of DIP by aquatic bacteria and algae results in rapid formation of small amount of labile low molecular weight DOP compound, which subsequently become associated with a high molecular weight colloid. The latter material was thought to represent the majority of nonparticulate P in water. Minear (1972) found that up to 20% of the DOP recovered from algal cultures and lake water was high molecular weight material consisting primarily of DNA fragments.

The particulate phosphorus (PP) fraction in lakes is even more heterogeneous than the DOP fraction. PP may include inorganic forms, e.g. phosphate sorbed on to clay suspended in the water and suspended precipitates of phosphates with such cations as Ca, Al and Fe. The PP fraction is also comprised of organic forms: detrital phosphorus from dead and decomposing cells, bacteria (freeliving and attached to detritus), phytoplankton and various zooplankton classes.

Several physical and biological processes affect the concentration of phosphorus in marine waters. The physical processes include precipitation and adsorption of soluble phosphate compounds. DIP is readily available to aquatic organisms and therefore consumed first in many situations. Organic forms require enzymatic activity, provided by phosphatase. Phosphorus bound in recalcitrant organic matrices within particles may possibly resist enzymatic extraction and remain unavailable. Sorbed phosphorus and polyphosphates can become available quite readily. Calcium and iron bound phosphorus may become available under the right physical, chemical and biological conditions. Microbial activity in sediments can also affect the dissolved phosphate levels in shallow estuarine systems.

Regeneration of phosphate from anaerobic sediments, takes place due to the fact that reduced phosphate salts are more soluble. In organic rich coastal sediments, there is significant diffusion of phosphate out of reduced sediments to the overlying water. Regeneration of phosphate by sediments is thus important in coastal waters. The above discussion suggests that the concentration of phosphate in water and sediments is determined by biological activity. Therefore, the oxygen uptake by organisms in water is well correlated to phosphorus concentrations (Stumm and Morgan, 1981), since nutrients are released during aerobic respiration of organic matter. All the dissimilative reactions result in regeneration of phosphorus.

Concentrations of dissolved inorganic phosphorus in mangrove waters are as low as μ molar range. Values in unpolluted mangrove water ways range from <0.1 to ~20 μmol. Diphosphoric acid and all polyphosphoric acid may also be present due to pollution of detergents in the coastal waters. Differences in concentrations among mangrove estuaries can be ascribed to local characteristics, such as the extent of fresh water and ground water input, and probably productivity of the biota. Lowest dissolved phosphorus concentration is usually coincident with dry periods as primary production is the highest.

The dissolved phosphorus is taken up by phytoplankton in the creek waters and thus enters the food chain in sea. After death and decay of organisms and plants a proportion of this phosphorus is returned to the water. The higher DIP concentration in eastern Brazilian shelf suggests a benthic nutrient regeneration (Millero, 1996). The earlier studies on nutrient status of Cochin estuary concluded that one of the major factors governing the distribution of nutrients may be variations in the regenerative property of the bottom mud rich in organic matter due to biological and chemical oxidation (Nair *et al.*, 1988; Sarala Devi *et al.*, 1991). The relative difference in phosphorus availability is ultimately a function of the abiotic controls of phosphorus sorption characteristics of the sediments (Sundereshwar and Morris, 1999).

Thus quantification of DIP, DOP and PP in water column, may generate some information on the major processes controlling phosphorus cycling in this aquatic system.

Dissolved inorganic phosphate (DIP)

In the creek waters, which are fringed by mangroves, showed a large variation in DIP concentration, where the values ranged between 0.40μmol L^{-1} at Station 3 (post-monsoon) and 32.06μmol L^{-1} at Station 1 (monsoon) (Table 3.12). Maximum DIP concentrations were recorded during pre-monsoon at all Stations, except at Station 1, which exhibited maximum concentration during monsoon season. Minimum concentration in DIP, were recorded during post-monsoon at all Stations except Station R, where minimum recorded during monsoon. The annual mean values of DIP showed a variation from 1.51μmol L^{-1} (Station 3) to 10.70μmol L^{-1} (Station 2). Station R recorded an annual mean value of 2.07μmol L^{-1} (Table 3.12). Monthly variations in DIP concentrations are given in Fig. 3.21. Significantly high values were obtained at Station 1 and Station 2 during the months of July and May respectively. Higher values were also found during the months of April, May, August, September and October at Station 1. However at Station 2, higher values were recorded during the months of April, September and October. Station 3 and Station R, recorded highest values during April and March respectively. Higher values were also found during the months of May and July at Station 3 while at Station R, higher values were recorded during July, August and October. Comparatively low values were recorded during post-monsoon at all Stations.

Table 3.12 Seasonal variation of DIP ($\mu molL^{-1}$) in surface waters

Stations	Season	Min	Max	Mean
Station 1	Pre-monsoon	2.18	13.40	7.73
	Monsoon	12.80	32.06	20.34
	Post-monsoon	2.61	11.30	5.00
	Annual mean			10.09
Station 2	Pre-monsoon	6.58	35.9	16.345
	Monsoon	5.67	18.97	10.7
	Post-monsoon	3.85	14.00	6.174
	Annual mean			10.70
Station 3	Pre-monsoon	1.40	4.28	2.48
	Monsoon	0.48	2.64	1.52
	Post - monsoon	0.40	1.20	0.74
	Annual mean			1.51
Station R	Pre-monsoon	1.16	4.01	2.39
	Monsoon	0.60	2.23	1.65
	Post - monsoon	1.28	3.45	2.07
	Annual mean			2.07

Remarkably higher concentration of DIP was found during monsoon at Station 1 (Fig. 3.22). High influx of river water during monsoon season into the estuary causes the desorption of dissolved phosphorus from Fe (OOH) minerals, into the water column. A large amount of surface runoff into the creek also resulted in remarkably higher concentration of DIP during monsoon season. Besides, as the shore of this creek is used and inhabited by people the anthropogenic input in to the water is higher. Species composition, bloom formation and production of diatoms were comparatively low during monsoon due to high rate of seaward flushing and poor light conditions (Kannan and Krishnamurthy, 1985). The decrease in DIP concentration during post-monsoon at Station 1 might be attributed to the increase in productivity during this season. The gradual increase in salinity during this post-monsoon season may also leads to increase in number of cations present in brackish water, which forms an insoluble calcium phosphate thus decreasing water-soluble phosphorus.

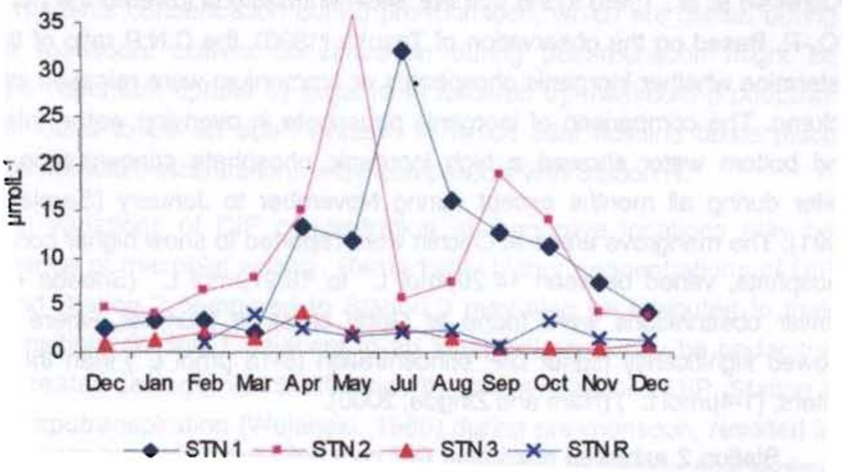


Fig 3.21 Monthly variation of DIP in surface waters

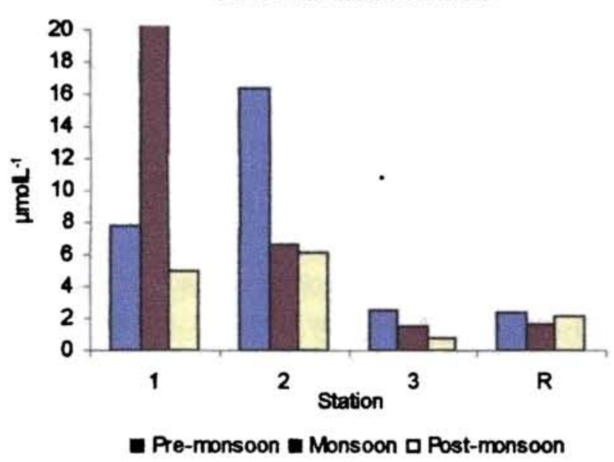


Fig. 3.22 Seasonal mean variation of DIP in surface waters

The DIP concentration at Station 1 and Station 2 varied from 2.18µmol L^{-1} to 13.40µmol L^{-1} and 6.58µmol L^{-1} and 35.9µmol L^{-1} respectively during pre-monsoon (Table 3.12). The microbially mediated benthic remineralisation of debris is another major recycling pathway and it can supply a significant fraction to the overlying water during pre- monsoon. The laboratory studies on role of bacteria in nutrient exchange (Kairesalo *et al.*, 1995) found that live sediment bacteria lowered the net retention of PO_4-P. Based on the observation of Tezuka (1990), the C:N:P ratio of the substrate determine whether inorganic phosphates or ammonium were released into the water column. The comparison of inorganic phosphate in overlying water, interface water and bottom water showed a high inorganic phosphate concentration in interface water during all months except during November to January (Sarala Devi *et al.*, 1991). The mangrove areas at Cochin were reported to show higher concentration of phosphate, varied between 14.29µmol L^{-1} to 18.97µmol L^{-1} (Sheeba *et al.*, 1996). Similar observations were found at Gorai creek in Mumbai, where creek water showed significantly higher DIP concentration (5-15 µmol L^{-1}) than the open shore waters, (1-4µmol L^{-1}) (Ram and Zingde, 2000).

Station 2 exhibited maximum DIP concentration during pre-monsoon, followed by monsoon and post-monsoon. The high concentration of dissolved inorganic phosphate during pre-monsoon may be as a result of the evapotranspiration. During pre-monsoon due to low fresh water discharge into the creek and with high rate of evaporation, the upper reaches of mangrove creek become completely isolated from the near shore zone. This phenomenon occurs if the water acquires salinity greater than that of the seawater. The greater salinity was acquired because of evaporation over the creek. (Wolanski *et al.*, 1989). A significantly higher salinity was also observed in this creek water during pre-monsoon. The significantly higher values of DIP at Station 1 and Station 2 suggest that ground water is also, probably an important source of phosphorus in mangrove areas.

The maximum concentration of dissolved inorganic phosphate was registered at Station 2 during the months of May followed by September. The station experienced almost dry conditions at the creek due to the formation of a bund at the mouth of the creek, during May and September, to supply water for an aquaculture pond resulted in no tidal flushing. The sediment collected during these months had the smell of hydrogen sulphide indicating the prevalence of anoxic conditions within the sediments. This anoxic conditions facilitate desorption of phosphate from the sediments to the overlying water which in turn increases the DIP concentration in creek water. The omission of these anomalous values for the calculation of the seasonal averages, the DIP concentrations found were 9.83 µmolL^{-1}, 6.58 µmolL^{-1} and 6.17 µmolL^{-1} during pre-monsoon, monsoon and post-monsoon respectively.

The maximum DIP concentration was observed in pre-monsoon, followed by monsoon and post monsoon at Station 3 (Fig. 3.22). The benthic microbial action increases the nutrients concentration during pre-monsoon, which are diluted during the southwest monsoon. Lowest concentration during post-monsoon might be attributed to the maximum uptake by organisms followed by maximum production. Station 3 was found to be an open system, in which tidal flushing takes place regularly, hence nutrient concentrations were comparable with Station R.

Seasonal variations of DIP concentration at mangrove locations may be under the influence of microbial activity. Remarkably higher concentrations of DIP at Station 1 and Station 2 compared to Station 3 may also be attributed to their geographical position. Station 1 adjacent to an inhabited area may be under the influence of untreated sewage, which influence the concentration of DIP. Station 2 experiencing evapotranspiration (Wolanski, 1989) during pre-monsoon, resulted in higher salinity and elevated concentration in DIP. Also due to the low tidal regime at the creeks at Station 1 and Station 2 reduce the transport of accumulated organic matter in the creek. This in turn enhance bacterial activity, which may reduce oxygen concentrations in sediment water interface in turn a reduced iron minerals release inorganic phosphate to the water column. The relationship between seasonal pattern of phosphate in water and flux of phosphate from sediments is an evidence for the regeneration of benthic phosphate affects water column concentrations (Nixon, 1980).

The DIP concentrations of mangrove fringed creek waters recorded positive correlations with concentrations of TSS, PP and TP ($p< 0.0$, $p<0.001$) (Table 3.2a). DIP concentrations recorded positive correlation with dissolved ammonium-N concentrations at all Stations ($p<0.0.05$, $p<0.01$) (Table 3.2a, 3.2b). ANOVA of DIP showed that a significant difference exists between stations ($p<0.05$) (App.11). The LSD at 5% level for stations is 5.8μmolL^{-1}. Significantly higher inorganic phosphate was noticed at Station 1 and Station 2 as compared to Station 3 and Station R. No significant difference between either Station 1 and Station 2 or between Station 3 and Station R were recorded.

Dissolved Organic phosphate (DOP).

Phosphorus occurs in all living organisms in the form of organic compounds. As a result of decay and decomposition it is liberated into water as dissolved substances, which on oxidation presumably by bacterial action, is released as phosphates in ionic form (Redfield *et al.*, 1963). The dissolved organic phosphorus pool has been indicated as a potentially important source of phosphorus for phytoplankton (Riley and Chester, 1971). In the process of regeneration, particulate phosphorus from the algal cells and detritus (including animal matter) is oxidized into inorganic phosphate. The intermediate stage during the process is dissolved organic phosphate. The organic phosphates include nucleic acid material, phospholipids, and many decomposition products. A little of the organic phosphorus material is present as enzyme hydrolysable phosphate esters.

Table 3.13 Seasonal variation of DOP (µmolL^{-1}) in surface waters

Stations	Season	Min	Max	Mean
Station 1	Pre-monsoon	2.26	11.96	7.02
	Monsoon	0.50	1.08	1.08
	Post-monsoon	0.67	10.95	3.21
	Annual mean			4.16
Station 2	Pre-monsoon	1.19	5.15	5.15
	Monsoon	0.49	4.99	2.99
	Post-monsoon	0.82	8.69	4.32
	Annual mean			3.24
Station 3	Pre-monsoon	0.01	2.15	0.75
	Monsoon	0.62	1.33	0.92
	Post - monsoon	0.08	2.74	1.30
	Annual mean			1.02
Station R	Pre-monsoon	0.13	3.23	1.68
	Monsoon	0.40	2.50	1.46
	Post - monsoon	0.07	2.45	2.24
	Annual mean			1.29

Monthly variation in DOP concentrations are depicted in Fig. 3.23. Generally higher values were recorded during April, May and October at Station 1, Station 2, and Station 3. However Station R showed higher values during February, August, November and December. The seasonal variations in DOP are given in Table3.13. The DOP concentration recorded a variation from 0.01µmolL^{-1} at Station 3 (pre-monsoon) to 11.96µmolL^{-1} at Station 1 (post-monsoon) at the mangrove fringed creek waters. Large variations in DOP concentrations were found at Station 1 and Station 2. Minimum concentrations at these Stations were 0.67µmolL^{-1}

(post-monsoon) and 0.49µmolL^{-1} (monsoon) respectively. Maximum concentrations recorded were 11.96µmolL^{-1}(pre-monsoon) and 8.69 µmolL^{-1}(post-monsoon). However at Station 3, DOP concentrations showed a variation from 0.01µmolL^{-1} (pre-monsoon) to 2.74µmolL^{-1} (post-monsoon). However minimum and maximum concentrations were recorded during pre-monsoon at Station R were 0.13 µmolL^{-1} and 3.23µmolL^{-1} respectively.

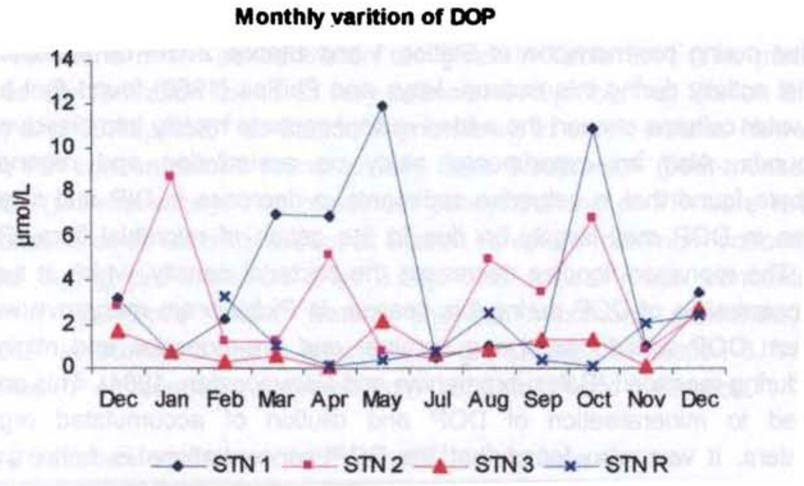


Fig 3.23 Monthly variation of DOP in surface waters

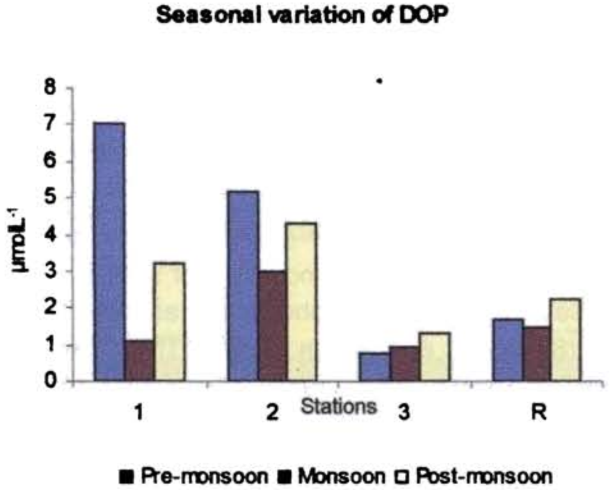


Fig. 3.24 Seasonal mean variation of DOP in surface waters

DOP concentrations of the present investigation recorded remarkably higher values compared to the earlier reported values. In Pichavaram waters, (south east coast of India) DOP concentration ranged from 0.5 to 2.75 with maximum levels within the salinity range of 5 to 22 x 10^{-3} (Balasubramanian and Venugopalan, 1984). At Hinchinbrook Island, Australia, DOP concentrations found to vary from 0.1 to 0.6µM (Boto and Wellington, 1988). The accumulation of DOP occurs after the removal processes such as utilization by bacteria and other heterotrophs and adsorption to particulate matter and sediments. The maximum concentration of DOP recorded during pre-monsoon at Station 1 and Station 2 can be attributed to high bacterial activity during this season. Hays and Phillips (1958) found that bacteria in fresh water cultures convert the added radiophosphate rapidly into dissolved organic compounds. Also an experimental study on assimilation and regeneration of phosphate found that in estuarine sediments, a decrease in DIP and simultaneous increase in DOP may largely be due to the action of microbial flora (Rajagopal, 1973). The monsoon flooding decreases the bacterial density, which in turn reduce the concentration of DOP during this season. In Pichavaram mangrove waters, the maximum DOP was found during summer and pre-monsoon and minimum was found during monsoon (Balasubramanian and Venugopalan, 1984). This pattern was attributed to mineralisation of DOP and dilution of accumulated organics by floodwaters. It was also found that the DOP concentrations in bottom waters of Pichavaram were significantly higher than those at the surface waters. This also suggests the influence of sediments in the concentration of DOP.

Seasonal variations showed a general pattern of minimum concentration during monsoon season at all Stations except at Station 3 (Fig. 3.24). However maximum concentrations of DOP recorded during pre-monsoon at Station1 and Station 2. Unlike DIP, at Station 3 and at Station R maximum concentrations of DOP were recorded during post-monsoon. The annual mean variation of DOP concentrations, recorded the maximum at Station 1 and minimum at Station 3 (Table 3.13).

The elevated concentration of DOP during post monsoon at Station 2 and Station 3 might be associated with the productivity of surface water. Algal growth produces an increase in particulate phosphorus and as algae senesce release as DOP takes place (Strickland and Austin, 1960). The DOP concentrations in mangrove creek waters were positively correlated with POC concentrations. This suggests a release of DOP during algae senesce. The dissolved oxygen level found to influence the mineralization of organic phosphorus (Sankaranarayan and Reddy, 1970). The present observation in creek waters also recorded a negative correlation of organic phosphate with dissolved oxygen (Table 3.2a).

The ANOVA of DOP showed that a significant difference exists between stations ($p<0.05$) (App.12). The LSD at 5% level for stations is 2.311μmolL^{-1}. Station 1 and Station 2 are having significantly higher organic phosphate compared to Station 3 and Station R. No significant difference either between Station 1 and Station 2 or between Station 3 and Station R were recorded.

Particulate Phosphorus (PP)

Spatial and seasonal variations were observed in PP concentrations. The seasonal variations of PP concentration are given in Table 3.14. The particulate phosphorus concentration found to vary between 0.49μmolL^{-1} at Station 2 (post-monsoon) and 55.40μmolL^{-1} at Station 2 (monsoon) in creek waters. However at Station R, PP concentrations found to vary from 0.58μmolL^{-1} (post-monsoon) to 8.40μmolL^{-1} (pre-monsoon). The maximum concentrations of PP were recorded during monsoon at all Stations except at Station R, where maximum concentration was found during pre-monsoon (Fig. 3.26). The annual mean concentrations recorded in mangrove creek waters showed maximum concentration of 16.26μmolL^{-1} at Station 2 and a minimum of 5.04μmolL^{-1} at Station 3. While at Station R the PP concentrations ranged from 0.58μmolL^{-1} and 8.40μmolL^{-1}.

Table 3.14 Seasonal variation of PP (μmolL^{-1}) in surface waters

Stations	Season	Min	Max	Mean
Station 1	Pre-monsoon	8.22	14.33	10.59
	Monsoon	8.52	13.92	10.59
	Post-monsoon	3.22	7.69	5.62
	Annual mean			8.93
Station 2	Pre-monsoon	9.98	40.48	20.63
	Monsoon	9.87	55.40	27.29
	Post-monsoon	0.49	1.22	0.86
	Annual mean			16.26
Station 3	Pre-monsoon	3.11	6.61	4.99
	Monsoon	4.43	10.86	8.29
	Post - monsoon	1.19	2.79	1.83
	Annual mean			5.04
Station R	Pre-monsoon	5.02	8.40	7.09
	Monsoon	1.52	6.00	3.32
	Post - monsoon	0.58	1.64	1.02
	Annual mean			3.68

Monthly variations in PP concentration are depicted in Fig. 3.25. Generally higher values were observed during April and July at all Stations. Remarkably higher values were obtained at Station 2, during May and September.

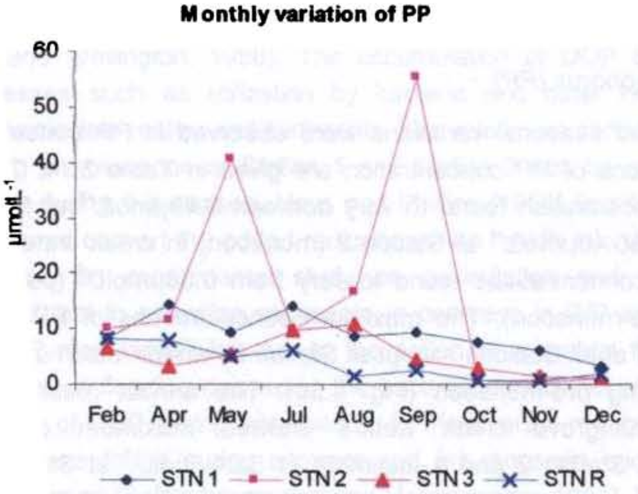


Fig 3.25 Monthly variation of PP in surface waters

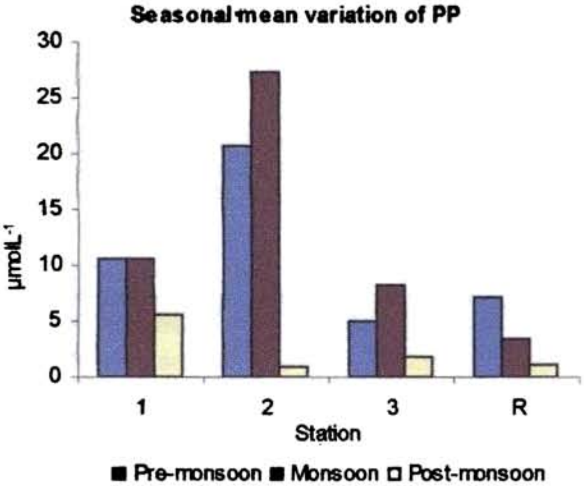


Fig. 3.26 Seasonal mean variation of PP in surface waters

Monsoon months were associated with maximum suspended load. The maximum concentrations of PP obtained during monsoon, may be associated with the load of suspended sediment transported to the estuary. A similar observation was found at Pitchavaram mangrove area (Subramanian and Venugopalan 1983). In their observation in shallow waters, the distribution of particulate phosphorus depend on the suspended sediment brought in, by the river discharge and not on the particulate matter formed on the estuarine mixing. It was found in the estuary of Purari river of Papua New Guinea where rain fall is very high most of the available phosphorus is bound, either as particulate or as phosphate adsorbed on to clays, in the suspended load, rather dissolved free in the water column (Viner, 1982). Remarkably higher concentration of PP at Station 2, during May and September may be attributed to the prevalent dry condition at this station. During post monsoon, PP concentrations were mainly due to phytoplankton biomass. Comparatively less phosphate found in phytoplankton biomass than sediments. Hence the minimum concentrations recorded during post-monsoon were associated with phytoplankton biomass at these stations. Higher values of particulate phosphorus were registered at Station 1 and Station 2 as compared to Station 3. The more denser plant distribution at these sites may be contributed to the particulate matter and organic detritus. The concentrations of PP were positively correlated with the concentrations of TSS, POC and SRP. A negative correlation was also recorded with DO (Table 3.2a). No significant difference in PP concentration was found between months or between stations using ANOVA (App. 13).

Total phosphate (TP)

The TP concentrations showed a variation similar to DIP concentrations. The seasonal variations of TP are given in Table 3.15. TP concentration at three mangrove locations found to vary between 2.00$\mu molL^{-1}$ at Station 3 (post-monsoon) and 77.87$\mu molL^{-1}$ at Station 2 (monsoon). At Station R, TP showed a variation from 3.46$\mu molL^{-1}$ (monsoon) to 12.79$\mu molL^{-1}$ (pre-monsoon). Similar to PP, monsoon season was characterized by maximum concentrations of TP at three mangrove locations. However at Station R, maximum concentration of TP recorded during pre-monsoon (Fig. 3.28). Minimum concentrations of TP were observed during post-monsoon at all Stations. The annual mean concentrations of TP showed maximum value at Station 2 and minimum value at Station R. Monthly variation (Fig. 3.27) of TP concentrations recorded higher values during April. May, July, and August at all Stations. Exceptionally higher TP values were recorded during September at Station 2 and during September and October at Station 1. The TP concentrations were found to be linear at Station R. TP concentrations indicated phosphorus loading in the water column of mangrove creeks at Station 1 and Station 2 than at Station 3 and Station R. Phosphorus may enter a water body through the inflows, precipitation, dry fallout and from the sediments, and it may be removed by sedimentation and through the outflow. Bacterial reduction of ferric hydroxy-phosphate complexes results in large amounts of soluble inorganic phosphorus and ferrous iron diffusing across the sediment-water interface causing internal loading. Ferrous iron is deoxidised when it encounters oxygen (from the trophogenic zone) to insoluble ferric iron which binds with orthophosphate. Phosphorus is also released from lake sediments to well aerated water. Exceptionally high TP concentrations were recorded in the water column at Station 2 except during post-monsoon might be associated with desorption of Fe-bound phosphorus due to the above reasons. Since these high values were associated with dry conditions of the creek during the months of May and September.

Table 3.15 Seasonal variation of TP (µmolL^{-1}) in surface waters

Stations	Season	Min	Max	Mean
Station 1	Pre-monsoon	13.98	34.62	27.20
	Monsoon	23.20	46.98	32.05
	Post-monsoon	11.03	29.93	18.46
	Annual mean			25.90
Station 2	Pre-monsoon	18.93	76.38	42.30
	Monsoon	16.03	77.87	40.99
	Post-monsoon	5.61	21.67	11.62
	Annual mean			31.64
Station 3	Pre-monsoon	7.39	9.57	8.64
	Monsoon	9.57	13.11	10.72
	Post - monsoon	2.00	4.75	3.75
	Annual mean			7.70
Station R	Pre-monsoon	6.78	12.79	10.05
	Monsoon	3.46	8.12	5.95
	Post - monsoon	4.10	5.37	4.56
	Annual mean			6.85

Station 1 recorded relatively higher TP concentration during monsoon and pre-monsoon. Remarkably high TSS (Table 3.15) during monsoon was recorded at all Stations. The major source of suspended sediment may be derived from river water inundation of the estuary and surface water runoff. Also At relatively higher temperatures in pre-monsoon, microanaerobic zones are formed very rapidly, and redox-controlled liberation of phosphate can occur to well-aerated water. An increase in temperature gives primarily indirect effects due to increased bacterial activity, which increases oxygen consumption and decreases the redox potential and pH-value. The production of phosphate-mobilizing enzymes and chelating agents might increase accordingly. The TP - minimum values (Table 3.15) observed at Station 1 and Station 2 were comparable. Station 3 and Station R recorded similar concentrations of TP with respect to minimum, maximum and mean values. The minimum TP was noticed during post monsoon at all Stations.

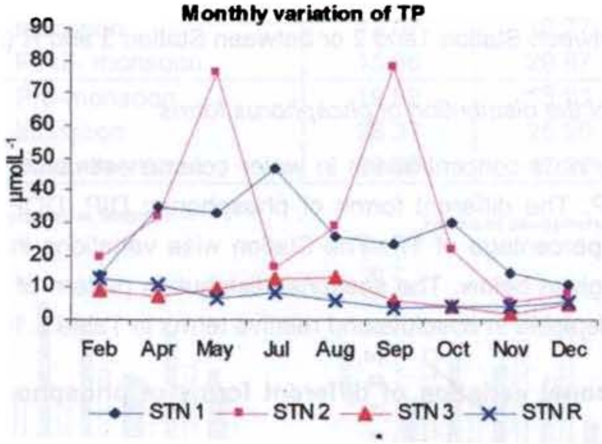


Fig 3.27 Monthly variation of TP in surface waters

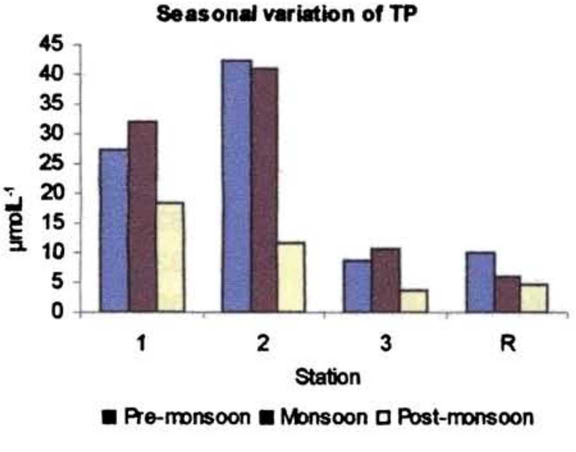


Fig. 3.28 Seasonal mean variation of TP in surface waters

Correlation analysis of TP concentrations with other physico-chemical parameters, in mangrove fringed creek waters, showed a positive relationship with TSS, POC, DIP, PP and ammonium-N concentrations. These correlations suggest a relationship of TP concentration with concentrations of suspended particles (Table 3.2a). No significant difference were recorded between months in TP concentrations in water column (App.14). However, significant differences were exhibited between Stations in TP concentrations. The LSD at 5% level between Stations was 5.711µmolL^{-1}. Stations 1 and Station 2 gives significantly higher TP concentrations than Station 3 and Station R. No significant differences were exhibited either between Station 1and 2 or between Station 3 and R (App.14).

Inter comparison of the distribution of phosphorus forms

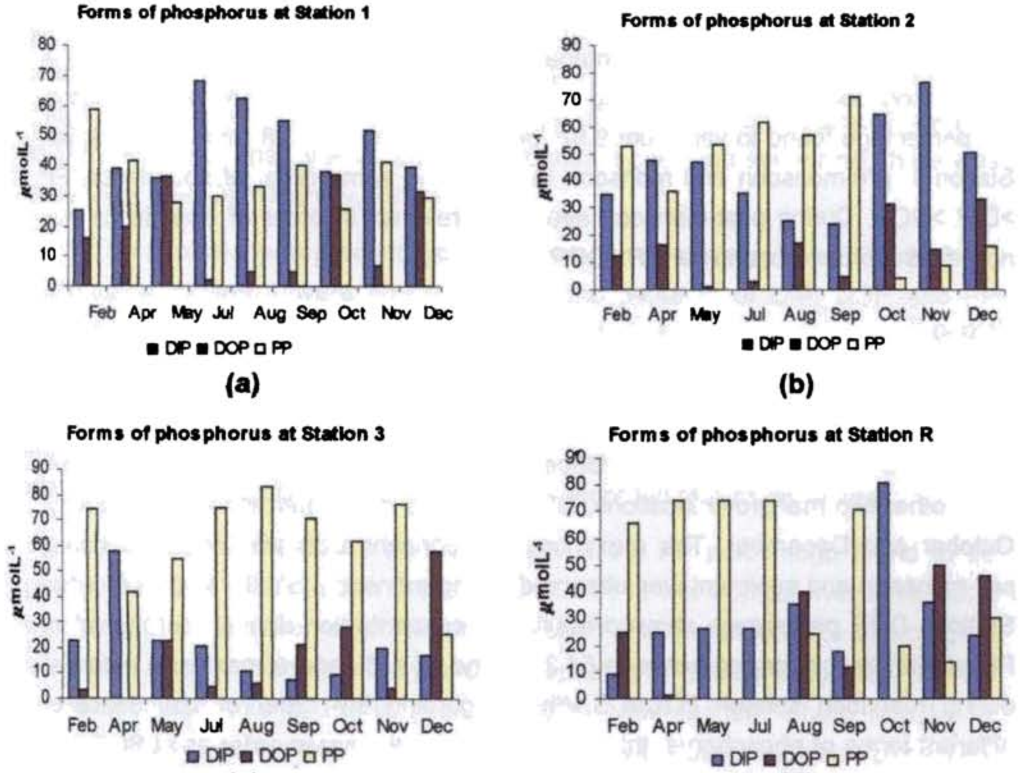
Total phosphorus concentrations in water column estimated as the sum of DIP, DOP and PP. The different forms of phosphorus: DIP, DOP and PP were estimated as the percentage of TP. The Station wise variations in percentage of each fraction are given below. The seasonal distribution pattern of different forms of phosphorus is depicted in absolute and relative terms in Table 3.16a and 3.16b.

Table 3.16a Seasonal variation of different forms of phosphorus in surface waters (µmol/L)

Stations	Season	SRP	SOP	PP	TP
Station 1	Pre-monsoon	7.73	7.02	10.59	25.34
	Monsoon	20.34	1.11	10.59	32.05
	Post-monsoon	5.00	3.21	5.62	13.68
Station 2	Pre-monsoon	19.16	3.76	20.63	42.30
	Monsoon	20.34	2.99	27.29	40.99
	Post-monsoon	7.38	3.38	0.86	11.62
Station 3	Pre-monsoon	2.84	0.82	4.99	8.64
	Monsoon	1.52	0.92	8.29	10.72
	Post - monsoon	0.55	1.36	1.83	3.75
Station R	Pre-monsoon	1.85	1.68	7.09	10.05
	Monsoon	1.65	1.46	3.32	5.95
	Post - monsoon	2.07	2.24	1.02	4.58

Table 3.16b Seasonal variation of different forms of phosphorus in surface waters as % of TP

Stations	Season	DIP	DOP	PP
Station 1	Pre-monsoon	33.21	24.09	42.70
	Monsoon	61.90	3.88	34.22
	Post-monsoon	42.93	25.03	32.04
Station 2	Pre-monsoon	43.09	9.94	47.30
	Monsoon	28.50	8.22	63.28
	Post-monsoon	63.97	26.42	9.62
Station 3	Pre-monsoon	34.52	8.60	56.88
	Monsoon	13.07	10.77	76.16
	Post - monsoon	15.66	29.97	54.37
Station R	Pre-monsoon	19.92	13.23	69.88
	Monsoon	26.37	25.95	57.39
	Post - monsoon	30.03	47.67	22.30


Forms of phosphorus at Station 1

Forms of phosphorus at Station 2

Forms of phosphorus at Station 3

Forms of phosphorus at Station R

(a) (b)

(c) (d)

Fig. 3.29 Monthly variation of forms of phosphorus

Station 1

Monthly variation in different forms of phosphorus (Fig. 3.29a) showed the major forms of phosphorus in water column were DIP and PP. However during the months of May, October and December, DOP concentrations also become substantial. A maximum DIP percentage recorded during monsoon season, while a minimum recorded during pre-monsoon (Table 3.16b). PP percentage showed a variation between 32.0 (pre-monsoon) and 42.7(post-monsoon). Concentrations of each fraction exhibited an order of abundance as PP >DIP >DOP during pre-monsoon and DIP >PP >DOP during post-monsoon and monsoon seasons.

Station 2

Similar to Station 1, the major forms of phosphorus identified in water column were DIP and PP. Substantial amount of DOP were recorded during the months of August, October and December (Fig. 3.29b). Seasonal pattern of distribution (Table 3.16a-b) recorded maximum percentage of DIP, during post-monsoon and minimum during monsoon, while DOP showed its maximum percentage during post-monsoon. PP percentage found to vary from 9.62 (post-monsoon) to 63.28 (monsoon). Unlike, Station 1, pre-monsoon and monsoon recorded the same order of abundance, PP >DIP >DOP. During post-monsoon season, a reversal in order of abundance was noticed, the order found to be DIP >DOP >PP.

Station 3

The temporal distribution of different forms of phosphorus identified are given in Fig. 3.29c This Station characterized by higher fraction of PP in water column, during all months except December. Next major form identified was DIP. As in other two mangrove locations, DOP recorded higher percentage during May, October and December. The maximum DIP concentration was recorded during pre-monsoon and minimum was observed during monsoon. Similar to the other two Stations DOP percentage showed maximum concentration during post-monsoon. PP at this Station ranged between 54.37% and 76.16% and a maximum recorded during monsoon season (Table 3.16b). Regarding the order of abundance of different forms of phosphorus, this Station followed the same order as at Station 2, during pre-monsoon and monsoon. However during post-monsoon, the concentration of different forms were in the following order : PP >DOP > DIP.

Station R

Similar to Station 3, PP found to be the major phosphorus fraction in water column, except during the months of November and December (Fig. 3.29d). DIP showed maximum percentage during post-monsoon. Significantly higher percentage of DOP was found during post-monsoon. PP percentage ranged between 22.30 and 69.88 and maximum percentage recorded during pre-monsoon. The order of abundance in different forms of phosphorus followed a similar pattern as at Station 2 and Station 3. However during post-monsoon Station R, recorded following order of abundance, *viz* DOP >DIP >PP.

In general, the entire studied water column exhibited, the percentage of PP to be greater than that of DIP, which in turn larger than DOP, other than certain exceptions. In lakes, it was found that, phosphorus is partitioned into about 60-70% PP, 20-30% DOP, and 5-12% DIP (Valiela, 1984). At all mangrove locations, the percentage of DIP found to be greater than DOP. However at Station R, almost similar concentrations of DIP and DOP were found. In aquatic systems where cell concentrations are lower than in lakes, DOP may be smaller than the inorganic fraction. It was found in English channel, most of the phosphorus present in winter as DIP, but in summer when there were abundant cells and senescing, there was more DOP than DIP (Harvey, 1955).

The annual mean percentage of different forms of phosphorus (Table 3.17) recorded at Station 1 were 48.4%, 17.1%, and 34.48 % of DIP, DOP and PP respectively. Remarkably higher percentage of DIP at this creek indicated a eutrophic condition. Jenson and Anderson(1992) have shown that Fe-bound P, when present in significant proportions in the sediment, may be a major source for internal P loading in shallow, eutrophic lakes, just as it may be in deeper, stratified lakes. In all other Stations, the PP percentage recorded maximum values.

At Station 2, Station 3 and at Station R the PP percentage found to be greater than DIP which in turn greater than DOP. In wet tropical river systems, it was found that the extremes of rainfall and runoff shift the importance of biological availability from dissolved inorganic phosphate to phosphorus tied to the suspended load, like in Purari river of Papua New Guinea, where rain fall is extremely high, most of the available phosphorus was bound, either as particulate or as phosphate adsorbed on to clays in the suspended load (Viner, 1982).

Table 3.17 Stationwise annual summary of percentage of different forms of phosphorus in surface waters

Stations	Season	Min	Max	Mean	%*
Station 1	SRP	3.50	32.06	12.54	48.41
	SOP	1.00	11.96	4.43	17.10
	PP	3.22	14.33	8.93	34.48
	TP	11.03	46.98	25.90	
Station 2	SRP	3.85	35.90	12.42	39.25
	SOP	0.49	6.80	3.33	10.52
	PP	0.49	55.40	16.26	51.39
	TP	5.61	77.87	31.64	
Station 3	SRP	0.40	4.28	1.64	21.24
	SOP	0.01	2.74	1.03	13.39
	PP	1.19	10.86	5.04	65.37
	TP	2.00	13.11	7.70	
Station R	SRP	0.61	3.45	1.99	26.67
	SOP	0.13	3.23	1.57	21.02
	PP	0.58	8.40	4.58	61.32
	TP	3.46	12.79	7.47	

* - as percentage of TP.

The low phosphorus concentration is typical of surface waters due to uptake by primary producers and bacteria. Phosphate is principally regenerated by the decay of particulate organic phosphorus and by animals. Death, shedding or molting of organisms plus adsorption of phosphate onto particles produce particulate organic phosphorus. Some particulate organic phosphorus is released as DIP, as particles decay in water column, but some settle on to sediments. In sediments further degradation of settled organic phosphorus to DIP can take place and some of this DIP is precipitated or adsorbed. A high percentage of particulate phosphorus (Table 3.17) recorded at all Stations except at Station 1.

At Station 1 and Station 3, during post-monsoon, a decrease in DIP was associated with an increase in DOP with percentage of PP remains the same. Therefore post-monsoon may be considered as most productive season at these

Stations. Since algae are the primary agent of phosphate removal and their ability to store nutrients also makes algae a more important reservoir than bacteria.

3.3 CONCLUSION

Seasonal salinity variations were experienced in Cochin estuary, due to the high volume of fresh water inundating the estuary, during South West monsoon. Although salinity variation in mangrove fringed creeks were also influenced by these seasonal variations in the estuary, Station 1 and Station 2 recorded significantly higher salinities during all seasons compared to Station R. High salinity values indicated that no real flushing taking place at these two Stations according to the tidal dynamics of the estuary. On the other hand Station 3 exhibited salinities that were similar to Station R. Remarkably higher salinities during pre-monsoon at Station 1 and Station 2 might be due to isolation of the head of the creek from near shores by the low fresh water discharge, in turn a maximum salinity regime found causes an increase in salinity of surface water than sea water.

Low pH values were recorded at Station 3, while all other Stations recorded alkaline pH values. During pre-monsoon season Station 1 also exhibited an acidic pH, probably due to microbial activity in surface waters.

Water temperatures were found to vary within normally expected ranges at all the stations. The lowest annual mean value of 29.1°C recorded at Station 1, 29.5°C at Station 2, and 30.2°C at Station 3. A clear seasonal variation was found at all three stations. As expected, the maximum temperature was recorded during pre-monsoon at all stations.

Suspended sediments associated with river influx and plant litter may contribute to the large amount of TSS at the creek waters under study area. The maximum concentrations of TSS varied between 150.13mgL^{-1} and 360.80mgL^{-1} at the three mangrove-fringed creek waters as against the 88.41mgL^{-1}, the maximum TSS concentration exhibited at Station R. At the mangrove creek waters, TSS concentrations showed significant positive correlations with POC, DIP, TP, PP and ammonium concentrations, while no such correlations were observed at Station R.

Mangrove-fringed creek waters exhibited maximum POC concentration during post-monsoon and minimum during monsoon season. An elevated POC concentration exhibited at Station 1,during pre-monsoon. The annual mean POC concentrations at three mangrove-fringed Stations were found to be 7.19mgL-^{1}, 6.85mgL-^{1}, and 5.06mgL-^{1} respectively. At Station R an annual mean value of 4.19mgL-^{1} recorded. Bacterial density, phytoplankton productivity as well as the presence of fine sediment in particulate matter resulted in an elevated concentration of POC in mangrove creek waters.

ANOVA on the general hydrographic parameters like, salinity, pH, TSS and POC values showed significant difference between months. Also the salinity values at Station 1 and Station 2, exhibited significantly higher values than at Station 3 and Station R.

The annual mean values showed almost similar concentrations of nitrate-N at three mangrove-fringed creeks with a minimum at Station 1 (1.82μmolL^{-1}) and maximum at Station 3 (1.97μmolL^{-1}) while Station R recorded an annual mean value of 7.74μmolL^{-1}. Uptake by trees and microorganisms, and by sorption on to the sediment matrix considerably reduces nitrate concentrations in mangrove forests, which in turn make it an effective sink for nutrients.

A general trend of nitrite nitrogen distribution showed minimum values during pre-monsoon at Station 1 and Station 2. The maximum values were recorded at Station 1 during monsoon and at station 3, during pre-monsoon were may be attributed to the bacterial activity in surface water.

Ammonium was the major dissolved inorganic nitrogen species at three of the mangrove-fringed creeks as well as at the reference station. The high concentration of ammonium was found at these sites indicated the net mineralisation of organic matter in this area. The annual mean ammonium concentrations recorded at Stations 1, 2, 3 and R were 13.28μmolL^{-1}, 32.90μmolL^{-1}, 11.54μmolL^{-1}, and 14.11μmolL^{-1} respectively. Remarkably high concentration at Station 2, may be due to the local regeneration from sediments.

The N:P ratio at mangrove-fringed creek waters were varied between 1.36 and 5.70 and Station R, showed an annual mean value of 4.48. The significantly lowered ratio at Station 1 and Station 2, were associated with an enhanced concentration of DIP. The above ratios suggest that the mangrove-fringed creeks of Cochin estuary represent an anthropogenically altered ecosystem.

Concentrations of nitrate, nitrite and ammonium showed significant difference between Stations (ANOVA). Significantly higher concentrations of nitrate and nitrite were recorded at Station R, while higher concentrations of ammonium were recorded at Station 2.

Seasonal variations of DIP concentration at mangrove locations were found to be under the influence of microbial activity. Remarkably higher concentrations of DIP at Station 1 and Station 2 compared to Station 3 may be attributed to their geographical position. Station 1 adjacent to an inhabited area may be under the influence of untreated sewage, which influence the concentration of DIP. Station 2 experiencing evapotranspiration during pre-monsoon, resulted in higher salinity and elevated concentration in DIP. Also due to the low tidal regime at the creeks, Station 1 and Station 2 reduce the transport of accumulated organic matter in the creek. Enhanced bacterial activity may reduce oxygen concentrations in sediment water interface in turn a reduced iron minerals, release inorganic phosphate to the water column. The relationship between seasonal pattern of phosphate in water and flux of phosphate from sediments is an evidence for the regeneration of benthic phosphate affects water column concentrations (Nixon *et al.*, 1984). The highest mean values of ammonium and DIP were recorded at Station 1 and Station 2 may be due to the high residence time for creek water which enhance the desorption processes. Nutrients are also trapped in sediments during the storage for a relatively longer period.

Total depletion of nutrients was not observed during the present study in the mangrove creek waters and estuarine reference site to limit the production of phytoplankton thereby making the waters sustainable for aqua cultural practices. ANOVA results showed, significantly higher DIP and DOP concentrations were recorded at Station 1and Station 2. Lower values recorded at Station 3 and Station R and no significant differences were observed, between the concentrations of DIP and DOP at Station 3 and at Station R. Regarding the PP concentration, no significant difference found, either between Stations or between months.

Station 1 recorded relatively higher TP concentration during monsoon and pre-monsoon. Remarkably high TP concentrations were also recorded in the water column of Station 2 except during post-monsoon, might be associated with desorption of Fe-bound phosphorus attributed to the bacterial reduction of ferric hydroxy-phosphate complexes. which diffusing across the sediment-water interface causing internal loading. Station 3 and Station R recorded similar concentrations of TP with respect to minimum, maximum and mean values. The minimum TP was noticed during post monsoon at all Stations. The correlations of TP concentration with TSS and POC concentrations suggest a relationship of TP with suspended particles.

The analysis of relative composition of each form of phosphorus revealed that the PP concentrations were greater than DIP concentrations which in turn was greater than DOP at all stations except at Station 1, where phosphorus was partitioned into about 34.5% PP, 48.4% DIP and 17.1% DOP. Anderson and Jensen (1992) have shown that Fe-bound P, when present in significant proportions in the sediment, may be a major source for internal P loading in shallow, eutrophic lakes, just as it may be in deeper, stratified lakes. At Station 2 the relative composition of each form of phosphorus observed were 51.4% PP, 39.3% DIP and 10.5% DOP. While Station 3, recorded the percentage composition of PP, DIP and DOP as 65.4%, 21.2% and 13.4% respectively. The reference Station gave a similar composition with 61.3% PP, 26.7% DIP and 21% DOP. Differences in speciation of phosphorus in water column among the studied area can be ascribed to local characteristics, such as extent of fresh water in put, land run-off, tidal amplitude and productivity of biota.

REFERENCES

Alongi, D.M. 1996 The dynamics of benthic nutrient pools and fluxes in tropical mangrove forests. *Journal of Marine Research* **54**, 123-148.

Alongi, D.M., Boto, K.G. & Robertson, A.I. 1992 Nitrogen and phosphorus cycles. In *Tropical Mangrove Ecosystems.* (Robertson, A.I. & Alongi, D.M., eds). American geophysical Union : Washington, D.C. pp. 251- 292.

Anderson, F.O. & Jensen, H.S. 1992 Regeneration of inorganic phosphorus and nitrogen from seston in a fresh water sediment, *Hydrobiologia*, **228**, 71-81.

Ayukai, T., Miller, D., Wolanski, E. & Spagnol, S. 1998 Fluxes of nutrients and dissolved and particulate organic carbon in two mangrove creeks in northeastern Australia. *Mangroves and Salt Marshes* **2**, 223-230.

Balasubramanian, T. & Venugopalan, U.K. 1984 Dissolved organic matter in Pichavaram mangrove environment, Tamil Nadu, South India; In *Proceedings of the Asian symposium on Mangrove environment: Research and Management* (Soepadmo, E, Rao, A.N. & Macintosh, D.J., eds). University of Malaya and UNESCO, Kuala Lumpur. pp. 496-513, Bhowmic, S.K., Roy, G.N. & Chowdhary, A. 1985 A list of twenty four strains of bacteria from the decomposed litter of mangrove areas of Sunderban complex. In *Proceedings of National Symposium on Biology, Utilization and Conservation of Mangroves* (Bhosale, L.J., ed). Shivaji University press, 467-472.

Boto, K.G. 1982 Nutrient and organic fluxes in mangroves. In *Mangrove ecosystems in Australia* (Clough, B.F., ed). Australian National University Press, Canberra, pp:239-257.

Boto, K.G. & Bunt, J.S. 1981 Dissolved oxygen and pH relationships in northern Australian mangrove water ways. *Limnology and Oceanography* **26**, 1176-1178.

Boto, K.G. & Wellington, J.T. 1988 Seasonal variations in concentrations and fluxes of dissolved organic and inorganic materials in a tropical, tidally dominated mangrove water- way. *Marine Ecology Progress Series* **50**, 151-160.

Chakraborty, S.K. 1995. Aquaculture potential of mangrove ecosystem of Sunderbans, West Bengal, India. *Proceedings Fisheries A Multibillion Dollar Industry, Madras, India during August 17-19* (Krishnamoorthy, B., Krishnamoorthy, K.N., Meenakshisundaram, P.T., Nayar, K.N., eds.) Madras, India. Aquaculture foundation of India, pp. 72-83.

Cundell, A.M., Brown, M.S., Standford, R. & Mitchell, R. 1979 Microbial degradation of Rhizophora mangle leaves immersed in the sea. *Estuarine, Coastal and Shelf Science* **9**, 281-286.

De, T.K., Mitra, A. & Choudhary, A. 1987 Studies on phytoplankton and productivity around Sagar Island and Prentice island. Sunderbans, India. *Proceedings of National Seminar on Estuarine Management*, Trivandrum, pp 327-329.

Dittmar, T. & Lara, R.J. 2001 Do mangroves rather than rivers provide nutrients to coastal environments south of the Amazon River? Evidence from long term flux measurements *Marine Ecology Progress Series* **213**, 67-77.

Grasshoff, K., Ehrhardt, M., Kremling, K. (Eds) 1983 Determination of nutrients. In *Methods of sea water analysis*. Verlag Chemie, Weinheim, 125-187.

Hays, F.R. & Phillips, J.E. 1958 Lake water and sediment IV Radiophosphate equilibrium with mud, plants and bacteria under oxidized and reduced condition. *Limnology and Oceanography* **3**, 459-475.

Jagtap, T.G. 1987 Seasonal distribution of organic matter in mangrove environment of Goa. *Indian Journal of Marine Sciences* **16**,103-106.

Kairesalo, T., Tuominen, L., Hartikainen, H. & Rankinen, K. 1995 The role of bacteria in the nutrient exchange between sediment and water in a flow-through system. *Microbial Ecology* **29**, 129-145.

Kannan,L. & Krishnamurthy, K. 1985 Nutrients and their impact on phytoplankton. *In Marine Plants* (Krishnamurthy, V., Untawale, A.G., eds). Papers presented at the All India symposium on marine plants, their biology, chemistry and utilization, Dona Paula, Goa, 73-78.

Kathiresan, K. 2000 A review of studies on Pichavaram mangrove, southeast India, *Hydrobiologia* **430**, 185-205.

Lean, D.R.S. 1973 Phosphorus dynamics in lake water. *Science* **179**, 678-680.

Millero F.J. 1996 Processes in the oceans In *Chemical Oceanography*, Boca Raton, Florida CRC press, 469pp.

Minear, R.A. 1972 Characterization of naturally occurring dissolved organophosphorus compounds. *Environmental Science and Technology* **6**, 921-927.

Nair K.K.C., Sankaranarayanan, V.N., Gopalakrishnan T.C., Balasubramanian, T., Lalithambika Devi, C.B., Aravindakshan, P.N. & Krishnankutty, 1988 Environmental conditions of some paddy-cum prawn culture fields of Cochin backwater, southwest coast of India. *Indian Journal of Marine Sciences* **17**, 24-30

Nixon, S.W. 1980 Between coastal marshes and coastal waters – A review of twenty years of speculation and research on the role of salt marshes in estuarine productivity and water chemistry. In *Marine Science*, vol, 11 Estuarine and Wetland Processes With Emphasis on Modelling, (Hamilton, P. & MacDonald, K.B., ed). 437-525.

Nixon, S.W., Furnas, B.N., Lee, V., Marshall, M., Ong, J.-E., Wong, C.-H., Gong W.K. & Sasekumar, A. 1984 The role of mangrove in the carbon and nutrient dynamic of Malaysia estraries. *Proceedings of the Asian Symposium on Mangrove Environment: Research And Management*, 534-544.

Ovalle, A.R.C., Rezende, C.E., Carvalho, C.E.V., Jennerjahn, T.C. & Ittekkot, V. 1999 Biogeochemical characteristics of coastal waters adjacent to small river-mangrove systems, East Brazil. *Geo-Marine Letters* **19**,179-185.

Parsons, T.R. 1975 Particulate organic carbon in the sea. In *Chemical Oceanography* (Riley, J.P. & Skirrow, G. eds). **Vol 2**, London, Academic Press, 365-383.

Preetha P.M. 1991 Eco-Biological studies of mangrove, Rhizophora- species. *M.Sc. dissertation submitted to Cochin University of Science and Technology*, Cochin.

Purvaja, R. & Ramesh, R. 2000 Natural and anthropogenic effects on phytoplankton primary productivity in mangroves. *Chemistry and Ecology* **17**, 41-58.

Qasim, S.Z. 1972 Taxonomy and biology of blue-green algae, (Desikachary, T.V. ed). University of Madras, Centre for advanced Study in Botany, Madras, pp. 433.

Rajagopal, M.D. 1973 On assimilation and regeneration of phosphorus in two different environments. *Mahasagar* 7,143-149.

Rajendran,N. & Kathiresan, K. 1999 Seasonal occurrence of juvenile prawn and environmental factors in a *Rhizophora mangal*, southeast coast of India. *Hydrobiologia* **394**, 193-200.

Ram, A. & Zingde, M.D. 2000. Interstitial water chemistry and nutrients fluxes from tropical intertidal sediment. *Indian Journal of Marine Sciences* **29**, 310-318.

Rama Raju, V.S., Udaya Varma & Pylee, A. 1979 Hydrographic characteristics & Tidal Prism at the Cochin harbour mouth. Indian Journal of Science **8**, **78-84**.

Rathna Kala, 1995 Microbial production of antibiotics from mangrove ecosystem. *Ph.D. Thesis submitted to Cochin University of Science and Technology under the Post Graduate Education and Research Programme in Mariculture*, CMFRI, P.O. Box. 1603, Cochin 14.

Redfield, A. C., Ketchum, B.H. & Richards, F.A. 1963 The influence of of organisms on the composition of seawater. In *The sea* (Hill, M.N., ed). **Vol 2**. Interscience publishers, New York, pp. 26-77.

Ridd, P.V. Sandstorm, M.W. & Wolanski, E. 1988 Outwelling from tropical tidal salt flats. *Estuarine Coastal and Shelf Science* **26**, 243-253.

Riley, J.P. & Chester, R. 1971 Micronutrient elements In *Introduction to Marine Chemistry* Academic Press, New York pp 152-181.

Rivera – Monroy, V.H. & Twilley, R.R. 1996 The relative role of denitrification and immobilization in the fate of inorganic nitrogen in mangrove sediments (Terminos Lagoon, Mexico) *Limnology and Oceanography* **41**, 284-296.

Rivera-Monroy, V.H., Day,W.J., Twilley, R.R., Vera-Herra, F. & Coronado-Molina, C. 1995 Flux of nitrogen and sediment in a fringe mangrove forest in a terminus lagoon, Mexico *Estuarine, Coastal and Shelf Science* **40**, 139-160.

Rivera-Monroy, V.H., Madden, J.C., Day Jr.,W.J., Twilley, R.R., Vera-Herra, F.& Alvarez-Guillen, H. 1998 Seasonal coupling of a tropical mangrove forest and an estuarine water column: enhancement of aquatic productivity. *Hydrobiologia* **379**, 41-53.

Rizzo, W.M. 1990 Nutrient exchanges between the water column and a subtidal benthic macroalgal community. *Estuaries* **13**, 219.

Sankaranarayanan, V.N. & Reddy, C.V.G. 1970 *Bulletin of the National Institute of Sciences of India* **38**, pp 138-162.

Sarala Devi K., Jayalakshmi, K.V. & Venugopal, P. 1991 Communities and co-existence of benthos in northern limb of Cochin backwater. *Indian Journal of Marine Science* **20**, 249-254.

Sarkar, S.K., Singh, B.N. & Choudhary, A. 1986 The ecology of copepods from Hooghly Estuary, West Bengal, India. *Mahasagar- Bulletin of National Institue of Oceanography* **19**, 103-112.

