STUDIES ON THE ROLE OF SEDIMENTS ON THE NUTRIENT DYNAMICS AND FERTILITY OF KUTTANAD WATERS

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CERTIFICATE

This is to certify that the thesis entitled "Studies on the Role of Sediments on the Nutrient Dynamics and Fertility of Kuttanad Waters" is an authentic record of the research work carried out by Smt. Lizen Mathews., under my supervision and guidance in the Department of Chemical Oceanography, School of Marine Sciences, Cochin University of Science and Technology, in partial fulfillment of the requirements for the Ph.D. degree of Cochin University of Science and Technology and no part thereof has been presented before for any other degree in any University.

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PREFACE

Estuarine and Coastal waters always maintained an intimate relation to the developmental activities of man. Along with the over exploitation of aquatic resources, discharges of wide varieties of wastes have considerably modified this relation during the last few centuries. The industrialization, applications of new teechnologies in agriculture, enhanced navigational activities, etc. have contributed to the present state. The deterioration of this most productive zone in the aquatic system have attracted considerable attention of the scientists all around. The most affected character of this waters is the sharp changes in the fertility due to modification in the nutrient level.

The Cochin estuarine system along with the Vembanad lake constitutes the most productive aquatic systems in the west coat of India. Serious changes in the character and behaviour of this system were noticed by many investigators. In the present study the nutrient dynamics and fertility of Kuttanad waters is addressed. Kuttanad represent a wetland system with considerable agricultural activities.

The hydrographical features of the Kuttanad waters are controlled by discharges from Manimala, Meenachil, Pamba, Achencoil and Muvattupuzha rivers and also by tidal intrusions of saline waters from Cochin backwaters during summer. The construction of Thanneermukkom bund, for the regulation of saline water intrusion has considerably modified the water characteristics of this aquatic system.

The thesis is divided into 5 chapters

Chapter I give a brief note on the estuarine environment and its behaviour with special reference to nutrients. The character of the Kuttanad waters and the details of previous work along with aim and scope is included in this chapter.

The description of the study area and the details of analytical techniques used for the estimation of different parameters forms the first part of chapter II. The analysis of results of the hydrographical parameters and general characteristics of sediments are the second part of chapter II.

Chapter III deals with the distribution of nutrients in water and sediments. The study of nutrients in the dissolved and sedimental form would help in understanding the potential availability of life supporting elements in any particulate region of the aquatic system. Understanding of the distributions, variations and transfer processes of nutrients in the Kuttanad water system, is therefore vital for an assessment of the water pollution problems and study of ecology in the area. Eventhough considerable amount of study has been done on the distribution of nutrients in the in the Cochin estuarine system, there is a shortage of data on the nutrient dynamics in this area. The third chapter reports the temporal and spatial variations of different forms of nitrogen and phosphorus in water and sediment.

Chapter IV deals with the speciation of phosphorus and nitrogen in the sediments. The Four phosphorus fractions identified are exchangeable and carbonate bound phosphorus, iron and aluminium bound phosphorus, calcium bound phosphorus and residual phosphorus. The different forms of nitrogen identified are exchangeable, fixed and organic nitrogen

Chapter V gives a conceptual model for the dynamics of nutrients.

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CHAPTER I

INTRODUCTION

The hydrosphere, which covers more than 70% of the earth crust, supports about 71 percent of the life on earth. Though coastal and estuarine waters constitute only a very small fraction of the hydrosphere, it accounts for about 25% of the aquatic productivity. These waters at the same time are the most affected by the human activities. Along with the significant load of substance due to the normal activity of the system, the development in the agriculture, industries and urbanisation have lead to the discharge of a heavy load of waste to the aquatic systems. This input has resulted in serious modifications in the coastal and estuarine environment and productivity. The management of these systems are so is the prime agenda of scientists all over the world.

Estuaries

Estuaries are defined as a semi- enclosed coastal body of water which has a free connection with the open sea and within which sea water is measurably diluted with fresh water from land drainage (Pritchard, 1967). Estuaries are thus unique water systems as they are the interface between river water and saline water. Based on geological mode of formation the estuaries are classified as Drowned river valleys, Bar built estuaries, Fjords, Estuaries formed by tectonic processes and Composite estuaries. On the basis of the Pitchard's definition of estuaries, they can also be classified on the basis of hydrologic characteristics.

1. Positive estuaries- They are those which have a measurable amount of dilution of sea water by surface and sub surface run-off
2. Inverse estuaries- They are those which have a higher rate of evaporation than fresh water inflow from precipitation and surface or sub surface run-off.
3. Neutral estuaries- They are those which are between the first two where neither fresh water inflow nor evaporation dominate.

Estuaries are like great chemical reaction vessels in which solutions with different chemistries are mixed in the presence of reactive particles (Goldberg, 1978). The fate of conservative chemicals supplied in solution from rivers or the ocean is usually predictable from a linear relation between the concentration changes of the chemical and salinity (Biggs & Cronin, 1981). Most chemicals, however, are highly reactive in the unstable estuarine environment. They may be assimilated by organisms or partitioned by particulate form through processes like ion exchange, precipitation, complexation with organic substances, co precipitation with iron and manganese, and incorporation into mineral lattices and faecal material. They are strongly adsorbed on fine particles. Consequently, sedimentary processes largely govern their movement and behaviour. By altering the flux of river-borne material to the oceans, estuary sediments can play an important geochemical role and affect global chemical budgets.

The chemistry of river water may be extensively modified during its passage through an estuary to coastal waters. Sediment- water exchange influences both transformations of pollutants and the overall nutrient budget within the estuary. The sediment water interface together with the water layer immediately above it and the sediment below form a zone which has a vital role in controlling pollutant and nutrient chemistries within the estuary. Microbial degradation of organic detritus within the sediment and on suspended particles regenerates nutrients and may release pollutants. These degradation processes occur in biogeochemical zones in which successively less energy efficient electron acceptors are utilised (Froelich et al., 1979). In estuaries the sediment receives comparatively high concentration of organic matter (Santschi et al., 1990), which results in these zones being compressed into a few centimetres.

Once formed, estuaries make good sediment traps. The nature and distribution of sedimentary matter in an estuary are controlled by the interaction between the kinds and quantity of available sedimentary components (such as shells, organic matter, quartz, sand grains, fecal pellets, and clay minerals), hydrodynamic processes and bottom morphology (Allen et al., 1973). Sediment is a suitable substrata for biological and chemical reactions, it plays an important role in biochemical and geochemical processes, and also serves as a surface for adsorption processes and bacterial activity. Estuaries are complex sedimentary environment and estuarine sediments may originate from a number of sources, both upstream and marine. Aston and Chester (1976) have pointed out that the two extreme sources of sediments in estuaries, ie. landward and seaward, together with intermediate sources such as river mouths and estuarine slopes, impose severe limitations on the geochemical interpretation of estuarine sedimentary processes The most important sedimentary and chemical interactions in estuaries may be subdivided in to two aspects: (1) the modification of sedimentary detritus during its transport to the oceans (11) the modification of estuarine sediments after deposition, ie. diagenetic changes.

The estuaries and coastal waters are considered to be the most productive zones. At the same time these waters are the most polluted of the aquatic system. The land run off is the main supporting sources for both the productivity and pollution. Apart from the recognized pollutants like trace metals, PHCs, PCBs, and other organic and inorganic substances, the heavy load of micro nutrients like nitrogen and phosphorus also, at times, deteriorate the productive environments present in these water bodies. .

Nutrients in aquatic systems

Recently attention has been drawn to the behaviour of nutrients such as phosphate, nitrate, nitrite, ammonia and urea in estuaries and coastal waters. This interest is due to partially from the importance of these substances in biological processes, including the control of productivity, and partially from concern about the possible effects of the input of nutrient- rich effluents such as domestic sewage, agriculture out puts, land run off etc to the estuaries.

A nutrient element is one, which is functionally involved in the process of living organisms. Traditionally, in chemical oceanography the term has been applied almost extensively to silicon, phosphorus, and nitrogen, but strictly a number of major constituents of sea water, together with a large number of trace metals, are also nutrient elements. The productivity of an aquatic system more or less depends on the availability of the inorganic ions of nitrogen and phosphorus. The regulation of the ions of these elements, thus have a prime role in the conservation and the sustainable management of the aquatic systems. Ions of phosphoric acid constitute the major phosphorus nutrients. Nitrite, nitrate, ammonia, and urea are the major nitrogen nutrients. Sediments play a key role in regulating the bioavailability of all these ions.