Selvam, V., Hariprasad, V., Mohan, R. & Ramasubramanian, R. 1994 Diurnal variations in the water quality of sewage polluted Adayar mangrove water, east coast of India. *Indian Journal of Marine Sciences* **23**, 94-97.

Sheeba, P., Sarala Devi, K. & Sankaranarayanan, V.N. 1996 Nutrients from mangrove areas of Cochin backwaters. *Proceedings of eighth Kerala Science congress*, Kochi. pp 87.

Shriadah, M.A. 2000 Chemistry of mangrove waters and sediments along the Arabian Gulf shoreline of United Arab Emirates. *Indian Journal of Marine Sciences* **29**, 224-229.

*Strckland, J.D.H. & Austin, K.H. 1960 Forms of phosphorus in NE pacific waters. *Journal of Fisheries Research Board Canada*, 7.

Stumm, W. & Morgan, J.J. 1981 An introduction emphasizing chemical equilibria in natural waters. In *Aquatic Chemistry* (2nd edn.). Wiley interscience, pp. 625-640.

Subramanian, A.N. & Venugopalan, V.K. 1983 Phosphorus and Iron distribution in two mangrove species in relation to environment, *Mahasagar*-Bulletin of the National Institute of Oceanography, **16**,183-191.

Sundareshwar, P.V. & Morris, J.T. 1999 phosphorus sorption characteristics of intertidal marsh sediments along an estuarine salinity gradient. *Limnology and oceanography* **44**, 1693-1701.

Tanaka, K.. & Choo, P. 2000 Influences of nutrient outwelling from the mangrove swamp on the distribution of phytoplankton in the Matang mangrove estuary, Malaysia. *Journal of Oceanography* **56**, 69-78.

Tezuka, Y. 1990 Bacterial regeneration of ammonium and phosphate as affected by the carbon:nitrogen:phosphorus ratio of organic substrates. *Microbial Ecology* **19**, 227-238.

Trott, L.A. & Alongi, D.M. 1999 Variability in surface water chemistry and phytoplankton biomass in two tropical, tidally dominated mangrove creeks *Marine Fresh Water Research* **50**, 451-457.

Twilley, R.R. 1985 The exchange of organic carbon in basin mangrove forest in a south west Florida estuary. *Estuarine, Coastal and Shelf Science* **20**, 543-557.

Valiela, I. 1984 Nutrient Cycles:Phosphorus, Nitrogen and Sulfur *In Marine Ecological Processes*, Springer Verlag, New York, 312-340.

Venkatesan V. 2001 Sediment and water characteristics of selected prawn farming sites at Cochin during pre-monsoon month. *M.F.Sc. Dissertation submitted Cochin University of Science and Technology, under the Post Graduate Education and Research Programme in Mariculture,* CMFRI, P.O. Box. 1603, Cochin 14.

*Viner, A.B. 1982 A quantitative assessment of the nutrient phosphate transported by particles in a tropical river. *Revue Hydrobiologie Tropicale* **15**, 3-8.

Wells, M.L., Mayer, L.M. & Guillard, R.R.L. 1991 Evaluation of iron as a triggering factor for red tide blooms. *Marine Ecology Progress Series* **69**,93 –100.

Wolanski, E., Mazda, Y. & Ridd, P. 1992 Mangrove hydrodynamics. In *Tropical Ecosystems* (Robertson, A.I. & Alongi, D.M., eds). American Geophysical Union, Washington, D.C. pp 43-62.

*Wolanski, E. 1989 Measurements and modeling of the water circulation in mangrove swamps. *COMARF Regional project for Research and Training on Coastal Marine Systems in Africa- RAF/87/038.* **Serie Documentaire No.3**, 1-43.

Woodroffe, C.D. 1985 Studies of a mangrove basin, Tuff Carter, New Zealand. III The flux of organic and inorganic particulate matter. *Estuarine Coastal and Shelf Science* **20**, 447-462.

* Not referred in original

Chapter 4

SEDIMENT CHARACTERISTICS AND NUTRIENT STATUS

4.1 INTRODUCTION

Carbon, nitrogen and phosphorus are the most significant macronutrient elements studied in aquatic system. In a specific aquatic system nutrient dynamics partition these elements among water, sediment and biota to attain a natural balance. This balance may change as nutrients are introduced from agricultural, industrial and urban sources. Studies on nutrients in aquatic sediments are mainly related to the assessment of the effect of their increasing concentrations originating from different sources. Accumulation of nutrients in water and sediments can result in eutrophication of lakes, ponds and rivers. The eutrophication is often accompanied by depletion of oxygen in the water and decrease of biodiversity in the affected water body (Vollenweider, 1968; Foehrenbach, 1973; Sutcliffe and Jones, 1992). Bonani *et al.* (1992) showed that sediments play an important role in the accumulation and regeneration of nutrients. Organic matter produced by phytoplankton in eutrophic shallow lakes settles to the sediment and decompose by aerobic and anaerobic processes, during which different carbon, nitrogen and phosphorus compounds are produced (Anderson and Jenson, 1992). Furthermore, decomposing organic material affects changes in oxygen concentrations and redox potential, which in turn affects nitrogen and phosphorus release from the sediments to the overlying water. Sediments are often thought of as nutrient sinks by their capability to adsorb and accumulate different forms of nutrients (Bailey, 1968).

The ecological significance of carbon as a nutrient is through its organic forms. The concentration of organic carbon in marine surface sediments depends on the extent of supply of organic matter, preservation condition and dilution by mineral matter. The results of organic carbon measurements are usually expressed as total organic carbon (TOC) or C_{org} values in percentage of dry sediment. Within sediment, the organic carbon content decreases with increasing depth due to mostly microbiological remineralisation as well as abiological oxidation during early diagenisis. Carrying out the analysis to the molecular level could arrive at the chemical composition of this organic matter. The concentration of total organic carbon is often used in correlation with other elements. The carbon to nitrogen and carbon to phosphorus is used to characterise the association of nitrogen and phosphorus in organic matter. Nitrogen found in sediments in various forms dissolved in pore water, adsorbed on the sediment and contained in particulate organic detritus and living organisms of various sizes. Some of the forms defined analytically as exchangeable ammonium, exchangeable nitrate and total nitrogen/total Kjeldahl nitrogen. Biological activity in living and dead tissues produces reduced form of organic nitrogen ranging from simple amines to complex proteins. Ammonia is the most reduced form of inorganic nitrogen, and is the product of decomposition of organic matter. Bacterial oxidation in the nitrification cycle produces nitrite and nitrate. Phosphorus species in the environment include organic phosphorus compounds, inorganic phosphate and mineralised inorganic complexes with iron, calcium and aluminium. Phosphorus precipitates to form low solubility compounds and metallic complexes, and is relatively immobile compared to carbon and nitrogen. The natural abundance of these nutrients is in the order were carbon, nitrogen and phosphorus. Being the least abundant phosphorus is considered as the limiting nutrient.

The amount of organic carbon in soil is important in soil classification and chemical characterization. Many soil bacteria require organic carbon as an energy source. Hence organic soil (organic carbon >6%) are likely to exhibit greater microbiological activity than mineral soils. Nitrogen exist in variety of forms in soils, such as inorganic and organic forms like proteins, amino acids etc. The inorganic forms, i.e., ammonium, nitrate and nitrite ions, are the only forms that can be directly utilized by plants. Phosphorus also exists in a variety of chemical forms, which again can be broadly subdivided into organic and inorganic forms. Organic matter in sediments relative to the primary producers is enriched particularly in carbon and hydrogen, whereas it is depleted in oxygen, (but the degree depend on the extent of sedimentary organic matter), nitrogen and phosphorus. Loss of nitrogen occurs by preferential degradation of organic nitrogen compounds. Depletion of phosphorus is due to facile hydrolytic cleavage of bound phosphate groups.

Tropical mangrove forests are very productive, and their associated food chains and nutrient cycles are often closely linked to those in adjacent coastal waters (Woodroffe, 1992). Tropical mangrove sediments possess reduction, oxidation properties, and other physicochemical characteristics such as pH, grain size etc typical of other estuarine and marine intertidal deposits (Boto and Wellington, 1984). Physical, chemical and biological processes, operating in mangrove ecosystems to sustain high levels of productivity are due to the wide range of interactions among different structural components such as soil, water, flora and fauna of the ecosystem. The cycling of nutrients in a mangrove ecosystem begins with the litter decomposition. The litter decomposition takes place by the combination of two processes. The leaching of either elements or compounds (Steinke *et al.*, 1993) and also by the microbial degradation (Lee *et al.*, 1990). The leaching eventually attracts, more bacterial population (Rajendran and Kathiresan, 1999). Bacteria and fungi contribute to decomposition of the mangrove material and to the transformation and cycling of nutrients. A number of factors like the species of the plant, tidal height, rainfall, temperature etc affect the rate of litter decomposition and therefore the rate of nutrient cycling. The degrading plant litter is consumed by wide variety of organisms as well as it releases nutrients to mangrove ecosystem for recycling. The mangrove insects and macrobenthic community act as macro degrader by braking the large, thick, wax coated mangrove leaves into smaller fragments. Then mangrove microbial communities (viz., bacteria, fungi and protozoa) complete the degradation of the litter into detritus. The deposit feeders (viz., crabs, molluscs, polychaetes, nematode etc) through their feeding activities turn over the surface sediment layer thereby exposing new litter surfaces to microbial attack. Edaphic factors that influence the productivity are anaerobiosis, nutrient availability and salinity. Factors that prevent build up of entirely anoxic conditions in mangrove mud are not known, but this characteristic has been ascribed to several factors such as crab burrowing, poor quality of organic matter, high bacterial activity and translocation of oxygen by mangrove trees to their roots.

Mangroves are shallow rooted, the roots being concentrated mainly in the top 50-100 cm of the soil and seldom penetrating to the depths beyond 2 m. Water and nutrients are absorbed by a dense mat of fibrous roots that usually originate from underground cable roots or smaller secondary roots in close proximity to the aerial "breathing" roots and in the case of Rhizophora, at the points of entry of the prop roots to the soil (Gill and Tomlinson, 1977). The shallowness of the root system, together with the close physical coupling of the smaller metabolically active roots and the aerial roots minimises the distance through which gases such as oxygen must diffuse in order to reach the extremities of the root system. In view of the fact that most of the fine absorbing roots are found near the soil surface, the physical and chemical properties of the rooting depth of the soil are probably more important than those at greater depth.

This chapter is concerned with the contributions of mangrove detritus to adjacent near shore areas in terms of sediment nutrient levels. Although much of the deposited plant litter is highly refractory, the amount of sedimented material appears to enrich the bulk concentration of carbon and nitrogen in sediments (Alongi, 1990). Grain size analysis of surface and core sediments, total organic carbon, total nitrogen, and total phosphorus were determined and their seasonal discourse was found out. The spatial and temporal variations in stoichiometries of carbon, nitrogen and phosphorus were also computed.

4.2 RESULTS AND DISCUSSION

4.2.1 Properties of Surface Sediments

Grain size distribution

A great variety of grain sizes are typical for the sediments on the near shores, with very coarse sand or gravel accumulating in high-energy environments and very fine-grained material accumulating in low-energy environments. The development and the hydrodynamic history of terrigenous sediments are described in its essentials by the grain- size distribution and the derived sediment characteristics. Therefore a classification on the basis of textural features appears suitable to describe the terrigenous sediments. The subdivision of sedimentary particles in the present study encompasses three major categories: sand (>63µm), silt (4-63µm) and clay (<4µm), each further divided into a number of subcategories.

Plotting the percentages of these grain sizes in a ternary diagram results in a basically quite simple and clear classification of the terrigenous sediments. The classification of clastic sediments as proposed by Folk (1974) is made use of in the present study.

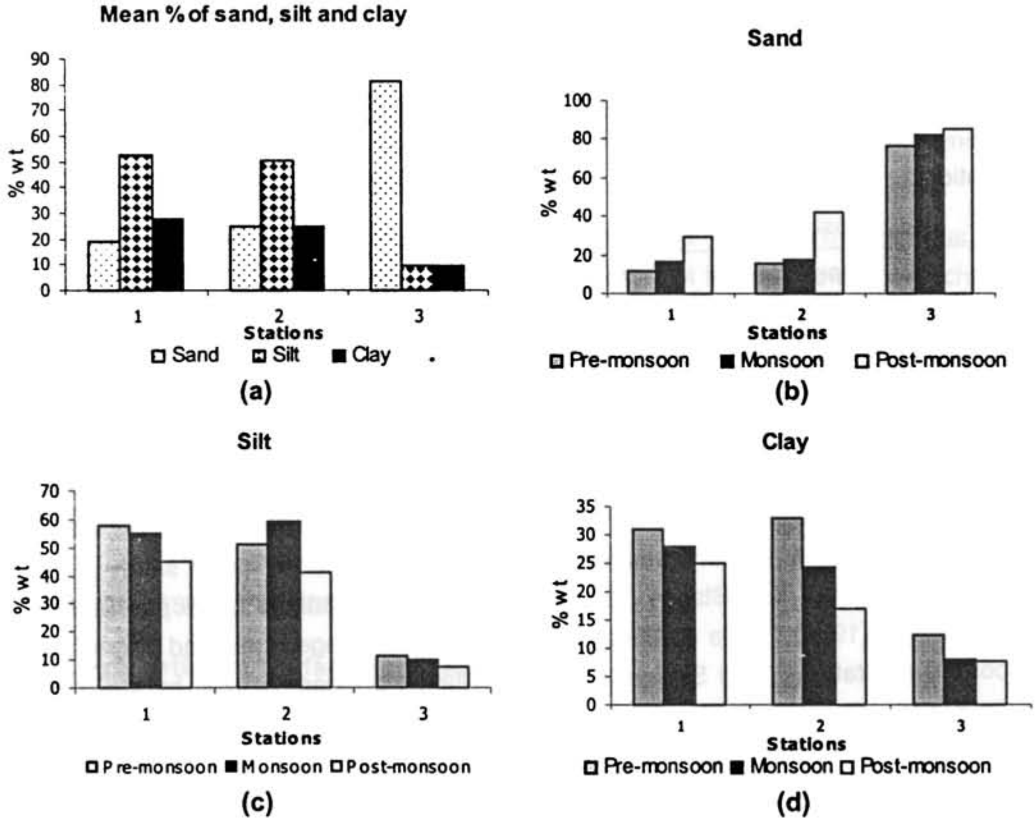
Table 4.1 Seasonal variations of GSA of surface sediments

Stations	Season	Sand %	Silt %	Clay %	Nature of sediment*
Station 1	Pre-monsoon	11.33	58.04	31.12	sandy mud
	Monsoon	16.89	55.10	28.07	sandy mud
	Post-monsoon	29.57	45.27	25.16	sandy mud
Station 2	Pre-monsoon	16.17	51.07	33.08	sandy mud
	Monsoon	17.72	58.96	24.29	sandy silt
	Post-monsoon	41.72	40.91	16.93	sandy silt
Station 3	Pre-monsoon	76.13	11.75	12.39	muddy sand
	Monsoon	81.91	10.31	8.12	muddy sand
	Post - monsoon	85.21	7.15	7.64	muddy sand

* According to Folks classification

The surface sediments showed substantially high content of mud (silt + clay) at Station 1 and Station 2, while the sediments at Station 3 showed a higher percentage of sand. Surface sediment in the study area were found sandy mud (Station 1), sandy silt (Station 2) and muddy sand (Station 3) as per Folk's classification (1974) (Table 4.1). Remarkably high percentage of silt and clay were recorded at Station 1 and Station 2 whereas Station 3, characterized by the high percentage of sand. The annual and seasonal variation in the percentage composition of sand, silt and clay were furnished in Figures 4.1a-1d. The sandy mud sediment (Station 1) recorded the composition of 45.27 to 58.04% silt, 25.16 to 31.12% clay and 11.33 to 29.57% sand, during three seasons. Sediments at Station 2 composed of two textural classes, sandy mud, during pre-monsoon and sandy silt, during monsoon and post-monsoon. Sand, silt and clay in sandy mud sediment were 16.17, 51.07 and 33.08% respectively. Post-monsoon season characterised by a remarkable increase in sand percentage at Station 2. Station 3 revealed the predominance of muddy sand during all three seasons. The percentage of sand was observed to increase from 76.13% during pre-monsoon to

85.21% during post-monsoon. The mean percentage composition of each fraction (Figure 4.1a) also showed substantially high percentage of silt at Station 1 and Station 2 while sand at Station 3. The characteristic root system of mangroves has a dense grid of vertical pnuematophores and arial roots. This structure traps floating detritus and reduces tidal flow, eventually creating conditions where suspended clay and silt particles settle (Soto-Jimmenez and Paez-Osuna, 2001).



(a) (b)

(c) (d)

Fig. 4.1 Annual and seasonal variations of %sand, % silt, % clay

The thick mangrove canopy and comparatively low tidal effects at Station 1 and Station 2 might promote siltation and accumulation of mud rich sediments. The mangrove area of Kannur was also found to have sandy mud sediment nature where there is rich mangrove vegetation (Badarudeen *et al.*, 1998). Muddy sand nature predominated at Station 3 which experience tidal effect. The flooding and ebbing of tidal waters promote washing off finer particles, particularly silt and clays, leaving the coarser sand grains as lag concentrates. The low density of plants at this site also promotes the winnowing process to a greater extent. The mud rich sediment observed at Stations 1 and 2, showed the minimum tidal effect at these sites and sand dominated sediment at Station 3, had resulted from maximum tidal effect at this site. The finer fractions (silt + clay) of the sediment found to be removed where there is maximum tidal influence and impact of waves.

Moisture.

The moisture content (percentage by weight) of the surface sediment varied from 35.15% (Station 3) to 72.14% (Station 1) (Table 4.2). The mean moisture percentages observed were higher at Station 1 and Station 2, while low percentages were recorded at Station 3. The seasonal variations in moisture percentage were depicted in Figure 4.2. Seasonal variations in moisture percentage recorded the general pattern, with a maximum during monsoon and minimum during pre-monsoon except at Station 2. However, pre-monsoon season was associated with maximum percentage of moisture at Station 1 attributed to the high organic carbon.

Table 4.2 Seasonal variation of moisture (%) in surface sediments

Stations	Season	Min	Max	Mean
Station 1	Pre-monsoon	65.51	72.14	68.83
	Monsoon	62.43	63.40	62.92
	Post-monsoon	61.25	62.56	61.91
	Annual mean			64.55
Station 2	Pre-monsoon	61.49	65.72	63.60
	Monsoon	65.37	70.31	67.84
	Post-monsoon	61.68	63.45	62.57
	Annual mean			64.16
Station 3	Pre-monsoon	35.15	42.44	38.80
	Monsoon	41.55	47.50	44.53
	Post - monsoon	38.49	46.52	42.51
	Annual mean			39.92

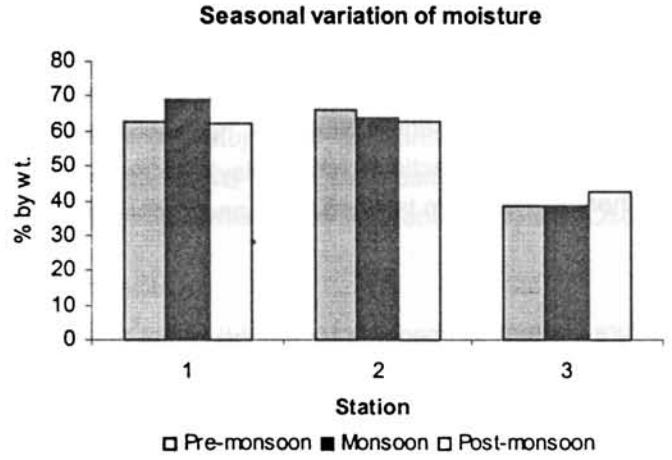


Fig. 4.2 Seasonal mean variation of moisture (%) in surface sediments

Remarkably higher moisture percentages were recorded at the first two Stations and lowering at Station 3 might be associated with the nature of sediments. The high proportion of fine fractions in sediment texture enables them to hold more water than the coarse sediments. The higher percentage of moisture observed at Station 2, during pre-monsoon might be associated with organic matter present in the sediment. It was well established that, an increase in moisture in sediment was associated with an increase in organic matter. In the present investigation, moisture percentages were positively correlated with percentage of clay, and percentage of silt and organic carbon. A significant negative correlation was also observed with the percentage of sand. The present observation indicated the spatial and seasonal variation in moisture content could be attributed to the variation of organic matter and grain size of the sediment.

pH

The pH of the mangrove sediments is governed by the concentrations of reduced iron and manganese hydroxides and carbonates, carbonic acid and humic acid (Patric and Mikkelsen, 1971). The pH values of the surface sediments recorded were in the range 7.63 to 8.63 at Station1, 8.08 to 8.81 at Station 2 and 6.02 to 8.08 at Station 3 (Table 4.3). Sediments at Station 1 and Station 2 were generally alkaline while that at Station 3 were acidic. Seasonal variations of pH values are depicted in Figure 4.3. Minimum pH values were recorded either during pre-monsoon or post-monsoon at all stations. Monsoon season was characterised by maximum value of pH at all stations. A significantly low pH value was recorded at Station 3 during post-monsoon.

Table 4.3 Seasonal variation of pH in surface sediments

Stations	Season	Min	Max	Mean
Station 1	Pre-monsoon	8.63	7.63	8.13
	Monsoon	8.23	8.38	8.31
	Post-monsoon	7.97	8.22	8.09
	Annual average			8.18
Station 2	Pre-monsoon	8.08	8.28	8.18
	Monsoon	8.57	8.81	8.69
	Post-monsoon	8.23	8.53	8.38
	Annual average			8.32
Station 3	Pre-monsoon	7.03	8.08	7.56
	Monsoon	7.66	7.92	7.79
	Post - monsoon	6.02	7.30	6.66
	Annual average			7.34

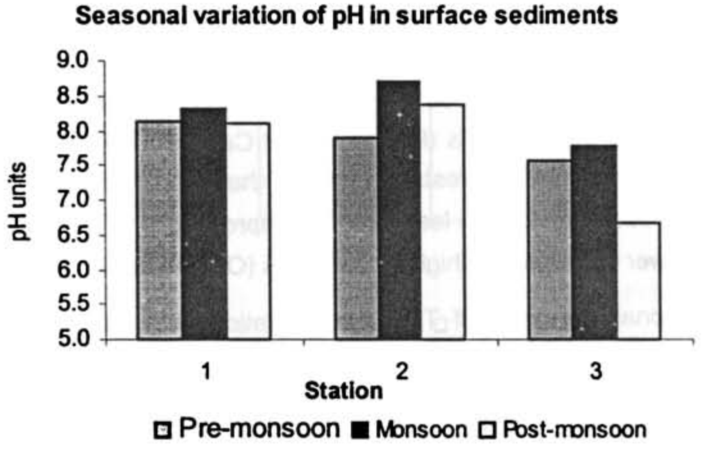


Fig.4.3 Seasonal mean variation of pH in surface sediments

Seasonal variation of pH (Figure 4.3) may be attributed more riverine environment prevalent at Station 3. Decreasing of pH values during pre-monsoon and an increasing trend during monsoon indicated an enhanced microbial activity in summer months. Also marked low pH values recorded at Station 3 post-monsoon, might be associated with the productivity of surface sediment. pH values observed were positively correlated with total organic carbon (TOC), total nitrogen and ammonium concentrations.

4.2.2 Nutrient levels in surface sediments

Total Organic Carbon (TOC)

The preservation of mangrove forests rests on the belief that carbon and energy fixed by mangrove vegetation is the most important nutritive source for animal communities in and near mangrove wetlands (Saenger *et al.*, 1983). The relative contribution of mangrove carbon to total estuarine or wetland primary production varies with forest types, and the amount of clear, open water in the system. The dominant source of carbon is the forest itself, in a riverine mangrove system, where the ratio of forested to open water habitat is high. In a fringing forest, phytoplankton, benthic algae and also other macrophytes become major source of carbon (Day *et al.*, 1982).

Biogenic organic matter is considered labile under most sedimentary conditions due to its sensitivity to oxidative degradation, either chemically or biologically mediated. This is true in well-oxygenated waters. Therefore abundant accumulation of organic matter is associated with anoxia. While recently it was established that high primary productivity in a dynamic system might also contribute to the organic matter in sediments (Pedersen and Calvert, 1990; Demaison, 1991). The food chain in mangrove forests suggested that the principal flow of energy was along the route, mangrove leaf litter → saprophytic community → detritus consumers → lower carnivores → higher carnivores (Odum and Heald, 1975).

The seasonal variations of TOC concentrations in surface sediments are depicted in Table 4.4. The concentrations varied between 21.67mg g^{-1} (Station 3) and 117.80mg g^{-1} (Station 1). Remarkably higher TOC concentrations were recorded at Station 1 and Station 2, compared with Station 3. Generally minimum TOC concentrations were recorded during pre-monsoon at all stations while maximum values were recorded during post-monsoon except at Station 3 (Figure 4.4). However Station 3 recorded similar TOC concentrations during all seasons.

Table 4.4 Seasonal variations of TOC (mg g^{-1}) in surface sediments

Stations	Season	Min	Max	Mean
Station 1	Pre-monsoon	61.93	66.42	64.18
	Monsoon	84.21	99.94	92.07
	Post-monsoon	94.29	117.80	106.04
	Annual mean			87.43
Station 2	Pre-monsoon	69.13	75.82	72.47
	Monsoon	72.75	106.16	89.46
	Post-monsoon	99.20	104.06	101.63
	Annual mean			87.85
Station 3	Pre-monsoon	24.72	31.71	28.22
	Monsoon	21.67	41.07	31.37
	Post - monsoon	26.54	32.76	29.65
	Annual mean			29.75

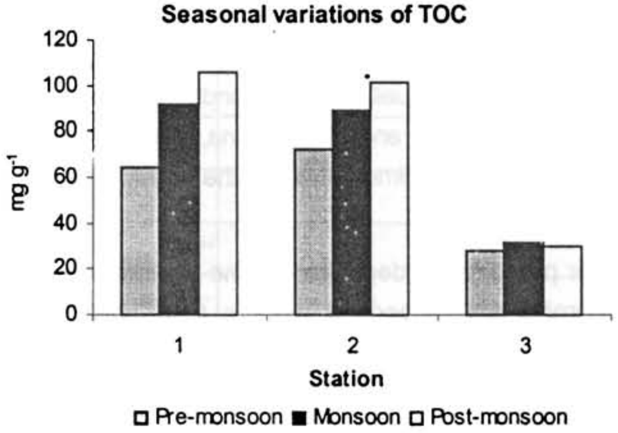


Fig. 4.4 Seasonal mean variation of TOC in surface sediments

The organic content of mangrove sediments is usually high with carbon levels typically ranging from 2 to 15% dry weight (Boto and Welligton, 1984; Kristensen *et al.*, 1988). The total carbon in surface sediments of south Andaman varies from 0.65% to 2.37% (Dinesh, R *et al.*, 1998). Alongi *et al.* (2000) observed that an equal or greater proportion of mangrove carbon is stored in above and below ground biomass than in sedimentary pools, hence the high retention of fixed carbon is one of highly efficient mechanism to conserve essential nutrients. In the

Bangrong area, (Phuket island, Thailand) organic carbon content of mangrove sediments found varied from 0.5 mmol g^{-1} to 3.7mmol g^{-1}dry weight of sediment (Kristensen *et al.*, 2000). The mangrove environment of Goa, India, exhibited TOC concentration ranged from 0.17% to 3.86% of sediment dry weight, and a marked variation in its distribution also observed (Jagtap, 1987).

Remarkably high TOC concentrations were noticed in the surface sediments at Station 1 and Station 2 which were varied between 61.93 mg g^{-1} and 117.80 mg g^{-1} (6.2% to 11.7%). However, Station 3 characterized by relatively low concentration of TOC, varied between, 21.67 mg g^{-1} and 41.07 mg g^{-1} (2.2% to 4.1%). The annual mean value of TOC concentration recorded similar values at Station 1 and Station 2. Earlier reports on concentration of TOC at mangrove areas of Cochin showed that the values ranged between 0.17% and 4.05% (Sunil Kumar, 1996) 0.64 to 7.94% (Badaruddin, 1997). It is well known that coarser sediments usually have lower concentration of elements and pore water solutes than finer deposits. The prevalent hydrodynamics and the presence of mangrove roots which are well developed at Station 1and Station 2, retained fine fraction of sediment. The characteristic root system of mangroves has a dense grid of vertical pnuematophores and arial roots. This structure traps floating detritus and reduces tidal flow, eventually creating conditions where suspended clay and silt particles settle (Soto-Jimmenez and Paez-Osuna, 2001). Thus the plant density together with the low energy tidal regime enhances the concentration of TOC at Station 1and Station 2.

Organic matter produced or deposited on the sediment surface in mangrove forests supports aerobic and anaerobic detritus food chain. Aerobic microbial decomposition of organic matter is usually more rapid than the rate of oxygen diffusion into surface sediments, and oxygen quickly becomes limiting. Anaerobic bacteria below the upper few millimeters of sediment therefore carry out most decomposition, except where animal burrows and plant roots channel oxygen to deeper sediment layers (Anderson and Kristensen, 1988; Aller, 1994). Anaerobic decomposition in marine sediments is performed by a wide variety of bacterial types utilizing a number of electron acceptors (e.g., nitrate, oxidized iron and manganese and sulphate) to oxidize carbon. The present investigation observed a seasonal variation of TOC concentrations, which might be associated with the variation in bacterial density. Pre-monsoon season associated with high temperature as well as restricted flow of water flourish the growth of bacteria and associated mineralisation resulted in lowering of organic carbon. Several factors like warm temperature, release of nutrients by mangrove roots, rapid deposition of organic matter etc account for the bacterial numbers and activity (Alongi *et al.*, 1993). These conditions were optimum during pre-monsoon, hence decomposition, followed by lowering of TOC at Station 1 and 2. However Jagtap (1987) found seasonal variations of TOC could also be attributed to their oxidation and living organisms present in the few centimeters of the sediment.

The statistical analysis exhibited a significant positive correlation of TOC concentrations with percentage of clay, percentage of silt, percentage of moisture, TN, TP and ammonium concentrations ($p< 0.01$, 0.001) (Table 4.5). The percentage of TOC in surface sediment from three stations was found to be relatively higher than the earlier observations at the mangrove habitats of Cochin estuary. The results indicate that the lack of microbial break down of organic carbon with respect to the organic load at these sites. Maximum TOC was noticed at Station 1, which was characterized by more anthropogenic input.

Table 4.5 Correlation matrix between parameters of surface sediments

	% of clay	% of silt	%of sand	% of moisture	pH	TOC	TN	TP	Ex.Amm.	Ex.NO_3
% of clay	1									
% of silt	0.9225***	1								
%of sand	-0.9621***	-0.9927***	1							
%of moisture	0.8403***	0.9482***	-0.9315***	1						
pH	0.5753*	0.7083**	-0.6786**	0.7343***	1					
TOC	0.6250**	0.7803***	-0.7499***	0.8219***	0.6837**	1				
TN	0.6979**	0.8087***	-0.7916***	0.8454***	0.6900**	0.8932****	1			
TP	0.5165	0.5211*	-0.5314	0.6486**	0.4365	0.6470**	0.6372**	1		
Ex.Amm.	0.6286**	0.7011**	-0.6915**	0.8177***	0.5358*	0.5929*	0.7598***	0.7738***	1	
Ex.NO_3	0.4932*	0.4833*	-0.4949*	0.5143*	0.4431	0.3909	0.4592	0.6780**	0.6327**	1

$p<0.05^{*}$ $p<0.01^{**}$ $p<0.001^{***}$

Total Nitrogen (TN)

Nitrogen is the second most abundant element and like carbon, exist in a wide range of organic forms. Unlike inorganic carbon, transformation between inorganic nitrogen species occur almost exclusive through biological processes with physical equilibria assuming a mirror role. Nitrogen enters mangrove sediments primarily via autochthonously produced leaf litter, microalgae and epiphytes. Other sources include nitrogen fixation by bacteria and cyanobacteria as well as possible particulate and dissolved nitrogen from adjacent coastal zone (Alongi *et al.*, 1992). Due to high content of nitrogen-poor structural carbohydrates in mangrove litter entering the sediment, the nitrogen content of sediment detritus is relatively low, varied from 0.05% to 0.4 % dry weight (Kristensen *et al.*, 1988). There are several studies, which establishes that the largest part of the total soil nitrogen was present in sedimented organic matter (Cartaxana *et al.*, 1999).

Total nitrogen (TN) concentration in surface sediments exhibited spatial and seasonal variations. The minimum concentration recorded at Station 3 (0.97mgg^{-1}) and maximum concentration was recorded at Station 2 (4.90mgg^{-1}) (Table 4.6). The annual mean values recorded were similar to TOC at Station 1 and Station 2, which exhibited remarkably higher concentration of TN than at Station 3. Seasonal variation in TN concentrations are depicted in Figure 4.5. Unlike TOC, maximum concentrations of TN were recorded during pre-monsoon and minimum was recorded during monsoon at all stations.

Table 4.6 Seasonal variations of TN (mg g^{-1}) in surface sediments

Stations	Season	Min	Max	Mean
Station 1	Pre-monsoon	2.90	3.19	3.05
	Monsoon	2.38	4.01	3.20
	Post-monsoon	3.63	4.00	3.82
	Annual mean			3.38
Station 2	Pre-monsoon	4.17	4.50	4.34
	Monsoon	3.77	4.35	4.06
	Post-monsoon	4.80	4.90	4.85
	Annual mean			4.46
Station 3	Pre-monsoon	1.21	1.44	1.32
	Monsoon	0.97	1.23	1.10
	Post - monsoon	1.00	1.21	1.10
	Annual mean			1.31

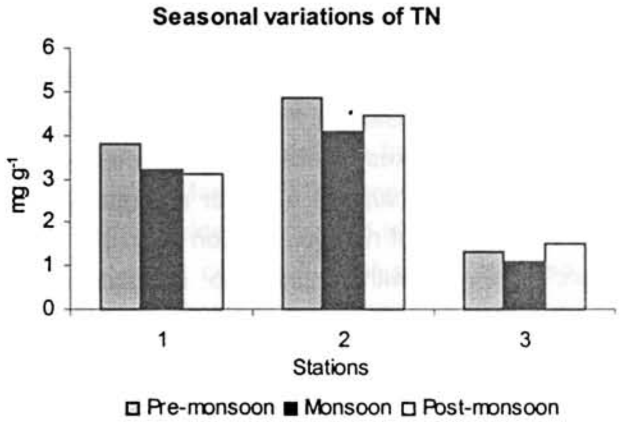


Fig. 4. 5 Seasonal mean variations of TN in surface sediments

Published literatures on TN concentrations in sediments of Cochin mangroves are rare. However, Remani *et al.* (1980) have reported a range of 0.70-3.73mg g^{-1} for TN concentrations in sediments of the Cochin estuary. They found that the maximum value recorded at a Station near a fertilizer factory during monsoon months. TN concentrations in sediments of Pichavaram mangrove area (south east India) were varied between 2.33 gm^{-2} and 3.4 gm^{-2} (Kathiresan *et al.*, 1996). Robertson and Phillips (1995) reported that the nitrogen content in mangrove soil is 0.6-2.0mg g^{-1}, with organic nitrogen being the main form. TN in sediments from mangrove habitats on the Clarence River, Australia, was varied between 1.02mg g^{-1} and 1.12mg g^{-1} (Smith, 1996). While Wahab and Sterling (1991) reported that in the accumulating sediment of culture ponds, the TN averaged between 3.5mg g^{-1} and 8.7mg g^{-1}. Holmer and Olsen (2002) have reported a range of 0.24 to 0.25% DW for mangrove sediment of Bangrong (Phuket Island, Thailand). Thus during the present study, Station 1 and Station 2 showed TN concentrations, which were found not high as that of culture pond sediments but greater than that of Bangrong mangrove sediments (Table 4.5). Station 3 (0.97-1.44mg g^{-1}) exhibited concentrations similar to that of other mangrove ecosystem and reported values of Cochin estuary.

It was well established that nitrogen fixation by cyanobacteria and heterotrophic bacteria are the important nitrogen transformation processes in mangrove forests, occurs on all inhabitable surfaces within the forest like sediment surface, prop roots, bark, logs and leaf litter (Sheridan, 1991; Alongi *et al.*, 1992).

TN concentrations recorded during the present study (Station 1 and 2) were in the maximum range of what reported in earlier studies of Cochin estuary. Remarkably higher concentrations of TN, at Station 1 and Station 2 may be attributed to an increased nitrogen fixation takes place at this site. Also elevated TOC concentrations at these stations support a higher nitrogen fixation. Clough *et al.*, (1983) found an increased rate of nitrogen fixation after the experimental addition of organic carbon. However with respect to inorganic nitrogen, mangrove sediments are poor in release and transformation processes but are efficient in microbial assimilation (Kristensen *et al.*, 2000).

Other than nitrogen fixation, bacteria also serves as an agent for assimilation of organic nitrogen pool. Pedersen *et al.* (1999) found that bacteria incorporated nitrogen from the indigenous particulate organic nitrogen pool, where as detritus served as energy source. Seasonal variation of TN (Figure 4.5) might be associated with the rate of change of microbial assimilation of nitrogen. The studied area was recorded minimum TOC concentration during pre-monsoon, associated with an elevated microbial activity, in turn an increased assimilation of nitrogen was observed during pre-monsoon. Also many studies in mangrove areas reported bacterial fixation of nitrogen (Ravikumar, 1995; Palaniselvam, 1998). Furthermore, maximum TN concentrations were recorded during post-monsoon, indicated maximum nitrogen fixation in optimum conditions.

TN concentrations were positively correlated with percentage of clay, percentage of silt, percentage of moisture, concentrations of TP and exchangeable ammonium ($p<0.01$, $p<0.001$) (Table 4.5). The positive correlation of TN and exchangeable ammonium concentrations indicated their closed cycling. Seasonal variation in concentration of TN may also associated with adsorbed ammonium present in the sediment. During the present study an increase in concentrations of TN at different stations was observed with respective increase in TOC concentrations at these stations, indicated nitrogen fixation through cyanobacteria and heterotrophic bacteria.

Total phosphorus

Total phosphorus concentration in mangrove sediments appears to fall within the range 0.2-1.5 mg g^{-1} (Shanmukhappa, 1987; Dinesh *et al.*, 1998; Alongi *et al.*, 2000). Because of their high organic content mangrove sediments may contain relatively large amount of organic phosphorus. The organic phosphorus accounted for 75-85% of the total phosphorus in mangrove sediments from Sierra Leone and Nigeria (Clough *et al.*, 1983). Most of the organic phosphorus in mangrove sediments probably occurs as complexes with humic and fulvic acids (Sommers *et al.*, 1972). Paludan and Morris (1999) reported that phosphorus can be preferentially bound to humic acids and trapped in the Fe(III) and aluminium pools. This suggests that the mineral composition of sediments also contribute to the observed difference in their phosphorus exchange properties. The phosphorus sorption potential of sediment appears to be controlled by abiotic mechanism such as salinity, sediment surface area, cation exchange capacity and the mineral composition of sediments (Sundereswar and Morris, 1999).

Table 4.7 summarises the measurements of TP in surface sediments from mangrove habitats. Station 3 had the minimum level of TP, while sediment from the Station 1 and Station 2 had the maximum levels. The concentrations recorded were similar at Station 1 and Station 2, were varied from 1.12mg g^{-1} to 2.11mg g^{-1} but those from Station 3 were significantly lower, ranges from, 0.49mg g^{-1} to 0.80mg g^{-1}. The annual mean concentration recorded maximum at Station 2 and minimum at Station 3. Seasonal variations in TP concentrations are depicted in Figure 4.6. Minimum concentrations of TP were recorded during pre-monsoon at all stations, while maximum were recorded either during post-monsoon or during monsoon.

Table 4.7 Seasonal variations of TP (mg g-1) in surface sediments

Stations	Season	Min	Max	Mean
Station 1	Pre-monsoon	1.12	1.48	1.30
	Monsoon	1.35	1.64	1.49
	Post-monsoon	1.69	1.96	1.82
	Annual mean			1.54
Station 2	Pre-monsoon	1.41	1.61	1.51
	Monsoon	1.71	2.11	1.63
	Post-monsoon	1.50	1.63	1.57
	Annual mean			1.66
Station 3	Pre-monsoon	0.49	0.63	0.56
	Monsoon	0.58	0.80	0.69
	Post - monsoon	0.66	0.78	0.72
	Annual mean			0.66

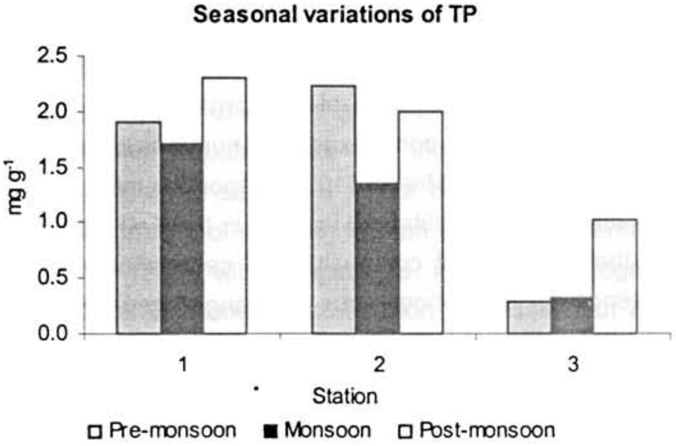


Fig. 4.6 Seasonal variations of TP in surface sediments

The observed TP concentrations at first two stations were higher than that reported in other mangrove habitats but however, comparatively lower than the TP concentrations reported in earlier studies undertaken in Cochin mangroves (Badaruddin, 1997). Remarkable spatial variation with higher values at first two stations might be attributed to different hydrodynamic regime play at these sites. Station 3 marked by the overbearing of coarse fraction, which inhibits accumulation of phosphorus in sediments.

Immobilisation of phosphorus in chemical complexes is a major process occurring in sediments. The oxidative reactions associated with iron and manganese hydroxides would immobilize phosphorus in sediments (Boto, 1992). However, the capacity of sediments to adsorb or immobilize phosphorus is limited by availability of exchange sites and by redox status. The highly reduced mangrove soils have far less capacity to absorb and occlude phosphorus because of the greater solubility of ferrous sesquioxides in the reduced soils. Thus the seasonal variation (Figure 4.6) observed during the present study might be attributed to the variation in redox status of the soil. Pre-monsoon season characterised by low fresh water input into the creeks and weak tidal regime lead to the accumulation of organic matter. The oxidation of organic matter resulted in the development of anoxic microzones on the sediment surface. Thus iron mineral acts as electron donors, subsequently soluble iron phosphate would be produced. Thus the anaerobic decomposition taking place in these ecosystems by a wide variety of bacterial types, utilizing iron minerals as electron acceptors to oxidise carbon might be an important mechanism to decrease the level of sediment associated TP. The increase in TP concentration during monsoon might be associated with the oxidised iron minerals in surface sediment. Anaerobisis exerts profound influence on the chemistry of phosphorus and nitrogen (Clough *et al.*, 1983).

TP concentrations showed significant positive correlation with percentage of silt, clay, moisture, TOC and ammonium concentrations ($p<0.05$, 0.01)(Table 4.5). The positive relationship between TP and ammonium again confirms the anaerobic decomposition taking place in sediments. Organic nitrogen mineralisation in sediments was found to be a significant source of ammonia nitrogen to the overlying water (Blackburn *et al.*, 1988). The cycling of phosphorus in the studied area is highly dynamic at least at first two stations, where the sediments act as an efficient sink for phosphorus as far as an aerobic environment prevailed.

Exchangeable ammonium.

Ammonium is the main form of inorganic nitrogen in anaerobic mangrove soils because nitrification of organic nitrogen stops at ammonium due to the lack of oxygen to oxidise it further to nitrate (Ponnamperuma, 1972). Like other cations, ammonium is capable of occupying cation exchange sites in soils. However the high level of sodium in most mangrove sediments tend to swamp the cation exchange sites, thereby displacing ammonium. Consequently ammonium associated with sediments concentrate more in dissolved phase than in solid phase. Interstitial ammonium is highly mobile and is thus susceptible to being leached by heavy rain or lost through drainage following tidal inundation. The permeability of mangrove sediments are quite low, particularly in sediments with high clay and silt content, so that the loss of ammonium and other soluble nutrients through leaching and drainage may not necessarily be severe. The low permeability of the sediment may be offset by drainage via channels, which form as the result of the burrowing activity of animals and the decomposition of roots.

The exchangeable ammonium concentrations varied between 0.08μmol g^{-1} (Station 3) and 0.84μmol g^{-1} (Station 1 and Station 2), (Table 4.8). Similar to other elements, ammonium concentrations also recorded maximum values at Station 1 and Station 2. Seasonal variations of exchangeable ammonium concentrations are depicted in Figure 4.7. Higher values were recorded during pre-monsoon at Station 1 and no significant seasonal variation at other two stations.

Table 4.8 Seasonal variation of exchangeable ammonium in surface sediments (µmolg^{-1})

Stations	Season	Min	Max	Mean
Station 1	Pre-monsoon	0.41	0.84	0.61
	Monsoon	0.32	0.42	0.37
	Post-monsoon	0.22	0.40	0.32
	Annual mean			0.44
Station 2	Pre-monsoon	0.38	0.84	0.55
	Monsoon	0.47	0.59	0.52
	Post-monsoon	0.57	0.66	0.60
	Annual mean			0.55
Station 3	Pre-monsoon	0.08	0.19	0.15
	Monsoon	0.17	0.26	0.20
	Post - monsoon	0.12	0.20	0.16
	Annual mean			0.17

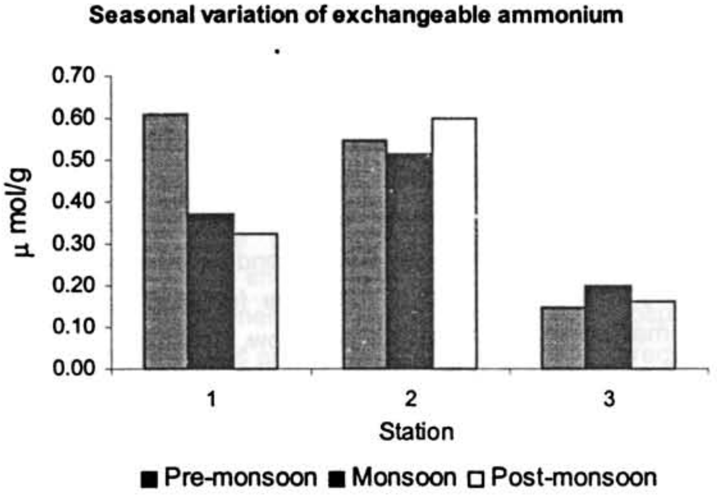


Fig. 4.7 Seasonal mean variation of exchangeable ammonium in surface sediments

The exchangeable ammonium concentration in Futian mangrove forest (Shenzhen, South China) found to vary from 68.35 µg g^{-1} to 71 µg g^{-1} (Li, 1997). In salt marsh ecosystem in Portugal, the exchangeable ammonium concentrations were found to vary from 1.33 to 33 µg N g^{-1} dry weight (Cartaxana *et al.*, 1999). Here a clear seasonal variation in concentration of ammonia was found, showing a maximum during hot season. In Australian mangrove ecosystem (Clarke, 1985) found the variation as 8-111 µM in a fringe forest and 7-39 µM in a riverine mangrove. Low concentration of exchangeable ammonium was observed in the present study may be due to its removal to interstitial phase and in turn leached by tidal water. Clay rich sediment at Station 1 and Station 2, may be attributed to the remarkably high concentrations of ammonium observed at these sites. Exchangeable cations found to be high in soils having high organic carbon and clay as they provide greater surface area for adsorption of the cations. A clayey soil rich in organic matter encourage the growth of benthic algae which, along with the associated micro-organisms, form the main food of fishes. Also the microorganisms responsible for nitrogen fixation and mineralisation of organic matter thrive well in muddy bottom. Observed minimum concentration at Station 3, associated with sandy bottom sediment as well as a regular tidal incursion may also remove ammonium from the soil as it is soluble in water.

The seasonal variation in ammonium at this site was attributed to variation in the amount of organic matter. Comparatively higher values were observed during pre-monsoon and post monsoon at Station 1 and Station 2. The high concentration of available ammonium was attributed to high early summer nitrogen mineralization (Cartaxana *et al.*, 1999). Maximum concentration of exchangeable ammonium was observed during monsoon, at Station 3. This was due to the ammonium that was brought into the system through the allochthonous matter.

Statistical analysis on correlation revealed the positive relationship (Table 4.5) of concentration of ammonium with percentage of clay, silt, concentrations of TOC, TP, and TN ($p<0.05$, $p<0.01$, $p<.001$). The positive correlation of exchangeable ammonium and percentage of clay indicated that the higher percentage of this exchangeable ammonium was due to the decreased mobility in interstitial phase.

Exchangeable nitrate

Two key processes, nitrification and denitrifiction primarily drive dynamics and fluxes of nitrate in marine sediments. Chemoautotrophic oxidation of ammonium to nitrate by nitrifying bacteria in oxic zones of the sediment, and subsequent reduction of nitrate to nitrogen gas by heterotrophic denitrifiers in anoxic zones, are known to be an efficient sink for combined nitrogen in most marine environments (Jenkins and Kemp, 1984; Lindau and DeLaune, 1991; Binnerup *et al.*, 1992). However, only a few attempts have yet been made to determine rates and processes of nitrate transformation in mangrove sediments

(Alongi *et al.*, 1993; Nedwell *et al.*, 1994). Insufficient oxygen diffusion through the waterlogged soil may reduce rates of nitrification and explain the low nitrate concentration in sediments. Denitrification of nitrate formed to gaseous nitrogen and nitrous oxide may also have contributed to low nitrate concentration found in salt marshes (Cartaxana *et al.*, 1999). In their study a salt marsh ecosystem in Portugal, the exchangeable nitrate found to vary from 2-50 nmol Ncm^{-3}. One important sink for nitrate at the sediment-water interface in mangrove sediments is the active community of benthic microalgae (Alongi *et al.*, 1993).

Generally, very low exchangeable nitrate concentrations, nanomol, range were observed at all stations. Significantly higher concentrations were recorded at Station 1 and Station 2, while lower values were recorded at Station 3. The values ranged between, 3.29 μmolg^{-1} (Station 3) and 64.31μmolg^{-1} (Station 1) (Table 4.9). Remarkable seasonal variations of exchangeable nitrate concentrations were found at all stations (Figure 4.8). Station 1 and Station 3, recorded maximum values during monsoon while at Station 2, maximum value observed during pre-monsoon. Minimum values recorded at all stations during post-monsoon.

Table 4.9 Seasonal variation of exchangeable nitrate (nmol g^{-1}) in surface sediments

Stations	Season	Min	Max	Mean
Station 1	Pre-monsoon	20.64	35.50	29.63
	Monsoon	16.61	64.31	32.63
	Post-monsoon	5.26	12.68	8.13
	Annual mean			23.46
Station 2	Pre-monsoon	16.47	49.23	34.43
	Monsoon	16.59	26.28	20.50
	Post-monsoon	13.59	28.84	19.48
	Annual mean			24.80
Station 3	Pre-monsoon	8.09	12.25	9.64
	Monsoon	7.55	30.71	17.17
	Post - monsoon	3.29	5.02	4.03
	Annual mean			10.28

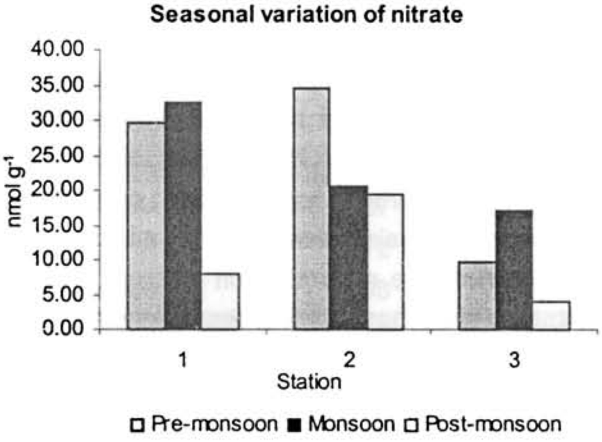


Fig. 4.8 Seasonal mean variation of exchangeable nitrate in surface sediments

Blackburn *et al.*, (1988) reported that in reduced sediments in earthen marine fishponds nitrification of ammonia to nitrate was absent, denitrification insignificant and much of the sedimenting organic detritus was mineralised. Consistent with this observation, Smith (1996) observed organic nitrogen as the main form of nitrogen in pond sediment as well as in the mangrove habitats of Clarence River, Australia. Hence, exchangeable nitrate concentrations may be associated with the assimilation by sediment microalgae (Alongi *et al.*, 1993). Spatial variation may also be associated with the oxygen availability in sediments. The higher concentrations at Station 2 may be associated with an oxic environment at this site as the mangroves translocate oxygen to their roots. While the minimum concentration observed at Station 1 and Station 2, during post-monsoon may be due to the maximum uptake by plant for their luxurious growth during post-monsoon. The maximum concentration at Station 3 during monsoon may be as a result of the high river runoff. The matrix of correlation of exchangeable nitrate concentrations and other parameters exhibited a positive relationship with percentages of clay, silt, moisture, TP, and exchangeable ammonium ($p<0.05$, $p<0.01$)(Table 4.5).

4.2.3 Stoichiometries of C, N and P in surface sediments

Carbon:Nitroen ratio (C/N)

Detrital material is the major component of the sediment organic matter in wetlands, and it acts as a major food source for deposit feeders. (Lopez and Levinton, 1987; Tenore *et al.*, 1984). The amount of detritus and its further decomposition influence the carbon and nitrogen content of the sediment. Ammonium immobilisation and assimilation mainly by microbes and plants, always accompanies and counteracts the mineralisation processes. Boto (1982) pointed out that the extent to which these processes balance each other is highly dependent on the C:N ratio of the decomposing organic matter. Substances rich in nitrogen (low C:N) favour net mineralisation, whereas those poor in nitrogen (high C:N) favour net immobilisation. The generally high C:N ratio of mangrove tree components for example leaves, wood etc. and high rates of bacterial cell production (Alongi, 1988) indicate that the rates of immobilization may be high in mangrove sediments.

The organic content of magrove sediments is usually high, with carbon levels typically ranging from 2 to 15% dw (Boto and Wellington, 1984; Kristensen *et al.*, 1988). Due to high content of nitrogen-poor structural carbohydrates in mangrove litter entering the sediment, the nitrogen content of sediment detritus is relatively low ranging from .05 to 0.4%dw (Kristensen *et al.*, 1988, 1991). Accordingly, the high bulk C:N molar ratio (25-40) reflects the origin of the sediment detritus. The algal detritus, an important source of organic matter, in subtidal marine sediments supported predominantly has a C:N ratio around 10 (Lancelot and Billen, 1985).

Generally higher values (Table 4.10) of C:N ratio were recorded at Station 1 and Station 3 while comparatively lower ratios were recorded at Station 2. The ratios found to ranged from 20.79 to 35.32 at Station 1, 16.57 to 28.18 at Station 2 and 20.39 to 33.32 at Station 3. The minimum ratio of 16.57 was recorded at Station 2 and maximum ratio of 35.32 was recorded at Station 1. Seasonal variations of the ratios are given in Figure 4.9. Remarkably higher C:N ratios were recorded during monsoon and minimum ratios were observed during pre-monsoon at all stations.

Table 4.10 Seasonal variation of C/N in surface sediments

Stations	Season	Min	Max	Mean
Station 1	Pre-monsoon	20.79	21.38	21.07
	Monsoon	24.91	35.32	28.79
	Post-monsoon	25.95	29.45	27.78
	Annual average			25.88
Station 2	Pre-monsoon	16.57	16.85	16.71
	Monsoon	16.72	28.18	22.04
	Post-monsoon	20.68	21.24	20.96
	Annual average			19.90
Station 3	Pre-monsoon	20.39	22.09	21.31
	Monsoon	22.42	33.32	28.53
	Post - monsoon	26.47	27.14	26.84
	Annual average			25.56

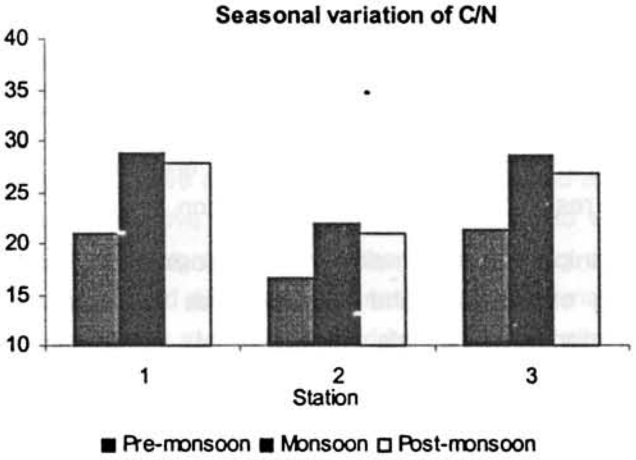


Fig. 4.9 Seasonal mean variation of C/N in surface sediments

The low C/N ratio at Station 2 suggests the mangrove litter detrital at this site. The C/N ratio of sediments of mangrove area of Bangrong forest (Thailand) reported to be 18.3 to 19.3 (Holmer and Olsen, 2002). They suggest that the larger loss of carbon compared to nitrogen in the mangrove leaves led to an overall decrease in C:N ratio of the mangrove detritus. A decrease in ratio usually attributed to colonization by bacteria (Stienke *et al.*, 1993; Wafar *et al.*, 1997). Also

Pedersen *et al.*, (1999) found that bacteria incorporated nitrogen from the indigenous particulate organic nitrogen pool, where as detritus served as energy source. The comparatively higher C/N at Station 1, indicated an accumulation of carbon. It was reported that the sediments from the periphery of prawn farms were found to be similar to that of intertidal mangrove habitat, which reflect the similar rate of organic enrichment that both habitats receive (Smith, 1996). Boyd (1992) reported that for shrimp prawn ponds from four countries, where sediment organic carbon varied from 1.8mg g^{-1} to 72 mg g^{-1}, showed an average C/N of 5.87. Wahab and Stirling (1991) reported that in the accumulating sediment of five earthen ponds used for culture trouts (where nitrogen averaged between 3.58mg g^{-1} and 8.78mg g^{-1}), C/N ratio was 7.9 to 11.6. The fine-grained sediment at Bangrong (Thailand) rich in organic carbon, (12.6% -15.8%) the C/N ratio varied from 19 to 25. The present results at Station 1 and Station 2 were in close agreement with the C/N ratios of Bangrong mangrove area. While Station 3, with a comparatively low percentage of organic carbon (Table 4.4) also exhibited similar C/N as that of Station 1 (Table 4.10). This results suggest the origin of nitrogenous matter at Station 3. Generally higher C/N values also found in sediments with high concentration of humic acid which is known to have a very high C:N ratio (Shanmukhappa, 1987). Further, the nitrogen in sediments of Station 3 could be regarded as biogenic, since humic substances are derived mainly from plant material, are very resistant to microbial mineralisation.

High inorganic nitrogen demand in decomposing leaf litter may regulate an efficient recycling of nitrogen, and can serve as the mechanism for nutrient conservation in mangrove habitats (Twilley *et al.*, 1986a; Alongi *et al.*, 1992). Denitrification appears to be of minor importance for the nitrogen cycling in unpolluted mangrove forests (Nedwell, 1975). Low denitrification rates in sediments of Station 3. may therefore be the consequence of high C:N ratios in the decomposing detritus. On the other hand comparatively low C:N ratios at Station 2 indicated the presence of detritus that are rich in nitrogen. High ammonium demand may also be assigned to assimilation during microbial degradation of nutrient poor litter in the sediment (Alongi, 1996; Rivera-Monroy and Twilley 1996). It has been suggested that ammonium is trapped in the upper few cm of mangrove sediments due to tight coupling between microbial mineralisation and assimilation in this highly reactive zone (Alongi 1996, Kristensen *et al.*, 1998). In the present investigation it was observed that denitrification was less in mangrove sediments, ammonification (mineralisation) assisted by nitrifying bacteria is a rapid process at Station 2. It was found in nitrogen mineralisation studies of mangrove sediments, the net production of ammonium was found as dissolved inorganic nitrogen across the sediment-water interface and also as bacterial assimilated nitrogen at the sediment surface (Kristensen *et al.*, 2000). The above process occurs with a very rapid turn over time of about one day.