Estuaries have been subject to intense anthropogenic influences over recent decades by inputs of compounds of nitrogen and phosphorus as a consequence of fertilizer usage and sewage/waste input (Howarth et al., 1996). Thus the capacity of an estuary to buffer or remove additional nutrients is of importance in modifying the load of these nutrients to the aquatic systems. Enhanced nutrient discharge to rivers have sometimes been blamed for increased phytoplankton growth and toxic algae development in their receiving estuaries and coastal regions(Cadee, 1989; Reigman et al., 1992; Boynton et al., 1995). As far as the nutrient prediction is concerned, extremely large temporal and spatial variations occur in estuarine nutrient fluxes (Balls, 1994). In addition non linear coupling between the biology, chemistry and water and sediment transport influence nutrient concentrations, so that realistic flux predictions can be obtained from numerical modelling simulations (Muller et al., 1991; Wilkinson et al., 1997).

Phosphorus

Inorganic phosphorus species present in Earth's surface are the ions of ortho phosphoric acid (Riley & Chester, 1971). The ortho- phosphate present in river water is mainly from weathering of phosphate minerals of continental rocks and also from anthropogenic sources. In addition to the simple inorganic phosphate ions, the river water and sea water also contains a variety of dissolved organic phosphates derived from biological activity and also particulate phosphates of both organic and inorganic origin (Riley & Skirrow, 1975). The estuarine chemistry of phosphate was well studied by many workers. The greater interest is due to the influence of phosphate in the primary and secondary production and also the nature of pollution arising from the disposal of sewage effluents in to rivers or directly into estuaries.

In the aquatic environment, dissolved phosphate is consumed during the growth of phytoplankton and is regenerated during bacterial decomposition of organic matter. Much of the regeneration takes place in the water, but in relatively shallow environments, such as lakes, estuaries, and continental shelves, sediments may play an important role in the regeneration of phosphate ((Fisher et al, 1982). Sediments receive mixture of labile and organic and inorganic phosphorus compounds from the overlying waters and surrounding land masses. A part of these compounds act as inert material and are buried in their original form. The other part undergo decomposition and release phosphate to the 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 (Krom and Berner, 1981; Froleich, 1988).

Studies investigating the mechanism controlling sediment phosphorus have recently increased considerably over the last two decades. This has been in response to the resilience of many lakes which, despite reductions in external phosphorus loading, have maintained high phosphorus concentrations.

Nitrogen

The chemical forms in which nitrogen can exist in sea water are many fold (Oxidation state –3 to +5), relative proportions of different forms of nitrogen depend upon the ambient environment and are governed by conditions of temperature, redox (Eh), pH etc. All the species have significant role in the marine environment; nitrate and nitrite account for about 65% of the soluble combined nitrogen (Martin, 1970; Ryther and Dunstan, 1971).

The major processes by which nitrogen is brought to the sea are atmospheric precipitation, volcanic activity and continental drainage whereas the processes involved for the nitrogen removal are loss to deep marine sediments, migration of marine animals and loss of nitrogen to the atmosphere (Martin, 1970).

In addition to the various diagenetic and regeneration processes involved in the nutrient cycles of phosphorus nitrification, denitrification and fixation are also involved in the nitrogen cycle. Denitrification and nitrification are the main pathways responsible for inorganic nitrogen removal and speciation in estuaries.

Denitrification results from the microbial breakdown of organic substances in the absence of oxygen, where nitrate is preferentially used as the terminal electron acceptor. Nitrate is subsequently reduced to gaseous end products. Denitrification tend to occur in the upper few centimeters of anoxic sediments where nitrate is supplied by nitrate diffusion from the water column and nitrification processes in the oxic surface sediments.

Nitrification, the conversion of ammonium to nitrate, is the major biological pathway which increases the oxidation state of inorganic nitrogen. Nitrification can impose significant oxygen demand leading to localised oxygen minima in the upper reaches of estuaries under certain conditions (Balls et al., 1996). In the esaturine water column nitrification is usually associated with turbidity maxima, a consequence of bacterial association with periodically resuspended particles ensuring maximal reaction rates (Plummer et al., 1987). Estuarine sediments have a high organic content, due to high rate of sedimentation, which lowers the oxygen status, increasing the denitrification potential. Although denitrification is thought to predominate in sediments, oxygen minima in the water column may produce favourable conditions for the process (Hattori, 1983). The biogeochemical cycling of nitrogen is of a complex nature because of varieties of chemical species in which nitrogen is available for biological utilization.

Jorge and Julio (1985) studied about inorganic nitrogen in coral reef sediments and observed that ammonium is the dominant nitrogenous species in the pore water. Studies on the vertical distribution of nitrate concentration in interstitial water of marine sediments revealed that nitrification takes place in the upper few centimeters of sandy sediments but not in the muddy sediments (Jean and Gilles, 1975). An investigation conducted on the rates of nitrification and nitrate reduction in near shore marine sediments have concluded that there is no constant relationship between nitrification and nitrate reduction (Sarah & Douglas,1985). A study about the nitrogen limitation of secondary production revealed high rate of primary production, despite low nutrients

Aim and scope of the present study

Though the coastal waters and estuarine waters are the major contributors to the total productivity of the hydrosphere the quality and character of these water bodies are the most ill maintained. They receive considerable amount of water from the human activities, which adversely affect the fertility of the system. A proper management of these systems require sufficient data on the disposal characteristics, fate and transport of water and the chemical character of the water as well its chemical transformations. The Cochin estuarine system along with the Vembanad lake is a shallow semi enclosed water body and have more or less positive tropical estuarine characteristics. The discharges from the five major rivers, Manimala, Meenachil, Pamba, Achencoil and Muvattupuzha rivers transports nutrient rich alluvial soils from the western mountain ranges to this low lying area. The fertility of these water bodies were significantly high and supported good agricultural production. Kuttanad water forms the southern part of this aquatic systems and is considered as the most productive zones. As a part of the management scheme for a higher agricultural activity, the Thanneermukkom bund was constructed to block and regulate the intrusion of saline water. The increased use of artificial fertilisers along with stagnant character of the water body in this area have resulted in sharp decline in the water quality, productivity and aquatic resources.

The earlier studies on this part of the estuarine system were concentrated on the physical and biological aspects of Vembanad Lake due to its economic importance. Considerable attention is diverted to study the hydrographic, fishery resources, and environmental hazards of this area (Sureshkumar 1998;Harikrishnan, 1997). A study was conducted on the primary production in Vembanad lake by Ramachandran Nair et al (1975). In 1975, Kunjukrishnapillai (1975) investigated the plankton production in the Vembanad lake and in his study the reason for not maintaining the conversion ratio between the primary and secondary tropic level is possibly due to the interference of salinity. He concluded that primary production is not a limiting factor for the secondary production in the estuary. Except some random data compiled from the results of investigations for defining the biological or physical behaviour, significant gaps exist in the data of the nutrient characteristics of this water mass.

A comprehensive and systematic programme to assess the nutrient characteristics and dynamics is essential for the management of this aquatic system. The present work, so, is planned to generate data on these bases. The sediment is the major sink and source of many of the chemical entities including nutrients which reach in estuarine and coastal systems. It is so intended to quantify and speciate the sedimentary nutrients.

CHAPTER II

MATERIALS AND METHODS

2.1 Description of the study area

2.2 Sampling and storage

2.3 Analytical procedures

a. Hydrographic parameters

b. Sediment characteristics

c. Hydrochemical parameters-Nutrients.

d. Speciation of Phosphorus

e. Speciation of Nitrogen

2.4 Results of hydrographic parameters and sediment characteristics.

2.1 Description of the study area

The area of study, Kuttanad waters, is a part of Cochin Estuarine system and forms the southern part of the Vembanad lake. The lake is connected to Arabian Sea at Cochin through a 425m wide channel which is the only source for tidal intrusion in to the lake. Tides are of semidiurnal type, showing substantial range and time .The area of study, which extends from 9^0 28'- 10^0 10' N (Lat) and 76^0 13'- 76^0 31' E (Long) runs parallel to the southern part of the west coast of India. The hydrographic features of this part of the estuary are controlled mainly by discharges from five rivers, Manimala, Meenachil, Pamba, Achencoil and Muvattupuzha and also by tidal intrusions of saline waters from Cochin estuarine system. Pamba and Manimala rivers join together before meeting the Achencoil river at Veeyapuram and all these rivers influx at the southern most part of the lake. River Meenachil opens at the middle of the lake, whereas river Muvattupuzha opens at the northern part in the downstream region. The average depth of the water body varied between 1.5-10 meters. The lake and adjoining canals and rivers have been supporting a lucrative fishery. During south west monsoon,this cultivatable land is seriously affected by severe floods. Agriculture, fish catching, shell collection, lime production, tapping from coconut palms and duck farming are the main occupation of the people of Kuttanad area.