Most of the nitrogen appears to be immoblized at Station1 and Station 3. Seasonal variation of C:N showed minimum ratio during pre-monsoon which suggest mineralisation followed by denitrification in anoxic zones. Remarkable increase in C:N ratio found during monsoon and post-monsoon at Station 1 and Station 3, may be associated with land derived humic substances. The high C/N ratio during post-monsoon was associated high concentrations of TOC as well as high values of TN. Further, a large part of the nitrogen in sediments of Station 1 and Station 3 could be regarded as biogenic, since humic substances are derived mainly from plant material, are very resistant to microbial mineralisation. More evidence of this could be obtained from the exchangeable ammonium concentrations observed in the present study (Table 4.8). Low C:N ratio at Station 2, indicated a tight coupling between microbial mineralisation or nitrogenous organic matter and assimilation in this highly reactive surface sediment. These ratio suggest an origin of mangrove detritus in sediments of studied area. The sediment C/N ratio in Chuwei mangrove forest (Taiwan) were found to vary from 11-18.8, suggested a detritus of mangrove origin in the forest (Cheng and Chang, 1999). The high C/N ratios observed during the present investigation may be as a result of accumulated organic carbon at Station 1, and humic derived nitrogeneous organic matter (biogenic origin) at Station 3. Relatively lower ratios observed at Station 2, was associated with the tight coupling between microbial mineralization and assimilation in organic sediments of the studied mangrove area.

Nitrogen:Phosphorus ratio (N/P)

This ratio known as Redfield atomic ratio 16 N: 1P is fairly constant over much of the ocean, but is generally lower in coastal areas. The depletion of nitrogen compared to phosphorus was found in coastal sediments. This loss may be the result of denitrification. The nitrogen limitation in coastal waters may be due to remineralistion of 25-50% of the organic matter in the sediments, where nitrogen may be lost by denitrification (Valeila, 1984).

Generally very low N:P ratios observed at all stations (Table 4.11). The N/P ratios recorded, varied between 1.77 and 2.87 at Station 1, 2.07 and 3.27 at Station 2 and 1.50 and 2.47 at Station 3. Among them, minimum ratio was found at Station 3 (1.50) and maximum ratio observed at Station 2 (3.27). Comparatively higher ratios were noticed in sediments at Station 2. Seasonal variations observed with a maximum during pre-monsoon at Station 1 and Station 3, while Station 2, recorded maximum during post-monsoon (Figure 4.10). Minimum values recorded during post-monsoon at Station 1 and Station 3, while at Station 2, it was observed during monsoon.

Table 4.11 Seasonal variation of N/P in surface sediments

Stations	Season	Min	Max	Mean
Station 1	Pre-monsoon	0.97	3.72	1.59
	Monsoon	1.71	2.26	1.88
	Post-monsoon	1.22	2.48	1.66
	Annual average			1.71
Station 2	Pre-monsoon	1.13	5.91	1.94
	Monsoon	2.13	5.62	2.99
	Post-monsoon	1.51	6.43	2.43
	Annual average			2.45
Station 3	Pre-monsoon	4.01	5.29	4.51
	Monsoon	1.95	8.00	3.39
	Post - monsoon	0.87	1.49	1.07
	Annual average			2.99

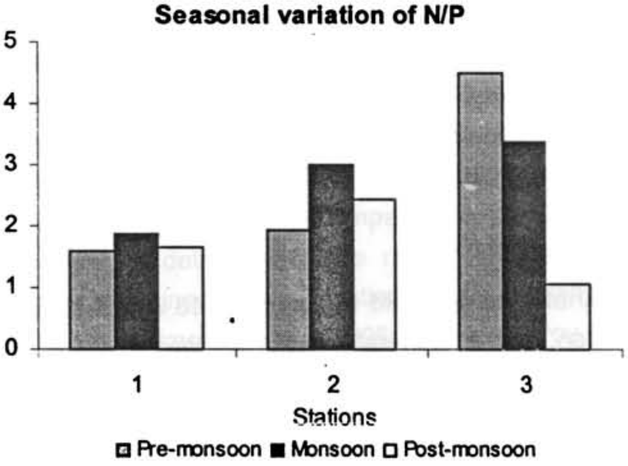


Fig. 4.10 Seasonal mean variation of N/P in surface sediments

Alongi (1990) reported that N:P ratio which ranged from 5.0 to 16.5, at the Hinchinbrook channel (Australia), and the ratio approached Redfield ratio only at one site. The variations found were due to several factors one of which was preferential release of nitrogen relative to carbon and phosphorus. At Pichavaram mangroves (south east coast of India) N:P ratio in sediments varied from 3.2 to 13.2 (Shanmukhappa, 1987). In the present observation the N:P values were found largely deviated from the Redfield ratio (Table 4.11). The previous findings at Cochin estuarine system also revealed low N/P ratio, which varied between 0.80 and 3.69 (Nair, 1992). The low N:P ratios were due to comparatively high concentration of total phosphorus. N:P ratio can be taken as an index of the extent of extraneous influence on a productive water body, since the nitrogen if produced is autochthonous, variation in N/P depend on phosphorus which is mostly external (Shanmukhappa, 1987). The relatively high amount of phosphorus might be due to external source since the mangrove detritus is known to consist of only comparatively low amount of phosphorus. The low N/P ratio indicates that the major portion of phosphorus in sediments of mangrove ecosystem was of abiogenic origin.

The seasonal variation in the quality and quantity of the settling phytoplankton affects the P dynamics at the sediment surface, both chemically and biologically (Tuominen, *et al.*, 1996). The seasonal variation in N/P ratio may be a function of seasonal variation in TP and TN. Remarkably higher N/P values noticed at Station 2, may be associated with the productivity of the mangrove creek waters during pre-monsoon and post-monsoon. Nair *et al.* (1975) found the productivity of the Cochin estuarine waters was high during pre- and post- monsoon months. Since this creek was shallow, after the bloom, the phytoplankton in the water column got deposited on the surface of the sediment. It is well known that fine-grained, silty clay sediments preserve the organic matter than sandy sediments. Thus both these factors most favourable at Station 2, which in turn resulted in a high concentration of TN in sediment and showed higher value of N/P. Although an enrichment of nitrogen during pre- and post- monsoon was found at Station 1 during these seasons, a simultaneous increase in TP also found. Station 3, sediments mostly composed of sand, exhibited low ratios on account of its low TN and high TP during monsoon and post-monsoon season. The spatial and seasonal variations of N/P observed during the present study indicated that the compositions of the mangrove sediment were influenced by allochthonous input during monsoon and high biological activity of the creek waters during pre-monsoon and post-monsoon.

Carbon:Phosphorus ratio (C / P)

C/P in sediments, of estuary is used an index of pollution by domestic sewage into an aquatic system, where C/P used to compare with the Redfield ratio. The sediments in mangrove environments are rarely in agreement with the theoretical Redfield ratio (Alongi, 1996). For e.g. the C/P in sediments of Hinchinbrook channel (Australia) varied from 29.4 to 397.3, and coral creeks of Hinchinbrook channel the ratios found as 392 in low intertidal site to 1291 at high inter tidal site (Alongi, 1990; 1996). The sediments at Bangrong mangroves (Thailand) exhibited a C/P, which varied from 195 to 263. In the Pichavaram mangrove (south east coast of India) sediments this ratio was found to range from 35.1 to 85.7 (Shanmukhappa, 1987). Outwelling of mangrove litter significantly influences sediment concentrations of organic carbon and total nitrogen, stoichiometric ratios of C:N:P (Alongi, 1990). Kairesalo *et al.* (1995) found that mineralisation of organic matter by bacteria may either mobilize or immobilize P, possibly depending on the C/N/P ratio in the available substrate. The richer the substrate is for P or N compared to bacterial biomass the more easily P or N will be released in the mineralization. Goldman *et al.* (1987) have reported that the C/N/P ratio of natural marine bacterial biomass is 45 : 9 : 1 (by atoms) or 17.6 : 4.1 : 1 (by mass). Therefore the decrease in sediment bacteria increased the concentration of inorganic phosphorus in the interstitial waters, in turn an accumulation in solid phase occurs (Tuominen *et al.*, 1996). Also the decrease in bacterial population decrease the ultimate release of phosphorus from sediment to lake water through decreased oxygen consumption leading to high phosphorus sorption at the oxic sediment-water interface (Kairesalo *et al.*, 1995).

Seasonal variation of C:P is depicted in Table 4.12. The values ranged from 41.88 to 62.71 at Station 1, 34.68 to 68.00 at Station 2, and 36.63 to 58.96 at Station 3. Among the ratios the minimum ratio of 34.68 and maximum ratio of 68.00 were, recoded at Station 2. The mean values of C/P showed higher ratios at Station 1. Similar lower values were recorded at Station 2 and Station 3. However remarkable seasonal variations in C/P were observed at all stations (Figure 4.11). Seasonal variations of C/P were not significant at Station 3, but are significant at Station 1 and Station 2.

Table 4.12 Seasonal variation of C/P in surface sediments

Stations	Season	Min	Max	Mean
Station 1	Pre-monsoon	41.88	59.89	50.88
	Monsoon	62.66	62.71	62.69
	Post-monsoon	55.54	60.23	57.89
	Annual mean			57.15
Station 2	Pre-monsoon	47.14	49.39	48.26
	Monsoon	34.68	62.12	48.40
	Post-monsoon	64.25	68.00	66.12
	Annual mean			54.26
Station 3	Pre-monsoon	48.71	49.66	49.19
	Monsoon	36.63	58.96	47.80
	Post - monsoon	39.91	41.45	40.68
	Annual mean			45.89

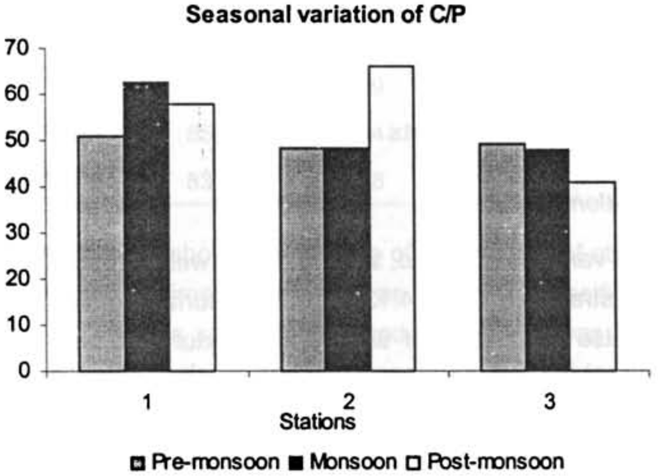


Fig.4.11 Seasonal mean variation of C/P in surface sediments

The observed ratios during the present investigation were far less than that reported at other mangrove sites. Among the mangrove sites investigated, the Station 1 and Station 2, showed high C/P ratios. According to the observations of Sinke and Cappenberg (1988) live sediment bacteria enhanced the release of P from the sediment. Comparatively higher C:P values recorded at Station 1 and Station 2, may be associated with an increased bacterial biomass in sediments.

Many studies have shown that bacterial activity is an important part of the inorganic phosphorus sorption capacity of the sediment (Gachter *et al.*, 1988). Therefore the comparatively lower C:P ratio at Station 3 may reflect a decrease in bacterial activity in the sediment. The seasonal variation observed at Station 1, exhibited a minimum ratio during pre-monsoon, which may be associated with maximum immobilization of phosphorus by bacterial biomass. A decrease in bacterial biomass might have occurred during monsoon flooding which enhanced the C/P during this season at Station 1. Associated with high productivity during post-monsoon season may deplete phosphorus in sediments in turn an increased ratio was noticed at Station 2.

The observed C/P ratio at the studied area reveal the accumulated phosphorus load in creek waters could be reduced by the mangrove plants and associated microorganisms. However to arrive at the cause of deviation from Redfield stoichiometry in the present investigation warrants more information on the kind of litter produced in this area, and also on the influence of microbes on carbon, nitrogen and phosphorus dynamics in this particular ecosystem.

4.2.4 Properties of Core Sediments

Grain-size distribution

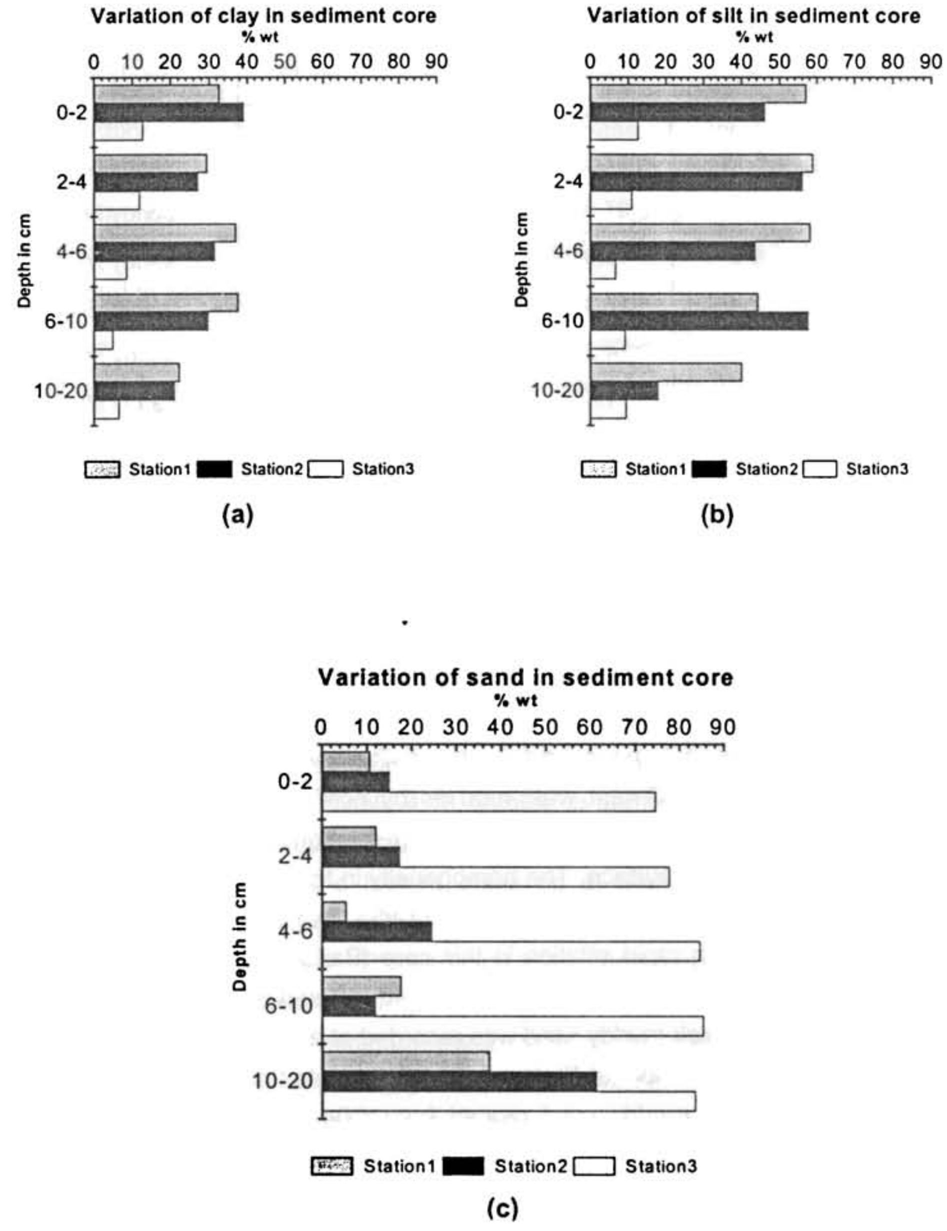
The vertical variations of sand, silt and clay in weight percentage of sediment dry weight are illustrated in Table 4.13. Similar to surface grain size analysis, the core sediments also composed of sandy mud textural facies at Station 1 and Station 2, while muddy sand texture observed at Station 3. Marked change in textural facies observed, a mud layer (4-6 cm layer) at Station 1 and a muddy sand layer (10-20 cm) at Station 2. The variation in percentage of sand, silt and clay at different depths are depicted in Figures 4.12a to 4.12c. Although there was some exceptions, maximum and minimum percentage of clay and silt were observed at Station 1 and Station 3 respectively. However a reversal was found in percentage of sand, recorded maximum at Station 3 and minimum at Station 1.

The distributions of relative percentage of each fraction at various depths are illustrated in Figures 4.13a to 4.13c. Generally higher fraction of silt found at Station 1 and Station 2, while Station 3 recorded higher percentage of sand.

Table 4.13 Grain size analysis in sediment cores

Station	Depth	% Sand	% Silt	% Clay	Nature of sediment
Station 1	0-2	10.64	32.72	57.14	sandy Mud
	2-4	12.02	29.53	58.95	sandy Mud
	4-6	5.46	37.03	58.17	Mud
	6-10	17.58	37.58	44.32	sandy Mud
	10-20	37.38	22.29	30.03	sandy Mud
Station 2	0-2	15.01	39.05	46.10	sandy Mud
	2-4	17.32	27.12	56.05	sandy Silt
	4-6	24.51	31.47	43.61	sandy Mud
	6-10	11.80	29.79	57.65	sandy Mud
	10-20	61.21	21.09	17.86	sandy Mud
Station 3	0-2	74.56	12.80	12.61	muddy Sand
	2-4	77.70	11.98	10.90	muddy Sand
	4-6	84.54	8.59	6.62	muddy Sand
	6-10	85.36	4.94	9.15	muddy Sand
	10-20	83.53	6.58	9.41	muddy Sand

The core at Station 1 showed a 1:2 ratio of silt and clay of about 4cm of depth. At the 4-6 cm interval, sediment was, mud as by Folk's classification. The major textural facies in this core is sandy mud. Sand percentage was found to increase from about 6 cm from the surface. The homogeneity in textural facies of the core as well as the dominance of mud over other size grades indicates the prevalence of a uniform hydroperiod with rapid siltation in this core (Badarudeen *et al.*, 1998). The core at Station 2 was predominantly composed of sandy mud sediment. An intercalation of 10 cm thick muddy sand was recorded at a depth of about 10cm from the surface. The core sediment at Station 3 is uniform in its textural facies index and is composed entirely of muddy sand ranged from 4.94 to 12.8% silt and 6.62 to 12.61% clay. The content of sand of this core was found to vary between 74.56% and 85.36% indicated a high-energy regime at this site. According to Flach and Heip (1996), a homogeneous distribution pattern of grain size in the vertical column of sediment suggests a constant mixture by bioturbation effects.

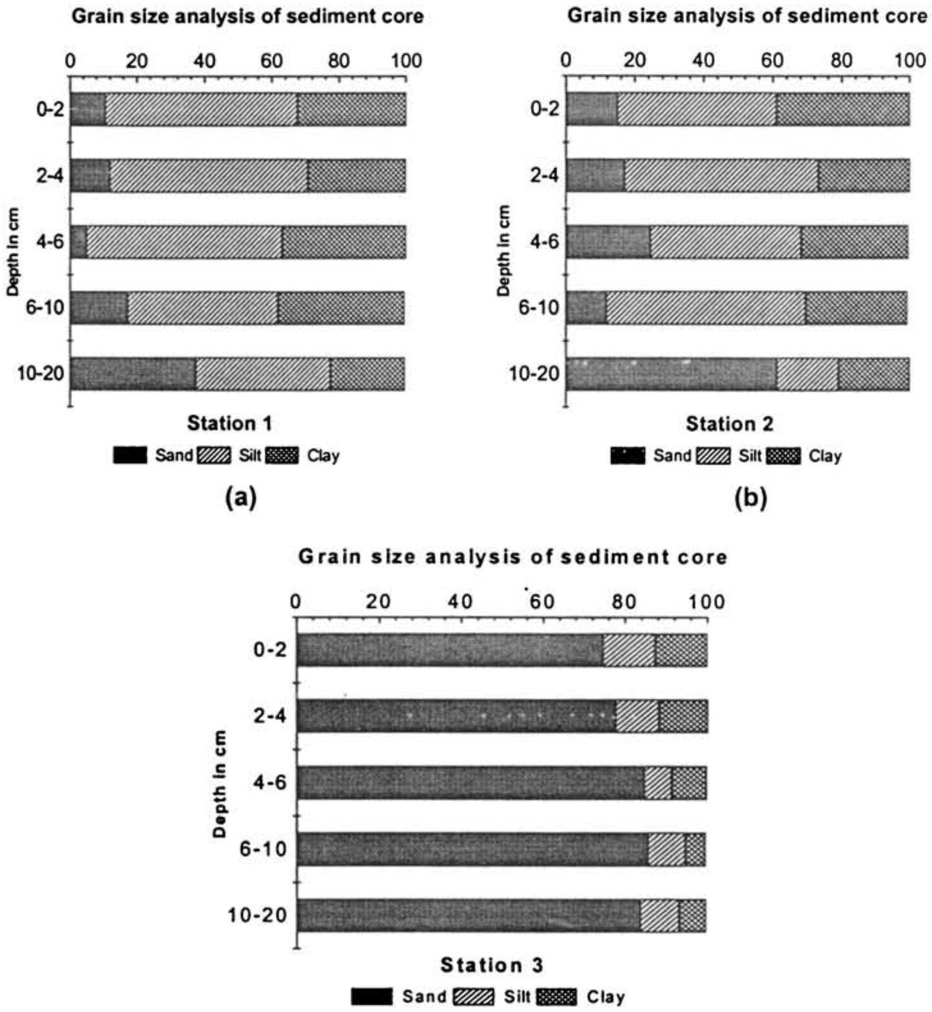


Variation of clay in sediment core

Variation of silt in sediment core

Variation of sand in sediment core

Fig. 4.12 Variation of % of sand, silt and clay in sediment cores



(a) (b)

(c)

Fig. 4.13 Relative composition of sand, silt and clay in sediment cores

Moisture

Table 4.14 summarises the measurement of moisture in sediment cores from the three mangrove fringed habitats. The values varied between 29.40% (Station 3) and 73.47% (Station 1). Generally moisture percentage decreases down the core at all stations (Figure 4.14a). Seasonal variations in percentage of moisture are depicted in Figures 4.14b - 14d. Higher moisture percentage was noticed during monsoon season at Station 1, while lower values were recorded during other two seasons. At Station 2 and Station 3, higher values were observed during pre-monsoon and post-monsoon respectively. An increase in moisture percentage was noticed during pre-monsoon and post-monsoon in subsurface sediment at Station 2.

Table 4.14 Station-wise summary statistics of moisture (%) in sediment cores

Station	Depth	Min	Max	Mean	SD	% of CV
Station 1	0-2	60.44	72.80	65.68	4.50	6.85
	2-4	59.57	73.47	64.45	4.77	7.41
	4-6	58.50	70.14	63.52	3.99	6.28
	6-10	55.76	68.78	60.72	4.91	8.09
	10-20	51.01	61.86	55.83	4.18	7.49
Station 2	0-2	57.79	71.57	64.96	5.32	8.19
	2-4	61.76	67.82	64.21	2.34	3.64
	4-6	57.80	71.54	64.54	4.47	6.93
	6-10	35.71	66.67	58.17	11.44	19.67
	10-20	53.81	64.95	59.31	4.39	7.40
Station 3	0-2	34.48	57.49	49.74	9.82	19.73
	2-4	35.12	57.73	47.85	8.16	17.05
	4-6	35.85	53.19	43.07	6.29	14.61
	6-10	31.84	45.71	37.94	5.61	14.78
	10-20	29.40	40.68	34.41	4.30	12.49

The spatial variation in moisture observed in the present investigation may be attributed to the fine sediment present at the first two stations. The moisture percentage showed a significant positive correlation with organic carbon. It was well established that in sediments, an increase in organic matter was observed with an increase in moisture at a given temperature. The annual mean values of moisture showed identical percentage at Station 1 and Station 2 due to the similar textural attributes at these stations, while less moisture percentage were recorded at Station 3, due to predominant muddy sand nature of the sediment.

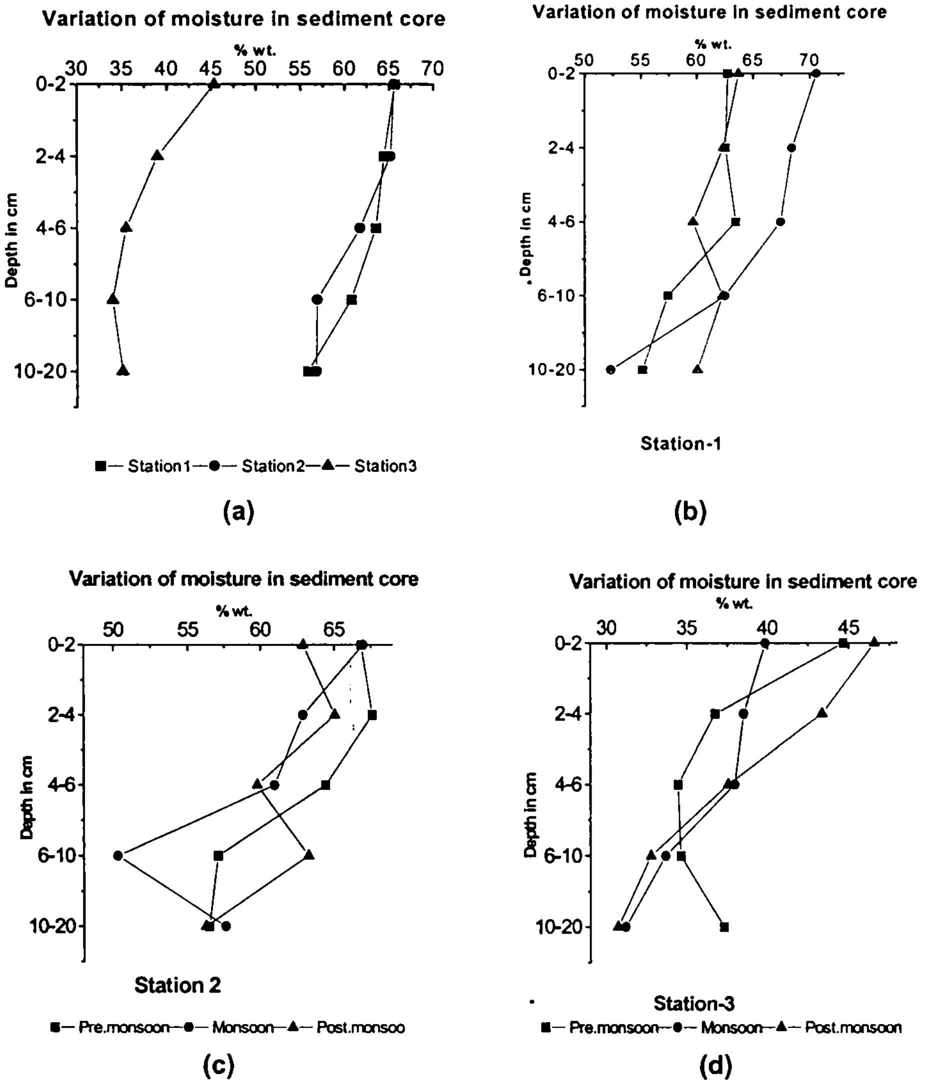


Fig. 4.14 Annual and seasonal variation of moisture in sediment cores

pH

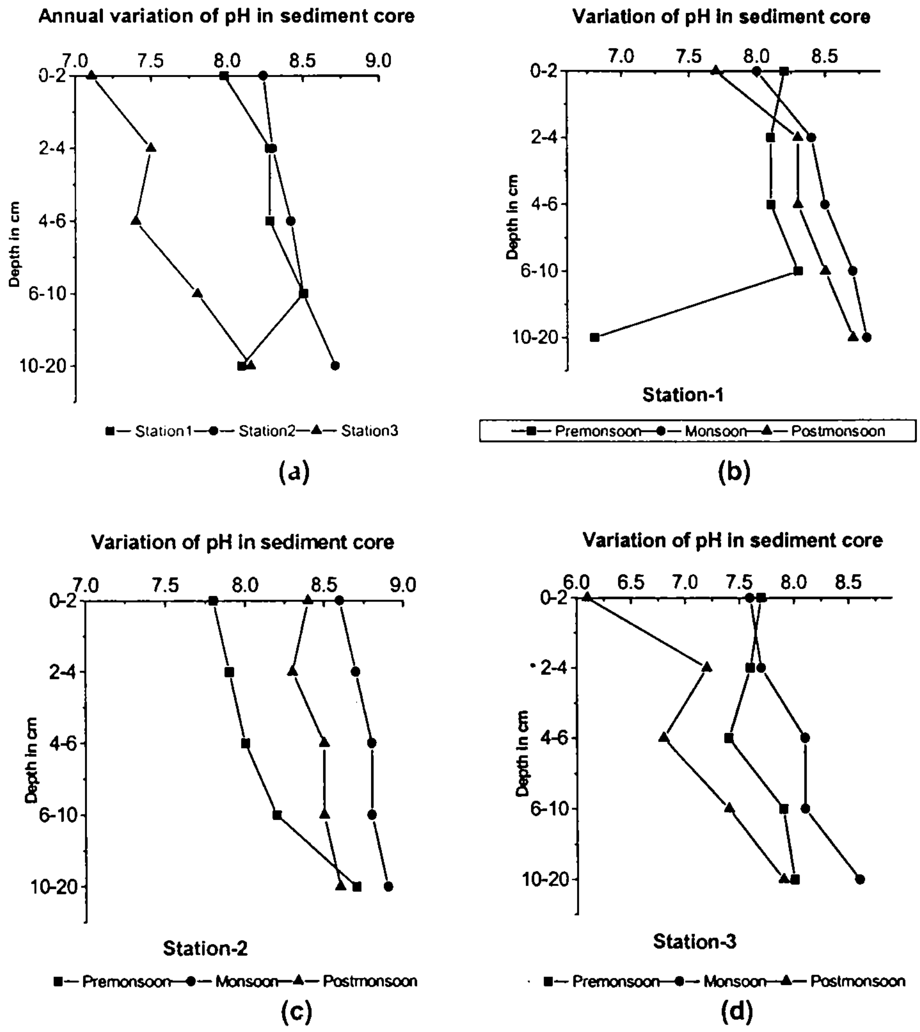
The pH influences the nutrient distribution in sediments, especially calcium bound inorganic phosphorus and iron bound inorganic phosphorus. With a more acid pH, the iron bound inorganic phosphorus is dominant although later even calcium bound phosphorus may be formed (Golterman, 1998). Also Bostrom *et al.*

(1988) found, the increase in pH was associated with coprecipitation or adsorption of phosphate on to calcite. Metal oxides carry a net positive charge at typical fresh water pH and a negative charge at sea water pH (Barrow *et al.*, 1980). The variations in pH values were also associated with macrophytic photosynthesis. Hence an estimate of pH variation was ideal in the study of nutrient dynamics.

Table 4.15 Station-wise summary statistics of pH in sediment cores

Station	Depth	Min	Max	Mean	SD	% of CV
Station 1	0-2	7.45	8.50	7.98	0.40	5.06
	2-4	7.50	8.70	8.28	0.46	5.54
	4-6	7.50	8.70	8.28	0.47	5.70
	6-10	7.70	8.90	8.50	0.49	5.77
	10-20	4.50	9.05	8.09	1.77	21.87
Station 2	0-2	7.30	8.70	8.24	0.49	5.96
	2-4	7.80	8.83	8.30	0.42	5.05
	4-6	7.70	8.90	8.42	0.44	5.23
	6-10	7.80	8.95	8.50	0.39	4.62
	10-20	8.50	9.07	8.71	0.20	2.34
Station 3	0-2	4.80	8.10	7.11	1.49	20.98
	2-4	7.07	8.00	7.50	0.40	5.32
	4-6	6.20	8.20	7.40	0.93	12.63
	6-10	7.10	8.47	7.80	0.59	7.60
	10-20	7.70	8.71	8.15	0.42	5.18

Table 4.15 summarises the measurement of pH in sediment cores to a depth of 20cms. The pH values varied between 4.50 (Station 1) and 9.07 (Station 2). Remarkably higher pH values were observed at Station 1 and Station 2 while lower values were noticed at Station 3. Generally an increase in pH values was recorded down the core at all stations, except beyond 10cm depth at Station 1 (Figure 4.15a). Seasonal variations of the pH values in sediment cores at each Station are depicted in Figures 4.15b-4.15d. At Station 1, pH values were showed an increase with increase in depth during monsoon and post-monsoon. However a remarkable decrease was noticed beyond 10cm depth at the same Station. All other stations, showed a down core increase in pH values during all three seasons.



(a) (b)

(c) (d)

Fig. 4.15 Annual and seasonal variation of pH sediment cores

pH values of mangrove sediments found to be less variable with depth at around pH 6.8-7.0 (Boto and Wellington, 1984). The present investigation showed an alkaline pH which was the impact of sea water in estuary. pH found to vary from 4.50 (10-20cm) to 9.05 at the same depth at Station 1. Other than these two remarkable variations, pH values at Station 1showed a gradual increase down the core. A sharp decrease 4.5 occurred at the 10-20 cm depth may be due to the anoxic condition resulting in the formation of hydrogen sulphide. A gradual increase down the core was observed at Station 2, showed variation from 7.30 (0-2cm) to 9.07 (10-20 cm). Station-wise summary statistics of pH values (Table 4.16) showed high variation at Station 3. At this Station, pH varied from 4.80 (0-2cm) to 8.71 (10-20cm).

The annual variation of pH values in core sediments showed a general increase down the core at all stations indicated an alkaline condition in sediment till 20cms of depth. However a gradual decrease of pH values was noticed at Station 1 during pre-monsoon. Also a marked decrease in pH was observed in 10-20 cm depth at the same Station. Seasonal variations in pH may be due to the anoxic environment created by microbial activity. During post-monsoon at Station 2, surface sediment showed low value compared to the subsurface sediments. This may be partly explained by the increased presence of phyto plankton biomass in the surface sediment, their photosynthesis lead to the formation of carbon dioxide. The Station 3, which exhibits more riverine characteristics, exhibited a low pH than the other two stations. The variations in pH values at the three mangrove locations may be ascribed to the microbial activity prevalent during different depths during different seasons.

4.2.5 Nutrient distribution in sediment cores

Total organic carbon (TOC)

Phytoplankton show relatively constant ratios between carbon content and the content of important nutrient elements, such as nitrogen and phosphorus, so studies of the production and fate of organic carbon are useful in understanding the overall biogeochemistry of aquatic system. The carbon produced within an ecosystem is known as autochthonous production and organic carbon derived from land run off is known as allochthonous production, which is an important source of respirable carbon in lakes. The decomposition of organic matter is orchestrated by a sequence of metabolic pathways that use different electron acceptors as chemistry changes with increasing depth (Canfield, 1993). There are evidences to show that in temperate environments, in intertidal muds, sulphate reduction and oxic respiration are the most important carbon oxidation path ways (Jickells and Rae, 1997; Alongi *et al.*, 1998). But in tropical intertidal muds carbon oxidation is driven proportionally more by suboxic processes than by sulphate reduction (Alongi *et al.*, 1999). The net carbon budget for a standard Rhizophora forest identified, three important sinks of carbon are litter export, crab feeding and bacterial mineralisation (via sulphate reduction) in the sediments, each account for about 20% of carbon removal from the mangrove (Kristensen and Pilgaard, 1999).

TOC concentration in the sediment cores varied between as low as 10.62mg g^{-1} (Station 3) and as high as 140.23mg g^{-1} (Station 1) (Table 4.16). Remarkably higher TOC concentrations were observed at Station 1 and Station 2 compared with Station 3. At Station 1 and at Station 2, TOC concentrations varied from 53.63mg g^{-1} (4-6cm) to 140.23mg g^{-1} (4-6cm) and 49.27mg g^{-1} (10-20cm) and 116.42mg g^{-1} (6-10 cm depth) respectively. While at Station 3, TOC concentrations ranged from 10.62mg g^{-1} (6-10cm) to 54.71mg g^{-1} (0-2cm). Generally TOC concentrations showed a decrease on increasing depth at all stations (Figure 4.16a). Seasonal down core variations in TOC concentrations are depicted in Figures 4.16b-4.16d. Station 1 recorded a remarkable increase at 4-6 cm depth during post-monsoon, while at Station 2, a remarkable decrease at depth beyond 10 cm was noticed. A gradual decrease of TOC concentration was observed at Station 3, down the core, during all seasons.

Table 4.16 Station-wise summary statistics of TOC (mg g^{-1}) in sediment cores

Station	Depth	Min	Max	Mean	SD	% of CV
Station 1	0-2	61.94	114.14	91.84	22.31	24.29
	2-4	59.87	105.52	84.69	20.28	23.94
	4-6	53.63	140.23	85.77	28.76	33.53
	6-10	55.10	114.11	77.08	21.11	27.39
	10-20	56.56	86.33	71.05	12.91	18.17
Station 2	0-2	69.12	111.87	91.97	18.35	19.95
	2-4	65.28	108.22	86.01	16.48	19.16
	4-6	57.81	111.24	85.58	20.70	24.19
	6-10	67.81	116.42	85.93	18.85	21.94
	10-20	49.27	74.96	61.71	11.28	18.29
Station 3	0-2	25.76	54.71	39.35	10.46	26.57
	2-4	24.70	38.91	30.09	5.44	18.07
	4-6	13.03	29.58	19.79	6.37	32.18
	6-10	10.62	16.80	14.26	2.13	14.95
	10-20	13.12	24.77	17.48	4.09	23.42

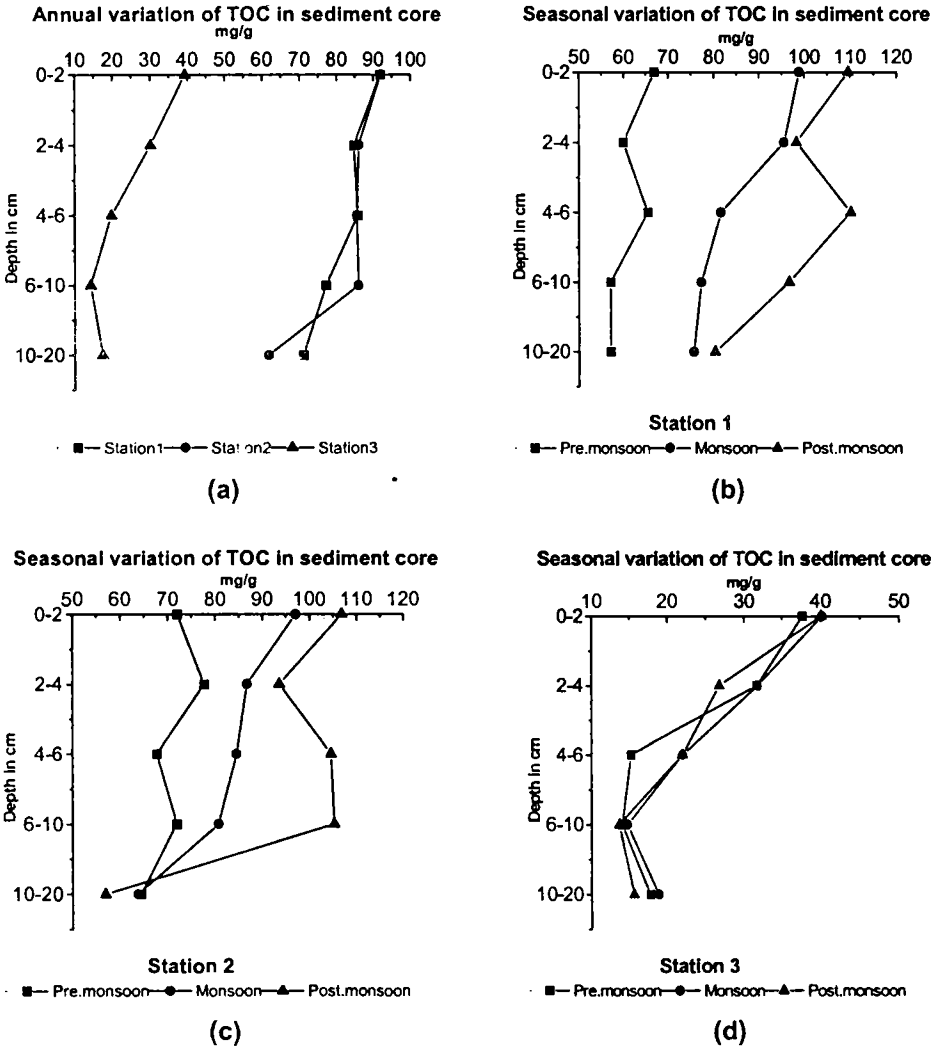


Fig. 4.16 Annual and seasonal variation of TOC in sediment cores

TOC concentrations in sediment cores of the mangrove areas of Kannur, Cochin and Veli found varied from 22.6mg g^{-1} to 69.8mg g^{-1} with highest values noticed at the top layer and lowest recorded at 30-40 cm layer Badarudeen (1997). General pattern of distribution showed a similar variation during the present study. Variation of total organic carbon among the top 3 cm of the sediment was mainly due to the macrobenthic activities (Cheng and Chang 1999). Since these activities return some decomposed products into the sediments as secondary input in the form of fecal pellets and carcasses from litter feeding crabs. Down core decrease may be associated with bacterial mineralisation. Below this depth, anaerobic conditions prevailed most of the time, mainly through organic matter degradation mediated by the sulphate reduction pathway (Kristensen *et al.*, 1991, 1992; Liu *et al.*, 1996, Morsel and Corredor 1993, Wafar *et al.*, 1997). In contrast to temperate salt marsh mud, mangrove mud are less anaerobic, rarely more negative than 300mV, and usually within range of 200 to +100 mV over a one meter profile (Limpsaichol, 1978; Boto and Wellington, 1984; Alongi, 1987).

Generally highest values of TOC recorded at the top, and lowest content recorded at 20-30 cm layer. The particles loosened and suspended by the wave action during inundation of the forest were flushed into the creek and deposit as a silt layer on the sediment surface. Nixon *et al.* (1984) suggested that mangrove forest in Malaysia act as a sink for suspended solids, and Rivera-Monroy *et al.* (1995) found import of microparticulate suspended solids from a mangrove forest in Mexico. The latter authors also found strong seasonal influence of particulate transport due to climate forcing, which can affect the magnitude and direction of water currents. A similar mechanism could explain the low concentrations of TOC observed during pre-monsoon at Station 1 and Station 2.

Litterfall is also considered as the most important primary source of detritus in mangrove environment, which account for about 45% of the total detritus in a mangrove area (Kristensen, 1997). Hence the availability of litter at the first two stations compared to the other also contributed to the high concentrations of TOC. The textural facies also contribute to the retention of organic matter. The fine-grained sediment at Station 1 and Station 2, facilitate trapping of fine particles entering the mangrove ecosystem. Where as the inability of sandy sediment to trap fine particles resulted in a decrease of TOC at Station 3. Furthermore the variation along the depth may also reveal the relationship between textural facies of the sediment and TOC concentrations. The remarkable decrease in TOC concentration in 10-20 cm depth at Station 2, may be due to the sand dominated texture of the sediment at this depth.

Among the seasonal variations, (Figures 4.16b-16d) certain subsurface increase in TOC was found. This increase may be attributed to the presence of bacterial assemblage in sediments. It was found that the grazing of crabs and their numerous burrows probably assist in oxidizing subsurface sediments and removing toxic metabolites like sulphides and ammonium thereby stimulate growth of microheterotrophs like bacteria and trees (Kristensen, 1988; Smith *et al.*, 1991). Subsurface increase in TOC were found only at Station 1 and Station 2, suggested oxidized subsurface sediment.

Significant positive correlation was exhibited between all depths with TOC ($p<0.001$) (Table 4.17). The positive correlation indicated that in all the depths there is high degree of association with TOC. The correlation of TOC concentrations (Table 4.18) with other parameters showed a significant correlation with percentage of clay, silt, TN ($p<0.01$) at all depths. A significant negative correlation was also exhibited with percentage of sand at all depths (Table 4.18a-4.18e).

Table 4.17 Correlation matrix between depths - TOC

	0-2	2-4	4-6	6-10	10-20
0-2	1.0000				
2-4	0.9803***	1.0000			
4-6	0.9817***	0.9663***	1.0000		
6-10	0.9736***	0.9748***	0.9890***	1.0000	
10-20	0.9082***	0.9547***	0.9184***	0.9106***	1.0000

$p<0.01^{**}$. $p<0.001^{***}$

Three way ANOVA was used to test the significance of station, depth and season on concentrations of TOC. A significant difference between stations was observed ($p < 0.001$) (App.15). The least significant difference (LSD) at 5% level for stations is 7.5 mg g^{-1}. Station 1 and Station 2 give significantly higher values of TOC. But there is no significant difference between these two stations. The very low concentration of carbon at Station 3 compared to other two sites may be due to the variability of sediment texture along with non-availability of litter. The maximum value of 110 mg g^{-1} was recorded at Station 1. A minimum value 13.2 mg g^{-1} was recorded at Station 3. Removal of organic carbon by tidal action would explain the low levels of organic carbon at this site. This site is characterised by maximum tidal influence and wave action as compared to the other two sites. The organic carbon was found to increase from the mangrove zone through the fringe forest in wetland in eastern Australia (Clarke, 1985).

The LSD at 5% level for depth is 0.96 mg g^{-1} The depths, 0-2, 2-4, and 4-6, layers showed higher amount of organic carbon as compared to 6-10 and 10-20 layers. The minimum value 13.1mg g^{-1} recorded at a depth of 20-30 cm. The accumulation of organic carbon in surface sediments might be due to plant litter associated with the forest. In mineralisation studies of organic matter, in an intertidal sediment of tropical semi-enclosed delta, the solid phase carbon and nitrogen found to decline with sediment depth (Alongi, *et al* 1999). The sediment cores of Gorai creek (near Mumbai) showed a decreasing trend of organic carbon with depth. They concluded that under tropical temperature, the excess organic loads are largely oxidized and remineralised by rich bacterial population at the sediment water interface apart from being consumed by benthic fauna such as polycheates and bivalves, which are present in high numbers in the creek (Ram and Zingde, 2000).

The LSD at 5% level for season is 7 mg g^{-1}. Significantly higher value of TOC was recorded during post-monsoon followed by monsoon and pre-monsoon seasons. Bacterial remineralisation of organic matter is enhanced by the increase in temperature (Klump and Martens, 1989).

Table 4.18a Correlation matrix between parameters in sediment cores - 0-2cm.

0-2	%clay	%silt	%sand	TOC	TN	TP	Ex.Amm.	Ex.NO$_3$	C/N	N/P	C/P
%clay	1										
%silt	0.8900***	1									
%sand	-0.9570***	-0.9840***	1								
TOC	0.8554***	0.8529***	-0.8769***	1							
TN	0.9570***	0.7690***	-0.8632***	0.6786**	1						
TP	0.8102***	0.8758***	-0.8738***	0.6124**	0.7860***	1					
Ex.Amm.	0.8424***	0.5778*	-0.6968**	0.5269*	0.9232***	0.61131**	1				
Ex.NO$_3$	0.3261	0.2215	-0.2684	0.2689	0.2770	0.2440	0.3441	1			
C/N	-0.3752	-0.0570	0.1829	0.0505	-0.5945**	-0.2669	-0.6597**	-0.0248	1		
N/P	0.1694	-0.0746	-0.0187	-0.1146	0.2935	-0.0598	0.5335*	0.5591*	-0.4114	1	
C/P	-0.6249**	-0.6530**	0.6596**	-0.4700	-0.6284**	-0.8381***	-0.5073*	-0.1134	0.0819	0.0453	1

$p<0.05^{*}$ $p<0.01^{**}$ $p<0.001^{***}$

Table 4.18b Correlation matrix between parameters in sediment cores – 2-4cm.

2-4	%clay	%silt	%sand	TOC	TN	TP	Ex.Amm.	Ex.NO$_3$	C/N	N/P	C/P
%clay	1										
%silt	0.9973***	1									
%sand	-0.9985***	-0.9998***	1								
TOC	0.9131***	0.9206***	-0.9191***	1							
TN	0.8957***	0.9239***	-0.9171***	0.8230***	1						
TP	0.7122***	0.7168***	-0.7160***	0.7341***	0.6591**	1					
Ex.Amm.	0.8718***	0.8832***	-0.8807***	0.7468***	0.8830***	0.4526	1				
Ex.NO$_3$	0.5748*	0.5707*	-0.5720*	0.4476	0.5520*	0.1344	0.4601	1			
C/N	-0.4284	-0.4679	0.4580	-0.2602	-0.7019**	-0.2344	-0.6086**	-0.2426	1		
N/P	0.01699	0.0439	-0.0369	0.0372	0.1530	-0.4573	0.1898	0.2656	-0.1947	1	
C/P	-0.5288*	-0.5325*	0.5318*	-0.4391	-0.5047*	-0.8116***	-0.3758	-0.1592	0.1043	0.4452	1

$p<0.05^{*}$ $p<0.01^{**}$ $p<0.001^{***}$

Table 4.18c Correlation matrix between parameters in sediment cores – 4-6cm.

4-6	%clay	%silt	%sand	TOC	TN	TP	Ex.Amm.	Ex.NO$_3$	C/N	N/P	C/P
%clay	1										
%silt	0.9958***	1									
%sand	-0.9989***	-0.9990***	1								
TOC	0.8978***	0.8787***	-0.8889***	1							
TN	0.8390***	0.7943***	-0.8169***	0.7974***	1						
TP	0.8245***	0.8062***	-0.8159***	0.8485***	0.8089***	1					
Ex.Amm.	0.6773**	0.6565**	-0.6673**	0.5230*	0.7582***	0.3194	1				
Ex.NO$_3$	0.5028*	0.4750*	-0.4890*	0.2063	0.6691**	0.3664	0.6716**	1			
C/N	0.0769	0.1112	-0.0946	0.2164	-0.2111	-0.0237	-0.1216	-0.4807*	1		
N/P	0.0204	-0.0342	0.0077	0.0656	0.2338	-0.1384	0.3498	0.4042	-0.3557	1	
C/P	0.0745	0.06858	-0.0715	0.1733	-0.0432	-0.2548	0.2754	-0.0353	0.5336	0.5707*	1

$p<0.05^{*}$ $p<0.01^{**}$ $p<0.001^{***}$

Table 4.18d Correlation matrix between parameters in sediment cores – 6-10cm.

	%clay	%silt	%sand	TOC	TN	TP	Ex.Amm.	Ex.NO_3	C/N	N/P	C/P
%clay	1										
%silt	0.8776***	1									
%sand	-0.9550***	-0.9803***	1								
TOC	0.8776***	0.9209***	-0.9313***	1							
TN	0.8038***	0.9615***	-0.9261***	0.8068***	1						
TP	0.5621*	0.7300***	-0.6833**	0.8722***	0.5979**	1					
Ex.Amm.	0.6948**	0.7564***	-0.7543***	0.6559**	0.7988***	0.4981*	1				
Ex.NO_3	0.8969***	0.8798***	-0.9139***	0.7771***	0.8509***	0.4857*	0.6586**	1			
C/N	0.0914	-0.1785	0.0729	0.0708	-0.3394	0.0357	-0.3315	-0.0501	1		
N/P	-0.0325	-0.0978	0.0739	-0.1168	-0.1216	-0.3233	-0.2183	-0.1494	-0.2652	1	
C/P	0.4504	0.1888	-0.3023	0.0526	0.2364	-0.4048	0.3231	0.3566	-0.1352	0.5688*	1

$p<0.05^{*}$ $p<0.01^{**}$ $p<0.001^{***}$

Table 4.18e Correlation matrix between parameters in sediment cores - 10-20cm.

	%clay	%silt	%sand	TOC	TN	TP	Ex.Amm.	Ex.NO_3	C/N	N/P	C/P
%clay	1										
%silt	0.7598***	1									
%sand	-0.8900***	-0.9727***	1								
TOC	0.9628***	0.7912***	-0.8987***	1							
TN	0.8970***	0.6358**	-0.7662***	0.8012***	1						
TP	0.7531***	0.8434***	-0.8604***	0.7219***	0.6832**	1					
Ex.Amm.	0.8065***	0.5205*	-0.6530**	0.6230**	0.8431***	0.6733**	1				
Ex.NO_3	0.3703	-0.0965	-0.0645	0.2550	0.5094*	0.1715	0.5647*	1			
C/N	-0.2133	-0.0452	0.1078	-0.1129	-0.4143	-0.0314	-0.3517	-0.2079	1		
N/P	-0.0617	-0.2210	0.1770	-0.1240	-0.0829	-0.4653	0.0606	-0.0725	-0.6092**	1	
C/P	0.0035	-0.2892	0.2016	0.0522	-0.1020	-0.5805*	-0.1681	-0.0739	-0.1076	0.6840**	1

$p<0.05^{*}$ $p<0.01^{**}$ $p<0.001^{***}$

Total nitrogen (TN)

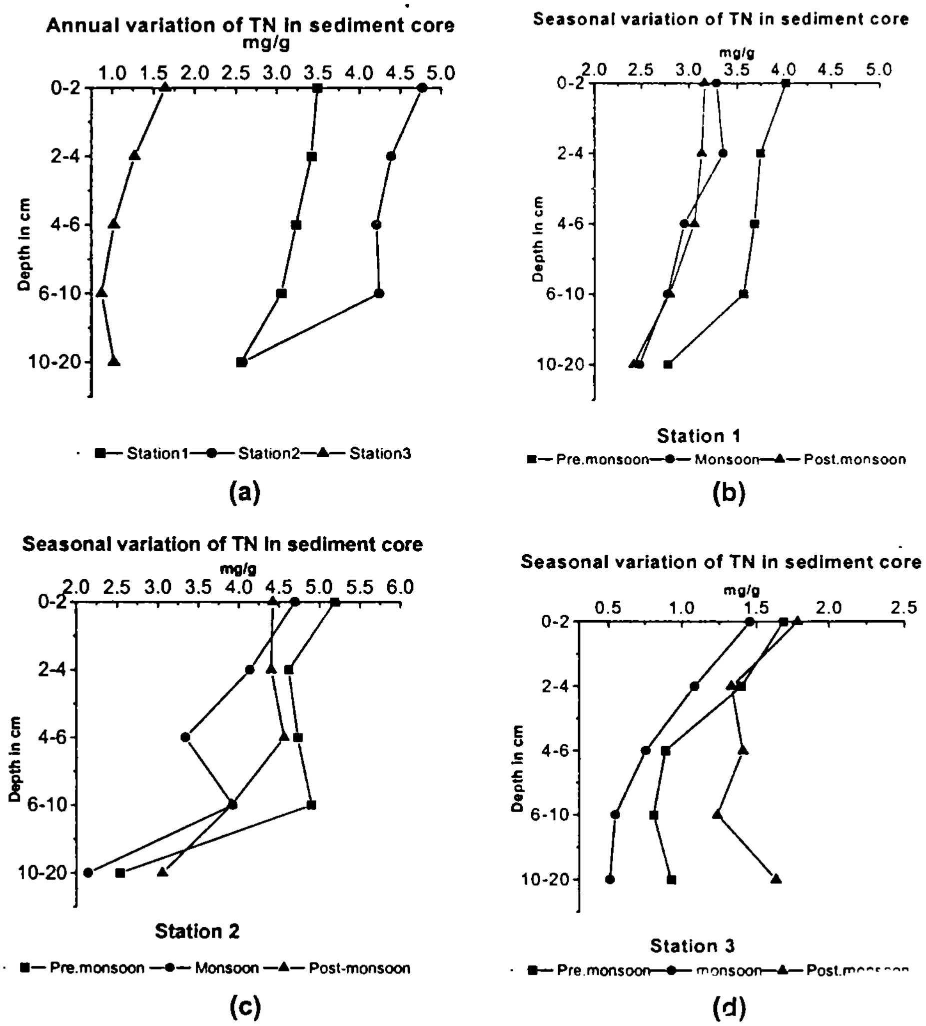
The nitrogen buried in sediments is in various organic and inorganic forms, and its abundance may decrease with depth in a manner similar to that of carbon (Haines *et al.*, 1977). A general feature of mangrove ecosystems is the very low levels of both dissolved and particulate nitrogen compounds (Boto and Wellington, 1984). The primary cause for this apparent nitrogen limitation is the low nitrogen content (high C:N ratio) of mangrove litter; the major source of organic input to the decomposer food chains. It has been suggested that mangrove forests are efficient in retaining and recycling nitrogen via several mechanisms that reduce export. These mechanisms include re-absorption or re-translocation of nitrogen prior to leaf fall, burial of fallen detritus by crabs, rapid and efficient uptake of dissolved materials by bacteria, and comparatively high nitrogen investment in chemical defences by the trees (Boto, 1984; Twilley *et al.*, 1986b). Nitrogen enters mangrove sediments primarily via autochthonously produced leaf litter, microalgae and epiphytes. Other sources include nitrogen fixation by bacteria and cyanobacteria as well as possible import of particulate and dissolved nitrogen from adjacent coastal zone (Alongi *et al.*, 1992). Both benthic microalgae (Kristensen, 1993) and bacteria are responsible for a very rapid turnover of nitrogen in mangrove sediments. Alongi (1988) estimated that the bacterial biomass accounts for nearly 8% of total particulate organic nitrogen pool in the upper 10 cm of the sediment in an Australian mangrove forest. It was also suggested by Alongi (1989) that bacteria and benthic microalgae in mangrove sediments are sinks for nutrient because the system is characterised by a closed internal cycling – death, decay uptake and growth – and thus serve as a mechanism for nutrient conservation i.e. reducing net system mineralisation.

Table 4.19 summarizes the measurement of TN in sediment cores to a depth of 20cms. The TN concentrations varied between 0.44mg g^{-1} (Station 3) and 5.84mg g^{-1} (Station 2). As in the TOC concentrations, Station 1 and 2 showed higher TN concentrations than Station 3. The TN concentrations ranged from 2.30mg g^{-1} (4-6cm) to 4.35mg g^{-1} (4-6cm) and 1.94mg g^{-1} (10-20) to 5.84mg g^{-1} (6-10) at Station 1 and Station 2 respectively. However, TN concentrations at Station 3 showed a variation from 0.44mg g^{-1} (6-10cm) to 1.81mg g^{-1} (0-2cm). TN concentrations showed the same decreasing pattern as TOC concentration with a remarkable decrease beyond 10-20 cm depth (Figure4.17a). The seasonal variations in depth pattern are given in Figures 4.17b-4.17d. Higher values of TN concentrations were recorded during pre-monsoon season at all stations except at Station 3. However at Station 3, higher TN concentration were observed during post-monsoon with an increase beyond 10cm of depth during all seasons.