Kuttanad is rightly called as the 'Rice Bowl of Kerala', contributing nearly 20% of the total rice production of the state Kerala. This region represents a wetland system which is considerably utilized for rice cultivation. The aquatic system was highly productive and contained high fishery resources. Total agricultural area is ~54935 ha. The amount of artificial fertilizers used in this area is about 8409 tones per year.

For the better management of this area, Thottappally spillway, for the release of flood water, Thanneermukom bund, to block the intrusion of saline waters, and a link road were constructed. Thannermukkom bund ,commissioned in 1976 was made for regulating the intrusion of saline water in to the Kuttanad paddy fields during December to March and thereby protecting 'Punja' crop. The barrier was originally envisaged to be closed for a period of three months from 15th of December to 15th of March every year while shutters remained open during monsoon months so as to facilitate the evacuation of flood water. However alterations in the operation schedule such as prolonged closure period up to April-May have brought in some adverse effects besides causing serious conflicts between fisherman and agriculturist. The deterioration of the water quality after the construction of Thanneermukkom bund is suspected to be one of the reasons of the massive spreading of fish diseases and fish mortality during the recent years. Furthermore, shifting of salinity gradient zone towards the north of the lake has also been resulted.

The area of investigation and station locations are given in the fig.2.1 The region lying between Thanneermukkom and Alleppey was divided in to nine stations. The stations are fixed in such a way that they reflect the complex environmental and geographical variability in a representative manner. The stations are,

1. Pallathuruthy

This station is situated near an urban town Alleppey. Agriculture is the main occupation of the people in this area. The water characteristics are mainly controlled by the riverine discharges from Pampa and Achenkoil.

2. Nedumudi

Agriculture is the main occupation of the people in this area. This station is also influenced by riverine discharges

3. Kavalam

An agricultural area influenced by riverine discharges.