Table 4.19 Station-wise summary statistics of TN (mg g^{-1}) in sediment cores

Station	Depth	Min	Max	Mean	SD	% of CV
Station 1	0-2	2.39	4.17	3.48	0.70	20.19
	2-4	2.46	4.26	3.41	0.63	18.57
	4-6	2.30	4.35	3.23	0.73	22.71
	6-10	2.46	4.06	3.05	0.55	17.90
	10-20	2.39	2.84	2.56	0.19	7.37
Station 2	0-2	4.12	5.40	4.75	0.55	11.50
	2-4	4.13	4.65	4.39	0.23	5.17
	4-6	3.06	4.82	4.10	0.74	18.08
	6-10	3.72	5.84	4.29	0.78	18.12
	10-20	1.94	3.92	2.57	0.70	27.46
Station 3	0-2	1.26	1.81	1.57	0.23	14.58
	2-4	0.95	1.55	1.15	0.24	20.60
	4-6	0.65	0.94	0.80	0.11	13.45
	6-10	0.44	0.57	0.54	0.07	12.21
	10-20	0.45	0.95	0.65	0.23	35.45

In Bangrong mangrove area (Thailand) TN concentrations reported a variation of 2.61mg g^{-1} to 2.14mg g^{-1} in cores of length 14-16cm (Kristensen *et al.*, 2000). Core sediment at this location showed a decrease in concentration with increase in depth. Alongi (1996) reported a decline concentration down the core in the intertidal mangrove forests of Hinchinbrook Island in Queensland, Australia. A similar soil organic nitrogen concentration of 3.74 mgg^{-1} was found in the fringe forest of eastern Australia (Clarke, 1985). Nitrogen fixation by cyanobacteria and heterotrophic bacteria are abundant on all inhabitable surfaces in mangrove ecosystem, enhance the TN concentration in surface sediment. Nitrogen mineralisation, where nitrogen is liberated from organic matter in the form of ammonium via hydrolyzation and catabolization of proteins and polynucleotides, is mediated by all nearly all heterotrophic organisms ranging from bacteria to macrofauna. Rates of bacterial ammonification found, rapidly decreasing with depth (Shaiful *et al.*, 1986). Rice and Tenore (1981) found that organic nitrogen accumulation in mangrove detritus was associated with an influx of dissolved inorganic nitrogen from water column. The ammonium assimilation by microphyto benthos and plants are always accompanied by mineralization processes in mangrove forests providing a net system immobilization. The maximum TN concentration exhibited at Station 2 may be attributed to ammonium assimilation by microphytobenthos and plants. Also Station 1 and Station 2 exhibited a remarkable decrease in TN concentrations at the depth of 10-20 cm while Station 3 showed a decrease at this depth. This observation support the assimilation of TN by micorphytobenthos at Station 1 and 2.



(a) (b)

(c) (d)

Fig. 4.17 Annual and seasonal variation of TN in sediment cores

The increase in total detrital nitrogen was also found to be associated with the production of mucopoly saccharide exudates by bacteria and their incorporation into humic compounds (Rice, 1982; Rice and Hanson, 1984). It was also established that mangrove leaf litter found to harbor a large population of bacteria that appear to be highly productive (Robertson, 1988; Benner and Hodson 1985). At the first two stations, a remarkable decrease in TN concentrations were noticed beyond 10 cm depth may be attributed to the bacterial biomass at this depth. While Station 3, exhibited a marked increase in TN concentration at this depth. Notable decrease of TN concentration beyond 10 cm depth at Stations 1 and 2 may also be associated with the muddy sand nature of the sediment, which were inefficient in binding mineralized ammonium.

Table 4.20 Correlation matrix between depths - TN

	0-2	2-4	4-6	6-10	10-20
0-2	1.0000				
2-4	0.9851***	1.0000			
4-6	0.9568***	0.9764***	1.0000		
6-10	0.9930***	0.9854***	0.9763***	1.0000	
10-20	0.8251***	0.8844***	0.9203***	0.8655***	1.0000

$p<0.01^{**}$ $p<0.001^{***}$

Significant positive correlation was found between TN concentrations in all depths ($p<0.01$) (Table 4.20). This positive correlation indicated a high degree of association of TN concentration at all depths. This may be attributed to the effective bioturbation at the studied area. The minimum amount of tidal flushing, at Station 1 and Station 2 may enhance the accumulation of ammonium formed by the mineralisation of organic matter. Also a significant positive correlation was observed with exchangeable ammonium at all depths ($p<0.01$) (Table 4.18a-18e) indicated the close association of TN and ammonium concentration in sediments. TN correlated positively with TOC and negatively with sediment C/N ratio at 0-2 and 2-4cm depth ($p<0.01$, $p<0.05$). This indicated the decrease in C:N ratio was mainly due to the increase of TN in the sediment. It is possible that the increase in TN and thus decrease in C/N ratio in the sediment partly to the increase of chlorophyll-containing labile materials (Cheng and Chang, 1999). TN was found to be positively correlated with percentage of clay, exchangeable ammonium and

TOCl at depths 0-2, 2-4, 4-6, 6-10 cm. Significant negative correlations were found with sand at these depths.

Three-way ANOVA analysis showed a significant difference of TN between stations, between depths and between seasons. The LSD at 5% level for stations is 0.314 mg g^{-1}. Among the stations, Station 2 showed significantly higher value of TN followed by Station 1, which in turn had significantly higher concentration than Station 3. The maximum value of 5.40 mgg^{-1} was recorded at Station 2. The LSD at 5% level for depth is 0.405. TN recorded significantly higher concentrations at the depth of 0-2cm and 2-4 cm. TN concentrations followed a decreasing order in the layers 4-6, 6-10 and 10-20 cm. The maximum value of 5.40 mg/g was recorded at a depth of 0-2 cm. The LSD at 5% level for season is 0.314. Significantly higher concentration of nitrogen was observed during pre-monsoon followed by post monsoon and monsoon. The maximum TN was found during pre monsoon irrespective of the stations may be associated with maximum nitrogen fixation during this season.

Exchangeable nitrate.

The nitrogen cycle is rather complex, involving processes such as nitrogen fixation, denitrification, uptake by plants, immobilization by micro-organisms and mineralisation. These processes are mediated by biological, mostly microbial, processes rather than by chemical means. By virtue of a wide range of oxidation states (-3 for ammonia to +5 for nitrate), nitrogen can serve as a reductant or an oxidant in the diagenesis of organic matter in addition to its role as a nutrient in microbial and plant assemblages. The presence of litter in the intertidal forested wetlands (mangroves) establishes different nutritional constraints on nitrogen transformations on sediments than those observed in subtidal sediments. Thus, rates of denitrification in mangroves are generally much lower than those of most estuarine sediments. Evaluating of the fate of inorganic nitrogen in mangrove sediments depend on time scales of sedimentary processes (Rivera- Monroy and Twilley, 1996). They also found that most of the inorganic nitrogen remains in the sediment. High inorganic nitrogen demand in decomposing leaf litter may regulate an efficient recycling of nitrogen that would serve as a mechanism for nutrient conservation (Twilley *et al.*, 1986 b; Twilley, 1988; Alongi *et al.*, 1992). The response of denitrification to supply of nitrate may depend on the nitrogen demand by decomposers as indicated by the C : N of sediments. Presence of nitrate and nitrite in anaerobic soils can be accounted for by nitrification in the aerobic rhizopheres near the roots of the wetland plant (Haines *et al.*, 1977).

The station-wise summary statistics of exchangeable nitrate are given in Table 4.21. The minimum and maximum values of exchangeable nitrate recorded were 2.71µmolg^{-1} (Station 3) and 90.67µmolg^{-1} (Station 2) respectively. Comparatively higher values were recorded at Station 1 and Station 2 than at Station 3. A general pattern of exchangeable nitrate concentrations, with an increase in sub-surface sediment followed by a gradual decrease down the core was noticed at all stations except at Station 3 (Figure 18a). However Station 3 recorded a gradual decrease of exchangeable nitrate concentration down the core. Seasonal variations in depth pattern are illustrated in Figures 4.18b-4.18d. The higher concentrations of exchangeable nitrate were recorded during pre-monsoon season with certain exceptions like a remarkable increase was recorded at 2-4 cm depth at Station 1 and Station 2 during monsoon season. However Station 3, recorded the subsurface increase only during pre-monsoon and post-monsoon seasons.

Table 4.21 Station-wise summary statistics of exchangeable nitrate (nmol g^{-1}) in sediment cores

Station	Depth	Min	Max	Mean	SD	% of CV
Station 1	0-2	12.68	20.64	16.76	3.98	23.77
	2-4	5.26	64.31	35.02	29.53	84.32
	4-6	6.45	32.75	18.60	13.26	71.27
	6-10	12.52	15.23	14.09	1.41	9.98
	10-20	8.40	14.01	10.75	2.91	27.06
Station 2	0-2	16.47	28.84	21.31	6.60	30.98
	2-4	13.59	49.23	29.70	18.06	60.83
	4-6	16.01	37.60	23.40	12.30	52.57
	6-10	11.10	16.32	13.90	2.63	18.92
	10-20	18.85	90.67	45.67	39.21	85.84
Station 3	0-2	3.29	30.71	14.03	14.64	104.39
	2-4	5.02	12.25	8.27	3.67	44.35
	4-6	3.80	13.24	8.53	4.72	55.28
	6-10	2.71	7.72	4.94	2.55	51.57
	10-20	2.76	10.47	5.88	4.06	69.08

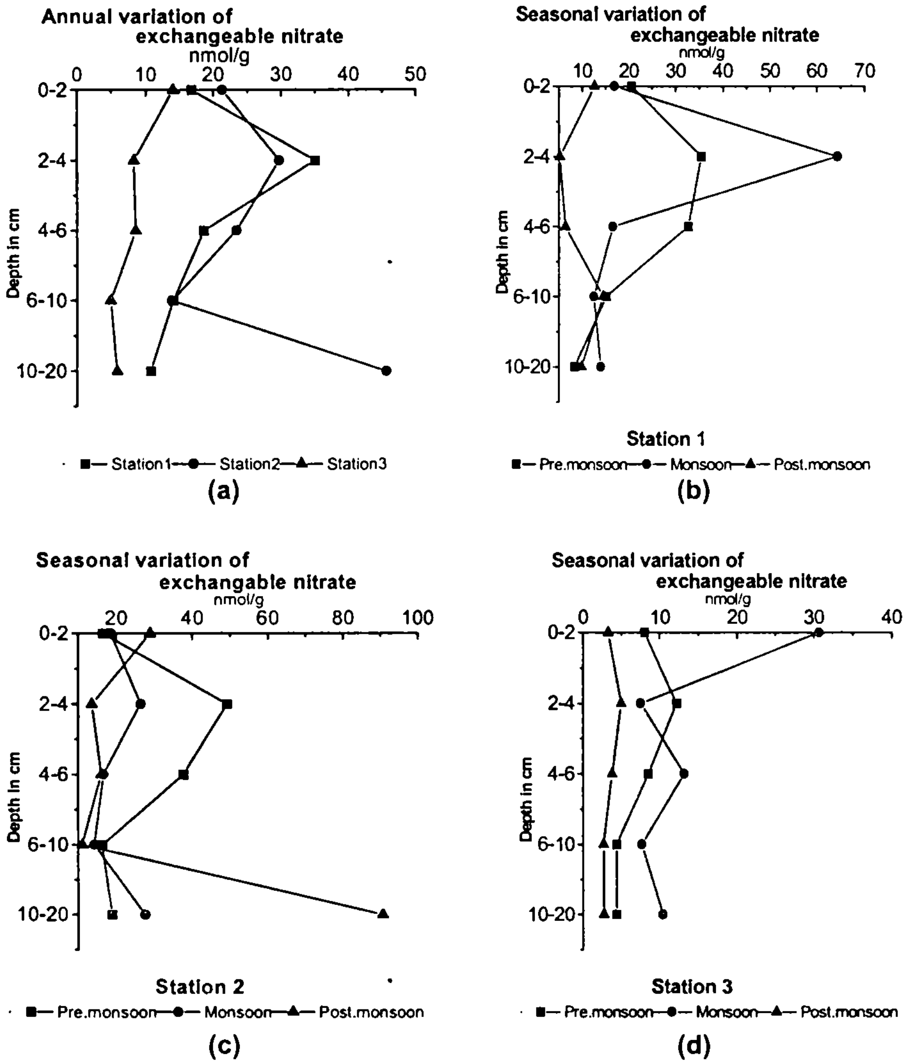


Fig. 4.18 Annual and seasonal variation of exchangeable nitrate in sediment cores

The highest concentration of exchangeable nitrate recorded at Station 2 associated with the luxuriant growth of plants at this Station. Presence of nitrate and nitrite in anaerobic soils can be accounted for by nitrification in the aerobic rhizopheres near the roots of the wetland plant (Haines *et al.*, 1977).

Nitrification in sediments might be the cause of increase in concentration of ammonia at this site. There exist a significant negative correlation between the exchangeable nitrate and ammonium at this station, during pre-monsoon. No significant difference of exchangeable nitrate exists between Station 1 and Station 3. Although the difference was not statistically significant in seasonal variations, monsoon season recorded maximum value of exchangeable nitrate. The 10-20 cm layer recorded a higher amount during post monsoon. Exchangeable nitrate recorded 12.6 nmolg^{-1}, 97.57 nmolg^{-} and 13.80 nmolg^{-1} at Station 1, Station 2, and Station 3 respectively.

The minimum values were recorded at depths of 6-10 cm or 10-20 cm observed mostly during monsoon or post monsoon (Table 4.21). Active growth of plants takes place during this season, which might cause the decrease of nitrate-N at this depth. Alternatively tidal incursions can also remove nitrate at Station 3 where tidal influence is maximum. Regular tidal incursions may remove nitrate, which is more soluble than ammonium from the soil (Clarke, 1985). There is significant correlation (Table 4.22) between depth ranges 2-4, 4-6 and 6-10 cm ($p < 0.01$). Correlation is not significant in other depth ranges may be due to the removal of nitrate from surface sediment by grazing organisms and 10-20 cm depth, major rooting zone of plants, plant uptake decide the concentration of exchangeable nitrate.

Table 4.22 Correlation matrix between depths – Ex. Nitrate

	0-2	2-4	4-6	6-10	10-20
0-2	1				
2-4	0.0842	1.0000			
4-6	0.3513	0.6702	1.0000		
6-10	0.3756	0.5631	0.6971*	1.0000	
10-20	0.5650	-0.0576	0.0905	0.1941	1.0000

$p<0.05^{*}$

ANOVA of exchangeable nitrate concentration recorded significant variation among stations but not with depth or season (App.17). The LSD at 5% level for station is 11.405nmol g^{-1}.

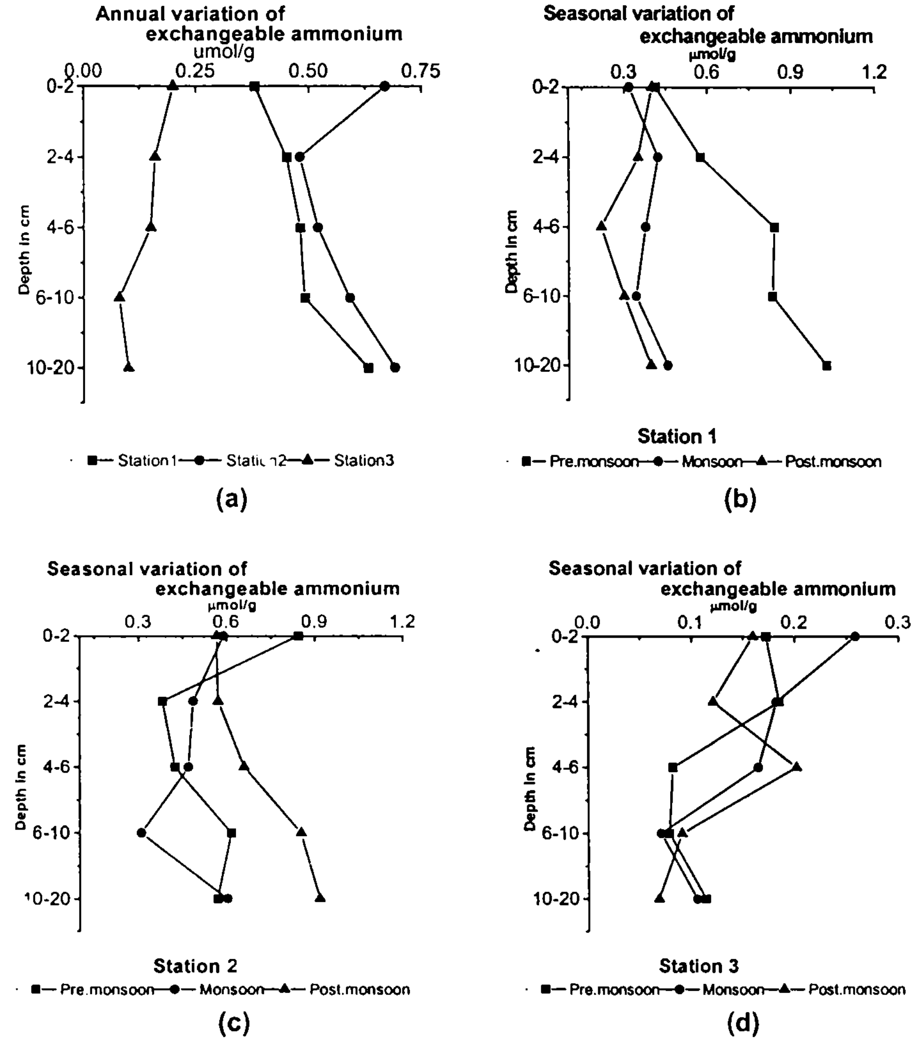
Exchangeable Ammonium.

Organic matter in wetland sediment accumulates on decadal time scales, and nitrogen immobilisation in sediments can eventually contribute to the burial of nitrogen in mangrove ecosystem. Some of this immobilized nitrogen in the early stages of decomposition may be recycled by ammonification and used in plant uptake. The measurements of inorganic nitrogen immobilization by ^{15}N technique refer to the accumulation of nitrogen in litter during early stages of decomposition (Rivera- Monroy and Twilley, 1996). Ammonium is the main form of inorganic nitrogen in anaerobic mangrove soils because nitrification of organic nitrogen stops at ammonium due to the lack of oxygen to oxidise it further to nitrate (Ponnamperuma, 1972). Like other cations, ammonium is capable of occupying cation exchange sites, but the high level of sodium in most mangrove soils tends to swamp the cation exchange sites, thereby displacing ammonium. Thus ammonium occurs mainly in the interstitial phase where it is highly mobile and susceptible to being leached by heavy rain or lost through drainage following tidal inundation. Boto and Wellington (1984) found that ammonium pools could be depleted by tree uptake during periods of rapid mangrove growth.

Table 4.23 summarises the measurements of exchangeable ammonium in sediment cores to a depth of 20cms. The ammonium concentrations varied between 0.07µmolg^{-1} (Station 3) and 1.03µmolg^{-1} (Station 1). Higher ammonium concentrations were noticed at Station 2 than other stations.

Table 4.23 Station-wise summary statistics of exchangeable ammonium (µmol g^{-1}) in sediment cores

Station	Depth	Min	Max	Mean	SD	% of CV
Station 1	0-2	0.32	0.41	0.38	0.05	13.59
	2-4	0.35	0.58	0.45	0.12	25.59
	4-6	0.22	0.84	0.48	0.32	67.60
	6-10	0.30	0.83	0.49	0.30	60.33
	10-20	0.40	1.03	0.63	0.35	55.51
Station 2	0-2	0.57	0.84	0.67	0.15	23.11
	2-4	0.38	0.57	0.48	0.10	19.82
	4-6	0.42	0.66	0.52	0.12	24.06
	6-10	0.31	0.85	0.59	0.27	45.99
	10-20	0.57	0.92	0.69	0.19	27.65
Station 3	0-2	0.16	0.26	0.20	0.05	27.24
	2-4	0.12	0.19	0.16	0.04	22.21
	4-6	0.08	0.20	0.15	0.06	41.07
	6-10	0.07	0.09	0.08	0.01	12.50
	10-20	0.07	0.11	0.10	0.02	25.42



(a) (b)

(c) (d)

Fig. 4.19 Annual and seasonal variation of exchangeable ammonium in sediment cores

Annual variation in depth pattern showed an increase in exchangeable ammonium concentrations with an increase in depth at Station 1 and Station 2 (Figure 4.19a). However a gradual decrease in ammonium concentrations, down the core was noticed at Station 3. Seasonal pattern of depth distribution are illustrated in Figures 4.19b-4.19d. The higher concentrations were observed during pre-monsoon at Station 1, with a gradual increase down the core. While at Station 2, higher concentrations were recorded during post-monsoon season, again an increase in concentration down the core was noticed. Unlike the other two stations, at some depths an increase in exchangeable ammonium concentrations recorded at Station3, the bottom sediments found to extract less ammonium than the surface sediments.

Table 4.24 Correlation matrix between depths – Ex. Ammonium

extr NH3	0-2	2-4	4-6	6-10	10-20
0-2	1.0000				
2-4	0.6240	1.0000			
4-6	0.5212	0.9037***	1.0000		
6-10	0.6526	0.8769**	0.9201***	1.0000	
10-20	0.6170	0.9675***	0.9652***	0.9544***	1.0000

$p<0.01^{**}$ $p<0.001^{***}$

The exchangeable ammonium at the depth range 2-4 is significantly correlated with 4-6, 6-10 and 10-20 cm depth ($p< 0.01$) (Table 4.24). The 4-6 cm layer is significantly positively correlated with 10-20 cm depth. While 0-2 cm depth range did not significantly correlate with any of the other depths. In general, however the surface layer of the sediments has the highest level of inorganic nitrogen, this is related to the faster rate of decomposition found on the surface of the sediments than at the depth (vander Valk and Attiwill, 1984). Correlation of exchangeable ammonium and other parameters showed a positive relationship with percentage of clay, total nitrogen, in 0-2, 2-4, 4-6 and 6-10 and 10-20 cm depth (Table 4.18a-18e). At 4-6 cm depth a positive relationship was observed with exchangeable nitrate.

Three way ANOVA analysis showed a significant difference of exchangeable ammonium between station, and between season but not between depth (App. 18). The LSD at 5% level for station and season is 0.122 µmolg^{-1}. Significantly higher concentration of exchangeable ammonium was recorded at Station 1 and Station 2. There is no significant difference between these two stations, while Station 3 recorded comparatively low concentration of exchangeable ammonium than the other to stations. Significantly higher value of exchangeable ammonium was observed during pre-monsoon followed by monsoon and post monsoon. Significantly low concentration was registered during post-monsoon The ammonium concentrations were found to increase and maximum were found at the

10-20 cm layer at Station 1 and Station 2. The ammonium concentration increases with depth in the anaerobic soil, indicating denitrification beyond rhizopheres.

Total Phosphorus (TP)

Many studies have revealed a permanent nutrient retention in aquatic system. The retention and dynamics of particulate matter and associated nutrients especially phosphorus are strongly affected by sedimentation and adsorption processes during low flow periods. The physical and chemical environment at the sediment-water interface largely governs phosphorus cycling in lakes, fluxes and redistribution patterns of phosphorus, in particular by the reduction of iron complexes at low redox potential (Mortimer, 1971). But in recent years, an increased understanding of microbial processes in aquatic ecosystem has provided a more advanced model, including the importance of sediment bacteria for phosphorus dynamics (Gachter and Meyer, 1993). Bacteria are known to have mechanisms for rapid uptake of phosphate and intracellular storage as poly-phosphate under aerobic conditions and the hydrolysis and release of phosphate when their environment turns anoxic. (Deinema *et al.*, 1985; Wentzel *et al.*, 1991). Much of the inorganic phosphorus in mangrove soils is adsorbed or incorporated within hydrated iron and aluminium colloidal sesquioxides. Regarding the vertical variation of TP in sediments, Delaune and Patric (1980) have found a marked decline with depth in a vertical profile of the distribution of solid phase TP in Lousiana Spartina marshes.

TP concentrations were found to vary between 296.70 $\mu g g^{-1}$ (Station 3, 10-20cm) and 2190.84$\mu g g^{-1}$ (Station 1, 10-20cm) (Table 4.25). The minimum at Station 1 recorded at a depth of 2-4cm (974.93$\mu g g^{-1}$) and maximum recorded at 10-20 cm (2190.84$\mu g g^{-1}$) depth. While at Station 2 minimum (974.93$\mu g g^{-1}$) observed at 10-20cm and maximum (2046.38$\mu g g^{-1}$) at 6-10cm depth. Station 3 recorded the minimum (296.70$\mu g g^{-1}$) at 10-20 cm depth and maximum (1412.85.$\mu g g^{-1}$) at 0-2 layer. TP concentrations were similar at Station 1 and in Station 2. The annual and seasonal depth distributions of TP are given in Figures 4.20a-20d. The overall picture of the annual variation followed the general pattern of decreasing phosphorus concentration with increasing depths at Station 1 and Station 3, except at 10-20 cm depth at Station 1 (Table 4.20). The TP concentrations exhibited comparatively lower coefficient of variation in 0-2cm layer at Station 1, 2-4 cm layer at Station 2 and 10-20 cm layer at Station 3. Station 2 showed a subsurface maximum and the values decreases down the core. However at Station 1 and Station 2 there was a reversal in the above trend at 10-20 cm depth and at 2-4 cm depth respectively.

Table 4.25 Station-wise summary statistics of TP (mg g^{-1})

Station	Depth	Min	Max	Mean	SD	% of CV
Station 1	0-2	959.60	1967.60	1590.51	361.05	22.70
	2-4	951.40	1954.21	1407.45	339.56	24.13
	4-6	1051.25	1947.46	1400.67	331.74	23.68
	6-10	1167.65	1922.13	1489.72	338.74	22.74
	10-20	1082.08	2190.84	1693.82	428.92	25.32
Station 2	0-2	1222.31	1819.23	1501.01	224.98	14.99
	2-4	1449.45	1777.34	1648.05	122.67	7.44
	4-6	1420.68	1768.37	1564.90	137.63	8.79
	6-10	1352.78	2046.30	1617.62	294.54	18.21
	10-20	974.93	1823.74	1331.14	303.79	22.82
Station 3	0-2	480.72	1412.85	847.28	320.82	37.87
	2-4	452.55	759.70	599.81	118.03	19.68
	4-6	357.01	608.57	475.93	85.87	18.04
	6-10	326.06	596.63	435.52	106.09	24.36
	10-20	296.70	476.06	415.91	73.96	17.78

Remarkably higher concentrations of TP were observed at Station 1 and Station 2 than at Station 3. The maximum concentration of 2190µgg^{-1} was recorded at Station 1. The spatial variation in distribution of TP is explained by the sediment grain size, presence or absence of macrophytes\ phytoplankton, bacterial assemblages etc. Redox potentials, pH and sorption/desorption processes have traditionally are regarded as important regulating factors for the exchange of phosphorus between sediment and overlying water (Bostrom *et al.*, 1988). Also the existence of denser vegetation at Station 1 and Station 2 as compared to Station 3 facilitates the trapping of nutrients discharged to this creek. Matrix of correlation between parameters showed that percentage of clay is positively correlated with TP at all depths (Table 4.18a-18e). Associated with the high silt and clay percentage (Table 4.13), the significantly high concentration of TP was recorded at the first two stations at all depths compared to the Station 3.

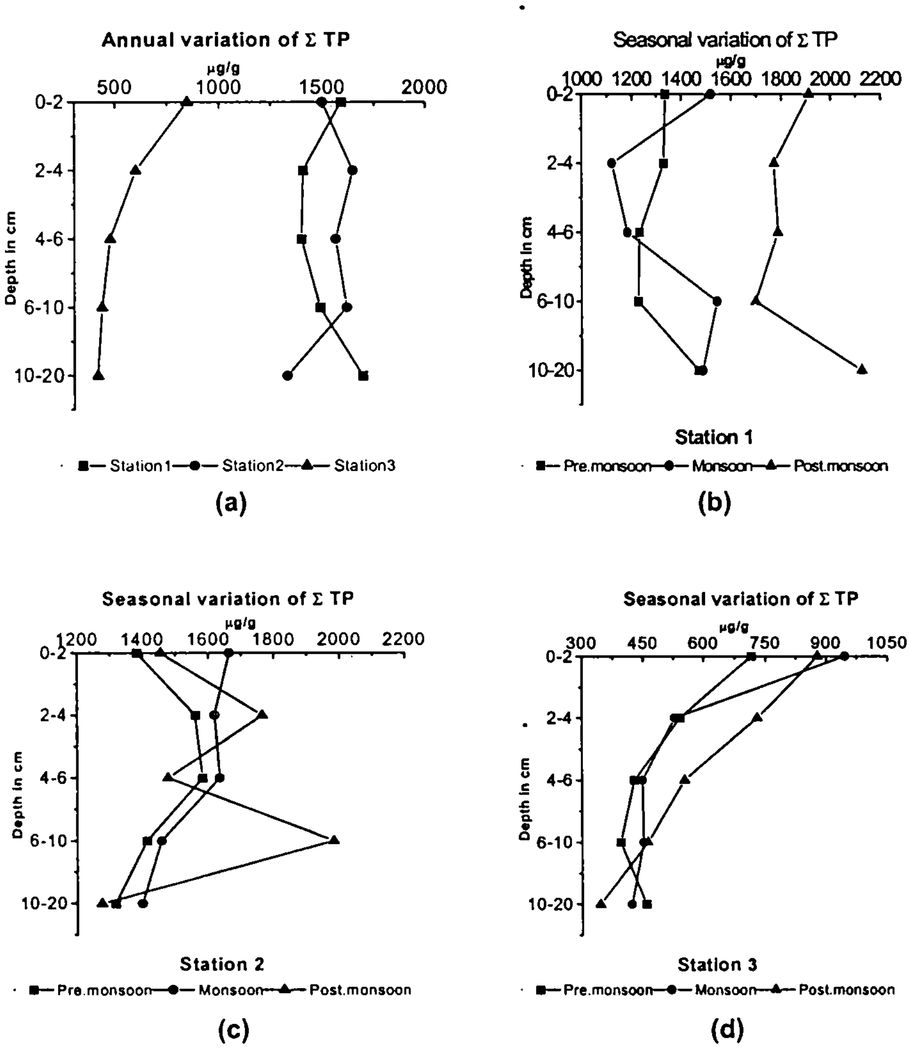


Fig. 4.20 Annual and seasonal variation of TP in sediment cores

Table 4.26 Correlation matrix between depths - TP

	0-2	2-4	4-6	6-10	10-20
0-2	1.0000				
2-4	0.8916**	1.0000			
4-6	0.9395***	0.9783***	1.0000		
6-10	0.8891**	0.9346***	0.9171***	1.0000	
10-20	0.9526***	0.8647**	0.9161***	0.8682**	1.0000

$p<0.01^{**}$ $p<0.001^{***}$

Generally at Station 2 and Station 3, 0-2cm and 2-4 cm layers exhibited higher TP concentrations than the other depths. In mangrove area (Fly Delta, Papua New Guinea) TP concentration were found high in surface sediments, suggesting oxidation near or at the sediment-water interface. The oxidative reactions would immobilize phosphorus and limit its availability to autotrophs and microheterotrophs, with phosphorus being bound to nonreactive metals, particularly as iron and manganese oxyhydroxides (Boto, 1992). The correlation matrix between depths, recorded significant positive correlation of TP concentration among the depth ranges 0-2, 2-4, 4-6 and 10-20 ($p< 0.05$) (Table 4.26). This positive relationship at different depths indicated an association of TP concentrations at different depths in the core sediment. TP concentrations were recorded high in surface and subsurface sediments, indicating the contribution of below ground roots in maintaining oxidised surface sediment. The oxidative reactions would limit its desorption of phosphate into overlying water, since most of the phosphorus being bound to non-reactive metals, particularly as iron and manganese oxyhydroxides. Also bacteria are known to have mechanisms for rapid uptake of phosphate and intracellular storage as poly-phosphate under aerobic conditions and the hydrolysis and release of phosphate when their environment turns anoxic.

Three way ANOVA showed a significant difference of TP concentrations between station ($p<0.001$) and between season ($p<0.01$) but not between depths (App.19). The LSD at 5% level for stations is 144µgg^{-1}. The LSD at 5% level for season is 0.145µgg^{-1}. Significantly higher concentration was observed during post-monsoon followed by monsoon and pre-monsoon. Maximum retention of phosphorus during post-monsoon may be associated with the oxidised iron minerals present in sediment. The present observation indicated the sediments at

Station 1 and Station 2 were better nutrient sink than at Station 3,due to its ability to immobilize phosphorus in an oxidised sediment-water interface.

4.2.6 Stoichiometries of C, N and P along core sediments

Carbon : Nitrogen ratio (C/N)

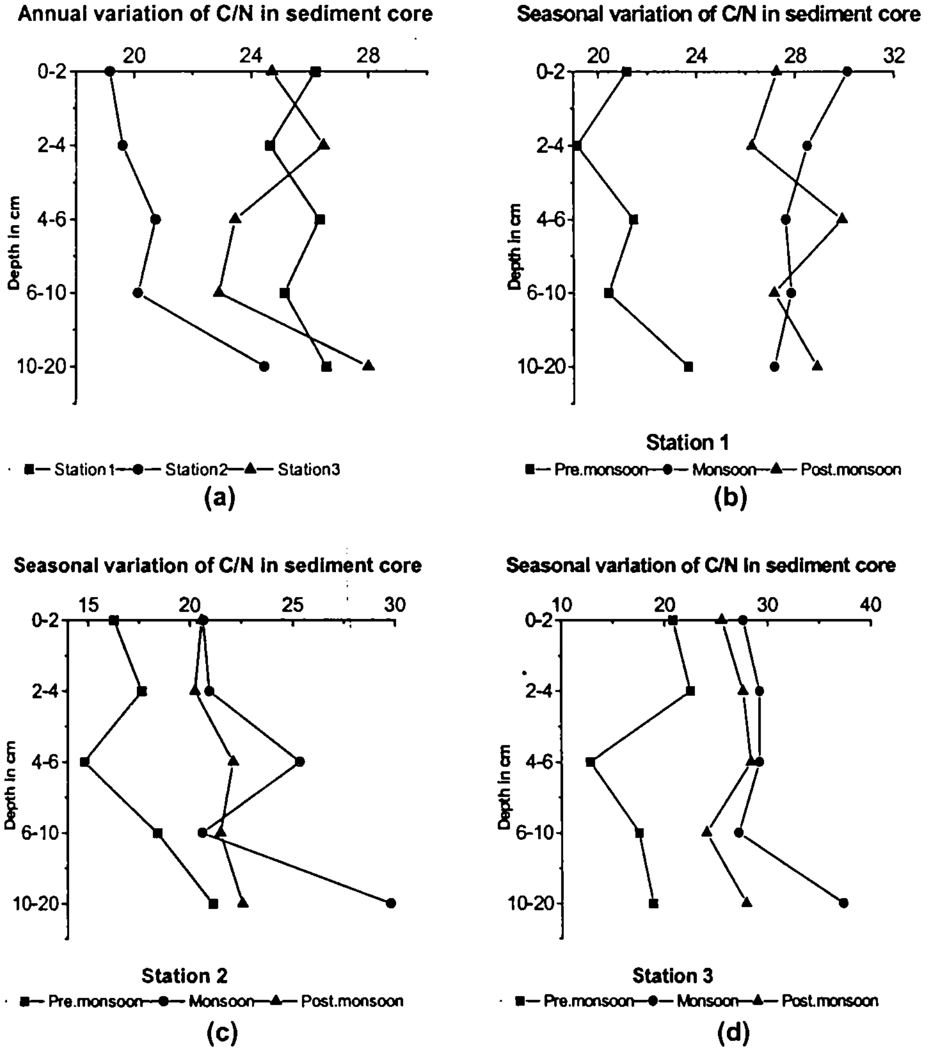
C/N ratio in sediments indicate rate of nitrogen mineraliztaion. Aerobial decomposition of organic matter is usually more rapid than the rate of oxygen diffusion into surface sediments, and oxygen quickly becomes limiting. Anaerobic bacteria below the upper few millimetres of sediment therefore carry out most decomposition, except where animal burrows and plant roots channel oxygen to deeper sediment layers (Anderson and Kristensen, 1988; Aller, 1994). Anaerobic decomposition in marine sediments performed by a wide variety of bacterial types utilizing a number of electron acceptors like nitrate, oxidised iron and manganese and sulphate to oxidise carbon. Macrophyte detritus from mangrove trees typically has high C/N ratios compared with the demands of decomposing bacteria (Kristensen, 1990; Wafar *et al.*, 1997). Since heterotrophic bacteria generally need organic substrates with a C/N ratio of 10 or less for maintanenace and growth (Fenchel and Blackburn, 1979) while mangrove litter with C/N ratio up to 100 are a highly insufficient substrate (Krtistensen, 1990).

Table 4.27 summarises the variation of C/N ratios observed in core sediments to a depth of 20cm. The minimum and maximum ratio observed were 10.48 (Station 3) and 56.62 (Station 3) respectively. The C/N ratios recorded at Station 1 were remarkably higher than the other two stations. C/N ratio varied from 19.09 (2-4cm) to 36.16 (10-20cm), 15.61 (4-6cm) to 38.33 (10-20cm), and 10.48 (4-6cm) to 56.62 (10-20cm) at Station 1, Station 2 and Station 3 respectively. Annual variations in depth profile showed a general pattern of a sub-surface decrease followed by a remarkable increase beyond 10 cm depth at all stations (Figure 4.21a). The seasonal depth distributions at all stations are illustrated in Figures 4.21b-d. The lower values were observed during pre-monsoon and higher values recorded during monsoon season at all stations. General pattern of depth distribution followed in seasonal pattern, except during monsoon season at Station 1.

Table 4.27 Station-wise summary statistics of C/N in sediment cores

Station	Depth (cm)	Min	Max	Mean	SD	% of CV
Station 1	0-2	20.75	35.01	26.57	5.15	19.37
	2-4	19.09	35.73	25.15	6.30	25.03
	4-6	20.21	35.20	26.56	5.98	22.53
	6-10	19.69	33.41	25.27	5.03	19.90
	10-20	23.13	36.16	27.74	4.77	17.19
Station 2	0-2	15.96	26.69	19.47	4.10	21.07
	2-4	15.81	26.23	19.62	3.85	19.60
	4-6	15.61	32.83	21.29	6.32	29.70
	6-10	17.48	23.73	20.04	2.66	13.25
	10-20	19.14	38.33	25.03	6.92	27.65
Station 3	0-2	18.64	23.64	19.86	1.89	9.53
	2-4	11.28	23.64	18.14	4.18	23.05
	4-6	10.48	25.89	19.18	6.33	33.01
	6-10	12.37	25.69	19.95	5.32	26.66
	10-20	20.49	56.62	30.39	13.27	43.66

Remani *et al.* (1980) have reported C/N values ranging from 2.87 – 45.44 in sediments of Cochin estuary. They suggest that the state of break down of organic matter, which depends on the environmental factors and textural characteristics of the sediment, rather than its absolute quantity influence the C/N ratio. The fringing mangrove zones have high C:N ratios indicating an accumulation of carbon relative to nitrogen; this carbon probably originates from debris washed on to strand lines (Clarke, 1985). A similar condition exists in the stations under investigation. According to C/N ratio accumulation of carbon was found maximum at Station 1. Based on the station-wise variation of exchangeable ammonium (Figure 4.19a) it can be concluded that ammonification was high in core sediments at Station 2. The C/N ratio together with the exchangeable ammonium concentration suggested maximum ammonification takes place at this site. Kristensen *et al.* (1998) suggested that, in mangrove sediments, due to tight coupling between microbial mineralisation and assimilation, ammonium is trapped in the sediments, which also estimated as TN. Though the TOC concentrations at Station 3 were very low, C/N was comparable as that of Station 2, indicate denitrification of the ammonium formed during organic mineralisation. The remarkably high ratios observed at beyond 10 cms of depth suggest a different pathway of mineralisation, probably as oxidised iron as electron acceptor.



(a) (b)

(c) (d)

Fig. 4.21 Annual and seasonal variation of C/N in sediment cores

Seasonal variations in C/N ratio in sediment cores at different sites exhibit variation similar to concentrations of TOC. Minimum C/N ratio observed during pre-monsoon associated with minimum TOC during the same season. However highest C/N ratios were observed during monsoon at all stations, may be associated with less mineralisation due to decrease in bacterial density.

C/N ratios recorded significant correlation between depth ranges 0-2, 2-4, 4-6 and 6-10 cm ($p<0.01$, $p< 0.05$) (Table 4.28). The C/N ratios at 2-4cm depth, significantly correlated with ratios at 4-6, 6-10, and 10-20cm depth ($p<0.05$, $p<0.01$). Positive correlations were also observed at C/N ratios at 4-6 cm layer with 6-10 and 10-20 cm depth. 6-10 cm layer, showed positive correlation with 10-20 cm depth ($p<0.01$, $p<0.05$)(Table 4.28). Between parameters correlation recorded a significant negative correlations of C/N ratios with exchangeable ammonium concentration at the 0-2 and 2-4 cm depths ($p<0.01$) (Table 4.18a and 18b).

Table 4.28 Correlation matrix between depths – C/N

	0-2	2-4	4-6	6-10	10-20
0-2	1.0000				
2-4	0.9402***	1.0000			
4-6	0.8021**	0.7336*	1.0000		
6-10	0.9327***	0.8574**	0.8969**	1.0000	
10-20	0.6496	0.6866*	0.8359**	0.7520*	1.0000

$p<0.05^{*}$ $p<0.01^{**}$ $p<0.001^{***}$

Three way ANOVA of C/N showed significant difference between station, depth and season (App. 20). The LSD at 5% level for station is 1.69. Station 1 and Station 3 have significantly higher value of C/N ratio than Station 2. Most of the ratio were larger than 14 which suggest that the detritus in the study site might be composed mainly of flora debris found in mangrove wet lands (Degrens, 1970; Valeila 1984; Kristensen, 1988; Alongi and Christoffersen, 1992). Despite the leaching of tannins and other deterrent substances and its highly refractory nature, this material still provides bulk particulate organic carbon for the benthic animals (Gonzalez and Mee, 1988). The LSD at 5% level for depth is 2.18. The 10-20 cm depth showed a significantly higher ratio than all other depths. Between other depths there is no significant difference. The LSD at 5% level for season is 1.69. Significantly higher value of C/N was observed during monsoon season followed by post monsoon and pre monsoon. Similar observation was found in the mangrove environment of Goa. The C/N ratio fluctuated, when fresh water discharge was greater (Jagtap, 1987). This indicated that besides mangroves and associated biota continuously add detritus to the mangrove ecosystem, terrigenous organic matter brought in by fresh water discharge also vary the stoichiometric ratios at these sites.

Nitrogen : Phosphorus ratio (N/P)

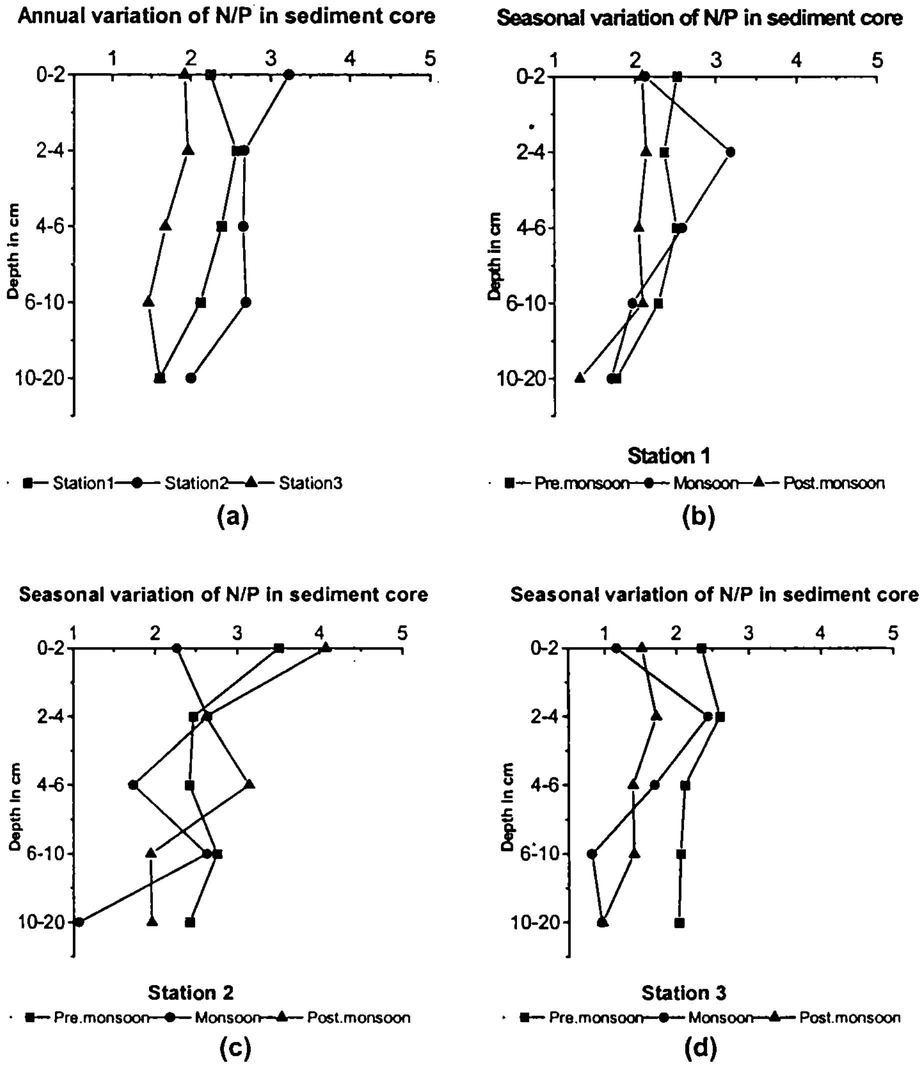
Coastal marine areas around the world are, to a large extent, influenced by human activities that lead into increased concentrations of nutrients and organic matter (Clough *et al.*, 1983; Conley, 2000). Bacteria are known to be important degraders of organic matter and they control the recycling of essential nutrients in coastal sediments (Alongi, 1994). A rapid immobilization of nutrients may occur during decomposition in mangrove forest sediments and other sediments as well (Alongi, 1991; 1994; 1996: Kristensen *et al.*, 1998). Immobilizations due to adsorption reactions further reduce the availability of phyosphorus. Thus an increased loading of phosphate and ammonium to the sediment due to increased human activities such as waste water outlet in shrimp farms in mangroves and urban waste water loading to mangrove fringed creeks may increase the rate of decomposition as the nutrient condition for the bacteria improved. Thus the examination of Redfield ratio (N/P) in core sediments may able to identify the loading of phosphorus in this system.

Table 4.29 summarises the variation of N/P ratios observed in core sediments to a depth of 20cm. The minimum and maximum ratio observed were 0.82 (Station 3) and 4.47 (Station 1) respectively. Comparatively higher ratios were observed at Station 2 (1.06-4.06) than the other two stations. Annual variations showed a general pattern of decreasing N/P ratio down the core, except at Station 1 where a subsurface increase was noticed (Figure 4.22a). Seasonal variations in N/P are illustrated in Figures 4.22b-d. Maximum values of N/P were recorded during pre-monsoon at Station 1 and Station 3, while at Station 2 maximum values were noticed during post-monsoon.

Table 4.29 Station-wise summary statistics of N/P in sediment cores

Station	Depth (cm)	Min	Max	Mean	SD	% of CV
Station 1	0-2	1.67	3.11	2.25	0.52	23.13
	2-4	1.89	4.47	2.57	0.97	37.73
	4-6	1.75	3.43	2.38	0.68	28.67
	6-10	1.28	2.65	2.11	0.46	21.98
	10-20	1.30	2.21	1.59	0.39	24.57
Station 2	0-2	2.26	4.08	3.23	0.61	18.89
	2-4	2.46	3.00	2.67	0.18	6.60
	4-6	1.73	3.27	2.65	0.56	21.17
	6-10	1.93	3.05	2.68	0.40	14.91
	10-20	1.06	2.60	1.99	0.53	26.78
Station 3	0-2	1.16	2.38	1.92	0.45	23.63
	2-4	1.27	2.75	1.96	0.66	33.63
	4-6	1.31	2.34	1.67	0.39	23.47
	6-10	0.82	2.13	1.45	0.56	38.79
	10-20	0.95	2.18	1.59	0.54	33.99

N:P ratios in core sediments showed a gradual decrease down the core may be attributed to the decrease of TN, since only TN concentrations showed a significant decrease with increasing depth (ANOVA). The highest N:P ratios were observed in surface/ subsurface sediment at all stations, where TN concentrations showed significantly higher values. Seasonal variation of N/P ratios were found in accordance with the seasonal variation of TP at all stations. The value of N/P ratio during the present study ranged between 0.82 and 4.47. The value of N/P for natural plankton is 13.8:1 while a ratio of 18.2:1 found for culture planktons. The values found in here were far below the above values indicated the abiogenic nature of phosphorus. Sankaranarayan and Panampunnayil (1979) have reported an abiogenic nature of phosphorus in sediments of Cochin harbour and adjacent areas.



(a) (b)

(c) (d)

Fig. 4.22 Annual and seasonal variation of N/P in sediment cores

The correlation matrix between depths showed significant correlation only in surface sediments (Table 4.30). Significant positive correlations observed among the depths 0-2cm, 2-4 cm and 4-6 cm ($p<0.01$, $p<0.05$). The correlation between other parameters showed a positive correlation with exchangeable nitrate concentration at 0-2 cm depth ($p<0.05$) (Table 4.18a).

Table 4.30 Correlation matrix between depths – N/P

	0-2	2-4	4-6	6-10	10-20
0-2	1.0000				
2-4	0.7834*	1.0000			
4-6	0.6690*	0.8543**	1.0000		
6-10	-0.4036	0.0614	-0.0759	1.0000	
10-20	0.2422	0.4528	0.3796	0.5686	1.0000

$p<0.05^{*}$ $p<0.01^{**}$

Three way ANOVA showed significant difference between station, between depth and between season (App.21). The LSD at 5% level for N/P ratios among stations is 0.34. Station 1 and Station 2 showed significantly higher ratio than observed at Station 3. No significant difference were found between the ratios found at Station 1 and Station 2. The LSD at 5% level for ratios observed at different depth is 0.44. Significantly higher value of N/P ratio were observed at 0-2cm, 2-4cm, 4-6cm depth than the other depths. The LSD at 5% level in N/P ratio during different seasons is 0.34. During pre-monsoon season, significantly higher ratios were noticed in sediment cores.

Carbon:Phosphorus ratio (C/P)

The C/P ratio is used as an index of pollution by domestic sewage in any aquatic environmental system. Several studies established that phosphate is immobilized in mangrove sediments (Hesse, 1962; Boto and Wellington, 1983). The capacity of mangrove soil to immobilize phosphate depends on the amount of organic matter, its C/P ratio and the type and amount of clay minerals present. Dissolution of mineral phosphate depends on physicochemical characteristics such as pH, available sulphides, alkalinity and redox state (Boto, 1988). These factors are affected by the activity of microbes and larger organisms. The variation of C/P ratio in core sediments may indicate the capacity of immobilization of phosphorus in sediments.

Table 4.31 Station-wise summary statistics of C/P in sediment cores

Station	Depth(cm)	Min	Max	Mean	SD	% of CV
Station 1	0-2	42.00	64.55	55.34	7.76	14.03
	2-4	42.88	76.83	57.81	12.70	21.97
	4-6	40.75	72.01	58.32	11.60	19.88
	6-10	42.78	61.36	49.40	6.53	13.21
	10-20	30.43	53.34	41.30	9.33	22.58
Station 2	0-2	40.83	83.22	59.23	14.89	25.13
	2-4	28.63	69.20	50.61	13.34	26.36
	4-6	34.57	72.48	52.95	15.63	29.51
	6-10	35.98	60.69	50.72	9.26	18.26
	10-20	40.79	66.69	48.96	9.43	19.25
Station 3	0-2	38.73	57.42	46.32	6.19	13.37
	2-4	36.02	77.09	51.15	17.23	33.68
	4-6	29.06	61.08	40.21	10.99	27.33
	6-10	25.67	37.41	31.61	4.32	13.67
	10-20	33.81	55.87	42.87	8.99	20.97

Table 4.31 summarises the variation of C/P ratios observed in core sediments to a depth of 20cm. The minimum and maximum ratios observed were 25.67 (Station 3) and 83.22 (Station 2) respectively. Generally a sub-surface increase in C/P ratios was observed at Station 1 and Station 3 (Figure 4.23a). Seasonal variations in C/P ratios are depicted in Figures 4.23b-d. Similar C/P ratios were recorded at Station 1 in all depths except at 2-4 cm depth, while remarkably higher C/P ratios recorded during post-monsoon at Station 2 in surface sediment. However Station 3 recorded maximum C/P ratios during pre-monsoon in surface sediments.

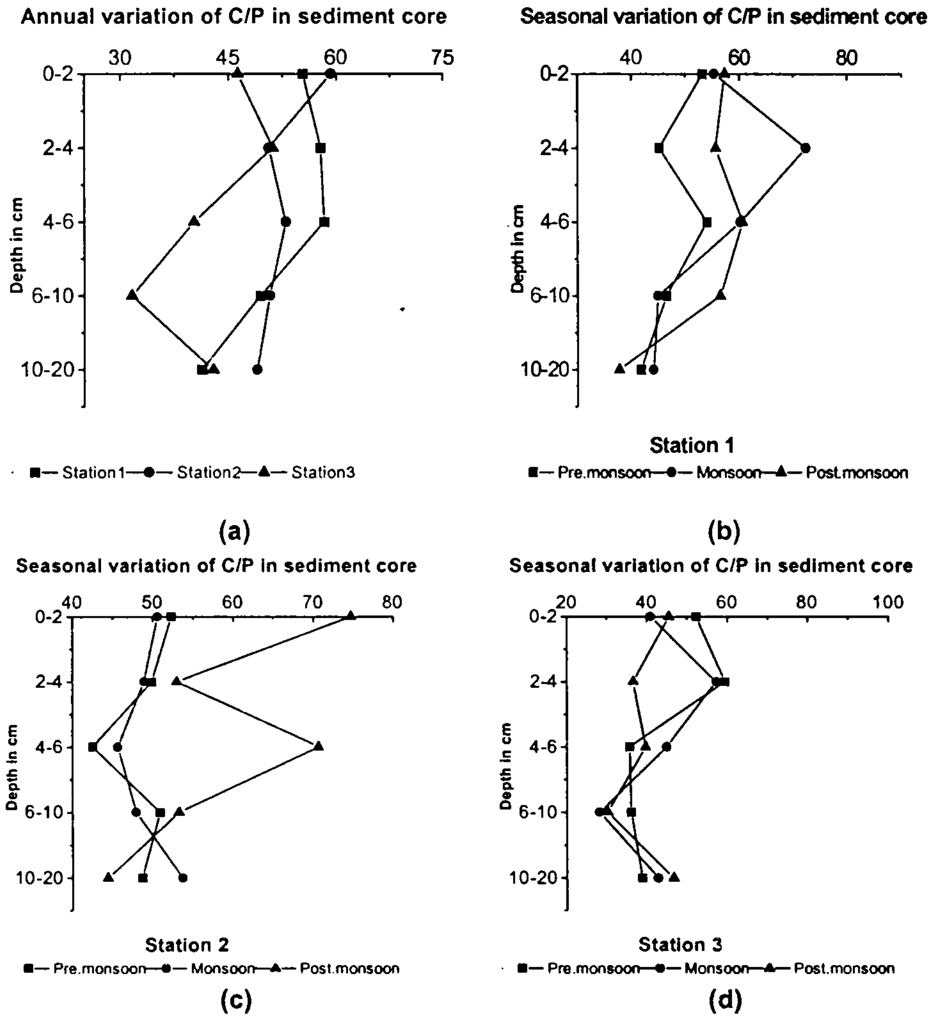


Fig. 4.23 Annual and seasonal variation of C/P in sediment cores

The C:N:P ratio in Pichavaram mangroves were reported to be 60.2:5.8:1 (Shanmukhappa, 1987). The C/P ratio reported in Cochin estuarine sediments were ranged from 4.662 to 38.27 (Nair, 1992). The observed C/P values during the present study ranged from 30.43 to 83.22 were found to be much higher than that found in the estuarine sediments of Cochin. Kairesalo *et al.* (1995) found the bacterial mineralization of organic matter depends on the C/N ratio of the available substrate. The richer the substrate for phosphorus or nitrogen compared to bacterial biomass the more easily phosphorus or nitrogen released in the mineralization. The C:N:P ratio of natural marine bacterial biomass was found as 45:9:1 (Goldman *et al.*, 1987). Tezuka (1990) however stated that this ratio could vary widely in natural assemblage of fresh water bacteria. However the studied area observed to compose of substrate richer in phosphorus than marine bacterial biomass. Comparatively higher C/P ratios found during the present study may be attributed to an increased bacterial phosphorus mineralization.

The depth profile of C/P ratio was similar during pre-monsoon and post-monsoon at Station 1. While at Station 2 and Station 3, monsoon and pre-monsoon season showed a similar depth profile. However maximum C/P were associated with post-monsoon season at Station 1 and Station 2 except at 2- 4cm depth at Station 1. The higher values observed during post-monsoon may be attributed to maximum concentrations of TOC. The depths beyond 10cms, showed minimum C/P ratios, associated with minimum concentrations of TOC in this layer. The high organic carbon as well as relatively high C/P ratio observed in this system indicted that a major portion of the phosphorus in sediment undergoes bacterial mineralisation. Further more it was also established that mangrove leaf litter found to harbor a large population of bacteria that appear to be highly productive (Robertson, 1988).

Table 4.32 Correlation matrix between depths – C/P

	0-2	2-4	4-6	6-10	10-20
0-2	1.0000				
2-4	0.9347***	1.0000			
4-6	-0.0115	0.0008	1.0000		
6-10	-0.2219	0.0799	-0.3022	1.0000	
10-20	-0.0310	0.0414	-0.2642	0.1060	1.0000

$p<0.001^{***}$

The C/P ratios were found, positively correlated between the depths 0-2cm and 2-4cm ($p< 0.001$) (Table 4.32). Correlation matrix between other parameters recorded significant negative correlation of C/P ratios with % silt and % clay at 0-2 and 2-4 cm depth $p<0.05$, $p<0.01$). Also C/P ratios exhibited positive relationship with TP concentrations at 0-2, 2-4 and 10-20 cm depth ($p<0.001$, $p<0.01$) (Table 4.18a, b, e).

Three way ANOVA showed significant difference between Station, between depth and between season (App.22). The LSD at 5% level for C/P ratios among stations is 6.027. Station 1 and Station 2 showed significantly higher ratio than observed at Station 3. No significant difference were found between the ratios found at Station 1 and Station 2. The LSD at 5% level for ratios observed at different depth is 7.78. Significantly higher value of C/P ratio were observed at 0-2cm, 2-4cm, 4-6cm depth than the other depths. No significant difference in C/P ratios was observed during three seasons.

4.3 CONCLUSION

Textural studies based on Folk's classification, the nature of surface sediment observed were sandy mud, sandy silt and muddy sand at Station1, Station 2 and Station 3 respectively. The well-developed mangroves at Station 1 and Station 2 support the root system of mangroves, which has a dense grid of vertical pnuematophores and arial roots. This structure traps floating detritus and reduces tidal flow, eventually creating conditions where suspended clay and silt particles settle, whereas the lack of vegetation as well as tidal influence and impact of waves remove finer fractions (silt + clay) of the sediment. The mean moisture percentages observed were higher at Station 1 and Station 2, while low percentages were recorded at Station 3. The spatial and seasonal variation in moisture content could be attributed to the variation of organic matter and grain size of the sediment. Generally higher pH values were observed at Station 1 and Station 2, while lower pH values were recorded at Station 3. Minimum pH values were recorded during pre-monsoon or post-monsoon at all stations and maximum values were recorded during monsoon season.

The concentrations of TOC in surface sediments of Station 1 and Station 2 were very high as that of Station 3. The prevalent hydrodynamics at Station 1 and Station 2 and the presence of mangrove roots that are well developed, retained fine fraction of surface sediment. The results indicate that Station 1 and Station 2 were composed of organic rich surface sediment. Generally minimum TOC concentrations were recorded during pre-monsoon at all stations while maximum were recorded during post-monsoon except at Station3. However Station 3 recorded similar TOC concentrations during all seasons. The present investigation observed a seasonal variation of TOC concentrations that might be associated with the variation in bacterial density. Pre-monsoon season associated with high temperature as well as restricted flow of water through the creek flourish the growth of bacteria and associated mineralisation resulted in lowering of organic carbon. The statistical analysis exhibited a significant positive correlation of TOC concentrations with percentage of clay, percentage of silt, percentage of moisture, TN, TP and ammonium concentrations. Total nitrogen (TN) concentration in surface sediments exhibited spatial and seasonal variations. The minimum concentration recorded at Station 3 (0.97mgg^{-1}) and maximum concentration was recorded at Station 2 (4.90mgg^{-1}). The seasonal variation of TN concentration showed maximum concentrations during pre-monsoon and minimum concentrations during monsoon at all stations. The TN concentrations varied between 0.97mg g^{-1} (Station 3) and 4.90mg g^{-1} (Station2). The seasonal variations may be attributed to the variation in TOC concentrations as well as with the adsorbed ammonium present in the sediment, since exchangeable ammonium found to be positively correlated with TN concentrations. Similar to TOC and TN concentrations, the concentrations of TP recorded were similar at Station 1 and Station 2, were varied from 1.12mg g^{-1} to 2.10mg g^{-1} but those from Station 3 were significantly lower, ranges from, 0.49mg g^{-1} to 0.80mg g^{-1}. Remarkable spatial variation with higher values at first two stations might be attributed to different hydrodynamic regime play at these sites. Station 3 marked by the overbearing of coarse fraction, which inhibits accumulation of phosphorus in sediments. The maximum salinity at Station 2 may cause precipitation of dissolved phosphorus and hence a maximum concentrations was recorded during pre-monsoon. The cycling of phosphorus in the studied area is highly dynamic at least at first two stations, where the sediments act as an efficient sink for phosphorus as far as an aerobic environment prevailed.

The exchangeable ammonium concentrations in surface sediments varied between 0.08µmol g^{-1} (Station 3) and 0.84µmol g^{-1} (Station 1 and Station 2). A regular tidal incursion at Station 3 may remove ammonium from the soil as it is soluble in water. Seasonal variations were found with comparatively higher values during pre-monsoon and post monsoon at Station 1 and Station 2. The high concentration of available ammonium was attributed to high early summer nitrogen mineralization (Cartaxana *et al.*, 1999). But at Station 3 the maximum was observed during monsoon. The surface sediments characterised by very low exchangeable nitrate concentrations, found to varied from 3.29 nmolg^{-1} to

64.31nmolg^{-1}. Spatial variation of exchangeable nitrate may also be associated with the oxygen availability in sediments. The higher concentrations at Station 2 may be associated with an oxic environment at this site as the mangroves translocate oxygen to their roots. While the minimum concentration observed at Station 1 and Station 2, during post-monsoon may be due to the maximum uptake by plant for their luxurious growth during post-monsoon. The maximum concentration at Station 3 during monsoon may be as a result of the high river runoff.

Although the C/N ratios varied between 16.57 and 35.32 at all stations, Station 2, surface sediments exhibited a variation of 16.57 and 28.18, which indicated an origin of mangrove detritus at this site. The high C/N ratios observed at Station 1 and Station 3, during the present investigation may be attributed to the accumulated organic carbon at Station 1, and humic derived nitrogeneous organic matter (biogenic origin) at Station 3. Relatively lower ratios observed at Station 2, suggest a mangrove detrital origin, and were associated with the tight coupling between microbial mineralization and assimilation in organic sediments of the studied mangrove area.

The low N:P ratios were due to comparatively high concentration of total phosphorus. N:P ratio can be taken as an index of the extent of extraneous influence on a productive water body, since the nitrogen if produced is autochthonous, variation in N:P depend on phosphorus which is mostly external (Shanmukhappa, 1987). These ratios indicated an abiogenic origin of phosphorus in the mangrove fringed creeks.

The C/P ratio varied between 34.68 (Station 2, monsoon) and 68.00 (Station 2, post-monsoon). The observed C/P ratio at the studied area reveal the accumulated phosphorus load in creek waters could be reduced by the mangrove plants and associated microorganisms. However to arrive at the cause of deviation from Redfield stoichiometry in the present investigation warrants more information on the kind of litter produced in this area, and also on the influence of microbes on carbon, nitrogen and phosphorus dynamics in this particular ecosystem. However outwelling of mangrove litter significantly influences sediment concentrations of TOC, TN and stoichiometric ratios of C:N:P (Alongi, 1990).

The grain size analysis of core sediments recorded similar observation as that of surface grain size analysis at all stations except in 4-6 cm layer at Station 1 and in 10-20 cm layer at Station 2. The major textural facies in sediment core at

Station 1 was sandy mud with a mud layer at 4-6 cm interval. However sediment core at Station 2 predominantly composed of sandy mud sediment with an intercalation of 10 cm thick muddy sand was recorded at a depth of about 10cm from the surface. According to Flach and Heip (1996), a homogeneous distribution pattern of grain size in the vertical column of sediment suggests a constant mixture by bioturbation effects.

The moisture percentage in sediment cores varied between 29.40% (Station 3) and 61.76% (Station 2). Generally moisture percentage decreases down the core at all stations. The moisture percentage showed a significant positive correlation with organic carbon. The annual mean values of moisture showed identical percentage at Station 1 and Station 2 due to the similar textural attributes at these stations, while less moisture percentage were recorded at Station 3, due to predominant muddy sand nature of the sediment. Seasonal variation in pH values in core sediments recorded the maximum values during monsoon while minimum were recorded during pre-monsoon at Station 1 and 2. However a remarkable decrease was noticed beyond 10cm depth at the same Station. All other stations, showed a down core increase in pH values during all three seasons. The three mangrove locations showed pH values as that of an alkaline nature of sediment up to 20cms of depth with certain exceptions during pre-monsoon at Station 1 and Station 3. The annual variation of pH values in core sediments showed a general increase down the core at all stations indicated an alkaline condition in sediment till 20cms of depth.

TOC concentration in the sediment cores varied between as low as 10.62mg g^{-1} at Station 3 and as high as 140.23mg g^{-1} at Station 1. Significantly higher values (LSD, 7.5 mg g^{-1}) TOC concentrations were observed at Station 1 and Station 2. The very low concentration of carbon at Station 3 compared to other two sites may be due to the variability of sediment texture along with non-availibility of litter. The depths, 0-2, 2-4, and 4-6, layers showed higher concentrations (LSD, 0.96 mg g^{-1}) of TOC as compared to 6-10 and 10-20 layers. Significantly higher value of TOC concentrations (LSD, 7 mg g^{-1}) was recorded during post monsoon followed by monsoon and pre monsoon seasons.

The TN concentrations varied between 0.44mg g^{-1} (Station 3) and 5.84mg g^{-1} (Station 2). Three-way ANOVA analysis showed a significant difference of TN between stations, between depths and between seasons. Among the stations, Station 2 showed significantly higher (LSD, 0.31 mgg^{-1}) value of TN followed by Station 1, which in turn had significantly higher concentration than Station 3. The LSD at 5% level for depth is 0.405mg g^{-1}. The layers 0-2cm and 2-4 cm showed significantly higher TN concentrations than the other depth ranges. TN concentrations followed a decreasing order in the layers 4-6, 6-10 and 10-20 cm. TN correlated positively with TOC and negatively with sediment C/N ratio at 0-2 and 2-4cm depth ($p<0.01$, $p<0.05$). This indicated the decrease in C:N ratio was mainly due to the increase organic nitrogen in the sediment. It is possible that the increase in TN and thus decrease in C/N ratio in the sediment partly to the increase of chlorophyll-containing labile materials (Cheng and Chang, 1999).

Significantly higher concentration (LSD, 0.314mg g^{-1}) of nitrogen was observed during pre-monsoon followed by post monsoon and monsoon.

Exchangeable nitrate concentrations were varied significantly among stations but not with depth or season. The highest concentration (LSD, 11.40 $nmolg^{-1}$) of exchangeable nitrate recorded at Station 2 associated with the luxuriant growth of plants at this Station.

The exchangeable ammonium concentrations varied between 0.07$\mu molg^{-1}$ (Station 3) and 1.03$\mu molg^{-1}$ (Station 1). Significant difference of exchangeable ammonium concentration observed between station, and between season but not between depth. The LSD at 5% level for station and season is 0.122 $\mu molg^{-1}$. Significantly higher concentration of exchangeable ammonium was recorded at Station 1 and Station 2 while Station 3 recorded comparatively low concentration of exchangeable ammonium. Significantly higher value of exchangeable ammonium was observed during pre-monsoon followed by monsoon and post monsoon. Significantly low concentration was registered during post-monsoon Although no significant difference between depths exist, an increase down the core observed at Station 1 and Station 2, during certain instances. The ammonium concentrations were found to increase with depth in the anaerobic soil, indicating denitrification beyond rhizopheres. Correlation of exchangeable ammonium and other parameters showed a positive relationship with percentage of clay, total nitrogen, in 0-2, 2-4, 4-6 and 6-10 and 10-20 cm depth. Also at 2-4 cm depth this is correlated with total iron and at 4-6 cm positive relationship showed with exchangeable nitrate.

TP concentrations were found to vary between 296.70 μgg^{-1} (Station 3, 10-20cm) and 2190.84μgg^{-1} (Station 1, 10-20cm). Significantly higher concentration

(LSD, 144μgg^{-1}) of TP was observed at Station.1 and Station 2 than at Station 3. The spatial variation in distribution of TP is explained by the sediment grain size, presence or absence of macrophytes\ phytoplankton, bacterial assemblages etc. Although significant difference does not exist among different depths, 0-2cm and 2-4 cm layers exhibited higher TP concentrations than the other depths. In mangrove area (Fly Delta, Papua New Guinea) total phosphorus concentration are high in surface sediments, suggesting oxidation near or at the sediment-water interface. Significantly higher concentrations of TP were observed during post-monsoon followed by monsoon and pre monsoon. The oxidative reactions would immobilize phosphorus and limit its availability to autotrophs and microheterotrophs, with phosphorus being bound to iron minerals.

The minimum and maximum C/N ratio observed were 10.48 (Station 3) and 56.62 (Station 3) respectively. Three way ANOVA showed significant difference between station, depth and season. The LSD at 5% level for station is 1.69. Station 1 and Station 3 have significantly higher (LSD,1.69) value of C/N ratio than Station 2. Most of the ratios were larger than 14 which suggest that the detritus in the study site might composed mainly of flora debris found in mangrove wet lands. The LSD at 5% level for depth is The 10-20 cm depth showed a significantly higher ratio (LSD, 2.18) than all other depths. Between other depths there is no significant difference. Significantly higher value (LSD, 1.69) of C/N was observed during monsoon season followed by post monsoon and pre monsoon. This indicated that besides mangroves and associated biota continuously add detritus to the mangrove ecosystem, terrigenous organic matter brought in by fresh water discharge also vary the stoichiometric ratios at this site.

The N/P ratios recorded in core sedimentd varied between 0.82 (Station 3) and 4.47 (Station 1) respectively. Three way ANOVA showed significant difference between Station, between depth and between season. The core sediments at Station 1 and Station 2 showed significantly higher ratio (LSD,0.34) than observed at Station 3. No significant differences were found between the ratios found at Station 1 and Station 2. Significantly higher value of N/P ratio (LSD, 0.44) were observed at 0-2cm, 2-4cm, 4-6cm depth than the other depths. During pre-monsoon season, significantly higher N/P ratios (LSD, 0.34) were noticed in sediment cores. The recorded values found in here were far below the N/P ratios for natural or cultured plankton, hence suggest the abiogenic nature of phosphorus.

Distrtibution of C/P ratios in sediment cores suggest a bacterial phosphorus mineralization, found to varied from 25.67 (Station 3) and 83.22 (Station 2). Station 1 and Station 2 showed significantly higher ratio (LSD, 6.027) than observed at Station 3. No significant differences were found between the ratios at Station 1 and Station 2. Significantly higher value (LSD, 7.78) of C/P ratio were observed at 0-2cm, 2-4cm, 4-6cm depth than the other depths. No significant difference in C/P ratios was observed during three seasons. It was also suggested by Alongi (1989) that bacteria and benthic microalgae in mangrove sediments are sinks of nutrients because the system is characterised by a closed internal cycling – death, decay uptake and growth – and thus serve as a mechanism for nutrient conservation.

Phosphorus is an abundant trace element and one of the most important nutrients. In a mangrove ecosystem the above ground biomass was significantly correlated with the soil exchangeable phosphorus (Boto and Wellington, 1983). These plants may remove a significant amount of phosphates from soil. Laborotary experiment on release of phosphates (PO_4-P) under anaerobic conditions, two Lake sediments behaved released differently. It is suggested that these differences are due to different amounts of organic matter in the sediment utilizable by the appropriate bacteria. It is further suggested that this is due to the greater degree of mineralization of detrital organic matter in one of the lake resulting in a lesser amount of utilizable organic matter. Tracer studies with ^{32} P showed very high fluxes, especially under anaerobic conditions. On an annual basis these varied from 50% to four orders of magnitude higher than the external loads of phosphorus to these Lakes (Rosich and Cullen, 1982).

It was also suggested that a large proportion of sediment nutrient is derived from mangrove detritus when the sediment depleted only in phosphorus but not with carbon and nitrogen.

REFERENCES

Aller, R.C. 1994 The sedimentary Mn cycle in long island sound: its role as intermediate oxidant and the influence of bioturbation, O_2 and C_{org} flux on diagenetic reaction of balances. *Journal of Marine Research* **52**, 259-295.

Alongi, D.M. 1987 Intertidal zonation and seasonality of meiobenthos in tropical mangrove estuaries. *Marine Biology* **95**, 447-458.

Alongi, D.M. 1988 Bacterial productivity and microbial biomass in tropical mangrove sediments. *Microbial Ecology* **15**, 59-79.

*Alongi, D.M. 1989 The fate of bacterial biomass and production in marine benthic food chain. In *Recent advances in microbial ecology* (Hattori, T., Ishida, Y., Maruyama, Y., Monta, R.Y. & Achida, A., eds). Japan Science Society Press, Tokyo, pp. 355-359.

Alongi, D.M. 1990 Effect of mangroves detrital outwelling on nutrient regeneration and oxygen fluxes in coastal sediments of the central great barrier reef lagoon. *Estuarine, Coastal and Shelf Science* **31**, 581-598.

Alongi, D.M. 1991 The role of intertidal mudbanks in the diagenesis and export of dissolved and particulate material from the Fly Delta, Papua New Guinea. *Journal of Experimental Marine Biology and Ecology* **149**, 81-107.

Alongi, D.M. 1994 The role of bacteria in nutrient recycling in tropical mangrove and other coastal benthic ecosystems. *Hydrobiologia* **285**, 19-32.

Alongi, D.M. 1996 The dynamic of benthic nutrient pools and fluxes in tropical mangrove forest. *Journal of Marine Research* **54**, 123-148.

Alongi, D.M. & Christoffersen, 1992 Benthic infauna and organism sediment relations in a shallow, tropical coastal area: influence of outwelled mangrove detritus and physical disturbance. *Marine Ecology Progress Series* **81**, 229-245.

Alongi, D.M., Boto, K.G. & Robertson, A.I., 1992 Nitrogen and Phosphorus cycles. In *Tropical Mangrove Ecosystems – Coastal and Estuarine Series 41* (Robertson, A.I. and Alongi, D.M., eds). American Geophysical Union, Washington, pp. 251-292.

Alongi, D.M., Christoffersen, P. & Tirendi, F.1993 The influence of forest type on microbial nutrient relationships in tropical mangrove sediments. *Journal of Experimental Marine Biology and Ecology* **171**, 201-223.

Alongi, D.M., Tirendi, F. & Clough, B.F. 2000 Below ground decomposition of organic matter in forests of the mangrove Rhizophora stylosa and Avicennia marina along the arid coast of western Australia. *Aquatic Botany* **68**, 97-122.

Alongi, D.M. Sasekumar, A., Tirendi, F. & Dixon, P. 1998 The influence of standage on benthic decomposition and recycling of organic matter in managed mangrove forests of Malaysia. *Journal of Experimental Marine Biology and Ecology* **225**, 193-217.

Alongi, D.M., Tirendi, F., Deixon., Trott, L.A., Brunskill, G.J. 1999 Mineralization of organic matter in intertidal sediments of a tropical semi-enclosed delta. *Estuarine, Coastal and Shelf Science* **48**, 451-467.

Alongi, D.M., Ayukai, T., Brunskill, G.J., Clough, B.F. and Wolanski, E. 1998 Sources, sinks, and export of organic carbon through a tropical, semi-enclosed delta (Hinchinbrook channel, Australia). *Mangroves and Salt Marshes* **2**, 237-242.

Andersen, F.O., Kristensen, E. 1988 Oxygen microgradients in the rhizosphere of the mangrove avicennia marina (Forsk) Vierh. *Marine Ecology Progress Series* **44**, 201-204.

Anderson, F.O. & Jenson, H.S. 1992 Regeneration of inorganic phosphorus and nitrogen from seston in a fresh water sediment, *Hydrobiologia* **228**, 71-81.

Badarudeen, A., 1997 Sedimentology and geochemistry of some selected mangrove ecosystems of Kerala, south west coast of India. *Ph.D. dissertation*, *Cochin University of Science and Technology*, Cochin-16.

Badarudeen, A. Padmalal, D. & Sajan, K., 1998 Hydrodynamic responses on mangrove sediments of Kannur region, southwest coast of India. *Indian Journal of Marine Sciences* 27, 262-265.

*Bailey, G.W. 1968 Role of soils and sediment in water pollution control – *Part 1: Reactions of nitrogen and phosphorus compounds with soils and geological strata , U. S. Department of the interior , Federal Water Pollution Control Administration,* South East Water Laboratory , 90-100.

Barrow, N.J., Bolland, M.D.A. & Allen, D.J. 1980 Describing the effect of electrolytes on adsorption of phosphate by a variable charge surface. *Australian Journal of Soil Research* **18**, 395-404.

Benner, R. & Hodson, R.E. 1985 Microbial degradation of the leachable and lignocellulosic components of leaves and wood from rhizophora mangle in a tropical mangrove swamp. *Marine Ecology Progress Series* 23, 221-230.

Binnerup, S.J., Jensen, K., Revsbech, N.P., Jensen, M.H. & Sorrensen. J. 1992 Denitrification dissimilatory reduction of nitrate to ammonium and nitrification in a bioturbated estuarine sediment as measured with ^{15}N and microsensor techniques. *Applied and Environmental Microbiology* **58**, 303-313.

Blackburn, T.H., Lund, B.A. & Krom, M.D. 1988 C- and N- mineralisation in sediments of earthen marine fishponds. *Marine Ecology progress series* **44**, 221-227.

Bonani, P., Caprioli, R., Ghiara, E., Mignuzzi, C., Orlandi, C., Paganin, G. & Monti, A. 1992 Sediment interstitial water chemistry of the Orbetello lagoon (Grosseto, Italy); nutrient diffusion across the water –sediment interface, *Hydrobiologia*, **235**, 553.

Bostrom, B., Andersen, J.M., Fleischer, S., Jansson, M. 1988 Exchange of phosphorus across the sediment water interface. *Hydrobiologia* **170**, 229-244.

Boto, K.G. 1982 Nutrient and organic fluxes in mangroves. In *Mangrove cosystems in Australia* (Clough, B.F. ed). Australian National University Press, Canberra, pp. 239-257.

Boto, K.G. 1984 Water logged saline soils. In *The Mangrove Ecosystems: Research Methods* (Snedaker, S.C. & Snedaker, J.G., eds). UNESCO, Paris, pp. 114-130.

Boto, K.G. 1988 The phosphorus cycle. In *Mangrove Microbiology* (Agate, A.D., Subramanian, C.V., & Vanucci, M., eds). *UNDEP/UNESCO regional project (RAS/86/1988)*, New Delhi, pp. 85-100.

Boto, K.G. 1992 Nutrients and mangroves. In *Pollution in Tropical Aquatic Systems* (Connel, D.W. & Hawker, D.W., eds). CRC Press, Boca Raton, pp. 129-145.

Boto, K.G. & Wellington, J.T. 1983 Phosphorus and nitrogen nutritional status of a northern Australian mangrove forest. *Marine Ecology Progress Series* 11, 63-69.

Boto, K.G. & Wellington, J.T. 1984 Soil characteristics and nutrient status in a northern Australian mangrove forest. *Estuaries* **7**, 61-69.

Boyd, C.E. 1992 Shrimp pond bottom soil and sediment management. In *Proceedings Special session on Shrimp farming* (Wyban ed.). World aquaculture society, Baton Rouge, LA, pp166-181.

Canfield, D.E. 1993 organic matter oxidation in marine sediments. In *Interactions of C,N,P and S in biogeochemical cycles and global change* (Wollaswt, R., Mackensie, F.T. & Chou, L., eds). Springer-Verlag, Berlin, pp. 333-363.

Cartaxana, P., Cacador, I., Vale, C., Falcao, M. & Catarino, F. 1999 Seasonal variation of inorganic nitrogen and net mineralization in a salt marsh ecosystem. *Mangroves and salt marshes* **3**, 127-134.

Cheng, I. J. & Chang, P.C. 1999 The relation between surface macrofauna and sediment nutrients in a mudflat of the Chuwei mangrove forest, Taiwan. *Bulletin of Marine Sciences* **65**, 603-616.

Clarke, P.J. 1985 Nitrogen pools and soil characteristics of a temperate estuarine wetland in eastern Australia. *Aquatic Botany* **23**, 275-290.

Clough, B.F., Boto, K.G. & Attiwill, P.M. 1983 Mangrove and sewage: a re-evaluation. In *Tasks for vegetation science* (Teas, H.J., ed). Dr. W. Junk Publishers, The Hague, **17**, 151-161.

Conley, D.J. 2000 Biogeochemical nutrient cycles and nutrient management strategies. *Hydrobiologia* **410**, 87-96.

Day, J.W., Day, R.H., Barriero, M.T., Ley-Lon, F. & Madden, C.J. 1982 Primary production in the Laguna de Terminos, a tropical estuary in the southern Gulf of Mexico. *Oceanologica Acta*, **5** (suppl), 269-272.

*De Laune, R.D. & Patric Jr. W.H. 1980 Nitrogen and phosphorus cycling in a gulf coast salt marsh. *Proceedings of International Estuarine Research Federation Conference,* Jeckyl Island, GA, Degrens, E.T. 1970 Molecular nature of nitrogenous compounds in sea water recent marine sediments. In *Organic matter in natural waters* (Hood, D.W. ed). Univ Alaska, pp. 59-103

Deinema, M.H., Van Loosdrecht, M. & Scholten, A. 1985 Some physiological characteristics of Acinetobactor spp. Accumulating large amount of phosphate. *Water Science and Technology* **17**, 119-125.

Demaison, G.J. 1991 Anoxia vs. productivity: what controls the formation of organic-carbon-rich sediments of and sedimentary rocks? *Bulletin of American Association of Petrology and Geology* **75**, 499-510.

Dinesh, R., Shome, B.R., Rajeshwari Shome & Bandyopadhay, A.K. 1998 Soil enzymes in mangroves: Activities and their relation to relevant soil properties. *Current Science* **75**, 511-512.

Fenchel, T. & Blackburn, T. H. 1979 *Bacteria and mineral cycling*. Academic press, London, pp. 225.

Flach, E., & Heip C. 1996 Vertical distribution of macrozoobenthos within the sediments on the continental slope of the Cogan Spur area (NE Atlantic). *Marine Ecology Progress Series* **141**, 55-66.

*Foehrenbach, 1973 Eutrophication. *Journal of Water Pollution Control Federation* **45,** 1237 –1240.

*Folk, R.L. 1974 *Petrology of sedimentary rocks*, Hemphill Publishing company, Austin, Tex, pp.182.

Gachter, R., Meyer, J.S. & Mares, A. 1988 Contribution of bacteria to release and fixation of phosphorus in lake sediments. *Limnology and Oceanography* **33**, 1542-1558.

Gachter, R.J., & Meyer, J.S., 1993. The role of microorganisms in mobilization and fixation of phosphorus in sediments. *Hydrobiologia* **253**, 103-121.

Gill, A.M. & Tomlinson, P.B. 1977 Studies on the growth of red mangrove (Rhizophora mangle L.,) The adult root system. *Biotropica* **9**,145-155.

Goldman, J.C., Caron, D.A. & Dennet, M.R. 1987 Regeneration of gross growth efficiency and ammonium regeneration in bacteria by subtrate C:N ratio. *Limnology and Oceanography* **32**, 1239-1252.

Golterman, H.L. 1998 The distribution of phosphate over iron-bound and calcium bound phosphate in stratified sediments. Hydrobiologia **364**, 75-81.

Gonzalez, F. & Mee, L.D. 1988 Effect of mangrove humic-like substances on biodegradation rate of detritus. *Journal of Experimental Marine Biology and Ecology* **199**, 1-13.

Haines, E.B., Chalmers, A., Hanson, R. & Sherr, B. 1977 Nitrogen pools and fluxes on a Georgia salt marsh, In *Estuarine processes* (Wiley, M., ed) vol 2, Academic Press, N.Y., 241-254.

Hesse, P.R. 1962 Phosporus fixation in mangrove swamp muds. *Nature* **193**, 295-296

Holmer, M. & Olsen, A.B. 2002 Role of decomposition of mangrove and seagrass detritus in sediment carbon and nitrogen cycling in a tropical mangrove forest. *Marine Ecology Progress Series* **230** , 87-101.

Jagtap T.G. 1987 Seasonal distribution of organic matter in mangrove environment of Goa. *Indian Journal of Marine Sciences* **16**, 103-106.

Jenkins, M.C. & Kemp, W.M. 1984 The coupling of nitrification and denitrification in two estuarine sediments. *Limnology and Oceanography* **29**, 609-619.

*Jickells, T.D. & Rae, J.E. (eds) 1997 Biogeochemistry of intertidal sediments. Cambridge University Press, Cambridge, pp. 193.

Kairesalo, T., Tuominen, T., Harikainen, K. & Rankinen, K. 1995 The role of bacteria in the nutrient exchange between sediment and water in a flow-through system. *Microbial ecology* **29**, 1219-144.

Kathiresan, K., Rajendran, N. & Thangadurai, 1996 Growth of mangrove seedlings in intertidal area of Vellar estuary southeast coast of India. *Indian Journal of Marine Sciences* **25**, 240-243.

Klump, J.V. & Martens, C.S. 1989 The seasonality of nutrient regeneration in an organic rich coastal sediment: Kinetic modeling of changing pore water nutrient and sulphate distribution. *Limnology and Oceanography* **34**, 559-577.

*Kristensen, E. 1988. Benthic fauna and biogeochemical processes in marine sediments: microbial activities and fluxes. In *Nitrogen cycling in coastal* *marine sediments* (Blackburn, T.H. & Sorrensen, J., eds). John Wiley, Chichester, pp. 275-299.

Kristensen, E. 1990 Characterization of biogenic organic matter by stepwise thermograveimetry (STG). *Biogeochemistry* **9**, 135-159.

Kristensen, E. 1993 Seasonal variation in benthic community metabolism and nitrogen dynamics in a shallow, organic poor Danish lagoon. *Estuarine, Coastal and Shelf Science* **36**, 565-586.

Kristensen, E. 1997 Carbon, Sulphur and Nitrogen Biogeochemistry of Tropical Mangrove sediments. *In Coastal Zone Management Imperative for Maritime Developing Nations* (Haq, B.U. *et al.*, eds). Kluwer Academic Publishers pp 199-232.

Kristensen, E. & Pilgaard, R. 1999 The role of faecal pellet deposition by leaf eating sesarmid crabs on litter decomposition in a mangrove sediment (Phuket, Thailand). In *Organism-sediment relations* (Aller, J.Y. & Aller, R.C., eds). University of South Carolina Press.

Kristensen, E., Anderson, F.O. & Kofoed, L.H. 1988 Preliminary assessment of benthic community metabolism in a South-East Asian mangrove swamp. *Marine Ecology Progress Series* **48**, 137-145.

Kristensen, E., Holmer, M., & Bussarawit, 1991 Benthic metabolism and sulphate reduction in a southeast Asian mangrove swamp. *Marine Ecology Progress Series* **73**, 93-103.

Kristensen, E., Devol, A.H., Ahemad, S.I., & Saleem, M. 1992 Preliminary study on benthic metabolism and sulphate reduction in a mangrove swamp of Indus delta, Pakistan. *Marine Ecology Progress Series* **90**, 287-297.

Kristensen, E., Anderson, F., Holmboe, N., Holmer, M. & Thongtham, N. 2000 Carbon and nitrogen mineralisation in sediments of the bangrong mangrove area, Phuket, Thailand. *Aquatic Microbial Ecology* **22**, 199-213.

Kristensen, E., Jensen. M.H., Banta, G. T., Hansen, K., Holmer, M. & King, G.M. 1998 Aspects of nitrogen cycling in sediments of a south east Asian mangrover forest. *Aquatic Microbial Ecology* **15**, 165-175.

Lancelot, C. & Billen, G. 1985 Carbon-Nitrogen relationships in nutrient metabolism of coastal marine ecosystems. Advances in aquatic microbiology **3**, 263-321.

Lee, K.H., Moran, M.A., Benner, R. & Hodson, R.E., 1990 Influence of soluble components of red mangrove (Rhizophora mangle) leaves on microbial decomposition of structural (lignocellulosic) leaf components in sea water. *Bulletin of Marine Science* **46**, 374-386.

Li, M.S. 1997 Nutrient dynamics of a Futian Mangrove Forest in Shenzhen, South China. *Estuarine coastal and Shelf Science* **45**, 463-472.

*Limpsaichol, P. 1978 Reduction and oxidation properties of the mangrove sediment, Phuket island, Southern Thailand. Phuket. *Marine Biological Center Research Bulletin*, No. **23**, 13 pp

Lindau, C.W. & DeLaune, R.D. 1991 Dinitrogen and nitrous oxide emission and entrapment in Spartina alterniflora saltmarsh soils following addition N-15 labelled ammonium and nitrate. *Estuarine, Coastal and Shelf Science* **32**, 161-172.

Liu, S-M., Kou, C-E & Hsu, T-B. 1996 Reductive dechlorination of cholorphenols and pentachlorophenol in anoxic estuarine sediment. *Chemosphere* **32**, 1287-1300.

Lopez, G.R. & Levinton, J.S. 1987 Ecology of deposit feeding animals in marine sediments. Quart. Rev. Biol. **62**, 235-260.

Morsel, J.M. & Corredor, J.E. 1993 Sediment nitrogen trapping in mangrove logoon. *Estuaries* **37**, 203-21.

Mortimer, C.H. 1971 Chemical exchanges between sediments and water in the Great Lakes – speculations on probable regulatory mechanisms. *Limnology and Oceanography* **16**, 387-404.

Nair, P.V.R., Joseph, K.J., Balchand, V.K. & Pillai, V.K. 1975 A study on the primary production in the Vembanad lake. *Bulletin of Department of Marine Sciences, University of Cochin* **7**, 161-170.

Nair, V. 1992 Biogeoorganic in the sedimentary environment of Cochin estuary, a dissertation submitted to Cochin University of Science and Technology, School of Marine Sciences, Cochin 682018.

Nedwell, D.B. 1975 Inorganic nitrogen metabolism in a eutrophicated tropical mangrove estuary. *Water Research* **9**, 221-231.

Nedwell, D.B., Blackburn, T.H., Wiebe, W.J. 1994 Dynamic nature of the turnover of the organic carbon, nitrogen and sulphur in the sediments of a Jamaican mangrove forest. *Marine Ecology Progress Series* **110**, 223-231.

Nixon, S.W., Furnas, B.N., Lee, V., Marshall, M., Ong, J.-E., Wong, C.-H., Gong, W.K. & Sasekumar, A. 1984 The role of mangrove in the carbon and nutrient dynamic of Malaysia estuaries. *Proceedings of Asian Symposium on Mangrove Environment Research and Management* pp. 534-544.

Odum, W.E., & Heald, E.J. 1975 The detritus-based food web of an estuarine mangrove community. In *Estuarine Research* (Cronin, L.E., ed) Academic Press Inc., New York. pp. 265-286.

*Palaniselvam, V. 1998 Epiphytic cyanobacteria of mangrove: ecological, physiological and biochemical studies and their utility as biofertilizer and shrimp feed. *Ph.D. Thesis, Annamalai University*, Parangipettai, India: 141pp

*Paludan, C. & Morris, J.T. 1999 Distribution and speciation of phosphorus along a salinity gradient in intertidal marsh sediments. *Biogeochemistry* **45**, 197-221.

Patric & Mikkelsen, 1971 Plant nutrient in flooded soil. In *Fertilizer Technology and Use* (Olson, R.A., ed). 2nd edition. Soil Science Society of America Inc. Madison,Wisconsin,USA. pp 187-215.

*Pedersen, T.F. & Calvert, S.E. 1990 Anoxia vs. productivity: What controls the formation of organic-carbon-rich sediments and sedimentary rocks? Reply. *Bulletin of American Association of Petrology and Geology* **75**, 500-501.

Pedersen, A.G.U., Bernstsen, J., Lomstein, B.A.A. 1999 The effect of eelgrass decomposition on sediment carbon and nitrogen cycling: a controlled laboratory experiment. Limnology and Oceanography 44, 1978-1992.

*Ponnamperuma, F.N. 1972 The chemistry of submerged soils. *Advances in Agronomy* **24**, 29-96.

Rajendran, N., Kathiresan, K. 1999 Seasonal occurrence of juvenile prawn and environmental factors in a *Rhizophora mangal*, southeast coast of India. *Hydrobiologia* **394,** 193-200.

Ram A., Zingde., M.D. 2000 Interstitial water chemistry and nutrient fluxes from tropical intertidal sediment *Indian Journal of Marine Sciences* **29**, 310-318.

*Ravikumar, S. 1995 Nitrogen fixing azotobactors from the mangrove habitat and their utilityas biofertilizers. *Ph.D. Thesis, Annamalai University*, Parangipettai, India: 102pp.

Remani, K.N., Venugopal, P., SaralaDevi, K., Lalitha, S. & Unnithan, R.V. 1980 Sediments of Cochin backwaters in relation to pollution. *Indian Journal of Marine Sciences* **9**, 111-113.

Rice, D.L. 1982 The detritus nitrogen problem: new observationa and perspectives from organic geochemistry. *Marine Ecology Progress Series* 9, 153-162.

Rice, D.L. & Hanson, R.B. 1984 A kinetic model for detritus nitrogen : role of the associated bacteria in nitrogen accumulation. *Bulletin of Marine Science* 35, 326-340.

Rice, D.L. & Tenore, R.B. 1981 Dynamics of carbon and nitrogen during the decomposition of detritus derived from estuarine macrophytes. *Estuarine Coastal and Shelf Science* **13**, 68-70.

Rivera- Monroy, V.H., Day, J.W., Twilley, R.R., Vera-Herrera, F. & Cornado-Molina, C. 1995 Flux of nitrogen and sediment in a fringe mangrove forest in Terminos Lagoon, Mexico. *Estuarine Coastal and Shelf Science* **40**, 139-160.

Rivera- Monroy, V.H., Twilley, R.R. 1996 The relative role of denitrification and immobilization in the fate of inorganic nitrogen in mangrove sediments (Terminos Lagoon, Mexico). *Limnology and Oceanography* **41** , 284-296.

Robertson, A.I 1988 Decomposition of mangrove leaf litter in tropical Australia *Journal of Experimental Marine Biology and Ecology* **116**, 235-247.

Robertson, A.I. & Phillips, M.J. 1995 Mangroves as filters of shrimp pond effluent: predictions and biogeochemical research needs. *Hydrobiologia* **295**, 311-321.

Rosich, R.S. & Cullen, P. 1982 Interaction of P,N and C at the sediment water interface *In* Cycling of C,N,S and P. In *Terrestrial and Aquatic Ecosystems* (Freney, J.F. & Galbally, eds). Springer – Verlag, Berlin, Heidelberg NY.

*Saenger, P., Hegerl, E.G. & Davie, J.D.S. 1983 Global status of mangrove ecosystems. *The Environmentalist* **3**, 1-88.

Sakaranarayanan, V.N. & Panampunnayil, S.U. 1979 *Indian Journal of Marine Science* **8** 27-35.

*Shaiful, A.A.A., Abdul Manan, D.M. Ramli, M. R. & Veerasamy, R. 1986 Ammonification and nitrification in wet mangrove soils. *Malay Journal of Science* 8, 47-56.

Shanmukhappa, H. 1987 Organic matter and C,N,P in sediments of Porto Novo. *Proceedings of National Seminar on Estuarine Management, 1987*, Trivandrum, pp. 128-133.

Sheridan, R.P. 1991 Epicalous, nitrogen-fixing microepiphytes in a tropical mangal community , Guadeloupe, French W.I. Biotropica **23**, 530-541.

*Sinke, A.J.C., Cappenburg, T.E. 1988 Influence of bacterial processes on the phosphorus release from sediments in the eutrophic Loosdrecht Lakes, The Netherlands. Arch Hydrobiol Beih Ergebn Limnol **30**, 5-13.

Smith III, T.J., Boto, K.G., Frusher, S.D. & Giddins, R.L. 1991 Keystone species and mangrove forest dynamics: the influence of burrowing by crabs on soil nutrient status and forest productivity. *Estuarine, Coastal and Shelf Science* **33**, 419-432.

Smith, P.T. 1996 Physical and chemical characteristics of sediments from prawn farms and mangrove habitat on the Clarence River, Australia. *Aquaculture* **146**, 47-83.

Sommers, L.E., Harris, R.F., Williams, J.D.H., Armstrong, D.E. & Syers, J.K. 1972 Fractionation of organic phosphorus in lake sediments. *Soil Science society of America Proceedings* **36**, 51-54.

Soto-Jimmenez, M.F., Paez-Osuna, F. 2001 Distribution and normalization of heavy metal concentrations in mangrove and lagoonal sediments from Mazatlan harbor (SE Gulf of California. *Estuarine, Coastal and Shelf Science* **53**, 259-274.

Stienke, T.D., Holland, A.J., Singh, Y. 1993 Leaching losses during decomposition of mangrove leaf litter. *South African Journal of Botany* **59**, 21-25.

Sundareshwar, P.V. & Morris, J.T. 1999 Phosphorus sorption characteristics of intertidal marsh sediments along an estuarine salinity gradient. *Limnology and oceanography* **44**, 1693-1701.

Sunil Kumar, R. 1996 Distribution of organic carbon in the sediments of Cochin mangroves, south west coast of India. *Indian Journal of Marine Science* **25**, 274 – 276.

Sutcliffe, D.W. & Jones, J.G. 1992 Eutrophication : research and application to water supply. *Freshwater Biology Association* **2**, 231-240.

Tenore, K.R., Hanson, R.B., Mc.Claim, J., Maccubbin, A.E. & Hodson, R.E. 1984 Changes in composition and nutritional value to a benthic deposit feeder of decomposing detritus pools. *Bulletin of Marine Sciences* **35**, 299-311.

Tezuka, Y. 1990 Bacterial regeneration of ammonium and phosphate as affected by the carbon:nitrogen:phosphorus ratio of organic substrates. *Microbial Ecology* **19**, 227-238.

Tuominen, L., Karesalo, T., Hartikainen, H. & Tollberg, P. 1996 Nutrient fluxes and microbial activity in sediment enriched with settled seston. *Hydrobiologia* **335**, 19-31.

Twilley, R.R. 1988 Coupling of mangroves to the productivity of estuarine and coastal waters. In *Coastal-offshore ecosystems: interactions. Lecture Notes Coastal Estuarine Studies* **22**. Springer. p. 155-180.

Twilley, R.R., Ejdung, G., Romare, P. & Kemp W.M. 1986a A comparative study of decomposition oxygen consumption and nutrient release for selected aquatic plants occurring in estuarine environments. *Oikos* **47**, 190-198.

Twilley, R.R., Lugo, A.E., & Patterson-Zucca, C. 1986b Litter production and turnover in basin mangrove forests in south west Florida. *Ecology* **67**, 670-683.

Valiela, I. 1984 Nutrient Cycles: Phosphorus, Nitrogen and Sulfur. In *Marine Ecological Processes,* Springer Verlag, New York, pp. 312-340.

Van der Valk, A.G. & Attiwll, P.M. 1984 Decomposition of leaf and root litter of Avicennia marina at Westernport Bay, Victoria, Australia. *Aquatic Botany* **18**, 205-221.

*Vollenweider, R. A. 1968 Scientific Fundamentals of the Eutrophication of Lakes and Flowing waters with Particular reference to Nitrogen and Phosphorus as

Factors in Eutrophication, Organization Economic Cooperation and Development, Paris, DAS/CSI/ **68**, 27.

Wafar, S. & Untawale, A.G., Wafar, M. 1997 Litter fall and energy flux in a mangrove ecosystem. *Estuarine, Coastal and Shelf Science* **44**, 111-124.

Wahab, M.A. & Stirling, H.P. 1991 Environment and development of benthos in earthern trout ponds in central Scotland. *Aquaculture* **97**, 335-352.

Wentzel, M.C., Lotter, L.H., Ekama, G.A., Loewenthal, R.E. & Mariais, G.v.R. 1991 Evaluation of biochemical models for biological excess phosphorus removal. *Water Science nd Technology* **23**, 567-574.

Woodroffe, C. 1992 Mangrove sediments and geomorphology. In *Tropical Mangrove Ecosystems – Coastal and Estuarine Series 41* (Robertson, A.I. & Alongi, D.M., eds). American Geophysical Union, Washington, pp. 7- 41.

* Not referred in original

Chapter 5

FRACTIONATION OF PHOSPHORUS IN SEDIMENT CORES

5.1 INTRODUCTION

Phosphorus is one of the key element affecting ecosystem productivity and perhaps the key nutrient in aquatic system. Unlike carbon and nitrogen, much of the phosphorus added stays within an ecosystem in a variety of forms like dissolved inorganic and organic forms, as minerals, associated with biota, sedimentary phosphate etc. (Reddy *et al.*, 1999). Sediment phosphorus undergoes various trasformations as it cycles through the inorganic phosphorus pool (associated with minerals) and the organic phosphorus pools (associated with plants, animals, microbes, and soil organic matter). The various forms of phosphorus determine the fate and transport of phosphorus in sediments. Inorganic phosphorus is mostly found in combination with Aluminium(Al), Iron(Fe), Calcium(Ca) and Magnesium (Mg). Phosphate minerals include apatite [$Ca_{10}(PO_4)_6F_2$], crandallite [$CaAl_3(PO_4)_6(OH)_2$], wavellite[$Al_3(PO_4)_2(OH)_3$], variscite [$Al_3(OH)_2H_2PO_4$] and strengite [$Fe(OH)_2H_2PO_4$]. Phosphorus may also be fixed through a variety of chemical reactions, by non crystalline oxides of Fe and Al, which often occur as coatings on soil particles. An indirect involvement of organic carbon through complex formation with Fe and Al has been suggested (Reddy *et al.* (1999) in cases where significant correlation with carbon in addition to Fe or Al, was obtained for the phosphorus sorbing capacity of a soil. As a result of biological and chemical processes a certain amount of phosphate is released from sediments and becomes available for algae and macrophytes. To determine the bioavailibility/mobility of sediment phosphate several methods - algae bioassays, chemical fractionation, exchange with anion resin, electrodialysis and isotopic exchange etc – have been employed. Chemical fractionation, involving sequential extraction procedures is, by far, the most widely used. Difficulties in identification of specific phosphorus minerals have led to the development of chemical fractionation schemes that attempt to characterize the forms of phosphorus in sediments. Such schemes have evolved from the assumption that particular chemical reagents preferentially extract discrete chemical forms of phosphorus from sediments. Common inorganic phosphorus pools identified in many sequential fractionation procedures include

1. Loosely bound (labile or exchangeable) phosphorus
2. Phosphorus fractions associated with Al, Fe and Mn oxides and hydroxides
3. Ca (and Mg) bound fractions of phosphorus
4. Phosphorus associated with minerals and organic material resistant to previous extractants

Because phosphorus in sediments exist in such a diversity of amorphous and mineral forms, it is best to consider that the various reagents extract a pool of phosphorus generally related to a given chemical group. Therefore, the chemical forms of phosphorus are often operationally defined and are subject to broad interpretations.

In order to study the role of sediments in the P-cycle of the mangrove ecosystems it is critical to choose a sediment P-fractionation procedure capable of discriminating among different org-P fractions and providing information about their bioavailibility. Two distinct schemes of extractions were recognized – operationally defined procedures and functional extraction procedures. Operationally defined procedures referred to sequential extractions with compounds such as NaOH and HCl.. The pH during the extraction is very different from the pH of the sediment. Functional extractions tried specific extractions with chelating compounds such as NTA or EDTA, supposed to react with specific compounds present in the sediments, which are carried out at a pH near to that of the sediment. For the operational extractions, Chang and Jackson (1957) pioneered the development of a comprehensive fractionation procedure that became one of the most widely used procedures for fractionating phosphorus present in soils and sediments.

Subsequently a variety of fractionation schemes (Williams *et al.*, 1971; Hieltjies and Lijklema 1980; Hedley *et al.* 1982; Ruttenburg, 1992) were developed to resolve various problems encountered with Chang and Jackson (1957) procedure to other research needs.

Functional extractions, *viz.* extraction with chelators like NTA/EDTA are supposed to react with specific species present in the sediment. Functional extractions make use of the chemical nature of the compounds to be extracted. The results obtained may enforce ideas about their structure (De Groot and Golterman, 1990). Kouwe and Golterman (1976) introduced Ca-NTA and EDTA solution as chelators of Fe-bound phosphorus and $CaCO_3$-bound phosphorus in sediments. The basic idea was first to extract the iron bound sediment phosphate with a solution of Ca-NTA, which is inactive towards calcium bound sediment phosphate, after which this compound might be extracted with Na_2-EDTA. At first these extractions took a long time, and the extractions were performed with columns in which sediment was extracted overnight. Eventhough the reaction between Fe-bound phosphorus and Ca-NTA is thermodynamically favored, it had a very low rate of reaction. This was found to be due to the lack of adsorption of the NTA on to the FeOOH. For the same reason Ca-EDTA reacted even less. Reducing agents like hydroxyl amine hydrochloride or ascorbic acid were introduced to accelerate the reaction. Later it was found that these compounds were active only at pH < 5.5 and might react with $CaCO_3$-bound phosphorus. Later, Golterman and Booman (1988) used dithionate as reducing agent, which is active even at pH, 8. The unstable nature of dithionate left as a disadvantage. Due to the insoluble nature of Ca-NTA at higher concentration than 0.02M, De Graff and Golterman (1989) suggested several extractions, during this step.

Since it is not feasible to repeat the extraction several times, Golterman (1996) replaced Ca-NTA by Ca-EDTA because, in the presence of dithionate, extraction would be complete within one or two hours. Also it was proved that Ca-EDTA extracts more Fe-bound phosphorus than Ca-NTA, which suggested a complexation of Fe-bound phosphorus with organic matter. Na_2-EDTA at pH 4.5 is more effective than at pH 8 and does not attack the acid soluble organic phosphorus. Although several adaptations /modifications were suggested by various workers, the refined EDTA method proposed by Golterman (1996) gained wide acceptances in view of its preferential ability to discriminate between different inorganic as well as different organic phosphorus fractions.

In fractionation using 'EDTA method', iron bound phosphate is extracted by Ca-EDTA (0.02M) and calcium bound phosphate is extracted by Na_2-EDTA (0.1M).

$$\mathrm{Fe(OOH)\quad P + Ca\text{-}EDTA} \longrightarrow \mathrm{Fe\text{-}EDTA + o\text{-}P + Ca^{2+}}$$

EDTA solution has the disadvantage of interference with ortho phosphate and Fe determination. For the ortho phosphate determination, 2ml of 0.1M EDTA can be used without interference. The Na_2-EDTA is found more effective at pH 4.5 than at pH 8 because it does not attack the acid soluble organic phosphate (Golterman, 1996). In the sediments of the River Garrone (Netherlands) Ca-NTA phosphorus appeared to be the best estimate of available P (Fabre *et al.*, 1996). Apatitic phosphate (extracted by EDTA) is generally considered not to be algal available phosphate (Williams *et al.*, 1980). Fabre *et al.*, (1996) however, found a spurious correlation between algal available phosphorus and EDTA phosphorus in Garrone sediments. A comparison of this method with that of the SEDEX extraction (Ruttenburg, 1992) and Heiltjes and Lijklema (1980), Golterman (1996) found that the SEDEX method extracted the same quantity of Fe-bound phosphorus, but less of $CaCO_3$ –bound phosphorus. The SEDEX method uses citric acid, dithionote and bicarbonate as extractants for Fe-bound phosphorus and sodium acetate followed by hydrochloric acid for the different forms of Ca- bound phosphorus. Heiltjes and Lijklema (1980) uses ammonium chloride, sodium hydroxide followed by hydrochloric acid is used to extract iron bound phosphorus. In Heiltjes and Lijklema (1980) method, much lower quantities of Fe-bound phosphorus was extracted than Ca-NTA (De Groot and Golterman, 1990).

Phosphorus transformation processes in mangrove sediments

Studies on sediment interaction in mangrove sediments have shown high phosphorus uptake. Total phosphorus content of mangrove sediments appears to fall within the range of 100-1600 $\mu g g^{-1}$. Mangrove sediments are expected to contain a high proportion of organic phosphorus compounds due to their generally high organic matter content. Boto (1988) pointed out that much of this organic phosphorus is in the phytate form and bound to humic compounds which are not readily available for microbial and mangrove plant nutrition. Although organic phosphorus is the major fraction, the inorganic phosphate probably represents the largest potential pool of plant available, soluble reactive phosphorus (Boto, 1988). Most of the inorganic phosphorus in mangrove sediments is either bound in the form of Ca, Fe and Al phosphates or present as soluble reactive phosphorus adsorbed onto, or incorporated into hydrated Fe and Al sesquioxides.

Macrophyte detritus from mangrove trees typically has high high C:N and C:P ratios (Kristensen, 1990; Wafar *et al.*, 1997) compared with the demands of decomposing bacteria. Therefore a rapid immobilization of nutrients may occur during decomposition in mangrove forest sediments (Alongi, 1988; 1991; 1994; 1996; Kristensen *et al.*, 1998). Mangrove sediments found to act as a sink for phosphates for example in experiments with waste water addition to mangrove sediment, Tam and Wong (1994; 1995; 1996) found a high retention of phosphate in the sediment. Wong *et al.* (1995) studied sewage discharge in a mangrove area (Shenzhen) with Kandelia candel and Aegiceras corniculatum, and observed that about 85% of the added P was retained in the sediment. Mangrove sediments in Australia were reported to have adsorption maxima in the range 250-700µg P g^{-1} dry weight sediment (Clough *et al.*, 1983). The effect of either increased ammonium or phosphate concentration was studied in Bangrong (Thailand) mangrove area and Wadden sea sediment (Holmboe *et al.*, 2001). Dissolved inorganic phosphorus (DIP) was released during anoxic decomposition in Wadden sea sediment, but was retained in Bangrong mangrove sediment. This study also found that added excess DIP was efficiently taken up by the sediment particles and primarily retrieved in the easily exchangeable and iron bound fractions and the sediment was thus found to act as a phosphorus sink.

Transformation of phosphorus in estuarine systems are categorized as two sets of processes: biotic and abiotic. Under biotic processes assimilation and excretion and hydrolysis were included. Precipitation, adsorption and chemisorption and dissolution and desorption were included under abiotic processes. The phosphate ions ($H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}) in dissolved phase were found to be strongly adsorbed to clay particles, particular to clay containing iron or manganese oxyhydroxides through different chemical and physical interactions. Clay such as kaolinite, abundant in tropical soils and sediments are particularly efficient in phosphate adsorption. It was also found that the capacity of mangrove sediments to immobilize phosphorus was probably limited by the availability of exchange sites, particularly in sediments already rich in phosphorus. However the capacity of sediments to immobilize phosphates may also depend on their incorporation into plant biomass (Clough *et al.*, 1983).

Phosphate immobilization by precipitation as Ca, Fe and Al salts also results in significant net removal of phosphorus into the large mineral pool, limiting the availability to living systems. In flooded salt marsh and mangroves, the grass and mangrove trees excrete oxygen through their root system, producing an oxygenated microenvironment (Silva *et al.*, 1991) capable of trapping phosphorus as ferric phosphate following the reaction:

$$4Fe^{+2} + O_2 + 4H^+ \longrightarrow 4Fe^{3+} + 2H_2O$$

$$Fe^{3+} + 3H_2O \longrightarrow Fe(OH)_3 + 3H^+$$

$$Fe(OH)_3 + H_2PO_4^- \longrightarrow FePO_4 + OH^- + 2H_2O$$

In the dry season, atmospheric exposure of the sediment would result in increased Fe^{3+} concentration leading to the precipitation of ferric hydroxide (Crosby *et al.*, 1984). Therefore the dominant reactions in the interstitial water are:

$$Me(OH)_{(S)} + DIP \longrightarrow MeDIP_{(S)} + OH^- + H_2O$$

where Me = Fe and DIP = $H_3PO_4 + H_2PO_4^- + HPO_4^{2-} + PO_4^{3-}$

In accordance with this, Fabre (1992) found similarly higher phosphorus concentration in the soils of the Garrone river with largest inundation periods.

Major fraction of phosphorus also found as bound to calcium minerals. The formation of inorganic solid phase P reservoirs in carbonate sediments is primarily driven by chemisorption of phosphorus on to calcite ($CaCO_3$) and / aragonite ($CaCO_3$ dimorph of calcite) followed by coprecipitation to form apatite (Stumm and Leckie, 1970; De Kanel and Morse, 1978; Kitano *et al.*, 1978). Common marine apatites are hydroxylapatite [$Ca_{10}(PO_4)_6(OH)2$], fluoroapatite [$Ca_{10}(PO_4)_6(F,OH)2$], and chloroapatite [$Ca_{10}(PO_4)_6Cl$] (Morel and Hering, 1993; Greenwood and Earnshaw, 1997; Yen, 1999). However, fluoroapatite (CFA) is to be the primary diagenetic sink in tropical marine carbonate sediments (Ruttenburg and Berner, 1993; Jensen *et al.*, 1998).

In general case, low redox potentials in mangrove and other water logged soils lead to the release of phosphate, particularly at low pH (<7). The mechanisms involved in this release as given in (Clough *et al.*, 1983) are as follows.

(i) Reduction of insoluble ferric phosphate to more soluble ferrous phosphate; (ii) the reduction of the hydrated ferric oxide coating on clay and silt particles resulting in the release of occluded phosphate; (iii) phosphate displacement from ferric and aluminium phosphates by organic anions; (iv) hydrolysis of ferric and aluminium phosphates; (v) anion (phosphate) exchange between clay and organic anions. The smaller grain size and the longer tidal inundation periods also affected the concentration of Fe-bound phosphorus. During inundation the respiratory activity of bacteria reduced the Fe^{3+} to Fe^{2+}, which resulted in the reactive capacity of iron (Patrick and Mahapatra, 1968).

The precipitation with Ca^{2+} or the adsorption of phosphate on to $CaCO_3$ is controlled by the solubility of apatite (Golterman, 1995). A lowering of the pH may also cause an increased mobilisation of phosphorus from hydroxy apatite (Bostrom *et al.*, 1988).

Diagenetic processes in sediments are driven by redox reactions that are mediated by the decomposition of organic carbon. The extent to which organic matter is preserved in sediment is critical in determining how far the diagenetic sequence progresses. Chester (2000) has suggested that diagenetic processes differ along sediment depth. Froelich *et al.*, (1979) given a vertical depth zone diagenetic model in hemipelagic sediments (sediments with intermediate sedimentation rates and organic carbon typically around 2%, the thickness of oxic layer ranges from a few centimeters to around a metre). The model is related to the sequential use of oxidants for the destruction of organic carbon and they were able to identify a number of distinct zone in the sediments. The major zones are, Zone 1, the oxygen being consumed for the destruction of organic matter, where ammonia is oxidized to nitrate. Just below this a zone, Zone 2 and Zone 5, where nitrate neither consumed nor produced so that to a certain depth, nitrate concentration become linear. Overlapping with this, Zone 3 and Zone 4, an interval over which organic carbon is oxidized by manganese oxides to release dissolved manganese ions into the interstitial waters. Below this region, Zone 6 and Zone 7, the organic carbon oxidation is effected by ferric oxides. Ferrous iron is released into solution, and diffuses upwards to be consumed near the top Zone 7 and in Zone 6.

But in their study (Silva and Sampio, 1998) they did not find any vertical variation with depth, might be due to bioturbation actions. Alongi *et al.*, (1998) compared vertical variation of sulphate reduction between mangrove and mudflat sediment found that labile organic matter is the major factor regulating rates of decomposition. The peaks obtained in subsurface sediments of mangrove suggested a source of labile organic matter, which are most likely derived from tree roots. Brunskill *et al.*, (1998) found a lack of clear vertical gradients in rates of sulphate reduction in pore water and solid profiles in mangrove sediments, (Herbert river region, Australia) attributed to the mixing of organic matter by benthic organisms like crabs. Earlier studies of this same area found extensive bioturbation, which greatly influencing nutrient concentrations and mangrove nutrient dynamics (Smith *et al.*, 1991). The exposed sediments with large amount of organic matter favored decomposition of organic matter with release of phosphate from organic fraction of the sediment. Silva and Sampaio (1998) found that the tidal inundation time, which varies with the topography of the soil, appears to the dominant process favoring the formation of iron compounds which in turn control phosphorus concentration in the soil. The relatively large amount of readily available ortho phosphorus could explain the high productivity of Donana ponds (Espejo *et al.*, 1999).

Biotic transformations of phosphorus in these systems are affected by uptake and excretion by organisms. Every organism participates to some extent in the phosphorus cycle by virtue of its need to assimilate organic/ or inorganic phosphorus for growth and maintenance, and by excreting phosphorus-containing byproducts. Bacteria, algae and higher plants, including mangroves, take up dissolved orthophosphate. The organic phosphates could either be taken directly or they were assimilated after hydrolyzing them by extracellular alkaline phosphatases. Organic phosphorus found to be very resistant to hydrolysis and not readily assimilable to organisms. Orthophosphate is coupled to ADP to form ATP in cells, and is essential for energy transfer and phosphorylations, and for synthesis of nucleic acids, phospho lipids and phosphoproteins (Ingraham *et al.*, 1983).

The cycling of phosphorus through mangrove food web is presumably similar to that in other aquatic system. At the base of pelagic and benthic food webs a microbial loop exists in which interaction among bacteria, microalgae and nano protozoans and larger protists facilitates net release of phosphorus into the water column and pore water (Alongi *et al.*, 1992).

The sequential extraction of P in sediment sample is important for understanding the mechanisms that control the release/uptake of phosphorus in sediment. These mechanisms could be chemical or biological in nature or a combination of both, and the nature of the mechanisms would decide if the element was available or not to flora and fauna (Silva and Mozeto, 1997). Thus the knowledge of the distribution of phosphorus among chemical forms is useful for understanding P availability to aquatic plants under varying sediment environments, predicting the fate and transport of phosphorus in environmental studies, and evaluating the interaction of phosphorus between sediments and overlying water. The objective of the present study is to attempt phosphorus fractionation in core sediments, and to explore the impact of environmental factors on the distribution and also to provide basic data for the study of mangrove sediments as internal sources of releasing phosphate into the overlying water.

To this end a sequential extraction procedure adapted from the EDTA method (Golterman, 1996) was designed with slight modification and made use of. The first step of the extraction was done using distilled water as suggested by Pardo, *et al* (1998). The details of chemical analysis for fractionation of phosphorus by EDTA method are given in Chapter 2. There were six steps in the extraction procedure and the first three extractions were analysed for both inorganic and organic phosphates. Each functional extraction is named after the functional group with which phosphate is associated with in the sediment. The first three extractions, extractants were analysed for inorganic phosphate and total phosphate. The various steps in the extraction facilitated the separation of following fractions: 1. water extractable phosphate (water extractable inorganic phosphate and water extractable organic phosphate) 2. CaEDTA/dithionate extractable phosphate (iron bound inorganic phosphate and iron bound organic phosphate) 3.NaEDTA extractable phosphate (calcium bound inorganic phosphate and calcium bound organic phosphate) 4.Acid extractable organic phosphate 5.NaOH extracted organic phosphate and 6.Residual organic phosphorus. The sum of fractions at each depth at every Station is given by ΣTP.

Abbreviations used in text, tables and graphs for these fractions are as follows:

1. Water extractable inorganic phosphate and water extractable organic phosphate (W-IP and W-OP)
2. Iron bound inorganic phosphate and iron bound organic phosphate (Fe-IP, Fe-OP)
3. Calcium bound inorganic phosphate and organic phosphate (Ca-IP, Ca-OP)
4. Organic phosphate acid extractable (Ac-OP)
5. Organic phosphate alkali extractable (Alk-OP)
6. Residual organic phosphorus (ROP)

5.2 RESULTS AND DISCUSSION

5.2.1. Vertical variation of phosphorus forms in sediment cores

Water extractable Inorganic Phosphate (W-IP)

W-IP is the easily exchangeable phosphate fraction in sediment. Exchangeable fraction includes the phosphorus dissolved in interstitial water as well as the phosphorus loosely bound to the absorbing surfaces of sediments. This fraction comprises of phosphorus forms, which would be readily available to the biota such as benthic bacteria or susceptible to diagenetic transformation, *e.g.* Complexation with Fe, Al, Ca or humic substances. In the present study this fraction was extracted with distilled water.

Station-wise summary statistics of W-IP are given in Table 5.1.

Table 5.1 Station-wise summary statistics of W-IP (μg/g) in sediment cores

Station	Depth	Min	Max	Mean	SD	% of CV
Station 1	0-2	3.52	54.02	14.30	19.61	137.13
	2-4	1.69	42.23	15.98	16.34	102.23
	4-6	3.85	56.19	17.04	19.76	115.97
	6-10	6.04	71.32	26.20	23.62	90.13
	10-20	22.67	82.56	42.86	21.59	50.38
Station 2	0-2	1.17	45.84	16.20	19.46	120.15
	2-4	0.99	75.41	20.90	28.47	136.25
	4-6	1.30	85.31	26.64	32.25	121.05
	6-10	2.81	75.91	25.96	26.61	102.52
	10-20	6.44	51.54	22.71	15.52	68.37
Station 3	0-2	0.03	5.61	1.70	1.97	115.61
	2-4	0.69	10.09	2.85	3.65	128.29
	4-6	0.46	12.34	4.29	5.36	124.94
	6-10	0.92	12.53	4.48	4.52	100.92
	10-20	1.67	14.29	7.08	5.72	80.84

Seasonal and annual variations in vertical profiles of W-IP, at three mangrove stations are depicted in Fig. 5.1a to 5.1d. The concentration of W-IP ranged between 0.03μgg^{-1} (0-2 cm, Station 3) and 85.31 μgg^{-1} (4-6 cm, Station 2). Eventhough a large variation (Table 5.1) was found between stations, consistent values were recorded in 10-20cm layer at all Stations. This fraction showed general increase in concentration with increasing depth except at Station 2, where, a reversal in the above trend at depth beyond 10cm was noticed.

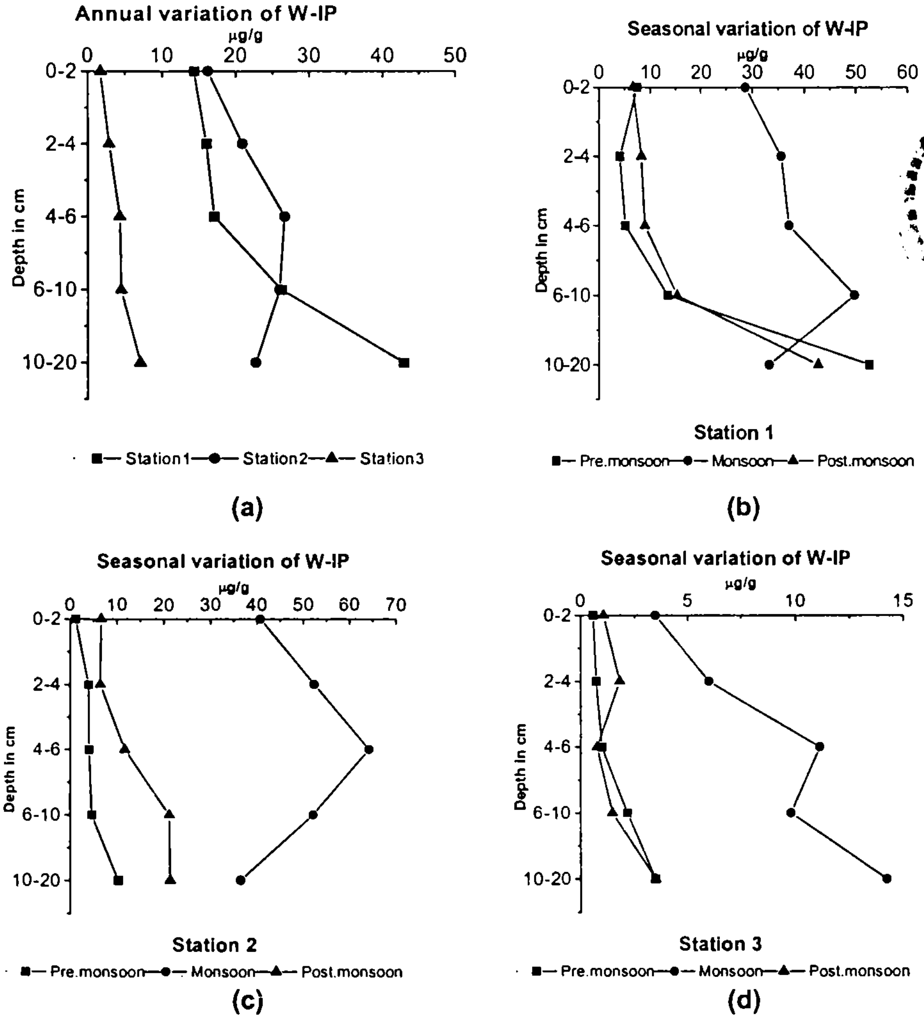


Fig. 5.1 Annual and seasonal variation of W-IP in sediment cores

The seasonal picture showed a W-IP concentration pattern, more or less similar during pre-monsoon and post-monsoon and higher during monsoon at all the three Stations. Station 1 exhibited a regular decrease in W-IP down the core, during pre-monsoon and post-monsoon, with a considerable increase at 10-20 cm depth. However during monsoon, W-IP found to decrease at 10-20 cm depth at this Station. Also at Station 2, W-IP recorded an increase in concentration during pre-monsoon and post-monsoon seasons, while during monsoon; the W-IP concentrations were found decreasing after 6cm of depth. At Station 3, W-IP showed an entirely different trend, with slight decrease followed by further increase at depths beyond 6cm during all seasons. An overall picture followed the general pattern of increasing W-IP concentration with increasing depth, except at Station 2 beyond 10cm.

The W-IP is the easily exchangeable phosphate fraction found in the sediment. The exchangeable fraction was found not to exceed 2% of the total phosphorus by Baldwin (1996). In a recovery determination of added phosphorus study it was observed that a large part of the added phosphorus was recovered in the exchangeable fraction, which is characterised as easily exchangeable phosphate adsorbed on to particle surfaces (Jensen and Thamdrup, 1993). This large adsorption of phosphorus may be due to very high silt+clay content of the sediment. Present study also confirms this by recording maximum exchangeable phosphorus at Station 2, at a depth of 4-6 cm (silt+clay, 95%). The general increase in W-IP down the core may be attributed to an elevated phosphate levels in interstitial waters of the sediment. The study undertaken by Joseph (2001) phosphates in pore water, in the same area also confirmed this observation. The increased W-IP concentration levels may be due to mineralisation of organic matter and dissolution of phosphate bearing iron oxides in the existing reducing conditions. Froelich *et al.* (1979) have observed large increase in pore water phosphate during mobilization of iron bearing oxy hydroxy coatings. In anoxic environments, another pathways for inorganic phosphate release from complex organic phosphate entities like phytate and poly phosphates stored in bacterial biomass were also observed (Suzumura and Kamatani, 1995). It was reported that bacterial biomass seem to store poly phosphate when they live in an aerobic environment and hydrolyse under anaerobic conditions (Comeau *et al.*, 1986). A typical anoxic environment may prevail in sediments cores of studied area with increasing depth. Thus increase in W-IP may be attributed clearly to the increased phosphate concentration in pore water levels.

Water extractable Organic Phosphate (W-OP)

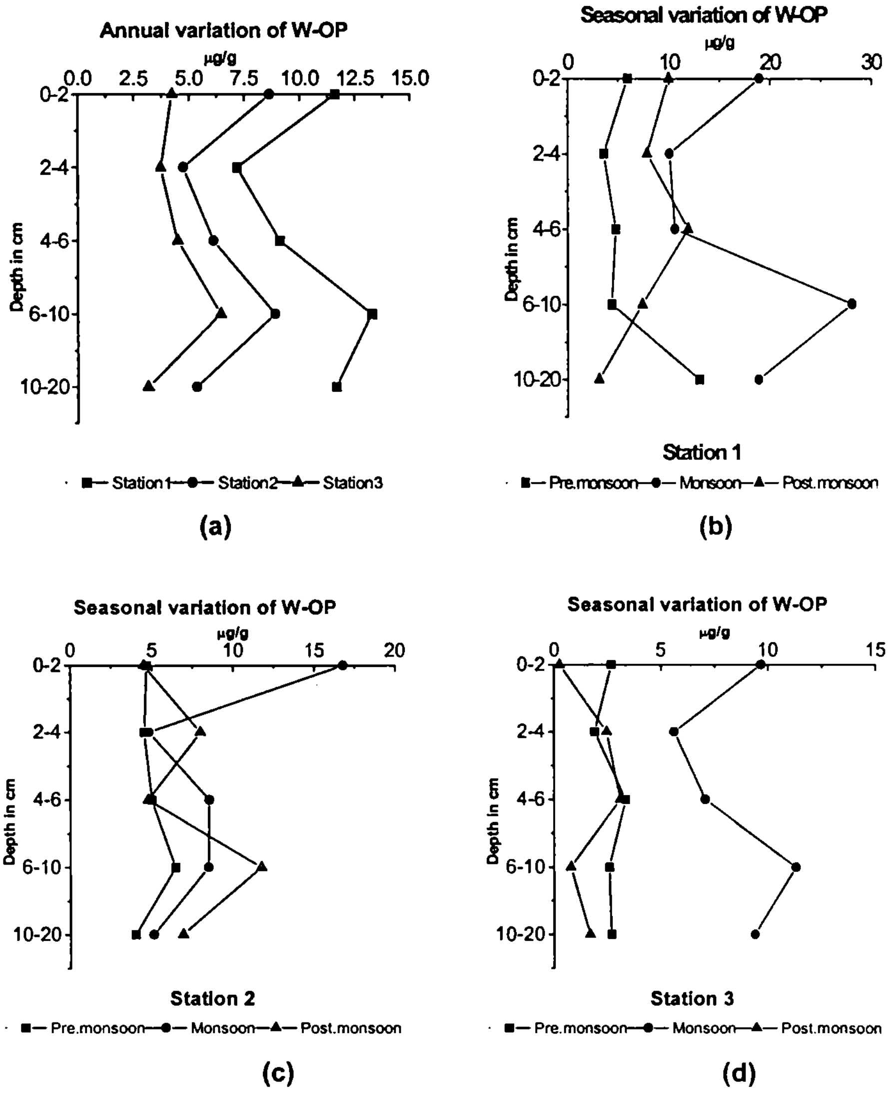
The water extractable organic phosphorus consists of mainly the organic phosphorus present in pore water.

The Station-wise summary statistics of W-OP are given in Table 5.2. The maximum concentrations of 52.95μgg^{-1} recorded at Station 2, 6-10 cm layer and minimum of not detectable were recorded at Station 3, 2-4, 4-6 and 6-10cm depths.

Table 5.2 Station-wise summary statistics of W-OP (μg g^{-1}) in sediment cores

Station	Depth	Min	Max	Mean	SD	% of CV
Station 1	0-2	1.47	21.06	11.62	8.23	70.87
	2--4	3.59	15.70	7.18	5.27	73.40
	4--6	0.54	23.31	9.11	8.09	88.86
	6--10	3.17	52.95	13.28	19.59	147.50
	10--20	1.55	27.79	11.68	11.10	95.00
Station 2	0-2	3.85	24.16	8.65	7.85	90.78
	2--4	0.24	12.82	4.75	4.32	90.99
	4--6	3.15	8.85	6.11	2.20	36.10
	6--10	1.92	15.08	8.90	5.20	58.47
	10--20	1.66	10.95	5.35	3.66	68.41
Station 3	0-2	0.00	19.44	4.23	7.57	179.18
	2--4	0.00	11.32	3.72	4.01	107.63
	4--6	0.00	15.21	4.49	5.57	124.23
	6--10	0.45	23.18	6.44	8.69	134.96
	10--20	0.00	10.25	3.15	3.68	116.59

Unlike W-IP, this fraction showed a general decrease with increasing depth except at 6-10 cm depth at all Stations (Fig. 5.2a). The W-OP concentrations observed were higher at Station 1 and Station 2 than at Station 3. The seasonal variations of W-OP are given in Fig. 5.2b to 5.2d. During monsoon, an increase at 6-10 cm depth was recorded at all Stations. The overall picture of the annual variation showed a distinct pattern with a decrease till 4cms of depth followed by a gradual increase till 10cms with a sharp decrease again beyond 10cms of depth (Fig. 5.2a). Monsoon season recorded maximum org-P at all stations. During pre-monsoon and post-monsoon similar concentrations were recorded at all stations. The sub-surface decrease was found maximum during monsoon. Unlike W-IP, less coefficient of variations in concentrations of W-OP were observed in surface and subsurface layers (Table 5.2).



(a) (b)

(c) (d)

Fig. 5.2 Annual and seasonal variation of W-OP in sediment cores

In sediments, dissolved organic phosphorus (DOP) was mostly used and recycled by bacteria without any significant net release of total phosphorus to the water column (Kairesalo *et al.*, 1995). Therefore, the sediment bacteria have an important role in the phosphorus dynamics of the sediment ecosystem. Sharp decrease in subsurface sediment may be due to the decrease in bacterial biomass, also due to the less amount of labile organic phosphorus. The gradual increase found till 10cm of depth may be attributed to the accumulation of organic phosphorus at this depth. Sinke and Cappenberg (1988) have observed that live sediment bacteria enhanced the release of phosphorus from the sediment. They stated that bacterial mineralisation would serve as driving force for the PO4-P release from the sediment. The decrease in W-OP at 10-20 cm may be attributed to an increased mineralisation of organic phosphorus compounds at this depth. Therefore the decrease of W-OP down the core sediment indicated a decrease in bacterial density on increasing sediment depth, as well as increase of W-OP may be associated with mineralisation of organic phosphorus aided by bacterial biomass. The bacteria capable of storing polyphosphates may play an important role in the PO_4-P release in anaerobic conditions (Hupfer and Uhlmann 1991).

Fe-bound inorganic phosphate (Fe-IP)

Phosphate extracted by Ca-EDTA/dithionite can be considered as the best predictor for algal available phosphate (Fabre *et al.*, 1996). Phosphate entering shallow water will be taken up rapidly by phytoplankton during the growing season, but during winter or less active period by far great amount will be bound on to settled sediments. The algal phosphate will be recycled several times during the growing season, but eventually it will become sediment phosphate, either as an inorganic or as an organic pool (Golterman, 1998). Both fixation of the inorganic phosphate onto the sediments, and its release from sediments to the overlying water, are controlled by the two mechanisms (Golterman, 1998). First by adsorption of dissolved orthophosphate (o-P) on to ferric hydroxide (goethite) Fe(OOH).x H_2O and second by precipitation with Ca^{2+} as apatite, $Ca_5\ (PO_4)_3.OH$, probably as co-precipitation with $CaCO_3$. The adsorption on to Fe(OOH) can be described by Freundlich adsorption isotherm, which in turn influenced by both Ca concentration and pH (Golterman, 1995). The inorganic fraction mainly iron bound phosphorus increase gradually with depth (25-100 cm) reflecting the influence of increasing anoxia particularly below the root layer (Alongi *et al.*, 1992).

The Station-wise summary statistics in depth profile of Fe-IP are given in Table 5.3. The concentrations of Fe-IP varied from 7.09μgg^{-1} (4-6cm, Station 3) to 1101.48μgg^{-1} (10- 20 cm, Station 1). Remarkably higher Fe-IP concentrations were recorded at Station 1 and Station 2 than at Station 3. The seasonal and annual mean distributions of Fe-IP at three stations are given in Fig. 5.3a to 5.3d. The

Fe-IP showed general decrease down the core at these Stations, except at Station 1 beyond 10cm depth. Seasonal variations of Fe-IP showed remarkably higher values during post-monsoon at all Stations. At Station 1 during pre-monsoon and monsoon, generally, Fe-IP concentration increased down the core. However at Station 2, monsoon and post-monsoon showed a similar trend, with a subsurface increase followed by a sharp decrease at 10-20 cm depth. The pre-monsoon concentration at this Station found to decrease with increasing depth. The overall picture of the annual variation followed the general pattern of decreasing trend down the core at Station 3. At Station 1, a small subsurface maximum and sharp increase recorded at 10-20 cm layer. Station 2 showed a subsurface maximum followed by general decrease downwards. The annual summary statistics (Table 5.3) showed comparatively consistent values at the depth, 6-10 cm at Station 1 and Station3 as well as in 10-20 cm depth at Station 2.

Table 5.3 Station-wise summary statistics of Fe-IP ($\mu g\ g^{-1}$) in sediment cores

Station	Depth	Min	Max	Mean	SD	% of CV
Station 1	0-2	43.61	849.32	412.12	323.58	78.51
	2--4	46.08	916.14	425.06	359.67	84.62
	4--6	45.20	850.10	392.23	347.25	88.53
	6--10	49.51	689.16	345.68	248.71	71.95
	10--20	40.66	1101.48	495.36	409.44	82.66
Station 2	0-2	35.74	827.58	427.08	296.49	69.42
	2--4	50.90	952.25	477.99	375.34	78.52
	4--6	45.83	830.24	414.48	315.31	76.07
	6--10	41.52	768.26	422.49	305.06	72.20
	10--20	48.47	492.24	282.63	190.89	67.54
Station 3	0-2	13.82	189.74	102.76	57.56	56.02
	2--4	11.30	167.32	90.73	56.43	62.20
	4--6	7.09	112.53	70.52	38.89	55.14
	6--10	7.21	78.07	52.41	25.23	48.14
	10--20	14.62	91.46	58.69	28.82	49.11

In general, capacity of mangrove soil to immoblize phosphate depends on the amount of organic matter, its C/P ratio, and the type and amount of clay minerals present. Dissolution of mineral phosphate also depends on physicochemical characteristics such as pH, available sulphides, alkalinity and redox state (Boto, 1988). Generally the Fe-IP found to decrease down the core at

Station 1 and Station 3. This is not in accordance with the observation of Alongi *et al.* (1992). The Fe-IP found to increase only at 10-20 cm depth at this station. At this depth bacterial mineralisation will be less, hence added phosphorus get adsorbed on to sediment. The added phosphate was found to retain in Bangrong mangrove sediment, primarily by binding large phosphate loadings as easily exchangeable phosphorus and Fe-bound phosphorus. (Holmboe *et al.*, 2001).

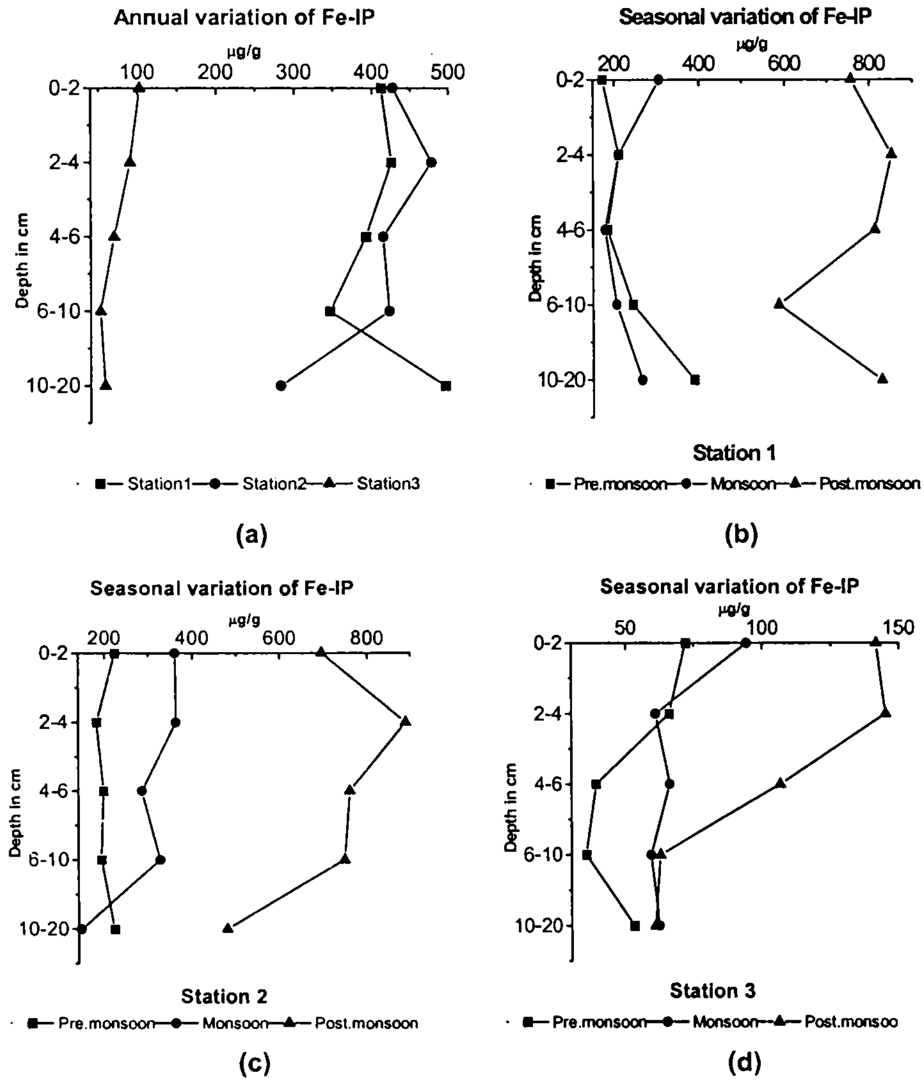


Fig. 5.3 Annual and seasonal variation of Fe-IP in sediment cores

The phosphorus sorption capacity of the sediment containing Fe(OOH) is expected to decrease along the salinity gradient due to corresponding changes in pH (Paludan and Morris, 1999). Under fresh water conditions (pH ranges from 4.5 – 7), hydroxides of metals such as Fe and Al carry a net positive charge that would facilitate phosphorus sorption, while under salt water condition (pH ranges from 7.0 – 8) they carry a negative charge (as given in Sundareshwar and Morris, 1999). Annual pH value in sediment cores ranges from (Table 4.15) 8.0 to 8.5 at Station 1, 8.2 to 8.7 at Station 2 and 7.1 to 8.2 at Station 3. An exceptionally high value, of Fe-IP concentration was observed at Station 1 in 10-20 cm layer, might be associated with a decrease in pH. This could be seen clearly during pre-monsoon, which gave a pH as low as 6.8 for this particular layer at Station1. While at Station 2 a minimum value of Fe-IP, 282.63$\mu g g^{-1}$ observed in this layer with an increasing trend of pH down the core. A decrease in Fe-IP concentrations was recorded also at Station 3, with an increase in pH.

The P-sorption potential, which is clearly related to the distribution of Fe species, is another factor that control the depth profile of phosphorus concentrations. Because Fe (III) is more efficient in binding P, the iron bound phosphorus rapidly declines with depth. It was observed by (Paludan and Morris, 1999) iron predominantly occurs in the Fe (III) state in surface sediments and in the Fe(II) state in the subsurface sediments. Study on effects of added phosphorus in sediments revealed that added P recovered mostly as exchangeable fraction and Fe-IP. The exchangeable fraction found to contain 35-38% in surface sediment and 51-54% in subsurface sediment. The added phosphorus recovered as 44-45% Fe-IP, in surface sediment and 20-22% in subsurface sediment (Holmboe, *et al.*, 2001). Therefore any conditions, which bring in phosphorus into the system, may increase the Fe-IP concentration in surface sediments than the subsurface sediments.

Seasonal variations were found at three stations with maximum during post-monsoon and minimum recorded during pre-monsoon at all three stations. Sundareshwar and Morris (1999) proposed that pH as well as salinity influence the binding capacity of phosphorus on to iron oxides. Alkaline conditions, promoted by sulphate reduction and or increased salinity, shift the charge of Fe-oxides from positive to negative (Stumm and Morgan, 1981) reducing phosphorus adsorption. Therefore increased salinity during pre-monsoon may be one of the reason to record minimum Fe-IP during this season. During pre-monsoon, at Station 2, pH was found to vary from 7.8 (0-2 cm) to 8.7(10-20 cm). This also support the fact that pH influence the concentration of Fe-IP. During rainy season these creeks are enriched with P leached by rainfall from their surrounding vegetation, soils, and sewage. In shallow lakes and marshes receiving a relatively large P input, nearly all phosphate is expected to enter the sediments during loading phase as given by Espejo *et al.* (1999).

The phosphorus adsorption capacity of sediments found to increase due to the increase of Fe (OOH) concentration in the sediment. This increase is explained by the upward leaching of oxides from deeper water in the soil during upwelling of water-table (Siljestrom and Clemente, 1990). An increase in Fe-IP was observed during desiccation of a fresh water marsh due to an increase in Fe(OOH) derived from the oxidation of FeS (De Groot and Fabre, 1993). Thus increase in Fe(OOH) in surface sediments during post-monsoon may be one of the reason to record maximum Fe-IP during this season. Furthur more an increase in total iron concentration was also recorded during post-monsoon and pre-monsoon.

Previous studies using estimates of free sorption sites have demonstrated the importance of total Al, Fe and Ca concentration on total sedimentary phosphorus (Lopez *et al.*, 1996). A comparison of the relative degree of free sorption sites on metal particles can be estimated by the sedimentary Fe:P ratio. In oxidized fresh water sediment with a molar Fe:P ratio above 8.5, the sediment was capable of retaining phosphate whereas below this value phosphate leached out of the sediment (Jensen *et al.*, 1992). The molar Fe:P ratio observed in the present study is given in Table 5.4. It was found to vary from 9.08 (Station 3) to 14.26 (Station 1). Thus, based on these ratios, both sediments had a high capacity for binding phosphate to iron. In tropical Bangrong mangrove forest (Thailand) this ratio found to vary from 16 and 20 in low inter tidal zone and 34 and 22 in mid inter tidal zone (Holmboe *et al.*, 2001). Hence considering all these factors, these mangrove zones appeared to be a sink for phosphorus.

Table 5.4 Station-wise summary statistics of total Fe/TP (molar ratio) in sediment core

Station	Depth	Min	Max	Mean	SD	% of CV
Station 1	0-2	4.60	20.19	12.38	5.10	41.19
	2-4	4.93	22.89	13.01	5.82	44.75
	4-6	4.70	23.75	13.08	6.74	51.49
	6-10	3.15	23.28	14.26	6.80	47.68
	10-20	4.37	22.07	12.07	5.67	47.00
Station 2	0-2	6.37	20.42	12.30	5.32	43.27
	2-4	5.50	17.38	11.80	4.90	41.51
	4-6	4.12	20.11	11.00	5.45	49.52
	6-10	5.38	16.68	12.48	4.51	36.12
	10-20	4.72	18.06	10.22	4.71	46.13
Station 3	0-2	0.92	19.60	11.34	6.67	58.79
	2-4	5.23	18.14	13.10	4.35	33.22
	4-6	3.62	12.62	9.08	3.72	40.98
	6-10	4.60	18.96	10.49	4.70	44.79
	10-20	3.82	22.63	12.26	7.38	60.18

Fe-bound organic phosphate (Fe-OP)

The total phosphate was determined in Ca-EDTA/dithionite extract by potassium persulphate digestion. The difference between total phosphorus in the extract and Fe-IP would give Fe-OP. The mixing of freshwater and and seawater causes a rapid precipitation of the dissolved humic compounds carried by rivers. The cations in seawater replace H+ on the exchange sites of the humic materials causing these materials to flocculate and sink to the bottom (Boyle *et al.*, 1977). Most dissolved humic compounds and metals such as Fe, that are carried with humus substances are precipitated in the estuary or within short distance of the mouth of the river (Boyle *et al.*, 1974). The flocculation of dissolved organic compounds and deposition of larger plant debris account for a major portion of the organic carbon in estuarine sediments (Hedges *et al.*, 1988). Most of the organic phosphorus will become ortho phosphate by mineralisation of the organic phosphate. A small part of the organic phosphoate will sediment and remain as refractory organic phosphate, of which phytate is probably the most important form (De Groot and Golterman, 1993).

The station wise summary statistics of Fe-OP are given in Table 5.5. Comparatively consistent values (less CV) were recorded in 2-4cm layer at Station 1, 4-6 cm layer at Station 2 and 0-2 cm layer at Station 3. At the three Stations, the concentrations ranged from 6.96μgg^{-1} (Station 3, 4-6cm) to 365μgg^{-1} (Station2, 4-6). The Fe-OP showed generally a decreasing trend down the core. Some exceptionally high values were recorded during post-monsoon at Station 1, 10-20cm depth and at Station 2, 4-6 cm depth. The annual and seasonal variations in depth profile of Fe-OP are given in Fig. 5.4a to 5.4d. Unlike the inorganic fraction the concentrations were similar during three seasons other than the exceptionally higher values at Station 2. The maximum value of Fe-OP, recorded at Station 2, 4-6 cm layer may be due to the incidental presence of some plant or animal debris.

Table 5.5 Station-wise summary statistics of Fe-OP (μg g^{-1}) in sediment cores

Station	Depth	Min	Max	Mean	SD	% of CV
Station 1	0-2	26.47	90.48	60.07	32.13	53.48
	2-4	41.02	83.90	61.77	22.28	36.06
	4-6	18.79	118.67	57.86	46.49	80.35
	6-10	9.22	78.38	44.28	35.94	81.17
	10-20	30.14	141.26	78.95	48.15	60.98
Station 2	0-2	30.95	79.42	57.28	21.04	36.74
	2-4	46.34	99.58	71.77	25.03	34.88
	4-6	54.28	365.20	172.84	168.09	97.25
	6-10	21.14	66.40	48.17	19.77	41.04
	10-20	35.25	97.87	60.73	32.90	54.17
Station 3	0-2	25.27	62.35	43.94	18.54	42.20
	2-4	15.77	41.98	29.09	14.53	49.94
	4-6	6.96	37.81	18.21	14.11	77.48
	6-10	9.25	84.91	30.85	36.36	117.85
	10-20	11.08	49.53	28.93	17.50	60.47

Together with P, large concentrations of humic substances of poly-phenolic nature are washed from mangrove vegetation into the creek water during monsoon. The importance of humic substances in water can be very large as they can regulate both abiotic and biotically mediated phosphorus cycling (Francko, 1986; De Haan 1992; Jones *et al.*, 1993). The formation of Fe-humic-P complexes in the water is partially reversible depending on ambient phosphorus concentration, changes in pH and exposure to light. As a result they may reduce instantaneous bioavailibility of inorganic phosphate, while maintaining potentially bioavailable dissolved organic phosphorus, by preventing the precipitation of P and iron (Jones *et al.*, 1993). Additionally, humic substances in water can retard the formation of $CaCO_3$ crystals and hence reduce the loss of inorganic phosphorus through co-precipitation with $CaCO_3$ (). Contrary to the Fe-IP, the maximum and minimum values were fluctuating down the core. Station 1 and Station 2 recorded similar values except at 4-6 cm layer at Station 2. The relatively higher values at 10-20 cm depth might be due to the presence iron bound humic matter at this depth. Earlier studies showed that total organic phosphorus concentration proportionally greater in 0-25 cm reflects the influence of roots (Hesse, 1963).

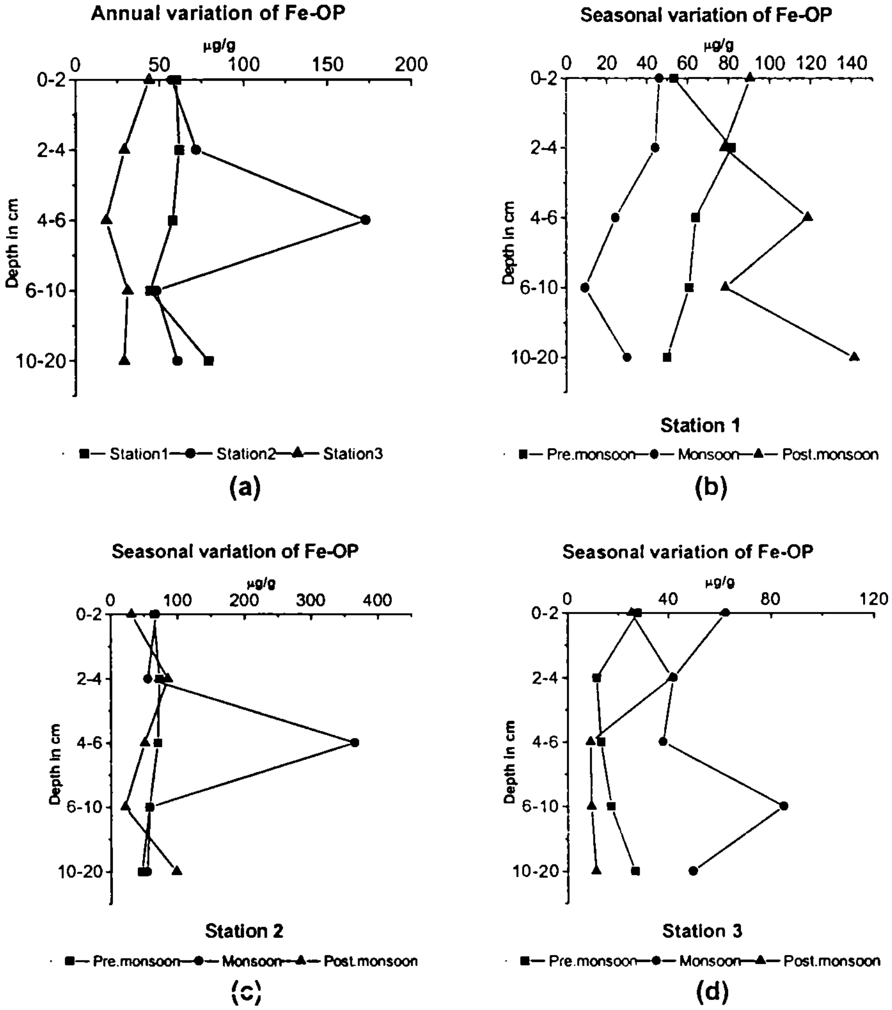


Fig. 5.4 Annual and seasonal variation of Fe-OP in sediment cores

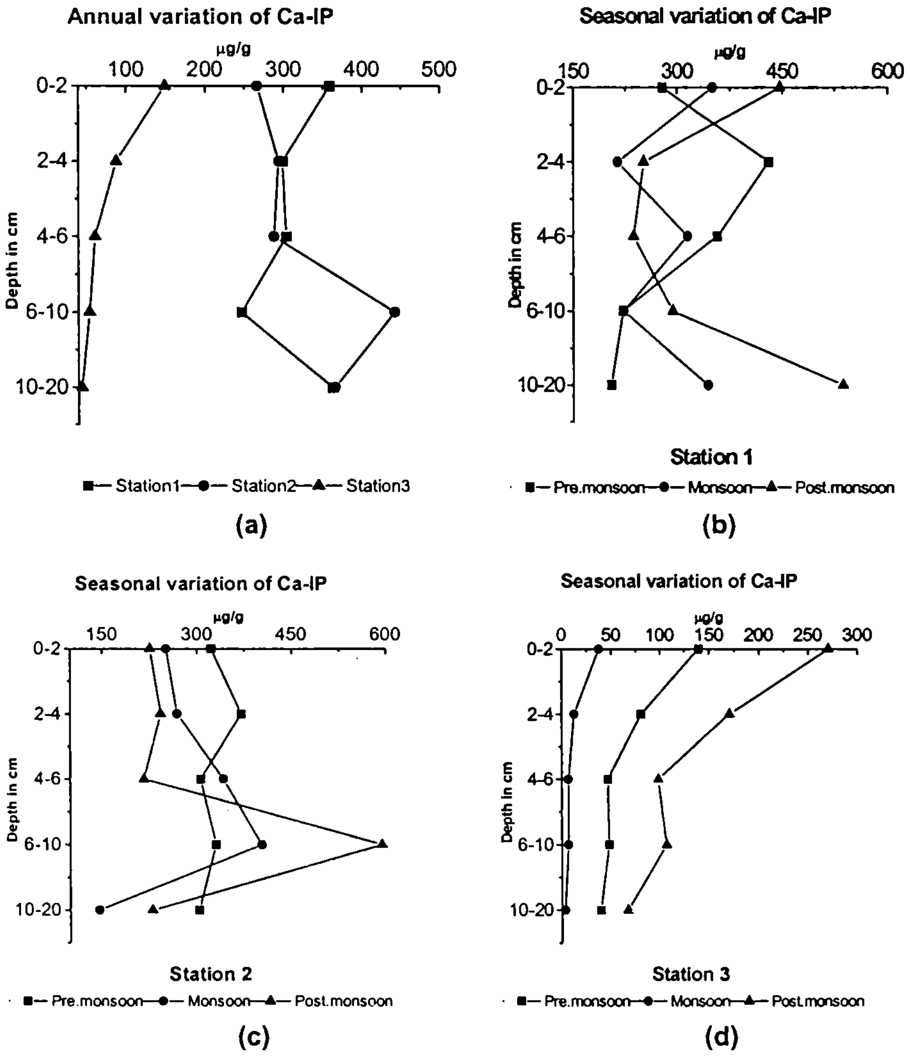
Calcium bound inorganic phosphate (Ca-IP)

Apatitic phosphate (extracted by Na_2 EDTA) is generally considered not to be algal available phosphorus (Williams *et al.*, 1980; DePinto *et al.*, 1981; Young *et al.*, 1985). The major biogeochemical process that transform inorganic phosphorus from a dissolved to solid state include anion adsorption onto iron and aluminium oxyhydroxides and carbonate minerals, precipitation and co-precipitation with minerals containing calcium, iron and aluminium; and uptake by microbes and plants (Jensen and Thamdrup, 1993). Dominance by a particular biogeochemical process is dependent on sediment type and other physicochemical factors. Because tropical and subtropical estuaries are typically dominated by calcium carbonate sediments, as opposed to silicate and clay-dominated sediments of coastal temperate regions, carbonate chemical equilibria can be more important than redox reactions in controlling sediment phosphorus transformations. In estuarine systems where Ca plays a major role in controlling the P concentration, phosphate adsorbs on to calcite (De Jonge and Villerius, 1989). Atkinson (1987) argues that if P is bound as $CaPO_4$ then its variation must be due to a contribution from calcifying organisms, where as if P is sorbed to $CaCO_3$, then its variation should be regulated by dissolved phosphate. Earlier studies found that (Jensen and Anderson 1992) that no significant effects on phosphorus release of pH change in the range 8.1 to 9.7 in lake Arreskov sediment. In an experimental study of comparison of phosphate release from sediments from a shallow lake (Lake, Vortsjarv), under oxic and anoxic conditions, there was no significant change in concentration of calcium bound inorganic phosphorus during the incubation (Noges and Kisand, 1999). This led them to conclude, calcium bound inorganic phosphorus (extracted by HCl) is rather immobile and not available for the phosphorus cycle in this lake. Diagenic processes may also increase calcium bound phosphorus in sediments (Goltermann, 1998). In Hooghly surfacial sediments lack of significant correlation between calcium and the calcium bound phosphorus have been reported by Vaithiyanathan *et al.*, (1993).

The annual summary statistics (Table 5.6) of Ca-IP concentrations recorded less CV at 0-2cm depth at all Stations. The concentrations varied from 4.47 $\mu g g^{-1}$ (Station 3, 6-10 cm) to 834.21$\mu g g^{-1}$ (Station 2, 10-20). The concentrations of Ca-IP showed an erratic behavior down the core at Station 1 and Station 2. At Station 1 the Ca-IP varied from 71.53$\mu g g^{-1}$ to 626.82$\mu g g^{-1}$. At Station 2 the variations found were from 144.13 μgg^{-1} to 834.56 μgg^{-1}. Station 3 showed a variation from 4.47μgg^{-1} to 271.95μgg^{-1}. Annual mean and seasonal variations in depth profile of Ca-IP, showed in Fig. 5.5a to 5.5d. At Station 3 this fraction showed a gradual decrease down the core, during all seasons. At Station 1 Ca-IP showed a decrease during monsoon and post-monsoon, with a sharp increase at 10-20 cm depth. At Station 2 a regular increase down the core with an exceptionally high value at 6-10 cm and a decrease beyond 10cm depth. At Station 3 gradual decrease down the core was found. The overall picture of the annual variation followed the general pattern at Station 3 with decreasing concentration down the core. Station 1 decreasing trend down the core except at 10-20 cm depth was noticed. While at Station 2 showed an increasing trend down the core with an exceptionally high value at 6-10 cm depth.

Table 5.6 Station-wise summary statistics of Ca-IP ($\mu g\ g^{-1}$) in sediment cores

Station	Depth	Min	Max	Mean	SD	% of CV
Station 1	0-2	159.26	509.34	358.83	117.88	32.85
	2-4	130.48	475.90	298.88	121.05	40.50
	4-6	136.44	494.21	303.38	147.45	48.60
	6-10	104.20	340.29	246.35	103.26	41.92
	10-20	71.53	626.82	362.04	199.40	55.08
Station 2	0-2	171.03	406.93	266.66	81.78	30.67
	2-4	170.41	490.80	293.88	115.74	39.38
	4-6	119.54	491.66	287.92	134.55	46.73
	6-10	166.72	685.38	442.21	194.95	44.09
	10-20	144.13	834.56	365.38	253.23	69.31
Station 3	0-2	12.29	271.95	149.43	116.14	77.72
	2-4	6.98	248.62	87.99	89.24	101.42
	4-6	10.64	145.55	61.06	55.58	91.03
	6-10	4.47	162.44	53.95	61.03	113.12
	10-20	6.44	90.21	44.36	37.63	84.82



(a) (b)

(c) (d)

Fig. 5.5 Annual and seasonal variation of Ca-IP in sediment cores

These variations down the core may be attributed to the surface area of the substrate sediment. On going down the core the percentage of sand increases and silt and clay decreases. Theoretically and experimentally there is a relationship between increasing phosphorus adsorptive capacity and decreasing grain size (Walter and Morse, 1984). pH conditions modified by primary production and mineralization play an important role in the phosphorus modification (Istvanovics, 1988). When sediments become anoxic, there is naturally a decrease in pH as a result of carbon dioxide produced. This decrease in pH will dissolve the apatite, as it strongly controls the solubility. Annual pH value in sediment cores ranges from (Table 4.15) 8.0 to 8.5 at Station 1, 8.2 to 8.7 at Station 2 and 7.1 to 8.2 at Station 3. In the present observation pH lies in the neutral to alkaline range, hence dissolution of Ca-IP may not takes place. The sharp increase at 10-20 cm depth at Station 1 may be due to the increase in percentage of calcareous sediment present at this depth. The increase in concentration at 6-10 cm may be also associated with the sediment nature at this depth. Considering these variations of Ca-IP contents of sediments it is to be inferred that, this fraction was modified by texture of sediments. In French Guanian mangroves the concentrations of Ca-IP were found to related to origin of the sediment rather than to chemical modification (Fabre *et al.*, 1999).

Calcium bound organic phosphate (Ca-OP)

Carbonate dominated marine ecosystems of the tropics have low dissolved organic matter in the surface waters, which, has been shown to influence nutrient uptake in these particular sediment type. Surface-active organic matter can compete for inorganic phosphate adsorption sites on carbonate particles, create organic coatings on carbonate surfaces that can physically reduce adsorptive sites (Morse, 1986). The organic matter can also modify other biogeochemical factors that influence the formation and release of solid phase phosphorus (e.g. pH and Eh). Organic phosphorus compounds (phospholipids) have also been shown to adsorb to carbonate particles, as organo-carbonate association (Suess, 1973), thus high DOC in surface and pore waters of coastal estuaries in the tropics could increase carbonate-associated organic phosphorus.

The organically bound calcium phosphates (Ca-OP) were determined as the difference of total calcium bound phosphorus and Ca-IP. The summary statistics of Ca-OP concentrations (Table 5. 7) showed more consistent values in 10-20 cm layer at Station 1 and Station 2 and 2-4 cm layer at Station 3. The concentrations found to varied from 1.10μgg^{-1} (Station 1, 2-4cm) to 105.80μgg^{-1} (Station 1, 6-10 cm). The annual and seasonal variations of Ca-OP are given in Fig. 5.6a to 5.6d. Ca-OP showed a general decrease in concentration with increasing depth. However an exceptionally high value recorded at 6-10 cm at Station 1. Unlike Ca-IP concentrations, at Station 2, Ca-OP concentrations were not deviating from general pattern. Station 3 recorded high values during pre-monsoon and post-monsoon. The overall picture of the annual variation showed a decrease down the core at Station 2 and Station 3. At Station 1 this fraction found to increase slightly in subsurface sediments and a large increase at 6-10cm depth.

Table 5.7 Station-wise summary statistics of Ca-OP (μg g^{-1}) in sediment cores

Station	Depth	Min	Max	Mean	SD	% of CV
Station 1	0-2	38.88	279.78	170.95	94.67	55.38
	2--4	30.17	291.67	157.74	91.30	57.88
	4--6	37.93	327.91	157.62	97.88	62.10
	6--10	56.47	283.99	164.30	90.35	54.99
	10--20	103.49	390.46	237.83	103.68	43.59
Station 2	0-2	29.46	348.66	151.72	106.48	70.19
	2--4	49.16	367.80	162.86	108.43	66.58
	4--6	43.66	431.74	149.76	149.49	99.82
	6--10	60.22	483.31	195.41	150.49	77.01
	10--20	70.59	491.53	171.13	159.86	93.42
Station 3	0-2	52.30	146.27	93.63	38.52	41.14
	2--4	34.87	156.76	84.65	40.08	47.35
	4--6	37.74	137.98	69.10	34.92	50.54
	6--10	42.11	159.31	73.59	43.37	58.94
	10--20	47.14	144.68	80.28	35.04	43.65

The increase in calcareous sediments associated with dissolved organic carbon in pore water could magnify the concentration of Ca-OP. The presence of dissolved organic matter in surface waters also found to influences the concentrations of Ca-OP. A general decrease in W-OP concentrations, except at 6-10 cm of depth, were found in these sediment cores, reflecting a decrease of organic phosphorus concentrations down the core. The same trend was found in Ca-OP concentrations, which suggested a decrease in organic phosphorus compounds resulted in a decrease in Ca-OP. An exceptionally high value of Ca-OP in 6-10cm depth might be associated with the presence of calcareous sediments at this depth.

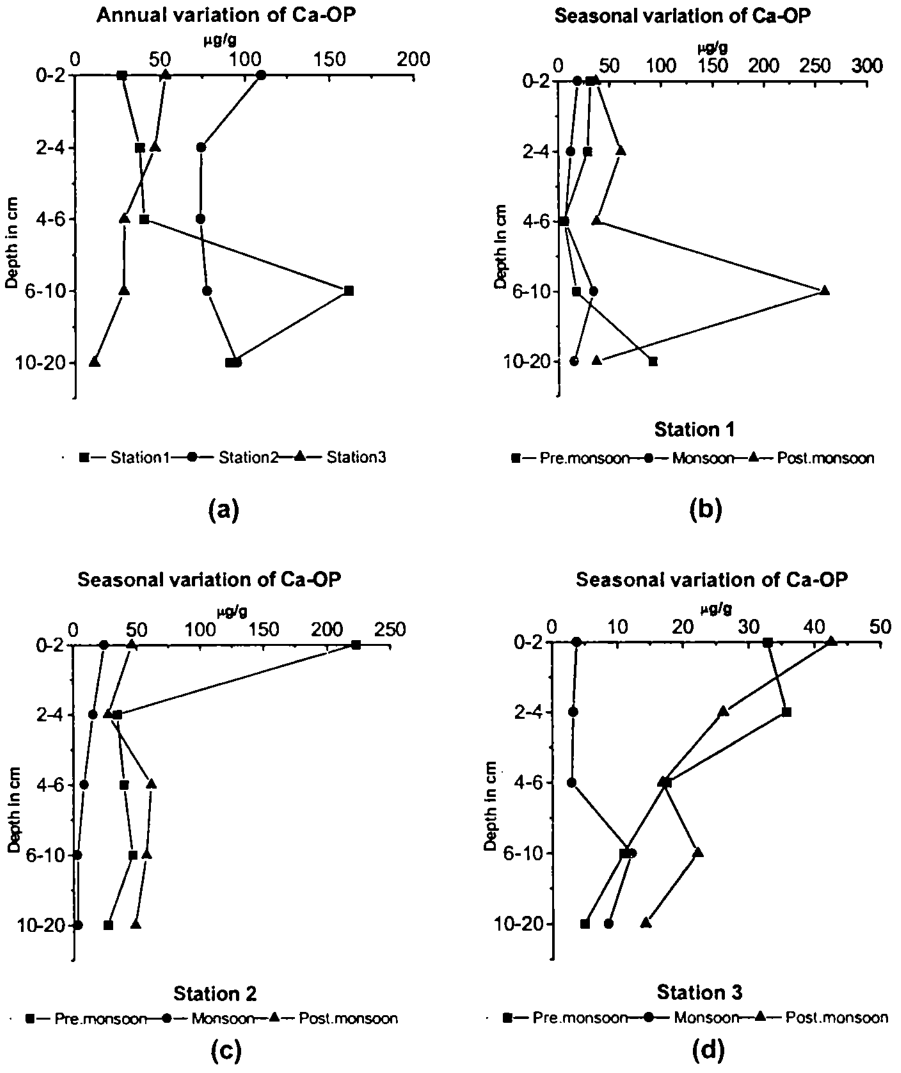


Fig. 5.6 Annual and seasonal variation of Ca-OP in sediment cores

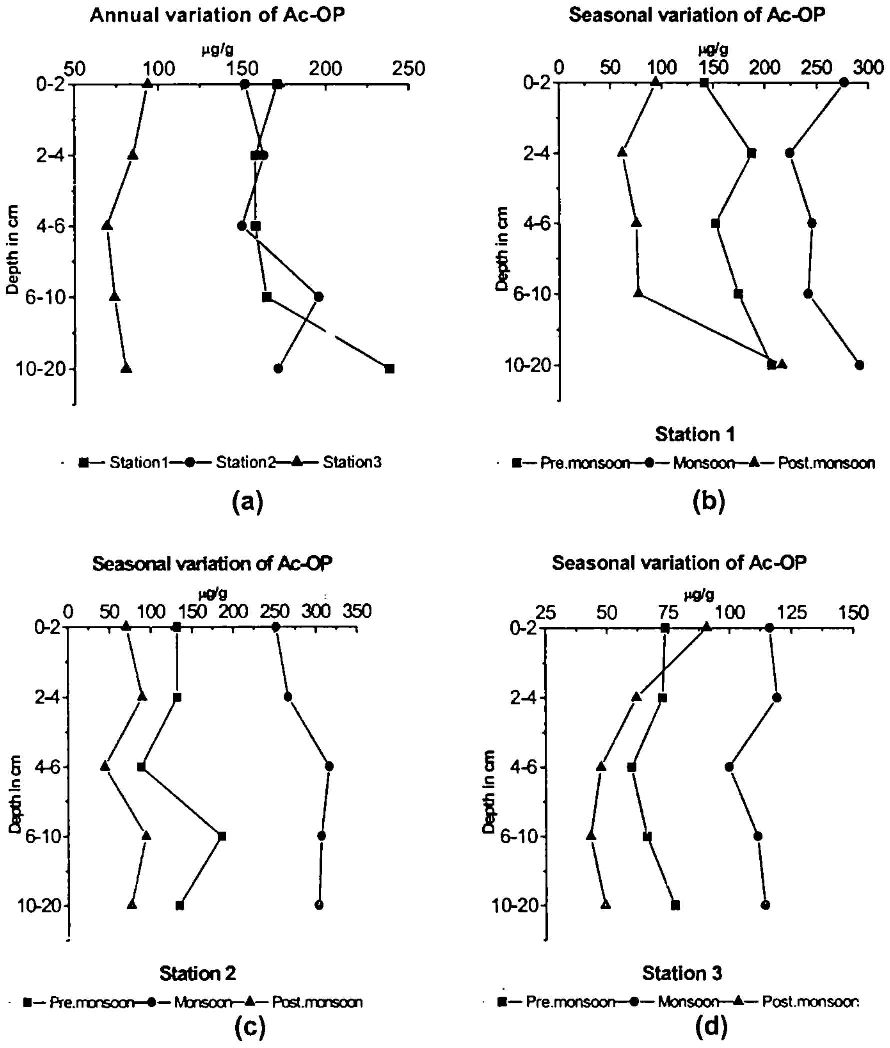
Acid soluble organic phosphate (Ac-OP)

The fractionation of organic phosphorus enable three main forms to be identified, acid soluble organic phosphorus, alkali soluble mostly composed of humic compounds, and residual organic phosphorus (Mesnage *et al.*, 2002). The phosphorus which fixes on to the fresh organic material gives compounds of the acid soluble organic phosphorus while the phosphorus which associates with more stable forms of organic material gives humic acid bound phosphorus forms. Ac-OP is a form of organic phosphorus, which is easily soluble in acid. This fraction usually represents only a small part of the sediment phosphorus and doesn't show any variation on a seasonal scale (Mesnage and Picot, 1995). The higher concentration of Ac-OP in the sediments in an ecosystem of France (Seine estuary) are interpreted as input of organic material which have come from micro algae, phyto plankton (Mesnage *et al.*, 2002).

Table 5.8 Station-wise summary statistics of Ac-OP (μgg^{-1}) in sediment cores

Station	Depth	Min	Max	Mean	SD	% of CV
Station 1	0-2	38.88	279.78	170.95	94.67	55.38
	2-4	30.17	291.67	157.74	91.30	57.88
	4-6	37.93	327.91	157.62	97.88	62.10
	6-10	56.47	283.99	164.30	90.35	54.99
	10-20	103.49	390.46	237.83	103.68	43.59
Station 2	0-2	29.46	348.66	151.72	106.48	70.19
	2-4	49.16	367.80	162.86	108.43	66.58
	4-6	43.66	431.74	149.76	149.49	99.82
	6-10	60.22	483.31	195.41	150.49	77.01
	10-20	70.59	491.53	171.13	159.86	93.42
Station 3	0-2	52.30	146.27	93.63	38.52	41.14
	2-4	34.87	156.76	84.65	40.08	47.35
	4-6	37.74	137.98	69.10	34.92	50.54
	6-10	42.11	159.31	73.59	43.37	58.94
	10-20	47.14	144.68	80.28	35.04	43.65

The Station-wise summary statistics of Ac-OP are given in Table 5.8. Both the minimum Ac-OP 29.46μgg^{-1}, (0-2cm), and maximum Ac-OP, 491.53μgg^{-1}' (10-20cm) were recorded at Station 2. The annual and seasonal depth profiles of Ac-OP are depicted in Fig. 5.7a-5.7d. Ac-OP showed generally a decrease in concentration down the core. There was a reversal in this trend at depths beyond 10cm at Station 1 and 6-10cm depth at Station 2. At all Stations more or less similar values were found during pre-monsoon and post-monsoon, but exceptionally high values recorded during monsoon. The concentration of acid extractable organic phosphorus found to be similar at Station 1 and Station 2. The overall picture of the annual variation showed generally a decrease down the core with an exception of 10-20 cm depth at Station 1 and a subsurface increase at Station 2.



(a)

(b)

(c)

(d)

Fig. 5.7 Annual and seasonal variation of Ac-OP in sediment cores

The general decrease down the core may be due to the decrease in microalgae in sediment. The exceptionally higher concentration at certain depths might be due to the incidental occurrence of root particles in the sediment. The depths, at which remarkably higher concentrations were recorded, showed high coefficient of variation (Table 5.8). Seasonal variations were found as against the observation of Mesnage and Picot (1995). The maximum concentrations were recorded during monsoon may be associated with the productivity. During monsoon season minimum Fe-IP recorded in the sediment which is the algal available fraction. This observation supports the fact that Ac-OP at these Stations were decided by the presence of microalgae.

Alkali soluble organic phosphate (Alk-OP)

NaOH extracts contain particularly humic compounds (Golterman, 1998). It was observed by Baldwin, (1996) that the NaOH extractable phosphorus has some inter-relation with the amount of phospholipids in the sediment. The phospholipids in the sediment could be derived from algae, zooplankton, leaf litter or bacteria. Phospholipid concentration has shown to give a good estimate of sedimentary bacterial biomass (White *et al.*, 1979). It has also been shown that NaOH can extract a large proportion of the P associated with the bacteria, Psuedomonas (Warra *et al.*, 1993), a large portion of which was in the non-reactive form. Therefore, it is possible that a proportion of the P extracted by NaOH may have been associated with sedimentary bacteria. Warra *et al.* (1993) stimulated bacterial growth in sediments and found a correlation between bacterial biomass and the P extracted by NaOH. In a study of polyphosphates in lake sediments it was found that poly-phosphorus was detected only in samples in which bacteria containing poly-phosphorus granules were present (Hupfer *et al.*, 1995). Changes in bacterial activity and biomass were directly related to the changes in the Alk-OP phosphorus (extracted with 0.1M NaOH and digested) and labile phosphorus pools in the sediment and to the uptake and subsequent release of phosphate by the sediments (Tornblom and Rydin 1998).

The concentrations of Alk-OP varied between 38.47 $\mu g g^{-1}$ (Station 3, 10-20) and 728.46$\mu g g^{-1}$ (Station 1, 0-2 cm). The annual summary statistics (Table 5.9), showed more consistent concentrations were recorded in 10-20 cm layer at Station 1, 0-2cm layer at Station 2 and Station 3. Seasonal and annual variations of Alk-OP in depth profile are given in Fig. 5.8a to 5.8d. Alk-OP showed general decrease in concentration down the core. Contrary to this an increase in Alk-OP concentration was observed at the sub-surface sediment of Station 2 during pre-monsoon and post-monsoon. Generally low concentrations were recorded during monsoon at all Stations. The concentrations during pre-monsoon and post-monsoon were close to each other. The surface sediment of Station 1 recorded considerably high value during pre-monsoon. Minimum values were recorded at 10-20 cm depth at all Stations. The annual mean variations of Alk-OP are given in Fig. 5.15. The overall picture of the annual variation followed the general pattern of decrease down the core at Station 1 and Station 3. Station 2 showed an entirely different picture of subsurface maximum and again decreases beyond 10cm depth.

Table 5.9 Station-wise summary statistics of Alk-OP (μg/g) in sediment cores

Station	Depth	Min	Max	Mean	SD	% of CV
Station 1	0-2	113.69	728.46	372.89	229.01	61.41
	2--4	114.78	576.29	292.74	171.49	58.58
	4--6	124.41	678.57	316.43	198.45	62.72
	6--10	122.51	410.70	266.62	106.96	40.12
	10--20	118.04	354.08	263.98	97.55	36.96
Station 2	0-2	127.36	380.94	277.32	102.82	37.07
	2--4	116.14	490.76	301.48	147.85	49.04
	4--6	129.34	485.19	296.09	144.81	48.91
	6--10	113.86	464.21	285.26	134.45	47.13
	10--20	83.13	452.15	237.74	127.12	53.47
Station 3	0-2	69.90	267.21	183.94	85.01	46.22
	2--4	56.21	272.44	149.85	89.42	59.67
	4--6	45.91	235.55	138.64	68.39	49.33
	6--10	47.58	232.57	133.42	67.23	50.39
	10--20	38.47	331.43	139.97	103.31	73.81

Other than humic compounds, NaOH also extracted polyphosphates found in bacterial biomass. Davelaar, (1993) recognized that poly-phosphates containing bacteria probably are ubiquitous in nature and that poly phosphate metabolism must be operative in sediments of aquatic environments. The bacterial biomass seems to store poly phosphorus mainly when they live in an aerobic environment and hydrolyse under anaerobic conditions (Comeau *et al.*, 1986; Wentzel *et al.*, 1991). Therefore the general decrease in Alk-OP concentration may due to the decrease in bacterial biomass down the core sediment. Bacterial biomass decreases with increasing sediment depth. (Gachter *et al.*, 1988). Therefore it is reasonable to infer that the poly-phosphorus content of sediment decreases quickly with increasing sediment depth and increasing redox potential. The maximum concentration of Alk-OP was recorded at surface sediment of Station 1. This could be due to an oxic environment in the surface sediment of Station 1, facilitating the bacterial biomass to store polyphosphates in their cells.

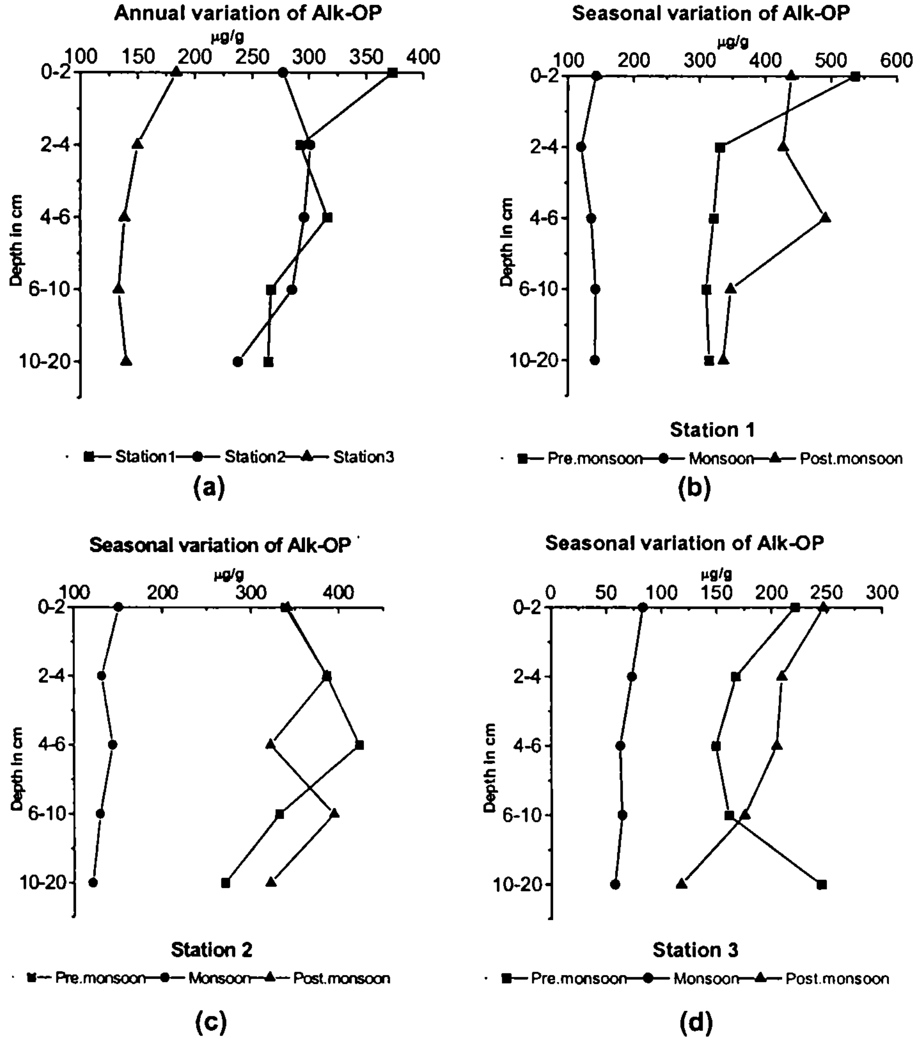


Fig. 5.8 Annual and seasonal variation of Alk-OP in sediment cores

Station 2 characterized by a subsurface increase in Alk-OP, suggest an oxic environment existing till 6cms of depth. Beyond this depth, Alk-OP showed a decreasing trend which may be due to anoxic conditions prevalent in this region.

Residual Organic Phosphorus (ROP)

The statiowise summary statistics of ROP are given in Table 5.10. Comparatively less CV were observed in ROP concentrations, 2-4 cm layer at Station 1, Station 3 and 10-20 cm layer at Station 2. The values found to vary from 2.61µgg^{-1} (Station 3, 4-6cm) to 345.51µgg^{-1} (Station 2, 2-4cm). The distribution of ROP in sediment cores is given in Fig. 5.9a to 5.9d. ROP showed general decrease in concentration with increasing depth. However at all three Stations a subsurface increase was found. At Station 2 and Station 3 maximum recorded at 2-4 cm depth. Mean variation of ROP is given in Table 5.10. Maximum concentrations were recorded during monsoon at all Stations. Pre-monsoon and post-monsoon season recorded similar concentrations at first two Stations. The overall picture of the annual variation followed general pattern of subsurface increase and decrease down the core at Station 1 and Station 2. At Station 3 gradual decrease recorded on increasing depth.

Table 5.10 Station-wise summary statistics of ROP (µg g^{-1}) in sediment cores

Station	Depth	Min	Max	Mean	SD	% of CV
Station 1	0-2	26.57	153.75	92.52	43.20	46.70
	2--4	42.94	125.98	83.96	31.19	37.15
	4--6	41.68	141.23	77.68	36.32	46.76
	6--10	48.30	142.02	80.05	34.56	43.17
	10--20	46.97	148.73	73.93	39.40	53.29
Station 2	0-2	46.81	201.64	84.13	59.28	70.46
	2--4	51.00	345.51	118.07	113.28	95.94
	4--6	50.53	181.64	91.59	48.86	53.35
	6--10	33.33	147.07	79.48	39.93	50.24
	10--20	38.39	111.24	65.10	25.64	39.39
Station 3	0-2	24.56	113.16	49.95	33.12	66.30
	2--4	19.69	220.57	78.54	82.38	104.89
	4--6	2.61	166.90	60.19	64.80	107.65
	6--10	14.12	126.62	45.55	43.13	94.69
	10--20	16.29	172.44	49.68	60.45	121.69

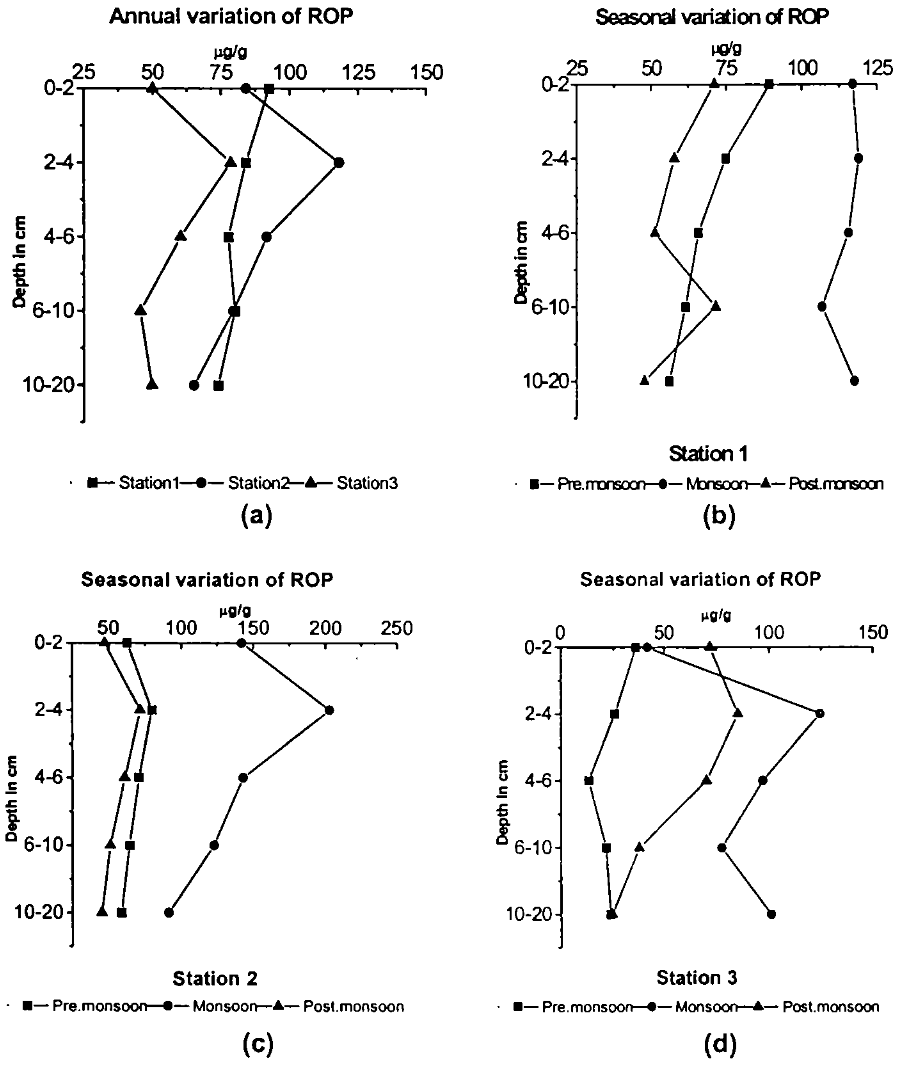


Fig. 5.9 Annual and seasonal variation of ROP in sediment cores

The depth profile of residual organic fraction points to the probability of sediment acting as a sink for phosphorus. The adsorbed phosphates concentrate in subsurface sediment. The ROP fraction concentrates at 2-4 cm depth, followed by 4-6 cm depth, at Station1 and Station 2. Station 3 showed a gradual decrease in concentration may be due to the tidal regime at this site. Due to wave action finer fraction of the sediment wash away and coarser particles settles down, which is poor in adsorbing phosphate.

Sum of fractions (ΣTP)

ΣTP concentrations were found to vary between 296.70 μgg^{-1} (Station 3, 10-20cm) and 2190.84μgg^{-1} (Station 1, 10-20cm). The minimum at Station 1 recorded at a depth of 2-4cm (974.93μgg^{-1}) and maximum recorded at 10-20 cm (2190.84μgg^{-1}) depth. While at Station 2 minimum (974.93μgg^{-1}) observed at 10-20cm and maximum (2046.38μgg^{-1}) at 6-10cm depth. Station 3 recorded the minimum (296.70μgg^{-1}) at 10-20 cm depth and maximum (1412.85.μgg^{-1}) at 0-2 layer. ΣTP concentrations were similar at Station 1 and in Station 2. The annual and seasonal depth distributions of ΣTP are given in Fig. 5.10a to 5.10d. The overall picture of the annual variation followed the general pattern of decreasing phosphorus concentration with increasing depths at Station 1 and Staion 3, except at 10-20 cm depth at Station 1 (Table 5.11). The ΣTP concentrations exhibited comparatively lower coefficient of variation in 0-2cm layer at Station 1, 2-4 cm layer at Station 2 and 10-20 cm layer at Station 3. Station 2 showed a subsurface maximum and the values decreases down the core. However at Station 1 and Station 2 there was a reversal in the above trend at 10-20 cm depth and at 2-4 cm depth respectively.

In Septia Bay, Silva and Mozeto (1997) found in mangrove sediments, total phosphorus concentrations varying from 170-270μgg^{-1}. In the four different kinds of mangrove sediments, investigated in French Guiana, Fabre *et al.* (1999) found, sum of all fractions of phosphorus varied between 600-800μgg^{-1}. In the three mangrove areas observed in this study, the values can be considered as high, values range from 296.70 μgg^{-1} to 2190.84μgg^{-1}. Nearly all phosphate is expected to enter the sediments in shallow lakes and marshes receiving a relatively large phosphorus input during the loading phase (Espejo et al., 1999). The seasonal variation showed comparatively higher values during post-monsoon at all Stations. Generally the ΣTP concentrations showed a decreasing trend during all seasons except at 10-20 cm depth at Station 1. While at Station 2, a sub-surface increase in concentration of ΣTP was recorded during post-monsoon and pre-monsoon. Station 3 recorded a gradual decrease in concentration of ΣTP during all seasons.

Table 5.11 Station-wise summary statistics of TP ($\mu g\ g^{-1}$) in sediment core

Station	Depth	Min	Max	Mean	SD	% of CV
Station 1	0-2	959.60	1967.60	1590.51	361.05	22.70
	2--4	951.40	1954.21	1407.45	339.56	24.13
	4--6	1051.25	1947.46	1400.67	331.74	23.68
	6--10	1167.65	1922.13	1489.72	338.74	22.74
	10--20	1082.08	2190.84	1693.82	428.92	25.32
Station 2	0-2	1222.31	1819.23	1501.01	224.98	14.99
	2--4	1449.45	1777.34	1648.05	122.67	7.44
	4--6	1420.68	1768.37	1564.90	137.63	8.79
	6--10	1352.78	2046.30	1617.62	294.54	18.21
	10--20	974.93	1823.74	1331.14	303.79	22.82
Station 3	0-2	480.72	1412.85	847.28	320.82	37.87
	2--4	452.55	759.70	599.81	118.03	19.68
	4--6	357.01	608.57	475.93	85.87	18.04
	6--10	326.06	596.63	435.52	106.09	24.36
	10--20	296.70	476.06	415.91	73.96	17.78

The lower concentration observed at Station 3 could be the reflection of the different geographical and geomorphological location of this Station. This result also suggests the existence of trapping mechanism for phosphorus in the mangrove ecosystem. The existence of denser vegetation at Station 1 and Station 2 as compared to Station 3 facilitates the trapping of nutrients discharged to this creek. It was observed by Silva *et al.* (1998) that 99% of total phosphorus (R.mangle trees plus sediment) were present in sediments, again suggests a trapping mechanism in mangrove sediments. The ΣTP concentrations at Station 2 were characterized by low concentrations in surface sediment and relatively higher in sub-surface sediments. The enrichment of P in sub-surface sediments may be due to the biogeochemical oxidation process occurring in this micro-environment (Silva *et al.*, 1998; Scholander *et al.*, 1955). The minimum concentration observed at 10-20 cm depth may be due to an anoxic environment, and is substantiated by the high concentration of dissolved inorganic phosphorus observed in pore water at this depth (Joseph, 2001). The same observation was found in Yangtze estuary (Min *et al.*, 2001). At Station1, 10-20cm, sediment exhibited maximum concentration of ΣTP. It may be due to the less mineralisation-taking place at this depth. In a comparative study undertaken to find the anoxic decomposition in sediments Holmboe *et al.* (2001) found that dissolved inorganic phosphorus (DIP) was released during anoxic decomposition in Wadden sea sediment, but was retained in Bangrong mangrove sediment. Their study also found that added excess DIP was efficiently taken up by the sediment particles and primarily retrieved in the easily exchangeable and iron bound fractions and the sediment was thus found to act as a phosphorus sink. The present investigation also recorded maximum concentration of Fe-IP. Comparatively less Alk-OP recorded at this layer also substantiate the fact that bacterial mineralization might be minimum at this depth, at Station 1.

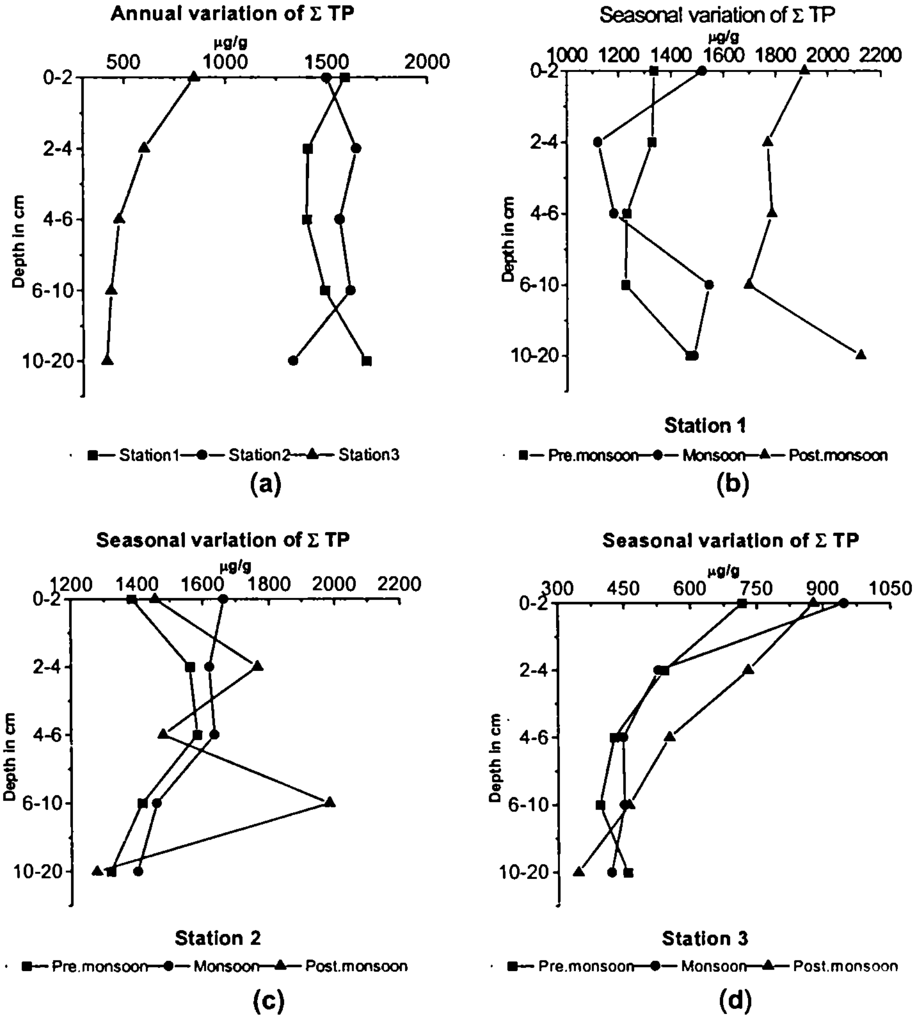


Fig. 5.10 Annual and seasonal variation of ΣTP in sediment cores

The depth profile of Station 3 showed an oxidized surface sediment, capable of retaining phosphate and decreasing concentration down the core, showed prevalent anoxic environment down the core. ΣTP concentrations were recorded, high in surface (0-2 cm) sediments due to oxidation near or at the sediment water interface. It was found that the oxidative reactions would immobilize phosphorus and limit its availability to autotrops and microheterotrops, with phosphorus being bound to non-reactive metals, particularly as iron and manganese oxy hydroxides.

5.2.2 Comparative study on the distribution of phosphorus fractions

Phosphorus, an important nutrient in aquatic system, undergoes tremendous chemical transformations during sedimentation. The comprehension of chemistry of phosphate is a pre-requisite for the study of phosphorus cycle in aquatic ecosystems. Hence a comparison of the various forms in which this entity remain in sediment during diagenesis is very essential to find out the major process governing P-cycle in this ecosystems. The concentrations of phosphorus forms found at the three mangrove locations are summarised in Tables 5.12a and 5.12b. They are expressed as annual mean concentrations of individual fractions and also as percentage of total phosphorus. The sum of all fractions was designated as the total phosphorus concentration (ΣTP). Station wise variations are presented below.

Station 1

At this Station, concentrations of Fe-IP fractions were recorded the maximum concentrations. It was found to be the abundant fraction of phosphorus at all depths and ranged between 345.68μgg^{-1} and 495.36μgg^{-1}. W-OP recorded a minimum with values ranging between 7.18μgg^{-1} and 13.28μgg^{-1}. Other major fractions found were Ca-IP (246.35μgg^{-1} and 362.04μgg^{-1}) and Alk-OP (263.98μgg^{-1} to 372.89μgg^{-1}). All other fractions gave intermediate values to those of W-OP and Alk-OP (Table 5.12a).

Regarding the percentage of different fractions at Station 1, Fe-IP was found to be the highest fraction at all depths and the percentage varied between 21.82 and 28.31. The minimum percentage was recorded for W-OP (0.48 – 0.84). Other major fractions found at this Station were Ca-IP, which varied from 15.55% to 20.47%, and Alk-OP which varied from 14.22% to 21.35%. Fe-OP and Ca-OP amount to 6.8 – 10.6% and 6.08 – 21% respectively. Ac-OP showed a variation of 9.75 to 12.82% at various depths. ROP concentrations were <10%. W-IP and W-OP fractions were the least extracted with a percentage 1.48 - 2.94% and 0.48 to 0.84% respectively (Table 5.12b).

Table 5.12a Annual mean concentration of fractions of phosphorus µg g^{-1}

Station	Depth	W-IP	W-OP	Fe-IP	Fe-OP	Ca-IP	Ca-OP	Ac-OP	Alk-OP	ROP	TP
Station 1	0-2	14.30	11.62	412.12	187.34	358.83	131.99	170.95	372.89	92.52	1752.56
	2--4	15.98	7.18	425.06	128.57	298.88	91.33	157.74	292.74	83.96	1501.43
	4--6	17.04	9.11	392.23	115.30	303.38	93.64	157.62	316.43	77.68	1482.43
	6--10	26.20	13.28	345.68	107.83	246.35	333.95	164.30	266.62	80.05	1584.26
	10--20	42.86	11.68	495.36	158.70	362.04	209.37	237.83	263.98	73.93	1855.75
Station 2	0-2	16.20	8.65	427.08	156.71	266.66	259.49	151.72	277.32	84.13	1647.95
	2--4	20.90	4.75	477.99	178.32	293.88	234.00	162.86	301.48	118.07	1792.25
	4--6	26.64	6.11	414.48	251.56	287.92	219.85	149.76	296.09	91.59	1744.01
	6--10	25.96	8.90	422.49	144.90	442.21	164.98	195.41	285.26	79.48	1769.59
	10--20	22.71	5.35	282.63	60.73	365.38	150.28	171.13	237.74	65.10	1361.04
Station 3	0-2	1.70	4.23	102.76	61.45	149.43	93.95	93.63	183.94	49.95	741.05
	2--4	2.85	3.72	90.73	44.74	87.99	77.65	84.65	149.85	78.54	620.71
	4--6	4.29	4.49	70.52	32.35	61.06	50.61	69.10	138.64	60.19	491.25
	6--10	4.48	6.44	52.41	54.24	53.95	99.15	73.59	133.42	45.55	523.23
	10--20	7.08	3.15	58.69	27.53	44.36	72.47	80.28	139.97	49.68	483.20

Table 5.12b Annual mean percentage of fractions of phosphorus

Station	Depth	W-IP	W-OP	Fe-IP	Fe-OP	Ca-IP	Ca-OP	Ac-OP	Alk-OP	ROP
Station 1	0-2	0.82	0.66	23.52	10.69	20.47	7.53	9.75	21.28	5.28
	2-4	1.06	0.48	28.31	8.56	19.91	6.08	10.51	19.50	5.59
	4-6	1.15	0.61	26.46	7.78	20.47	6.32	10.63	21.35	5.24
	6-10	1.65	0.84	21.82	6.81	15.55	21.08	10.37	16.83	5.05
	10-20	2.31	0.63	26.69	8.55	19.51	11.28	12.82	14.22	3.98
Station 2	0-2	0.98	0.52	25.92	9.51	16.18	15.75	9.21	16.83	5.11
	2-4	1.17	0.27	26.67	9.95	16.40	13.06	9.09	16.82	6.59
	4-6	1.53	0.35	23.77	14.42	16.51	12.61	8.59	16.98	5.25
	6-10	1.47	0.50	23.88	8.19	24.99	9.32	11.04	16.12	4.49
	10-20	1.67	0.39	20.77	4.46	26.85	11.04	12.57	17.47	4.78
Station 3	0-2	0.23	0.57	13.87	8.29	20.17	12.68	12.63	24.82	6.74
	2-4	0.46	0.60	14.62	7.21	14.18	12.51	13.64	24.14	12.65
	4-6	0.87	0.91	14.36	6.59	12.43	10.30	14.07	28.22	12.25
	6-10	0.86	1.23	10.02	10.37	10.31	18.95	14.06	25.50	8.71
	10-20	1.47	0.65	12.15	5.70	9.18	15.00	16.61	28.97	10.28

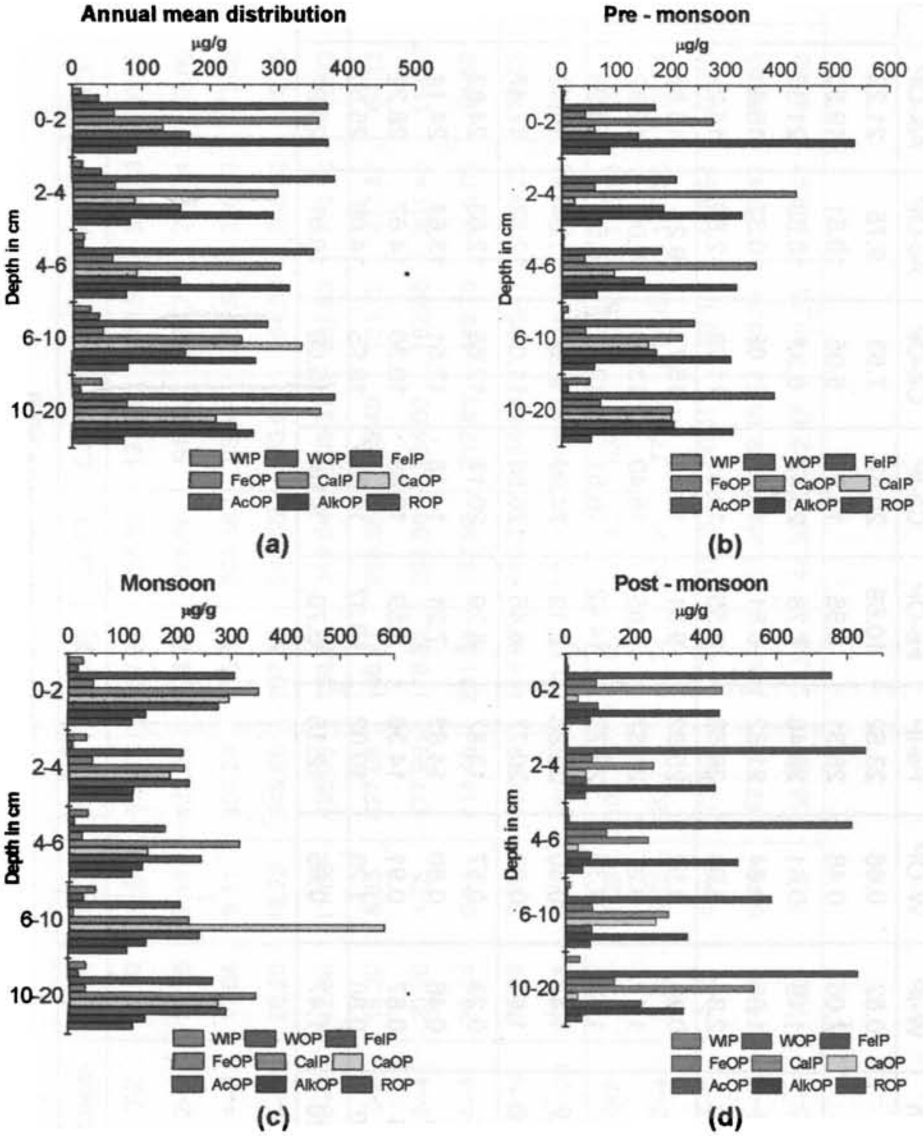


Fig. 5.11 Annual and seasonal variation of fractions of phosphorus at Station 1

The seasonal variations of different phosphorus species at this Station are depicted in Fig. 5.11b - 5.11d. Generally Fe-IP, Ca-IP and Alk-OP were the more abundant fractions extracted during the three seasons. During pre-monsoon, the above three fractions gave maximum concentrations at different depths. While Alk-OP was a maximum in 0-2 cm layer and 6-10 cm layer ; Ca-OP was a maximum in the 2-4 and 4-6 layers and Fe-IP was a maximum at the 10-20 cm layer. The concentration of Fe-IP was comparatively higher than any other fraction during post-monsoon.

The order of abundance of each phosphorus fraction, in the layers, 0-2, 2-4 and 4-6 cm were similar. Fe-IP was a maximum at all depths followed by Alk-OP, Ca-IP, Ac-OP, Ca-OP, ROP, Fe-OP, W-IP and W-OP (Fig.5.11a). The 6-10cm layer showed an order of abundance as follows. Fe-IP> Ca-IP> Alk-OP> Ca-OP> Ac-OP> ROP> Fe-OP > W-IP > W-OP. At 10-20 cm layer the order found to be Fe-IP > Ca-IP > Alk-OP > Ac-OP > Ca-OP > Fe-OP > ROP > W-IP > Fe-OP.

Station 2

Similar to Station 1, Station 2 core sediments also were generally composed of Fe-IP as the major fraction at all depths except at 6-10 and 10-20 cm depths. Fe-IP at this Station ranged between 282.63µgg^{-1}and 477.99µgg^{-1}. W-OP recorded minimum concentrations. (4.75µgg^{-1} to 8.90µgg^{-1}). Other major fractions at this site were Ca-IP, which ranged from 266.66µgg^{-1} to 442.21µgg^{-1} and Alk-OP, which ranged from 237.74µgg^{-1} to 301.48µgg^{-1} (Table 5.12a).

The percentage of different fractions at Station 2 showed a similar trend as the individual concentrations. Fe-IP fraction gave the maximum concentration in surface layers. The 6-10 and 10-20 cm depths consist of higher amounts of Ca-IP. W-IP fraction recorded minimum percentages at all depths. The other major fractions, Alk-OP and Ca-IP, gave almost similar percentages except at 6-10 and 10-20cm depth. These fractions varied from 16.18 to 26.85% and 16.12 to 17.47% respectively. The maximum percentage of Ca-IP was recorded at 10-20 cm depth. Fe-OP and Ca-OP amounts to 4.46 – 14.42% and 9.32 – 15.75% respectively. Ac-OP showed a variation of 8.59 to 12.57% at various depths. The ROP recorded <10%. The W-IP and W-OP fraction were the least extracted with a percentage 0.98 – 1.67% and 0.27 to 0.52% respectively. All these percentages were comparable to that of Station 1. (Table 5.12b).

The annual and seasonal variation of fractions of phosphorus at Station 2 are given in Figs. 5.12a-12d

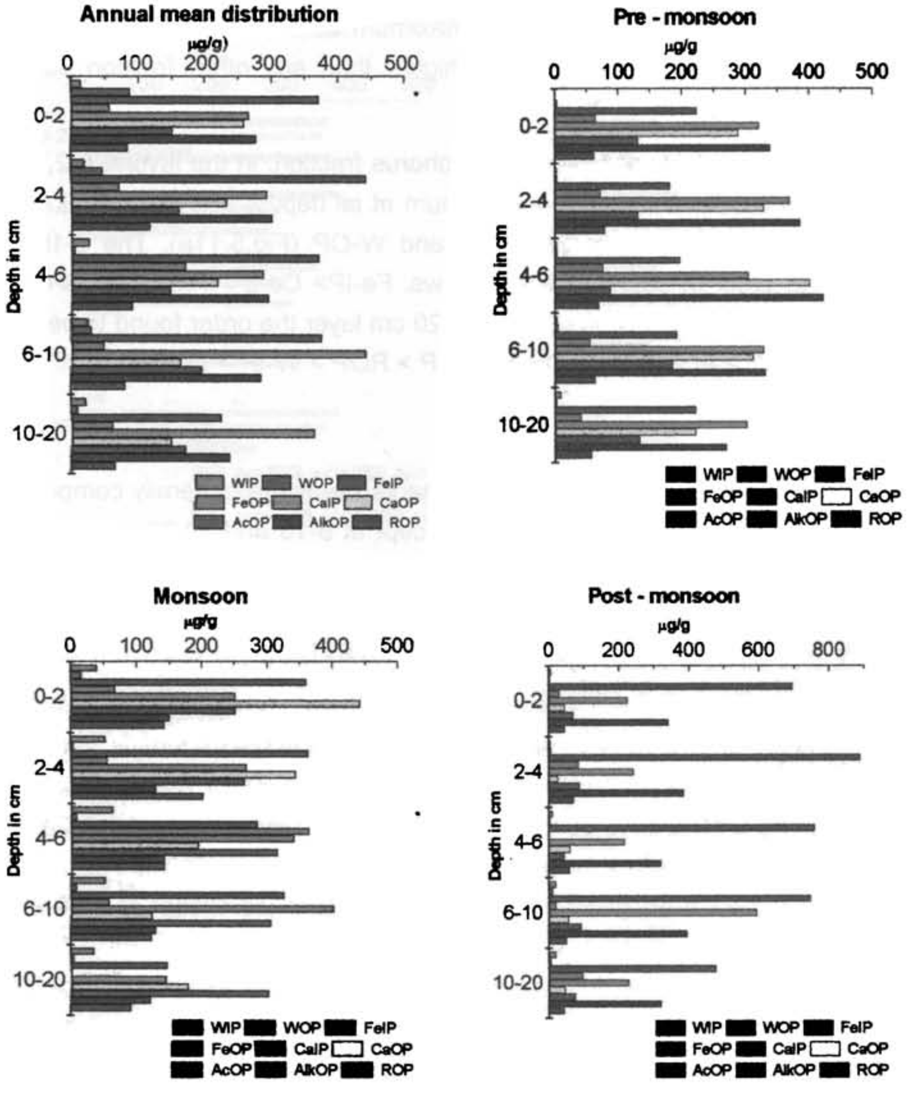


Fig. 5.12 Annual and seasonal variation of fractions of phosphorus at Station 2

The seasonal distribution of various fractions at Station 2 also showed variations. Ca-IP and Alk-Op were the two major fractions during pre-monsoon, while Ca-IP and Fe-IP were the major fractions during monsoon. During monsoon, there was a considerable increase in Ca-OP at 0-2 and 2-4 cm depth. Similar to Station 1, Fe-IP was the abundant fraction during post-monsoon, followed by Alk-OP.

The order of abundance of each fraction at the depths 0-2, 2-4 and 4-6cm layers were similar. Fe-IP was a maximum at these depths and was followed by Alk-OP, Ca-IP, Ca-OP, Ac-OP, ROP, Fe-OP, W-IP, W-OP. At 6-10 and 10-20 cm layers, Ca-IP was the major fraction identified. These layers showed an order of abundance of Ca-IP > Fe-IP > Alk-OP > Ac-OP > Ca-OP > ROP > Fe-OP > W-IP > W-OP (Fig.5.12a).

Station 3

Fractionation of sediment cores at Station 3 gave an entirely different pattern as that of Station 1 and Station 2. The major fraction at this site was Alk-OP. This fraction showed a variation from 133.42μgg^{-1} to 183.94μgg^{-1}. The minimum concentration fraction was also different from the other two Stations. Here W-IP showed minimum concentration at this site, which varied from 1.70μgg^{-1} to 7.08μgg^{-1}. The other major fractions obtained were Fe-IP (52.41 to 102.76μgg^{-1}) Ca-OP (50.61 to 99.15μgg^{-1}) and Ac-OP (69.10 to 93.63μgg^{-1}) (Table 5.12a)

At Station 3, Alk-OP percentage was the maximum 24.14 – 28.97%, followed by Ca-IP and Fe-IP, which were varied from 9.18 to 20.17% and 10.0 – 14.6% respectively. The Ca-OP concentration amounts to a significant fraction at this site, which varied from 10.3 to 18.95%. Ac-OP showed a similar percentage as that Ca-OP which amounts to 12.60 – 16.61%. Fe-OP concentration composed of 5.70-10.37% of total phosphorus. ROP, varied from 6.7 to 12.65% (Table 5.12b).

Seasonal distribution of different fractions of phosphorus at Station 3 are given in Fig. 5.13b-5.13d. Certain seasonal variations were observed in concentrations of major fractions. During pre-monsoon the abundant fraction obtained was Alk-OP at all depths. Ca-IP and Ca-OP showed exceptionally high values during this season. Ac-OP concentration was another major phosphorus fraction extracted during monsoon season. However Alk-OP fraction was the major phosphate fraction during post-monsoon, except at 0-2 cm layer. The Ca-IP concentration recorded a maximum in this layer.

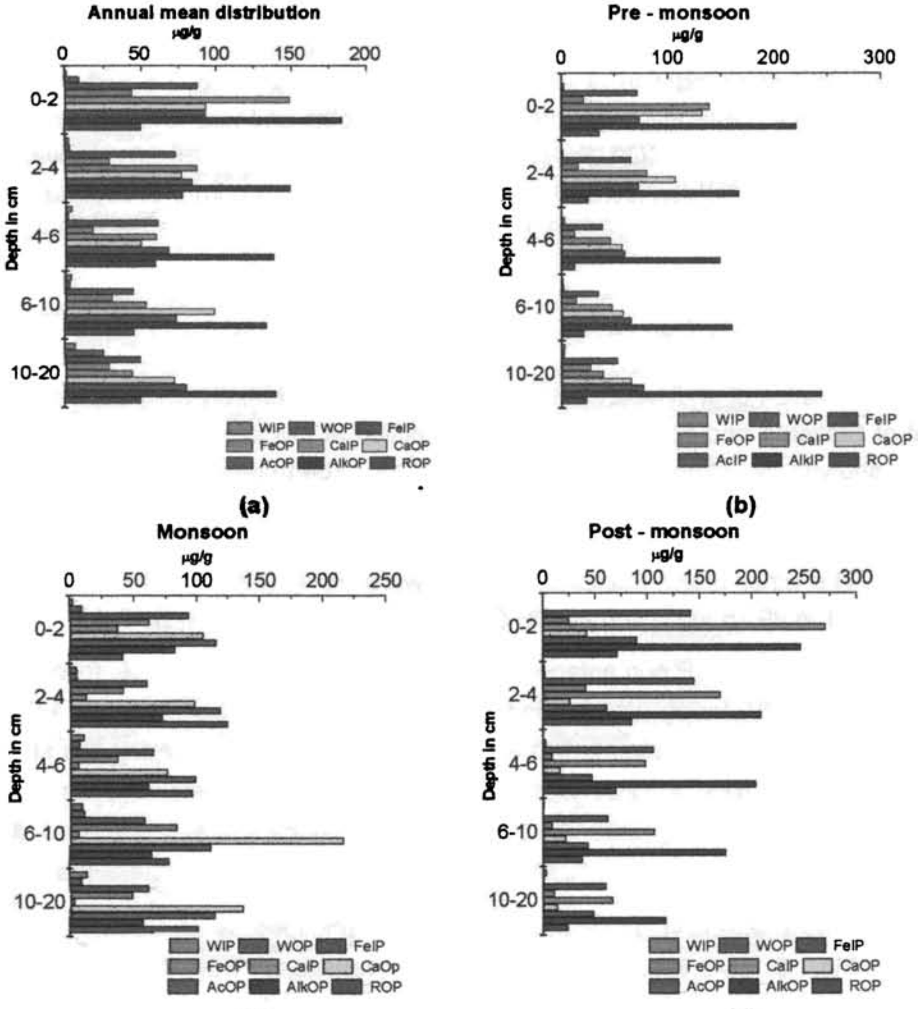


Fig. 5.13 Annual and seasonal variation of fractions of phosphorus at Station 3

Various fractions when arranged in their order of abundance at this Station, showed that Alk-OP was the major fraction till 10cm of depth. Ca-IP concentration was the major fraction at 10-20 cm depth. The order of abundance for the various fractions in 0-2cm and 2-4cm layers were Alk-OP > Ca-IP> Fe-IP> Ac-OP> Ca-OP> ROP> Fe-OP> W-OP>W-IP. The 4-6cm showed an order Alk-OP> Ca-OP> Ac-OP> Ca-IP> ROP> Ca-OP> Fe-OP> W-OP>W-IP. The 6-10 cm showed an order Alk-OP> Ca-OP> Ac-OP> Ca-IP> Fe-IP> ROP> Fe-OP> W-OP>W-IP. The

10-20 cm layer showed an order Ca-IP> Ac-OP> Ca-OP> Fe-IP> ROP> Ca-IP> Fe-OP> W-IP>W-OP in abundance (Fig. 5.13a)

The major phosphate forms identified in Cochin estuary are Ca- bound, resistant organic, hydrolysable organic and Fe and Al bound phosphorus with regional variability. The abundance of the above phosphorus forms points to the presence of calcareous materials as well as terrestrial transfer of organic material in the sediment facies (Balchand and Nair, 1994). It was also reported that, irrespective of the season, the sediments of fresh water arms of the estuary showed greater concentrations of Ca-bound phosphorus and resistant organic phosphorus. While the sediment in waters of intermediate salinity was found to bind hydrolysable as well as resistant organic forms of phosphorus, those in more saline environment exhibited a preference for hydrolysable and for Fe or Al bound phosphorus. The variations in the affinity of phosphorus forms are attributed to the difference in estuarine chemical reactivity. During the present investigation Station 1 and Station 2 are more saline than Station 3, which lie more adjacent to barmouth of Cochin estuary. The high saline area of this estuary exhibited a preference for Fe/Al bound phosphates. Station 3 is of intermediate salinity and showed a preference for hydrolysable organic phosphorus and calcium bound organic phosphorus. The speciation of phosphorus in other mangrove ecosystems also showed preferences of one form of phosphorus or the other with changing salinity. Regarding the phosphate concentration in mangrove sediments, available data are scares and there is a large variability among systems and methodology for data acquisition. Comparison of concentration are difficult task because of differential analytical technique are used for different speciation.

The major forms of phosphorus identified in Pichavaram (mangrove ecosystem on the south east coast of India) surfacial sediments were ferric Fe bound followed by authigenic calcium carbonate bound, exchangeable phosphorus, detrital apatite and organic phosphorus (Ramanathan, 1997). The above fractionation done using SEDEX method (Ruttenburg, 1992) was found to be related to chlorinity variations in the waterways.

In a speciation of Bangrong (Thailand) mangrove sediment, Holmboe *et al.* (2001) found the distribution as exchangeable inorganic phosphorus (IP) 0.8-1.1%, Fe IP 24.8 -30.4%, adsorbed IP 9.3 -10.3%, humic phosphorus 13.0 – 18.7%, Ca IP 15.9 - 25.3%, nonreactive phosphorus 12.6 – 15.9% and residual phosphorus

9.8 - 13.2%. Thus they found that Fe bound fraction was the abundant and the exchangeable fraction was the smallest in Bangrong sediments. The present study also found Fe-IP was the major fractions at Stations 1 and 2. The minor fraction, W-OP/W-IP is the loosely bound or exchangeable fraction.

Speciation study in French Guianese mangroves by EDTA method', Fabre *et al.* (1999) showed, Fe-IP concentrations varied from 34.6 to 61.2%; Ca-IP varied from 9.3 to 19.6%; Ac-OP varied between 6.8% and 15.8% and ROP varied between 11.8% and 40.5%. In this particular.

Seasonal variability of fractionation at Station 1 showed Alk-OP to be the major fraction at 0-2cm depth during pre-monsoon. The Ca-IP was the major fraction at 2-4 and 4-6 cm of depths. This phenomenon reflects the influence of sewage into this creek since studies on sediments under the influence of untreated sewage have revealed the major fractions to be organic and non-apatite phosphorus (Carreira and Wagener, 1998).

Relatively low concentrations of Fe-IP at Station 1 during pre-monsoon season reflect the anoxic conditions prevalent in sediment cores. Only at 10-20 cm depth significant amount of Fe-IP was recorded. At this depth bacterial mineralizing may be less due to decrease in bacterial density and phosphate was bind to fine fractions of sediment mainly as Fe-IP. In a comparative study undertaken to find the anoxic decomposition in sediments, (Holmboe *et al.*, 2001) it was found that dissolved inorganic phosphorus (DIP) was released during anoxic decomposition in Wadden sea sediment, but was retained in Bangrong mangrove sediment. Since the added excess DIP was efficiently taken up by the sediment particles and primarily retrieved in the easily exchangeable and iron bound fractions and the mangrove sediment was thus found to act as a phosphorus sink. Pre-monsoon season showed comparatively high concentration of Alk-OP, which also indicated a high bacterial biomass in sediments. Therefore the variation of phosphorus fraction down the core at Station 1 may primarily depend up on bacterial mineralisation during this season. 2-4, 4-6 and 6-10 cm of depth sediments experience anoxic condition, which were reflected in the Fe-IP concentrations. This may be partly due to the higher sulphate reduction due to higher bacterial biomass and subsequent reduction of Fe-oxides by sulphides. It was well established that the reduced Fe-oxides release of Fe-bound phosphate. The higher sulphate reduction caused a decrease of Fe-bound phosphorus in Wadden sea sediment (Holmboe *et al.*, 2001). Bacterial dynamics and sedimentation events were reported to be factors that affected the size of different phosphorus fractions in surfacial sediment in Lake Erken, Sweden (Goedkoop and Pettersson, 2000). Another factor, which control the Fe-IP, was salinity. The pre-monsoon season associated with higher salinity decrease the sites for adsorption on Fe-oxides. Alkaline conditions, promoted by sulphate reduction and or increased salinity, shift the charge of Fe-oxides from positive to negative (Stumm and Morgan, 1981) reducing phosphorus adsorption.

During monsoon there was a sharp decrease in Alk-OP, at Station 1, followed by an increase in Fe-IP. Monsoon flooding of the creek may dilute the bacterial biomass, which in turn may reflect on Alk-OP. Also decrease in temparature may reduce the bacterial activity. Another significant difference during this season was the increase in Ac-OP fraction, which gives an estimate of the phosphorus, which fixes on to the fresh organic material. This material may be increasing during monsoon, which in turn increases the productivity of sediment. The detritus, which carried through land run off, also may contain fresh organic material. The significant increase of Fe-IP during post-monsoon, indicate an aerobic environment down the core so that iron may be in Fe^{+3} oxidation state. Even though the Alk-OP was the next abundant fraction during post-monsoon, bacterial mineralistion may not take place in an aeorobic environment.

Station 2, also showed low concentrations of Fe-IP during pre-monsoon and a substantial increase in concentration of Ca-IP. Both fixation of the inorganic phosphate onto the sediments, and its release from sediments to the overlying water, are controlled by the two mechanisms (Golterman, 1998): First, by adsorption of dissolved orthophosphate (o-P) on to ferric hydroxide (goethite) $Fe(OOH).x\ H_2O$ and second by precipitation with Ca^{2+} as apatite, $Ca_5\ (PO_4)_3.OH$, probably as co-precipitation with $CaCO_3$. Two factors that control the distribution of phosphate between Ca-IP and Fe-IP are pH and water depths. With a more acid pH, Fe-IP is at first dominant while Ca-IP become dominant only later. If the phosphorus loading is high in shallower waters then, Ca-IP precipitation starts earlier (Golterman, 1998). pH values showed that an alkaline range recorded at this Station, hence phosphorus loading may influence the distribution of phosphorus between Fe-IP and Ca-IP. The adsorption on to Fe-oxides would be reduced due to high salinity of core sediments. The salinity of pore waters too found to increase down the core (Joseph, 2001). Similar to Station 1, the Alk-OP found to be the major fraction during pre-monsoon, which might be due to the bacterial biomass present in the sediment. Unlike in Station 1, Station 2 exhibited lower concentration of inorganic phosphates at 10-20 cm depth. Sediment texture with increasing sand percentage was one reason of lowering of phosphates at this depth. A study of phosphorus forms relating to sediment grain size and geochemical characteristics in French coastal areas showed that the exchangeable and Fe/Al phosphate were preferentially associated with the fine particles (<63µm) in three studied areas (Andrieux and Aminot, 2001). In more sandy sediments these forms were also found in significant correlation in the larger size classes. As at Station 1 Fe-IP was the major fraction obtained during post-monsoon again gives an indication of an oxic environment in sediment cores.

Seasonal variation of different fractions of phosphorus at Station 3 showed maximum Alk-OP, followed by Ca-IP. At lower depths as this fraction increases all other fractions decreased significantly. A large increase in Alk-OP at 10-20 cm depth showed the high amount of humic bound phosphorus at this Station. An increase in Fe-IP from pre-monsoon to post-monsoon found only for surface sediments. This indicates an anoxic environment at the bottom sediments of this Station. Since this Station is characterized by sediments of large grain size, adsorption of phosphate on to particles might be less. It was found that the low concentration of ortho phosphate in the water column favors its release from the sediment into the water (Fabre, 1988; Golterman, 1995). In mangroves regularly flooded by the tide, the repeated resuspension of the sediments caused by the wave action can favor exchange of orthophosphate from the solid to the liquid phases. The water movement or sediment resuspension have profound influence on the concentration of orthophosphate in water column. Neverthless, the results on the effects of resuspension upon ortho phosphate concentration in the water column are opposed. Adsorption of phosphorus by resuspended sediments has been recorded whereas the importance of resuspension in releasing phosphorus also has been noted (Lijklema, 1977; Rippey, 1977). Therefore the relatively low concentration of Fe-IP at Station 3, might be due to repeated phosphorus desorption from the resuspended sediments.

It has been established that sediment characteristics could serve as the basis to assume phosphorus species in sediments and ultimately predict potential rates of internal phosphorus loading. For example Williams *et al.* (1976) found correlations between sediment characteristics and phosphorus species in 48 surfacial sediments from Lake Erie. Ostrofsky(1987) also found significant correlations between iron and inorganic phosphorus species and between organic matter and organic phosphorus in surfacial sediments collected from sixty-six lakes in North Eastern America.

Table 5.13a Correlation matrix between different fractions of phosphorus in sediment cores - 0-2cm.

0-2	W~P	Fe ~P	Ca~P	Ac-OP	Alk-OP	ROP	% sand	%silt	%Clay	TOC	Fe
W~P	1										
Fe ~P	0.9989***	1									
Ca~P	-0.6182**	-0.5805*	1								
Ac-OP	-0.9936***	-0.9978***	0.5255*	1							
Alk-OP	-0.8511***	-0.8749***	0.1136	0.9050***	1						
ROP	-0.9982***	-0.9999***	0.5693*	0.9986***	0.8815***	1					
% sand	-0.9952***	-0.9895***	0.6920**	0.9778***	0.7958***	0.9874***	1				
%silt	0.9626***	0.9488***	-0.8080***	-0.9259***	-0.6772**	-0.9444***	-0.9845***	1			
%Clay	0.9782***	0.9869***	-0.4414	-0.9954***	-0.9417***	-0.9890***	-0.9532***	0.8853***	1		
TOC	0.9993***	0.9965***	-0.6462**	-0.9889***	-0.8316***	-0.9953***	-0.9981***	0.9718***	0.9700***	1	
Fe	0.9981***	0.9941***	-0.6655**	-0.9848***	-0.8172***	-0.9925***	-0.9993***	0.9775***	0.9635***	0.9997***	1

p<0.05* p<0.01** p<0.001***

W~P = W-IP+W-OP Fe ~P = Fe-IP+Fe-OP Ca~P = Ca-IP+Ca-OP

Table 5.13b Correlation matrix between different fractions of phosphorus in sediment cores - 2-4cm.

2-4	W~P	Fe ~P	Ca~P	Ac-OP	Alk-OP	ROP	% sand	%silt	%Clay	TOC	Fe
W~P	1										
Fe ~P	0.9787***	1									
Ca~P	0.1111	0.3127	1								
Ac-OP	-0.8623***	-0.9479***	-0.5992**	1							
Alk-OP	-0.8301***	-0.9271***	-0.6459**	0.9982***	1						
ROP	-0.9959***	-0.9933***	-0.2007	0.9046***	0.8775***	1					
% sand	-0.9890***	-0.9983***	-0.2570	0.9277***	0.9037***	0.9983***	1				
%silt	0.9850***	0.9994***	0.2807	-0.9366***	-0.9140***	-0.9966***	-0.9997***	1			
%Clay	0.9946***	0.9947***	0.2137	-0.9102***	-0.8838***	-0.9999***	-0.9990***	0.9976***	1		
TOC	0.9708***	0.9994***	0.3461	-0.9585***	-0.9398***	-0.9886***	-0.9956***	0.9976***	0.9905***	1	
Fe	0.9621***	0.9976***	0.3781	-0.9677***	-0.9509***	-0.9828***	-0.9919***	0.9947***	0.9852***	0.9994***	1

Table 5.13c Correlation matrix between different fractions of phosphorus in sediment cores - 4-6cm.

4-6	W~P	Fe ~P	Ca~P	Ac-OP	Alk-OP	ROP	% sand	%silt	%Clay	TOC	Fe
W~P	1										
Fe ~P	0.5200*	1									
Ca~P	0.6411**	0.9889***	1								
Ac-OP	-0.6478**	-0.9876***	-1***	1							
Alk-OP	-0.6607**	-0.9847***	-1***	0.9999***	1						
ROP	-0.3192	-0.9755***	-0.9320***	0.9287***	0.9222***	1					
% sand	-0.0893	-0.8972***	-0.8217***	0.8166***	0.8066***	0.9724***	1				
%silt	0.0511	0.8796***	0.7992***	-0.7939***	-0.7834***	-0.9628***	-0.9993***	1			
%Clay	0.1402	0.9187***	0.8498***	-0.8452***	-0.8358***	-0.9831***	-0.9987***	0.9960***	1		
TOC	0.3182	0.9752***	0.93168***	-0.9284***	-0.9218***	-1***	-0.9727***	0.9630***	0.9833***	1	
Fe	0.4757	0.9987***	0.9800***	-0.9783***	-0.9746***	-0.9854****	-0.9186***	0.9028***	0.9376***	0.9853***	1

Table 5.13d Correlation matrix between different fractions of phosphorus in sediment cores - 6-10cm.

6-10	W~P	Fe ~P	Ca~P	Ac-OP	Alk-OP	ROP	% sand	%silt	%Clay	TOC	Fe
W~P	1										
Fe ~P	0.0177	1									
Ca~P	0.5815	0.8237	1								
Ac-OP	-0.4614	-0.8952	-0.9901	1							
Alk-OP	-0.2379	-0.9754	-0.9285	0.9715	1						
ROP	-0.1841	-0.9860	-0.9067	0.9569	0.9985	1					
% sand	-0.2327	-0.9765	-0.9265	0.9702	0.9999	0.9988	1				
%silt	0.0432	0.9997	0.8379	-0.9063	-0.9807	-0.9899	-0.9817	1			
%Clay	0.5172	0.8648	0.9970	-0.9980	-0.9543	-0.9364	-0.9527	0.8774	1		
TOC	0.2030	0.9826	0.9147	-0.9624	-0.9994	-0.9998	-0.9995	0.9870	0.9430	1	
Fe	0.7697	0.6519	0.9669	-0.9215	-0.8031	-0.7691	-0.8000	0.6711	0.9445	0.7813	1

Table 5.12e Correlation matrix between different fractions of phosphorus in sediment cores - 10-20cm.

10-20	W~P	Fe ~P	Ca~P	Ac-OP	Alk-OP	ROP	% sand	%silt	%Clay	TOC	Fe
W~P	1										
Fe ~P	0.8807	1									
Ca~P	-0.0772	0.4042	1								
Ac-OP	-0.4014	-0.7873	-0.8822	1							
Alk-OP	-0.6268	-0.9211	-0.7285	0.9652	1						
ROP	-0.5509	-0.8805	-0.7895	0.9855	0.9956	1					
% sand	-0.8463	-0.9977	-0.4657	0.8276	0.9455	0.9108	1				
%silt	0.9468	0.9863	0.2476	-0.6747	-0.8441	-0.7901	-0.9727	1			
%Clay	0.5104	0.8568	0.8180	-0.9925	-0.9000	-0.9989	-0.89	0.7599	1		
TOC	0.5900	0.9018	0.7598	-0.9764	-0.9989	-0.9989	-0.9292	0.8181	0.9955	1	
Fe	0.8863	0.99993	0.3933	-0.7799	-0.9164	-0.8748	-0.9968	0.9882	0.8506	0.8966	1

The water extractable fraction showed significant positive correlation with percentage of silt, clay, organic carbon, and Fe content in 0-2 and 2-4 cm layers (Table 5.13 a and 5.13b). This shows that a large part of the exchangeable fraction found as adsorbed phosphorus. The increase in silt and clay increases the surface area of the sediment, facilitating the adsorption of phosphorus. The higher percentage of W-IP at Station 1 and Station 2 may be due to the high amount of silt and clay percentage at these sites. Relatively high percentage of W-OP than W-IP at Station 3 also indicates that the adsorbed phosphate is less at this site.

The Fe-bound phosphorus was found as, positively correlated with percentages of silt, clay, organic carbon and iron content at all depths except 6-10 cm layer. In this layer, positive relationship was found with percentage of silt and organic carbon. The Fe/Al –P were significantly correlated with fine fraction of the sediment in French coastal area (Andrieux and Aminot, 2001). It was well known that clay, such as kaolinite, which is abundant in tropical sediments, is very efficient in phosphate adsorption. This fraction showed a significant negative correlation with acid extractable organic phosphorus, ROP, and percentage of sand at all depths.

No significant correlation was exhibited by Ca-bound phosphorus at 0-2, 2-4, and 10-20 cm layers. At 4-6 and 6-10 cm layers this fraction was positively correlated with total organic carbon and iron content and negatively correlated with organic fraction. Although different phosphorus minerals, is formed in diagenetic processes, can contribute to this fraction, apatite is the most important among them (Petterson *et al.*, 1988).

The size of the adsorbing particles has a strong relationship with the reactive surface area of the sediment. But many biogenic carbonates have complex physical structures, which would considerably reduce their reactive surface area (Walter and Morse, 1984). This will facilitate adsorption on to larger particle (Mc Glathery *et al.*, 1994). The same phenomenon was observed at north east Florida Bay (Koch *et al.*, 2001). It was also reported that (Andrieux and Aminot, 2001) that Ca bound phosphate showed variable distribution over size classes and as a function of sedimentary calcium. It was suggested that a significant correlation with fine particles and calcium suggest a metamorphic origin of Ca-P while the absence of correlation suggest a marine origin. The absence of correlation of concentrations of Ca-IP with fine particles indicated a marine origin of calcium bound phosphorus at these sites. Further more Ca-IP may of apatitic nature since its concentration increases down the core, indicated an inability to resuspend.

The concentrations of Ac-OP showed a significant positive correlation with other organic fractions, at all depths. A negative relationship was exhibited by this fraction with percentages of silt, clay, organic carbon and iron content.

A significant or weak negative correlation showed with percentage of sand with Alk-OP at all depths. This extract showed negative relationship with total organic carbon, iron content and in some depths percentage of clay. The presence of high organic matter in the sediment increases the probability of iron getting bound onto the humic matter (Selig and Schlungbaum, 2002). However no such correlation was observed in the present study.

Correlation analysis showed that a similar mechanism governed the phosphorus speciation at 0-2 and 2-4 cm layers. These layers remain oxygenated layers at all seasons. The 4-6, 6-10 and 10-20cm layers may become anoxic and this could influence the amount of different species of phosphorus present.

The annual mean concentrations of ΣTP were similar at Station 1 (1482μgg^{-1} - 1855 μgg^{-1}) and at Station 2 (1361μgg^{-1} – 1792 μgg^{-1}) but concentration were lower at Station 3 (483μgg^{-1}–741μgg^{-1}). It reflects large spatial difference of phosphorus due to different geographical and geomorphological locations. This result also indicated a trapping mechanism is operating for phosphorus in the mangrove ecosystem. At Station 1 and Station 2, denser vegetation was seen compared to Station 3, which facilitates trapping of nutrients discharged to this creeks from nearby systems. Also, Station 1 and Station 2 appear to be the sites with high sedimentation. Therefore the causes of chemical differences among the first two Stations and the third Station can ascribe to sedimentation, through which the system can act as a sink of suspended matter. Fabre *et al.* (1999) found that the difference in the major form of phosphorus at different mangrove sites in French Guiana were due to the sedimentation pattern at each sites and also the ability of these sites to function as a sink for suspended matter. At Station 1 bottom sediment exhibited maximum concentration of ΣTP, reflecting the capacity of retaining phosphates by mangrove sediments. It was observed (Silva *et al.*, 1998), that 99% of total phosphorus was (*R.mangle* trees plus sediment) present in sediments, suggesting a trapping mechanism. Station 2 is characterised by lower ΣTP values in surface and bottom sediments and higher values in subsurface sediments. The enrichment of P in sub-surface sediments may be due to the biogeochemical oxidation process occurring in this micro-environment caused by oxygen excreted from the below ground roots as given by Silva *et al.* (1998) (Scholander *et al.*, 1955). A similar observation was reported from Yangtze estuary (Min *et al.*, 2001). Wetlands function as major sink for suspended particles. Low flow rates and vegetation resistance enhance particle settling and associated particulate phosphorus. This results in accretion of organic matter and the building of new soil material. Influences of biotic processes like bioturbation, plant uptake and transpiration and root zone decomposition are some factors which affect the mobilization of P in wetlands. The order of abundance of each fraction at various depths gave an indication of bioturbation at mangrove sites. At Station 1, the order of abundance was similar in the first three layers, which indicated bioturbation at this site. Similarly, the identical nature of the first three layers at Station 2 also indicated bioturbation at this site. Unlike Station 1 and Station 2. core sediments at Station 3 recorded different order of abundance. Station 3 is characterized by resistant organic fraction of phosphate, which might be less labile than the other fractions.

Statistical Analysis – Analysis of Variance (ANOVA)

The data were analysed using three factor ANOVA between site, depth and fractions. ANOVA was done using minimum, maximum and mean concentration of each fraction. No significant differences were observed between depths (Table 5.14) although there were significant differences between fractions and between stations.

Minimum value analyses showed significantly higher phosphorus concentration at Station 1 followed by Station 2 and Station 3. Among fractions, Fe-IP had a significantly higher value followed by Ca-IP, Alk-OP, Ac-OP, ROP, Ca-OP Fe-OP, W-IP and W-OP. No significant differences were found between Fe-IP and Ca-IP (App. 23).

Maximum value ANOVA showed significantly higher values at Station 1 followed by Station 2 and Station 3. Regarding the fractions, the Fe-IP was significantly higher followed by Alk-OP, Ca-IP, Ca-OP, Ac-OP, Fe-OP, ROP, W-IP and W-OP. Almost equal concentrations were exhibited by Alk-OP and Ca-IP (App. 24).

Mean value ANOVA showed that Station 1 and Station 2 had significantly higher concentration of phosphorus than Station 3. Regarding fractions, as in the minimum and maximum values, Fe-IP showed significantly higher value followed by Alk-OP. The fraction Ca-IP also showed significantly higher value followed by Ca-OP, Ac-OP, ROP, W-IP and W-OP.

On the basis of the above analysis it appears that the sediments of the studied area composed of Fe-IP fraction than any other fraction. The Ca-IP and the Alk-OP fractions are next two major fractions.

5.3 CONCLUSION

Sequential fractionation techniques, providing an increased resolution of the sediment phosphorus pool, can be a useful tool to quantify fluxes between phosphorus forms and to improve our understanding of the processes and mechanism affecting phosphorus dynamics in an aquatic system. The study on vertical variation of phosphorus fractionation in sediments indicated that the variation of phosphorus forms with depth was susceptible to multifactor influences such as sedimentary environment, early diagenesis, grain sizes and anthropogenic activities. Depth profiles of P fraction were examined to provide information on P diagenesis as a function of various storage forms.

Among the three mangrove areas investigated, its particular form of phosphorus characterizes each site. The Fe-IP concentration exceeded any other fraction at Station 1 and Station 2. However at Station 3, Alk-OP fraction gave maximum values. High Fe-IP concentration suggest a rapid mineralization of organic phosphorus and readsorption on Fe (OOH) during sediment resuspension. Furthermore, as the relation between Fe-IP and bioavailable phosphorus is now well established, a high potential productivity of the suspended sediments and overlying water in these mangrove systems are anticipated.

Sum of phosphorus fractions were similar at Station 1 (1482µg g^{-1} – 1855 µg g^{-1}) and at Station 2 (1361µg g^{-1} – 1792 µg g^{-1}) but concentration were lower at Station 3 (483µg g^{-1}–741µg g^{-1}). It reflects large spatial difference of phosphorus due to different geographical and geomorphological locations. These results indicated the occurrence of trapping mechanism for phosphorus in the mangrove ecosystem. The denser vegetation seen at Station 1 and Station 2 (as compared to Station 3) facilitates trapping of sediment and nutrients discharged to these creeks from nearby systems.

The maximum concentration of sum of all fractions recorded at different depths at different Stations. At the Station 1, 10-20 cm depth, at Station 2, sub-surface sediment and at Station 3, 0-2 cm layer recorded maximum values. The accumulation of phosphorus in bottom sediments at Station 1 might be due to the phosphate retaining capacity of this sediment. The enrichment of phosphorus at Station 2 in sub-surface sediments may be due to the biogeochemical oxidation process occurring in this micro-environment caused by oxygen excreted from the below ground roots. The retaining capacity of phosphate in bottom sediments of Station 2 was found to be less than that of Station 1. This difference might be attributed to the difference in textural facies of bottom sediments of Station 1 and Station 2. The relatively low concentration in surface sediments at both Stations may be resulted from repeated phosphorus desorption from resuspended sediments to the coastal water.

W-IP, the easily exchangeable fraction in the sediment showed a general increase in concentration with increase in depth except at Station 2 beyond 10 cm depth. The general increase may be attributed to the elevated phosphate levels in interstitial water of the sediment. Desorption of phosphorus into pore water may be attributed to the anaerobic conditions prevail in the bottom layers of the sediment. Unlike W-IP, WOP fraction showed a general decrease with increasing depth. The increase in W-OP may associate with the presence of live sediment bacteria. The Fe-IP fraction showed general decrease down the core at these Stations except at Station 2, where a subsurface maximum was recorded. Seasonal variations in Fe-IP were found at three stations with maximum during post-monsoon and minimum recorded during pre-monsoon at all three stations. The Fe:P ratio in sediments found to vary from 9.08 (Station 3) to 14.26 (Station 1). Thus, based on these ratios, the sediments had a high capacity for binding phosphate to iron. Unlike the inorganic fraction the concentrations of Fe-OP were similar during three seasons other than the exceptionally higher values at Station 2. The maximum value of Fe-OP, recorded at Station 2, 4-6 cm layer may be due to the incidental presence of some plant or animal debris. The concentrations of Ca-IP showed an erratic behavior down the core at Station 1 and Station 2. The overall picture of the annual variation followed the general pattern at Station 3 with decreasing concentration down the core. Station 1 decreasing trend down the core except at 10-20 cm depth was noticed. While at Station 2 showed an increasing trend down the core with an exceptionally high value at 6-10 cm depth. Variation of Ca-IP in the study area confirmed the influence of sediment texture in its distribution. Ca-OP concentration showed a decrease with the increase in depth except at 6-10 cm depth. The Ac-OP fraction exhibited a general decrease in concentration down the core. A reversal of this trend was observed at depths beyond 10 cm at Station 1 and 6-10 cm depth at Station 2. The Ac-OP fraction mainly consisted of fresh organic matter, which decreases with increasing depth. The exceptionally high values recorded at 6-10cm depth at Station 2 may be due to occasional presence of root particles in sediment core.

Alk-OP generally decreases down the core except at Station 2 where a subsurface increase was found. NaOH, extract the humic bound phosphates and poly phosphates associated with bacteria. Therefore the general decrease down the core may be attributed to the decrease in bacterial biomass with increase in sediment depth. The marked subsurface increase in Alk-OP at Station 2 may be associated with the oxic environment prevalent at this Station. Generally ROP concentration showed a decrease down the core. However the ROP fraction found to concentrate in subsurface sediment at Station 2 and Station 3.

Seasonal changes in the chemical characteristics of phosphorus fractions in sediment cores might be due to difference in bacterial biomass, oxic or anoxic environment prevalent in sediment and different adsorption capacity of textural facies. Alk-OP was the major fraction during pre-monsoon at Station 1, which indicated an impact of untreated sewage into the creek. The subsequent increase in bacterial biomass in sediment during this season caused an anoxic environment, might due to the higher sulphate reduction. This resulted in reduction of Fe-oxides and subsequently the release of Fe-bound phosphate occurs. The monsoon flooding dilute the bacterial biomass and an increase in Fe-bound phosphorus occurred and maximum Fe-IP, recorded during post-monsoon.

Station 2, also showed low concentration of Fe-IP during pre-monsoon and a substantial increase in concentration of Ca-IP. The increase in salinity during this season decreased the phosphate adsorption onto Fe-oxides in sediment. Hence precipitation on to Ca^{+2} might be a more favorable process occurred. The increase in salinity of pore waters with increase in depth also supports the above conclusion. Generally, Fe-bound phosphorus was the major fraction of phosphorus, at Station 1 and Station 2. However at depths beyond 6cms, Station 2, recorded a major fraction of Ca-IP.

Analysis of Variance showed that core sediments at Station 1 and Station 2 composed of significantly higher ΣTP concentration than at Station 3. The Fe-IP concentration recorded significantly higher concentration than any other fraction. However the concentrations of Alk-OP and Ca-IP also observed as significant fractions next to Fe-IP.

References

Alongi, D.M., Boto, K.G. & Robertson, A.I. 1992 Nitrogen and Phosphorus Cycles. In *Tropical Ecosystems* (Robertson, A.I. & Alongi, D.M., eds). Coastal Estuarine Studies 41, American Geophysical Union, Washington, D.C., 251-292.

Alongi, D.M. 1991 The role of intertidal mud banks in the diagenesis and export of dissolved and particulate material from the Fly Delta, Papua New Guinea. *Journal Experimental Marine Biology and Ecology* **149,** 81-107.

Alongi, D.M. 1994 The role of bacteria in nutrient cycling in tropical mangrove and other coastal benthic ecosystem. *Hydrobiologia* **285**, 19-32.

Alongi, D.M. 1996 The dynamics of benthic nutrient pools and fluxes in tropical mangrove forest. *Journal of Marine Research* **54**, 123-148.

Alongi, D.M. 1988 Bacterial productivity and microbial biomass in tropical mangrove sediments. *Microbial Ecology* **15**, 59-79.

Alongi, D.M., Sasekumar, A., Tirendi, F. & Dixon, P. 1998 The influence of standage on benthic decomposition and recycling of organic matter in managed mangrove forests of Malaysia. *Journal Experimental Marine Biology and Ecology* **225**, 193-217.

Andrieux-Loyer, F. & Aminot, A. 2001. Phosphorus Forms related to sediment grain size and geochemical characteristics in French coastal areas. *Estuarine, Coastal and Shelf Science* **52**, 617-629.

Atkinson, M.J. 1987 Low phosphorus sediments in a hyper saline marine bay. *Estuarine, Coastal and Shelf Science* **24**,335-347.

Balchand, A.N. & Nair, S.M. 1994 Fractionation of phosphorus in the sediments of a tropical estuary. *Environmental Geology* **23**, 284-294.

Baldwin, S.D. 1996 The phosphorus compounds in a diverse series of Australian sediments. *Hydrobiologia* **335**, 63-73.

Bostrom, B., Anderson, J.M., Fleischerand, S. & Janson, M. 1988 Exchange of phosphorus across the sediment-water interface. *Hydrobiologia* **170**, 229-244.

Boto, K.G. 1988 The phosphorus cycle. In Mangrove Microbiology (Agate, A.D., Subramanian, C.V. & Vanucci, M., eds). UNDEP/UNESCO regional project (RAS/86/1988), New Delhi, pp. 85-100.

*Boyle, E.A., Collier, R., Dengler, A.T., Edmond, J.M., Ng, A.C. & Stallard, R.F. 1974 On the chemical mass-balance in estuaries. *Geochimica et Cosmochimica Acta* **38**,1719-1728.

Boyle, E.A., Edmond, J.M. & Sholkovitz E.R. 1977 The Mechanism of iron removal in estuaries. *Geochimica et Cosmochimica Acta* **41**, 1313-1324.

Brunskill, G.J., Zagorskis, I. & Pfitzner, J. 1998 Carbon burial rates in sediments of the Herbert River region of the Great Barrier Reef continental shelf, North Queensland, Australia. In *CO_2 Fixation and Storage in Coastal Ecosystems,* *Phase 1 collected reports Report 4* (Ayukai, T., ed.). Australian Institute of Marine science, Townsville, pp 1-20.

Carreira,-R.S. & De-L.R.Wagener,-A. 1998 Speciation of sewage derived phosphorus in coastal sediments from Rio de Janeiro, Brazil. *Marine Pollution Bulletin* **36**, 818-827

Chang, S.C. & Jackson M.L. 1957 Fractionation of soil phosphorus. *Soil science* **84**,133-144.

Chester, R. 2000 Sediment Interstitial Waters and Diagenesis. In *Marine Geochemistry*. II Edition. Blackwell Science, pp 357-404.

Clough, B.F., Boto, K.G. & Attiwill, P.M. 1983 Mangrove and Sewage: a re-evaluation. In *Tasks for vegetation science*, Vol. 8. (Teas, H.J., ed.) Dr. W. Junk Publishers, The Hague. (17), 151-161.

Comeau, Y., Hali, K.J., Hanrock, R.E.W. & Oldham, W.K. 1986 Biochemical model for enhanced biological phosphorus removal. *Water* **20**,1511-1521.

Crosby, S.A., Millward, G.E., Butler, E.I., Turner, D.R., Whitfield, M. 1984 Kinetics of phosphate adsorption by iron oxyhydroxides in aqueous system. *Estuarine, Coastal and Shelf Science*, 257-270.

Davelaar, D. 1993 Ecological significance of bacterial polyphosphate metabolism in sediments. *Hydrobiologia* **253**, 179-192.

*De Graff Bierbrauwer-Wiirtz, I.M. & Golterman, H.L. 1989 Fosfaatfracties in de bodem van een aantal Nederlandse meren. (in Dutch, with English summary). H_2O: 411-414.

De Groot, C.J. & Golterman, H.L. 1990 Sequential fractionation of sediment phosphate. *Hydrobiologia* **192**, 143-149.

De Groot, C.J. & Golterman, H.L. 1993 On the presence of organic phosphate in some Camargue sediments: evidence for the importance of phytate. *Hydrobiologia* **252**, 117-126.

De Groot, K.J. & Fabre, A.C. 1993 The impact of desiccation of a freshwater marsh (Garcines Nord, Camargue, France) on the sediment-water-vegetation interactions. Part 3: The fractional composition and the phosphate adsorption characteristics of the sediment. *Hydrobiologia* **252**,105-116.

De Haan, H. 1992 Impacts of environmental changes on the biogeochemistry of aquatic humic substances. *Hydrobiologia* **229**, 59-71.

De Jonge, V.N. & Villerius, L.A. 1989 Possible role of carbonate dissolution in estuarine phosphate dynamics. *Limnology and Oceanography* **34**, 332-340.

De Kanel, J. & Morse, J.W. 1978 The chemistry of orthophosphate uptake from sea water on to calcite and aragonite. *Geochimica et Cosmochimica Acta* **42**, 1335-1340.

DePinto, J.V., Young, T.C., Martin, S.C. 1981 Algal available phosphorus in suspended sediments from lower Great Lakes tributaries. *Journal of Great Lakes Research* **7**, 311-325.

Espejo, D.A., Serrano, L., Toja, J. 1999 Changes in sediment phosphate composition of seasonal ponds during filling. *Hydrobiologia* **392**, 21-28.

Fabre, A. 1988 Experimental studies on some factors influencing phosphorus solubilization in connection with drawdown of a reservoir. *Hydrobiologia* **159**, 153-158.

Fabre, A.C. 1992 Inorganic phosphate in exposed sediments of the river Garonne. *Hydrobiologia* **228**, 37-42.

Fabre, A., Fr. Fromard & Trichon, V. 1999 Fractionation of phosphate in sediments of four representative mangrove stages (French Guiana). *Hydrobiologia* **392**,13-19

Fabre, A., Qotbi, A., Dauta, A. & Baldy, V. 1996 Relation between algal available phosphate in the sediments of the river Garrone and chemically determined fractions. *Hydrobiologia* **335**, 43-48.

Francko, D.A. 1986 Epilemnetic phosphorus cycling : influence of humic materials and iron on coexisting major mechanisms. *Canadian Journal of Fisheries and Aquatic Sciences* **43**, 302-310.

Froelich, P.N., Klinkhanmu, G.P., Beudu, M.L., Luedtke, N.A., Heath, G.R., Cullen, D., Dauphion, P., Hanmond, D., Hartman, B. & Maynard, V. 1979 Early oxidation of organic matter in pelagic sediments of the eastem equatorial Atlantic: suboxic diagenesis. *Geochimica et Cosmochimica Acta* **43**, 1075-1090.

Gachter, R.J., Meyer, J.S. & Mares, A. 1988 Contribution of bacteria to release and fixation of phosphorus in lake sediments. *Limnology and Oceanography* **33**, 1542-1558.

Goedkoop, W. & Petterson, K. 2000 Seasonal changes in sediment phosphorus forms in relation to sedimentation and benthic bacterial biomass in Lake Erken. *Hydrobiologia* **431** : 41-50.

*Golterman H.L. & Booman, A. 1988 Sequential extraction of iron-phosphate and calcium phosphate from sediments by Chelating agents. Verh. Int. Ver. Limonol. **23**, 904-909.

Golterman, H.L. 1995 The labyrinth of nutrient cycles and buffers in wetlands: results based on research in the Camargue (Southern France). *Hydrobiologia* **315**, 39-58.

Golterman, H.L. 1996 Fractionation of sediment phosphate with chelating compounds: a simplification and comparison with other methods. *Hydrobiologia* **335**, 87-95.

Golterman, H.L. 1998 The distribution of phosphate over iron-bound and calcium bound phosphate in stratified sediments. *Hydrobiologia* **364**, 75-81.

Golterman, H.L., Paing, J., Serrano, L. & Gomez, E. 1998 Presence of and phosphate release from polyphosphates or phytate phosphate in lake sediments. *Hydrobiologia* **364**, 99-104.

Greenwood, N.N. & Earnshaw, A. 1997 Phosphorus. In *Chemistry of the Elements.* Pergamon Press, New York, pp. 545-555.

Hedges, J.I., Clark, W.A. & Cowie G.L. Cowie. 1988 Organic matter sources to the water column and surficial sediments of a marine bay. *Limnology and Oceanography* **33**, 1116-1136.

Hedley, M.J., Stewart, J.W.B. & Chauhan B.S. 1982 Changes in inorganic and organic soil phosphorus fractions induces by cultivation practices and by laboratory incubations. *Soil Science Society of America Journal* **46**, 970-976.

Hesse, P.R. 1963 Phosphorus relationships in mangrove swamp mud with particular reference to aluminium toxicity. *Plant and soil* **19**, 205-218.

Hieltjes, A.H.M. & Lijklema, L. 1980 Fractionation of inorganic phosphates in calcareous sediments. *Journal of. Environmental Quality* **9**, 405-407.

Holmboe. N., Kristensen, E. & Anderson, F.O. 2001 Anoxic Decomposition in sediments from a tropical mangrove forest and the temperate Wadden sea; implications of N and P addition experiments. *Estuarine, Coastal and Shelf Science* **53**,125-140.

*Hupfer, M. & Uhlmann, D. 1991 Microbially mediated phosphorus exchange across the mud-water interface. Verh Internat Verein Limnol **24**, 2999-3003.

Hupfer, M., Gachter, R. & Rugger, H. 1995 Polyphosphate in lake sediments: ^{31}P NMR spectroscopy as a tool for its identification. *Limnology and Oceanography* **40**, 610-617.

*Ingraham J.L., Maaloe, O. & Neidhardt, F.C. 1983 Growth of the Bacterial Cell, Sinauer, Sunderland, 435 pp.

Istvanovics. 1988 Seasonal variation of phosphorus release from sediments of shallow lake Balaton. *Water Research* **22**, 1473-1481.

Jensen, H.S. & Thamdrup, B. 1993 Iron-bound phosphorus in marine sediments as measured by bicarbonate-dithionate extraction. *Hydrobiologia* **253**, 47-59.

Jensen, H. S. & Anderson, F.O. 1992 Importance of temparature, nitrate and pH for phosphate release from aerobic sediments of four shallow eutrophic lakes. *Limnology and Oceanography* **37**, 577-589.

Jensen, H.S., McGalathy, K.J., Marino, R. & Howarth, R.W. 1998 Forms and availability of sediment phosphorus in carbonate sand of Bermuda seagrass beds. *Limnology and Oceanography* **43,** 799-810.

Jones, R.I., Shaw, P.J. & De Haan, H. 1993 Effects of dissolved humic substances on the speciation of iron and phosphate at different pH and ionic strength. *Environmental Science and Technology* **27**,1052-1059.

Joseph, P.M. 2001 Distributional characteristics of phosphate and some trace metals in the interstitial waters of riverine, estuarine, and mangrove systems. *M.Phil. dissertation submitted to Cochin University of Science and Technology*, Cochin 16, 49pp.

Kairesalo, T., Tuominen, T., Harikainen, K. & Rankinen, K. 1995 The role of bacteria in the nutrient exchange between sediment and water in a flow-through system. *Microbial Ecology* **29**, 1219-144.

Kitano, Y., Okumara, M. & Idogaki, M. 1978 Uptake of phosphate ions by calcium carbonate. *Geochemical journal* **12**, 29-37.

*Kouwe, F.A. & Golterman, H.L. 1976 Rol van bodemfosfaten in het eutrophieringsproces. (In Dutch) H_2O **9**, 84-86.

Koch, M.S., Benz, R.E. & Rudnick, D.T. 2001 Solid phase phosphorus pools in highly organic carbonate sediments of Northeastern Florida Bay. *Estuarine Coastal and Shelf Science* **52**, 279-291.

Kristensen, E. 1990 Characterization of biogenic organic matter by stepwise thermogravimetry (STG). *Biogeochemistry* **9**, 135-159.

Kristensen, E., Jensen, M.H., Banta, G.T., Hansen, K., Holmer, M. & King, G.M. 1998 Transformation and transport of inorganic nitrogen in sediments of a Southeast Asian mangrove forest. *Aquatic Microbial Ecology* **15**, 165-175.

Lijklema, L. 1977 The role of iron in the exchange phosphate between water and sediments. In *Interactions between sediments and freshwater* (Golterman, H.G., ed). Dr. W. Junk Publishers, The Hague: 313-317.

Lopez, P., Lluch, X., Vidal, M. & Morgui, J.A. 1996 Adsorption of phosphorus on sediments of the Balearic Islands (Spain) related to their composition. *Estuarine, Coastal and Shelf Science*, Coastal and Shelf Science **42**,185-196.

Mc Glathery, K.J., Mariand, R., Howarth, R.W. 1994 Variable rates of phosphate uptake by shallow marine carbonate sediment: Mechanisms and ecological significance. *Biogeochemistry* **25**,127-146.

Mesnage, V. & Picot, B. 1995 The distribution of phosphate in sediments and its relation with eutrophication of a mediterranian coastal lagoon. *Hydrobiologia* **297**, 29-41.

Mesnage, V., Bonneville, S., Laignel, B., Lefebvre, D., Dupont, J.P. & Mikes, D. 2002 Filling of a wet land (Seine estuary, France): natural eutrophication or anthropogenic processes? A sedimentological and geochemical study of wetland organic sediments. *Hydrobiologia* **475/476**, 423-435.

Min, L., Shiyuan, X., Lijun, H. & Dongni, O. 2001 Phosphorus forms in sediments and their distribution in the Yangtze estuary and coastal areas. *Marine Science Bulletin* **3**, 55-62.

*Morel, F.M.M. & Hering, J.G. (eds) 1993 Principles and applications of Aquatic Chemistry, John Wiley and Sons, Inc., New York.

Morse, J.W. 1986 The surface chemistry of calcium carbonate minerals in natural waters: An overview. *Marine Chemistry* **20**, 91-112.

Noges, P. & Kisand, A. 1999 Horizontal distribution of sediment phosphorus in shallow eutrophic lake Vortsjarv (Estonia). *Hydrobiologia* **408/409**, 167-174.

Ostrofsky, M.L. 1987 Phosphorus species in the sacrificial sediments of lakes of Eastern North America. *Canadian Journal of Fisheries and Aquatic Sciences* **44**, 960-966.

Paludan, C. & Morris, J.T. 1999 Distribution and speciation of phosphorus along a salinity gradient in intertidal marsh sediments. *Biogeochemistry* **45**, 197-221.

Pardo, P., Lopez-Sanchez, J.F. & Rauret, G. 1998 Characterisation, validation and comparison of three methods for the extraction of phosphate from sediments. *Analytica Chimica Acta* **376**, 183-195.

Petterson, K., Bostrom, B. & Jacobsen, O.-S. 1988 Phosphorus in sediments-specification and analysis. *Hydrobiologia* **170**, 91-101.

*Patrick, W.H. & Mahapatra, I.C. 1968 Transformation and availability to rice of nitrogen and phosphorus in waterlogged soils. *Advances in Agronomy* **20**, 323-359.

Ramanathan, A.L. 1997 Sediment characteristics of Pichavaram mangrove environment, south east cost of India. *Indian Jornal of Marine Sciences* **26**, 319-322.

Reddy, K.R., Kadlec R.H., Flaig, E. & Gale, P.M. 1999 Phosphorus retention in streams and wetlands: A review. *Critical. Rev. Environmental Science and Technology* **29**, 1-64.

Rippey, B. 1977 The behaviour of phosphorus and silicon in undisturbed cores of Lough Neagh sediments. In *Interactions between sediments and freshwater* (Golterman, H.L., ed). Dr. W. Junk Publishers, The Hague: 348-353.

Ruttenburg, K.C. 1992 Development of sequential extraction method for different forms of phosphorus in marine sediments. *Limnology and Oceanography* **37**, 1460-1482.

Ruttenburg, K.C. & Berner, R.A. 1993 Authigenic apatite formation and burial in sedimentsfrom non-upwelling continental margin environments. *Geochimica et Cosmochimica Acta* **57**, 991-1007.

Scholander, P.F., Van Dam, L. & Scholander, S.I. 1955 Gas exchange in the roots of mangroves. *American Journal of Botany* **42**, 92-98.

Selig, U. & Schlungbaum, G. 2002 Longitudinal patterns of phosphorus and phosphorus binding in sediment of a low land lake-river system. *Hydrobiologia* **472**, 67-76.

Siljestrom, P.A. & Clemente, L.E. 1990 Geomorphology and soil evolution of a moving dune system in South-West Spain (Donana National Park). J. Arid Envir. **18**, 139-150.

*Silva, C.A.R., Lacerda, L.D., Silva, L.F.F. & Rezende, C.E. 1991 Forest structure and biomass distribution in a red mangrove stand, Septia Bay, Rio de Janeiro. *Revista Brasileira de Botanica* **14**, 21-25.

Silva C.A.R. & Mozeto, A.A. 1997 Release and retention of phosphorus in mangrove sediments: Sepetiba Bay, Brazil In *Mangrove Ecosystem Studies in Latin America and Africa* (Kjerfve, B., Lacerda, L.D. & Diop, E.H.S., eds). United Nations Educational Publisher, The Hague, 179-190.

Silva, C.A.R., Mozeto, A.A. & Ovalle, A.R.C. 1998 Distribution and fluxes as macrodetritus of phosphorus in red mangroves, Sepetiba Bay, Brazil. *Mangroves and Salt Marshes* **2**, 37-48.

Silva C.A.R. & Sampio, L.S. 1998 Speciation of phosphorus in a tidal floodplain forest in the Amazon estuary. *Mangroves and Salt Marshes* **2**, 51-57.

*Sinke, A.J.C. & Cappenberg, T.E. 1988 Influence of bacterial processes on the phosphorus release from sediments in eutrophic Loosdrecht Lakes, The Netherlands. Arch Hydrobiol Beih Ergebn Limnol **30**, 5-13.

Smith III, T.J., Boto, K.G., Frusher, S.D. & Giddins, R.L. 1991 Keystone species and mangrove forest dynamics: the influence of burrowing crabs on soil nutrient status and forest productivity. *Estuarine, Coastal and Shelf Science* **33**, 419-432.

*Stumm, W & and Leckie, J.O. 1970 Phosphate exchange with sediments; its role in the productivity of surface waters, In *advances in water pollution research.* Pergammon Press, New York, pp 1-16.

Stumm, W. & Morgan, J.J. 1981 Aquatic Chemistry An introduction emphasizing chemical equilibria in natural waters (2nd edn.). Wiley interscience. pp. 625-640.

Suess, E. 1973 Interaction of organic compounds with calcium carbonate - II. Organo-carbonate association in recent sediments. *Geochimica et Cosmochimica Acta* **37**, 2435-2447.

Sundareshwar, P.V. & Morris, J.T. 1999 Phosphorus sorption characteristics of intertidal marsh sediments along an estuarine salinity gradient. *Limnology and Oceanography* **44**, 1693-1701.

Suzumura M. & Kamatani A. 1995 Mineralization of inositol hexaphosphate in aerobic and anaerobic marine sediments: Implications for the phosphorus cycle. *Geochimica et Cosmochimica Acta* **59**, 1021-1026.

Tam, N.F.Y. & Wong, Y.S. 1994 Nutrient and heavy metal retention in mangrove sediment receiving waste water. *Water Science Technology* **29**, 193-200.

Tam, N.F.Y. & Wong, Y.S. 1995 Mangrove soils as sink for wastewater-borne pollutants. *Hydrobiologia* **295**, 231-241.

Tam, N.F.Y. & Wong, Y.S. 1996 Retention of wastewater-borne nitrogen and phosphorus in mangrove soils. *Environmental Technology* **17**, 851-859.

Tornblom, E. & Rydin, E. 1998 Bacterial and phosphorus dynamics in profoundal Lake Erken sediments following the deposition of diatoms: a laboratory study. *Hydrobiologia* **364**, 55-63.

Vaithiyanathan, P., Jha, P.K. & Subramanian, V. 1993 Phosphorus distribution in the sediments of the Hooghly (Ganges) Estuary, India. *Estuarine Coastal and Shelf Science* **37**, 603-614.

Wafar, S., Untawale, A.G. & Wafar, M. 1997 Litter fall and energy flux in a mangrove ecosystem. *Estuarine, Coastal and Shelf Science* **44**, 111-124.

Walter, L.M. & Morse, J.W. 1984 Reactive surface area of skeletal carbonates during dissolution: effect of grain size. *Journal of Sedimentary Petrology* **54,** 1081-1090.

Warra, T., Janson, M., Petterson, K. 1993. Phosphorus composition and release in sediment bacteria of the genus Psudemonas during anaerobic and aerobic conditions. *Hydrobiologia* **253**, 131-140.

Wentzel, M.C., Lotter, L.H., Ekama, G.A., Loewenthal, R.E. & Marais, G.V.R., 1991 Evaluation of biochemical models for biological excess phosphorus removal. *Water Science and Technology* **23**, 567-574.

White D., Davis, W., Nickels, J. & Bobbie R. 1979 Determination of the sedimentary microbial biomass by extractable lipid phosphate. *Oecologia* **40**, 51-62.

Williams, J.D., Shear, H. & Thomas, R.L. 1980 Availability to Scendesmus quadricauda of different forms of phosphorus in sedimentary materials from the Great Lakes. *Limnology and Oceanography* **25**, 1-11.

Williams, J.D.H., Jaquet, J.M. & Thomas, R.L. 1976 Forms of phosphorus in the surfacial sediments of lake Erie. *Journal of the Fisheries Research Board of Canada* **33**, 413-429.

Williams, J.D.H., Syers J.K., Harris, R.F. & Armstrong D.E. 1971 Fractionation of soil inorganic phosphate in calcareous lake sediments. *Soil Sci. Soc. Am. Proc.* **35**, 250-255.

Wong, Y.S., Lan, C.Y. & Chen, G.Z. 1995 Effect of wastewater discharge on nutrient contamination of mangrove soils and plants. In *Asia-Pacific Symposium on Mangrove Ecosystems* (Wong, Y.S. and Tam, N.F.,Y., eds). Kluwer Academic publishers, The Netherlands, pp. 243-254.

*Yen, T.F. 1999 Environmental Chemistry, Chemical Principles for Environmental Proccesses. Prentice-hall, Inc., New Jersey.

Young, T.C., DePinto, J.V., Martin, S.C. & Bonner, J. 1985 Algal available particulate phosphorus in the Great Lakes basin. *Journal of Great Lakes Research* **11**, 434-446.

* Not referred in original

Chapter 6

SUMMARY

The spatial and temporal distribution of nitrogen and phosphorus in mangrove fringed creek waters and sediments were investigated with a view to determine the variability of phosphorus speciation in water column as well as in sediments. General hydrographic features and sediment characteristics were also investigated to ascertain the influence of these factors on phosphorus speciation. Monthly observations were made during the period December 1999 to December 2000. Three mangrove-fringed creeks around Cochin estuary were selected according to plant density. Station 1 was located near the terminus of a 5-7 feet wide canal. It is about 1km distant from adjoining estuarine water body. Station 2, represented a carefully preserved mangrove habitat inside the premises of Kerala Agricultural University campus. Station 3, Aroor is located on the southern part of Cochin estuary while Station 1 and Station 2 were located in an island in Cochin estuary.

Surface water and sediment cores to a depth of 20cm were collected at monthly intervals. Without much of compaction sediment cores were taken out from the corer and fractionated into five layers at depths 2cm, 4cm, 6cm, 10cm and 20cm. General hydrographic features were noted. Surface and core sediments were analysed for basic sediment characteristics as well as for total elemental concentrations of carbon, nitrogen and phosphorus. Phosphorus fractionations were carried out by sequential extraction with chelating compounds.

The annual mean values of salinity, recorded a minimum of 11.28 x 10^{-3} at Station 3 and maximum of 18.41 x 10^{-3} at Station 2. Station R recorded a mean salinity value of 11.26 x 10^{-3}. High salinity values at Station 1 and Station 2 indicated that no real flushing took place at two Stations according to the tidal dynamics of the estuary. On the other hand Station 3 exhibited salinities that were similar to Station R. Remarkably higher salinities at Station 1 and Station 2 during pre-monsoon might be due to isolation of the head of the creek from near shores. The isolation resulted in low fresh water discharge, in turn a maximum salinity regime found at the head of the creek. Low pH values were recorded at Station 3, while all other Stations recorded alkaline pH values. During pre-monsoon season Station 1 also exhibited a low pH, probably due to microbial activity in surface waters. Water temperatures were found to vary within normally expected ranges at all the stations. The lowest annual mean value of 29.1°C recorded at Station 1, 29.5°C at Station 2, and 30.2°C at Station 3. A clear seasonal variation was found at all three stations. As expected, the maximum temperature was recorded during pre-monsoon at all stations. Suspended sediments associated with river influx and plant litter may contribute to the large amount of TSS at the creek waters under study area. The maximum concentrations of TSS varied between 150.13mgL^{-1} and 360.80mgL^{-1} at the three mangrove-fringed creek waters as against the 88.41mgL^{-1}, the maximum TSS concentration exhibited at Station R. The annual mean POC concentrations at three mangrove-fringed Stations were found to be 7.19mgL^{-1}, 6.85mgL^{-1}, and 5.06mgL^{-1} respectively. At Station R an annual mean value of 4.19mgL^{-1} was recorded. Bacterial density, phytoplankton productivity as well as the presence of fine sediment in particulate matter resulted in an elevated concentration of POC in mangrove creek waters.

Uptake by trees and microorganisms and by sorption on to the sediment matrix considerably reduces nitrate concentrations in mangrove forests, which in turn make it an effective sink for nutrients. Significantly higher concentrations of nitrate-N were recorded at Station R than the mangrove fringed creek waters. A general trend of nitrite nitrogen distribution showed minimum values during pre-monsoon at Station 1 and Station 2. The maximum value recorded at Station 1 during monsoon and during pre-monsoon at Station 3 might be due to the bacterial activity in surface water. The annual mean ammonium concentrations recorded at Stations 1, 2, 3 and R were 13.28µmolL^{-1}, 32.90µmolL^{-1}, 11.54µmolL^{-1}, and 14.11µmolL^{-1} respectively. Remarkably high concentration at Station 2, may be due to the localized regeneration from sediments.

The N:P ratio at mangrove-fringed creek waters were varied between 1.36 and 5.70 and Station R showed an annual mean value of 4.48. The significantly lowered ratio at Station 1 and Station 2 could be due to an enhanced concentration of DIP. The above ratios suggest that the mangrove-fringed creeks of Cochin estuary represent an anthropogenically altered ecosystem.

The annual mean values of DIP showed a variation from 1.51µmol L^{-1} (Station 3) to 10.70µmol L^{-1} (Station 2). Station R recorded an annual mean value of 2.07µmol L^{-1}. Remarkably higher concentration of DIP was found during monsoon at Station 1 and decrease of the same occurred during post-monsoon at Station 1. The relationship between seasonal pattern of phosphate in water and flux of phosphate from sediments is an evidence for the regeneration of benthic phosphate affects water column DIP concentrations. The high concentration of DIP at Station 2, during pre-monsoon may be as a result of the evapotranspiration. The DIP concentrations recorded at Station 3 and Station R were similar during the study period. The DOP concentrations in surface waters showed a variation from 0.01µmolL^{-1} at Station 3 to 11.96µmolL^{-1} at Station 1. The minimum and maximum DOP concentrations recorded at Station R were 0.13 µmolL^{-1} and 3.23µmolL^{-1} respectively.

Particulate phosphorus concentration found to vary between 0.49µmolL^{-1} at Station 2 and 55.40µmolL^{-1} at Station 2 in creek waters. However at Station R, PP concentrations varied from 0.58µmolL^{-1} to 8.40µmolL^{-1}. Seasonal variations showed maximum concentrations of PP during monsoon at all Stations except at Station R, where maximum concentration was found during pre-monsoon. The distributions of particulate phosphorus depend on the suspended sediment brought in by the river discharge and not on the particulate matter formed during the estuarine mixing. Low concentrations of TP were observed during post-monsoon at all Stations. The annual mean concentrations of TP showed maximum value at Station 2 and a minimum value at Station R. TP concentrations indicated phosphorus loading in the water column of mangrove creeks (Station 1 and Station 2) than Station 3 and estuarine reference Station. Station 1 recorded relatively higher TP concentration during monsoon and pre-monsoon. Phosphorus may enter a water body through the inflows, precipitation, dry fallout and from the sediments, and it may be removed by sedimentation and through the outflow.

Concentrations of nitrate, nitrite and ammonium showed significant difference between Stations (ANOVA). Significantly higher concentrations of nitrate and nitrite were recorded at Station R, while Station 2, recorded higher concentrations of ammonium. Contrary to the inorganic nitrogen species, DIP and DOP concentrations exhibited significantly higher concentrations at Stations 1 and 2 than at Stations 3 and R. At the mangrove creek waters, TSS concentrations showed significant positive correlations with POC, DIP, TP, PP and ammonium concentrations, while no such correlations could be observed at Station R. Correlation analysis of ammonium with other parameters showed significant positive correlation with TSS, DIP, PP and TP. However, dissolved ammonium levels were found to be negatively correlated with dissolved oxygen.

Analysis of relative composition of each form of phosphorus revealed that the PP concentrations were greater than DIP concentrations which in turn was greater than DOP at all stations except at Station 1; where phosphorus was partitioned into about 34.5% PP, 48.4% DIP and 17.1% DOP. The observed high percentage of DIP at Station 1 during the present study may be resulted from the high fraction of iron bound phosphate in the sediment. Anderson and Jensen (1992) have shown that Fe-bound P, when present in significant proportions in the sediment, may be a major source for internal P loading in shallow, eutrophic lakes, just as it may be in deeper, stratified lakes. At Station 2 the relative composition of each form of phosphorus observed were 51.4% PP, 39.3% DIP and 10.5% DOP while Station 3, recorded the percentage composition of PP, DIP and DOP as 65.4%, 21.2% and 13.4% respectively. The reference Station gave a composition with 61.3% PP, 26.7% DIP and 21% DOP. Differences in speciation of phosphorus in water column among the studied area can be ascribed to local characteristics, such as extent of fresh water in put, land run-off, tidal amplitude and productivity of biota.

Textural studies indicated the nature of surface sediment to be sandy mud, sandy silt and muddy sand at Stations 1, 2 and 3 respectively. The well-developed mangroves at Station 1 and Station 2 support the root system of mangroves, which has a dense grid of vertical pnuematophores and arial roots. This structure traps floating detritus and reduces tidal flow, eventually creating conditions where suspended clay and silt particles settle, whereas the lack of vegetation as well as tidal influence and impact of waves remove finer fractions (silt + clay) of the sediment.

The mean moisture percentages recorded higher values at Station 1 and Station 2. The spatial and seasonal variation in moisture content could be attributed to the variation of organic matter and grain size of the sediment. Generally, higher pH values were observed at Station 1 and Station 2, while lower pH values were recorded at Station 3. Minimum pH values were recorded during pre-monsoon or post-monsoon at all Stations and maximum values were recorded during monsoon season.

The concentrations of TOC in surface sediments of Station 1 and Station 2 were very high when compared with that of Station 3. The prevalent hydrodynamics at Station 1 and Station 2 and the presence of well developed mangrove roots retained fine fraction of surface sediment. The results indicate that Station 1 and Station 2 were composed of organic rich surface sediment, capable of trapping nutrients. Similarly TN concentrations, recorded a minimum of 0.97mg g^{-1} at Station 3 and maximum concentration of 4.90mg $g^{-1}$was recorded at Station2. The seasonal variation of TN concentration showed maximum concentrations during pre-monsoon and minimum concentrations during monsoon at all Stations. The seasonal variations may be attributed to the variation in TOC concentrations as well as with the adsorbed ammonium present in the sediment, since exchangeable ammonium was found to be positively correlated with TN concentrations. The concentrations of TP recorded were similar at Station 1 and Station 2, were varied from 1.12mg g^{-1} to 2.10mg g^{-1} but sediments of Station 3 were significantly lower, ranging from, 0.49mg g^{-1} to 0.80mg g^{-1}. Remarkable spatial variation with higher values at first two Stations might be attributed to different hydrodynamic regime. Station 3 was marked by the overbearing of coarse fraction, which inhibits accumulation of phosphorus in sediments. The maximum salinity at Station 2 may cause precipitation of dissolved phosphorus and hence a maximum concentration was recorded during pre-monsoon. The cycling of phosphorus in the studied area is highly dynamic at least at first two Stations, where the sediments act as an efficient sink for phosphorus as far as an aerobic environment prevailed.

The exchangeable inorganic nutrient concentrations were found to be low in other mangrove ecosystem due to plant intake and solubility of these in surface water. Exchangeable ammonium concentrations in surface sediments varied between 0.08μmol g^{-1} (Station 3) and 0.84 μmol g^{-1} (Station 1 and Station 2), while exchangeable nitrate concentration ranged between 3.29 nmolg^{-1} (Station 3) to 64.31nmolg^{-1} (Station 1). A regular tidal incursion at Station 3 may remove ammonium from the sediment as it is soluble in water. Seasonal variations were found with comparatively higher values during pre-monsoon and post monsoon at Station 1 and Station 2.

The C/N ratios of surface sediments were ranged between 16.57 and 35.32 at all Stations. However at Station 2, surface sediments exhibited a C/N variation of 16.57 and 28.18, which indicated an origin of mangrove detritus at this site. The high C/N ratios observed at Station 1 and Station 3, during the present investigation may be attributed to the accumulated organic carbon at Station 1, and humic derived nitrogeneous organic matter (biogenic origin) at Station 3. Relatively lower ratios observed at Station 2, indicate a mangrove detrital origin. The mangrove detritus were associated with the tight coupling between microbial mineralization and assimilation in organic sediments of the studied mangrove area.

The low N:P ratios (1.50 to 3.27) observed in the study area were due to comparatively high concentration of TP. N:P ratio can be taken as an index of the extent of extraneous influence on a productive water body, since the nitrogen if produced is autochthonous, variation in N:P depend on phosphorus which is mostly external. These ratios observed during the present study indicated an abiogenic origin of phosphorus in the mangrove fringed creek sediments.

The C/P ratios varied between 34.68 (Station 2, monsoon) and 68.00 (Station 2, post-monsoon). The observed C/P ratio revealed that the accumulated phosphorus load in creek waters could be reduced by the mangrove plants and associated micro-organisms. However to arrive at the cause of deviation from Redfield stoichiometry requires more information on the kind of litter produced in this area, and also on the influence of microbes on carbon, nitrogen and phosphorus dynamics in this particular ecosystem. Outwelling of mangrove litter significantly influences sediment concentrations of TOC, TN and stoichiometric ratios of C:N:P (Alongi, 1990).

Grain size analysis of core sediments recorded similar observation as that of surface grain size analysis at all Stations except in 4-6 cm layer at Station 1 and in 10-20 cm layer at Station 2. The major textural facies in sediment core at Station 1 was sandy mud with a mud layer at 4-6 cm interval. However sediment core at Station 2 was predominantly composed of sandy mud sediment with an intercalation of 10 cm thick muddy sand was recorded at a depth of about 10cm from the surface. According to Flach and Heip(1996), a homogeneous distribution pattern of grain size in the vertical column of sediment suggests a constant mixture by bioturbation effects.

The moisture percentage in sediment cores varied between 29.40% (Station 3) and 61.76% (Station 2). Generally moisture percentage decreased down the core at all Stations. The moisture percentage showed a significant positive correlation with organic carbon. The annual mean values of moisture showed identical percentage at Station 1 and Station 2 due to the similar textural attributes at these stations, while less moisture percentage were recorded at Station 3, due to predominant muddy sand nature of the sediment. Seasonal variation in pH values in core sediments recorded the maximum values during monsoon while minimum values were recorded during pre-monsoon at Station 1 and 2. However a remarkable decrease was noticed beyond 10cm depth at the same Stations. All other depths showed an increase in pH values with an increase in depth during all three seasons. The three mangrove locations showed pH values as that of an alkaline nature of sediment up to 20cm of depth with an exceptions during pre-monsoon at Station 1 and Station 3. The annual variation of pH values in core sediments showed a general increase down the core at all Stations indicated an alkaline condition in sediment till 20cm of depth.

TOC concentration in the sediment cores varied between as low as 10.62mg g^{-1} (Station 3) and as high as 140.23mg g^{-1} (Station 1). Remarkably higher TOC concentrations were observed at Station 1 and Station 2 compared with Station 3. Generally highest values of TOC observed at the top and lowest contents recorded at 20-30 cm layer may be attributed to the particles loosened and suspended by the wave action during inundation of the forest and flushed into the creek and deposit as a silt layer on the sediment surface. Litterfall in the forest floor accounted for about 45% of the total detritus in a mangrove area. However subsurface increases in TOC concentration were found only at Station 1 and Station 2, suggesting an accumulation of organic carbon in subsurface sediment. Higher values of TN concentrations were recorded during all seasons at Station 1 and Station 2 than at Station 3. Nitrogen fixation by cyanobacteria and heterotrophic bacteria which are abundant on all inhabitable surfaces in mangrove ecosystem, mineralization processes associated with the ammonium assimilation by microphyto benthos and plants, the production of mucopoly saccharide exudates by bacteria and their incorporation into humic compounds enhance the TN concentrations in surface sediment. Also TN correlated positively with TOC and negatively with sediment C/N ratio at 0-2 and 2-4cm depth This indicated that decrease in C:N ratio was mainly due to the increased organic nitrogen in the sediment. It is possible that the increase in TN and thus decrease in C/N ratio in the sediment may be partly attributed to the increase of chlorophyll-containing labile materials.

The minimum and maximum values of exchangeable nitrate recorded were 2.71μmolg^{-1} (Station 3) and 90.67μmolg^{-1} (Station 2) respectively. Comparatively higher values were recorded at Station 1 and Station 2 than at Station 3. A general pattern of exchangeable nitrate concentrations, with an increase in sub-surface sediment followed by a gradual decrease down the core was noticed at all Stations except at Station 3. Active growth of plants might cause the decrease of this nutrient with depth. Alternatively tidal incursions can also remove nitrate at Station 3 where tidal influence is maximum.

The ammonium concentrations varied between 0.08μmol g^{-1} (Station 3) and 0.84μmol g^{-1} (Station 1). Higher ammonium concentrations were noticed at Station 2 than other Stations may be attributed to high organic carbon and clay as they provide greater surface area for adsorption of the cations. Annual variation in depth pattern showed an increase in exchangeable ammonium concentrations with an increase in depth at Station 1 and Station 2. The ammonium concentration increases with depth in the anaerobic soil, indicating denitrification beyond rhizopheres.

TP concentrations were similar at Stations 1 and 2. The overall picture of the annual variation followed the general pattern of decreasing phosphorus concentration with increasing depths at Station 1 and Station 3, except at 10-20 cm depth at Station 1. Associated with the high silt and clay percentage, a significantly high concentration of TP was recorded at the first two stations. The present observation indicated the sediments at Station 1 and Station 2 were better nutrient sinks than at Station 3 due to its ability to immobilize phosphorus in an oxidised sediment-water interface. TP concentrations were high in surface and subsurface sediments indicated the contribution of below ground roots in maintaining oxidised surface sediment. The oxidative reactions would limit the desorption of phosphate into overlying water, since most of the phosphorus being bound to non-reactive metals, particularly as iron and manganese oxyhydroxides.

The C/N ratios recorded at Station 1 and 3 were remarkably higher than at the other two Stations. C/N ratio varied from 19.09 (2-4cm) to 36.16 (10-20cm), 15.61 (4-6cm) to 38.33 (10-20cm), and 10.48 (4-6cm) to 56.62 (10-20cm) at Station 1, Station 2 and Station 3 respectively. Annual variations in depth profile showed a general pattern of a sub-surface decrease followed by a remarkable increase beyond 10 cm depth at all stations. The fringing mangrove Station 1, have high C:N ratios indicating an accumulation of carbon relative to nitrogen; this carbon probably originates from debris washed on to strand lines. The C/N ratio fluctuated during monsoon season when fresh water discharge was greater and this indicated that besides mangroves and associated biota, terrigenous organic matter brought in by fresh water discharge continuously added detritus to the mangrove ecosystem also varied the stoichiometric ratios at these sites. N:P ratios in core sediments showed a gradual decrease down the core may be attributed to the decrease of TN, since only TN concentrations showed a significant decrease with increasing depth (App.16). The highest N:P ratios were observed in surface/ subsurface sediment at all Stations, where TN concentrations showed significantly higher values. The value of N/P ratio ranged between 0.82 and 4.47 and were far below the N:P ratio of planktons, indicating the abiogenic nature of phosphorus in the studied area.

The minimum and maximum C/P ratios observed in sediment cores were 25.67 (Station 3) and 83.22 (Station 2) respectively. Generally a sub-surface increase in C/P ratios was observed at Station 1 and Station 3. The decrease in C/P ratios beyond 10cm depth may be associated with minimum concentrations of TOC in this layer. The high organic carbon as well as relatively high C/P ratio observed at Station 1 and 3 indicted that a major portion of the phosphorus in sediment undergoes bacterial mineralisation. Further more it was also established that mangrove leaf litter found to harbour a large population of bacteria that appear to be highly productive.

Fractionation of phosphorus was carried out using the EDTA method (Golterman, 1996). The study on vertical variation of phosphorus fractions in sediments indicated that the variation of phosphorus forms with depth was susceptible to multifactor influences such as sedimentary environment, early diagenesis, grain sizes and anthropogenic activities. Depth profiles of P fraction were examined to provide information on P diagenesis as a function of various storage forms.

Sum of phosphorus fractions were similar at Station 1 ($1482\mu gg^{-1}$-$1855\ \mu gg^{-1}$) and at Station 2 ($1361\mu gg^{-1}$ – $1792\ \mu gg^{-1}$) but concentration were lower at Station 3 ($483\mu gg^{-1}$–$741\mu gg^{-1}$). It reflects large spatial difference of phosphorus due to different geographical and geomorphological locations. These results indicate the occurrence of trapping mechanism for phosphorus in the mangrove ecosystem. The denser vegetation seen at Station 1 and Station 2 (as compared to Station 3) facilitates trapping of sediment and nutrients discharged to these creeks from nearby systems. It appears that very high phosphate adsorption capacity exist in the sediments of Station 1 and Station 2 in accordance with the amount of iron bound phosphorus fraction while the major fraction obtained at Station 3 was organically bound phosphorus and calcium-bound inorganic phosphorus.

The W-IP concentrations recorded a general increase down the core may be attributed to the elevated phosphate levels in interstitial water of the sediment. Desorption of phosphorus into pore water may be attributed to the anaerobic conditions prevail in the bottom layers of the sediment. Unlike W-IP, WOP fraction showed a general decrease with increasing depth. The Fe-IP fraction showed general decrease down the core at these Stations except at Station 2, where a subsurface maximum was recorded. Seasonal variations in Fe-IP were found at three stations with maximum during post-monsoon and minimum recorded during pre-monsoon at all three Stations. The Fe:P ratio in sediments found to vary from 9.08 (Station 3) to 14.26 (Station 1). Thus, based on Fe:P ratios, the sediments had a high capacity for binding phosphate to iron. Unlike the inorganic fraction, the concentrations of Fe-OP were similar during three seasons other than the exceptionally higher values at Station 2. The concentrations of Ca-IP showed an erratic behavior down the core at Station 1 and Station 2. The overall picture of the annual variation followed the general pattern at Station 3 with decreasing concentration down the core. Variation of Ca-IP in the study area confirmed the influence of sediment texture in its distribution. Ca-OP concentration showed a decrease with the increase in depth except at 6-10 cm depth. The Ac-OP fraction exhibited a general decrease in concentration down the core. A reversal of this trend was observed at depths beyond 10 cm at Station 1 and 6-10 cm depth at

Station 2. The Ac-OP fraction mainly consisted of fresh organic matter, which decreases with increasing depth. The exceptionally high values recorded at 6-10cm depth at Station 2 may be due to occasional presence of root particles in sediment core. Alk-OP generally decreases down the core except at Station 2 where a subsurface increase was found. NaOH, extract the humic bound phosphates and poly phosphates associated with bacteria. Therefore the general decrease down the core may be attributed to the decrease in bacterial biomass with increase in sediment depth. Generally ROP concentration showed a decrease down the core. However the ROP fraction found to concentrate in subsurface sediment at Station 2 and Station 3.

The speciation of phosphorus in the mangrove ecosystems showed preferences of one form of phosphorus or the other with changing salinity. At Station 1, Fe-IP fractions were observed as the abundant fraction of phosphorus at all depths and ranged between 345.68µgg^{-1} and 495.36µgg^{-1}. W-OP recorded a minimum with values ranging between 7.18µgg^{-1} and 13.28µgg^{-1}. Other major fractions found were Ca-IP (246.35µgg^{-1} and 362.04µgg^{-1}) and Alk-OP (263.98µgg^{-1} to 372.89µgg^{-1}). All other fractions gave intermediate values to those of W-OP and Alk-OP.

Similar to Station 1, Station 2 core sediments also were generally composed of Fe-IP as the major fraction at all depths except at 6-10 and 10-20 cm depths. Fe-IP at this Station ranged between 282.63µgg^{-1}and 477.99µgg^{-1}. W-OP recorded minimum concentrations. (4.75µgg^{-1} to 8.90µgg^{-1}). Other major fractions at this site were Ca-IP, which ranged from 266.66µgg^{-1} to 442.21µgg^{-1} and Alk-OP, which ranged from 237.74µgg^{-1} to 301.48µgg^{-1}.

Fractionation of sediment cores at Station 3 gave an entirely different pattern from that of Station 1 and Station 2. The major fraction at this site was Alk-OP. This fraction showed a variation from 133.42µgg^{-1} to 183.94µgg^{-1}. The minimum concentration fraction was also different from the other two Stations. Here W-IP showed minimum concentration at this site, which varied from 1.70µgg^{-1} to 7.08µgg^{-1}. The other major fractions obtained were Fe-IP (52.41 to 102.76µgg^{-1}) Ca-OP (50.61 to 99.15µgg^{-1}) and Ac-OP (69.10 to 93.63µgg^{-1}). It was reported that the added excess DIP was efficiently taken up by the sediment particles and primarily retrieved in the easily exchangeable and iron bound fractions and the mangrove sediment was thus found to act as a phosphorus sink. Thus Stations 1 and 2 sediments which comprise majority of Fe-IP fractions may act as a phosphorus sink.

It has been established that sediment characteristics could serve as the basis to assume phosphorus species in sediments and ultimately predict potential rates of internal phosphorus loading. The water exchangeable fraction showed significant positive correlation with percentage of silt, clay, and TOC concentrations in 0-2 and 2-4 cm layers. The Fe-bound phosphorus was found as, positively correlated with percentages of silt, clay, organic carbon and iron content at all depths except 6-10 cm layer. No significant correlation was exhibited by Ca-bound phosphorus at 0-2, 2-4, and 10-20 cm layers. This fraction showed negative relationship with total organic carbon, iron content and in some depths, with percentage of clay. Correlation analysis showed that a similar mechanism governed the phosphorus speciation at 0-2 and 2-4 cm layers. These layers remain oxygenated layers at all seasons. The 4-6, 6-10 and 10-20cm layers may become anoxic and this could influence the amount of different species of phosphorus present. The concentrations of different fractions indicated a trapping mechanism operating for phosphorus in the mangrove ecosystem. At Station 1 and Station 2, denser vegetation was seen compared to Station 3, which facilitates trapping of nutrients discharged to this creeks from nearby systems. Also, Station 1 and Station 2 appear to be the sites with high sedimentation. Therefore the causes of chemical differences among the first two Stations and the third Station can ascribe to sedimentation, through which the system can act as a sink of suspended matter. Fabre *et al.*, (1999) found that the difference in the major form of phosphorus at different mangrove sites in French Guiana were due to the sedimentation pattern at each sites and also the ability of these sites to function as a sink for suspended matter. Influences of biotic processes like bioturbation, plant uptake and transpiration and root zone decomposition are some factors which affect the mobilization of P in wetlands. The order of abundance of each fraction at various depths gave an indication of bioturbation in the studied area. At Stations 1 and 2, the order of abundance was similar in the first three layers, which indicated bioturbation at this site, while Station 3 showed different order of abundance in these layers. The statistical ANOVA carried out between station, fraction and depth, showed significant difference in concentrations of phosphorus exist between Station, and between fraction and not between depths. Among fractions, Fe-IP fractions recorded significantly higher concentrations followed by Ca-IP concentrations and Alk-OP concentrations.

REFERENCES

Alongi, D.M. 1990 Effect of mangroves detrital outwelling on nutrient regeneration and oxygen fluxes in coastal sediments of the central great barrier reef lagoon. *Estuarine, Coastal and Shelf Science* **31**, 581-598.

Anderson, F.O. & Jensen, H.S. 1992 Regeneration of inorganic phosphorus and nitrogen from seston in a fresh water sediment, *Hydrobiologia*, **228**, 71-81.

Flach, E. & Heip C. 1996 Vertical distribution of macrozoobenthos within the sediments on the continental slope of the Cogan Spur area (NE Atlantic). *Marine Ecology Progress Series* **141**, 55-66.