4. Vattakayal

Paddy and coconut are the main agricultural crops in this area. The

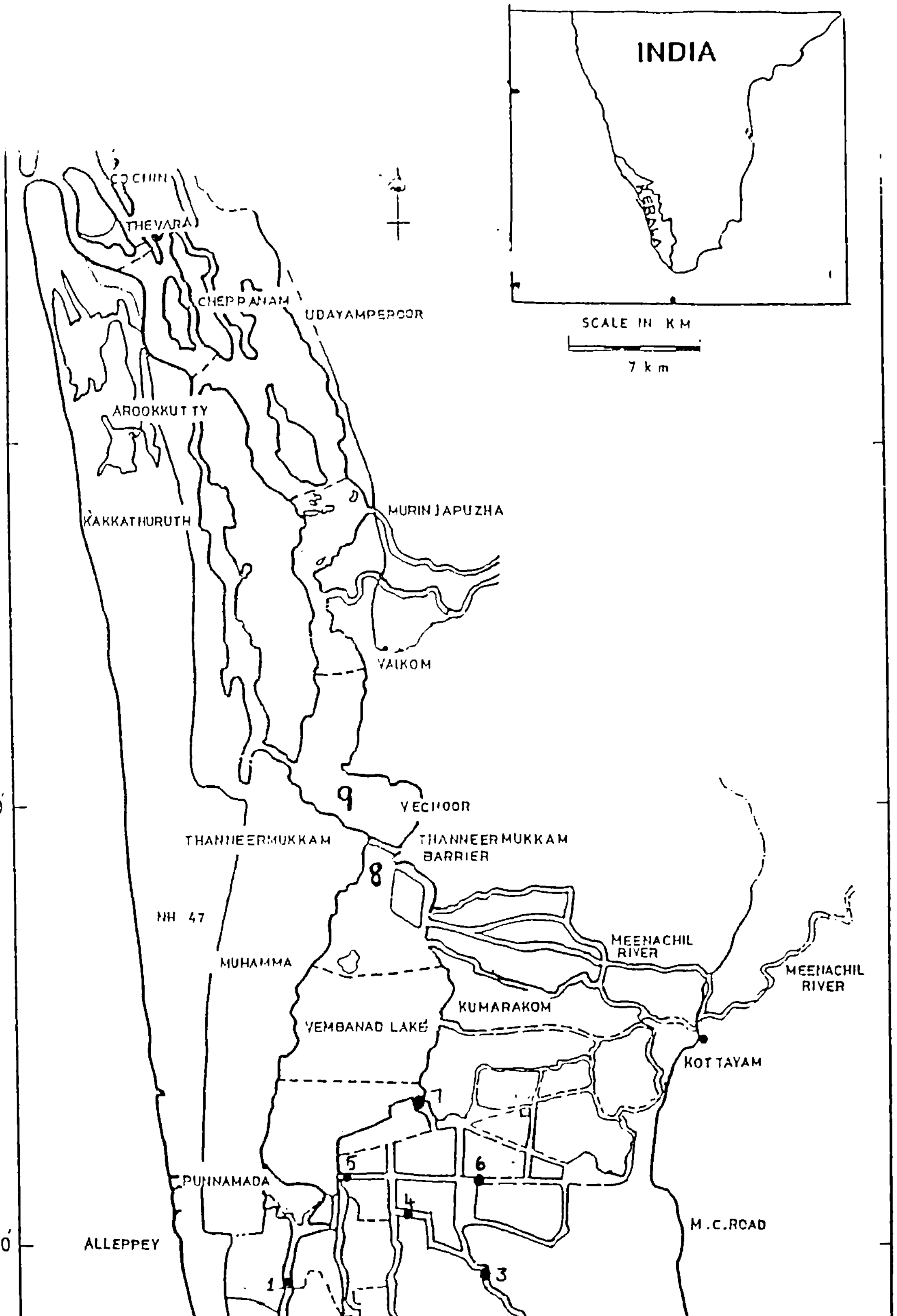


Fig 2.1 Location of the study area

quality of water is influenced by the discharges from various rivers.

5. C Block

6. 24000

7. Chithira

Paddy is the main cultivation in this area and this water body is influenced by discharges from paddy fields.

8. Thanneerrmukkom south

This station is situated near to the bund and showed slightly estuarine characteristics.

9. Tanneerrmukkom north

This station is located north of the Thanneerrmukkom bund and is estuarine in character.

Considering the salinity distribution, geographical character and the nature of various human activities prevailing in this area, the study area was divided in to three zones. The first zone is constituted by stations1 to 4, the second zone contains the stations 5 to 7 and the stations 8 & 9 make the third zone. All the zones exhibit riverine character during monsoon season. Zone 1 is completely riverine in nature during the pre monsoon and post monsoon seasons also. The main occupation in this area is agriculture. During pre monsoon the second zone shows estuarine characteristics while during the other two seasons they are fresh water dominated.. Stations 8 & 9, the third zone, is estuarine in nature during the pre monsoon and post monsoon seasons.

2.2 Sampling and storage

Samples of water (surface and bottom) and sediments were collected from May-1996 to May-1997, at monthly intervals. All the surveys were carried out using a 25 feet fibre glass boat, M.B. King Fisher of the School of Industrial Fisheries, Cochin University of Science and Technology, Cochin.

Surface samples were collected using a clean plastic bucket and bottom samples by a pre-cleaned Teflon coated High Tech water sampler. Sediments were collected by stainless steel plastic lined van-Veen Grab ($0.032m^2$). Sediments were kept stored at –4° C till analyses were performed. The surface and bottom samples were deep frozen in polythene containers and were analyzed within a week. The dissolved oxygen of surface and bottom samples was fixed in situ. All the reagents used are analytical grade and Milli- Q water is used for the preparation of standards and reagents solutions

2.3Analytical Methods

a. Hydrographical parameters

pH was measured in situ and temperature was measured using a sensitive thermometer. Salinity of the water samples was estimated by Mohr-Knudsen method (Strickland and Parson, 1972) .Modified Winkler method was used for the estimation of Dissolved Oxygen (Grasshoff, 1983).

b. Sediment Characteristics:

Analysis of grain size and dissolved organic carbon were conducted in sediment samples. The method of Gaudett and Flying (1974) was followed for the determination of total organic carbon. Grain size of the sediments was determined by the method of Carvar (1971). Moisture content of the sediment was estimated by oven drying the sediment at 105°C for 24 hours.

b. Hydrochemical parameters : Nutrients

All the nutrients were estimated sphectrometrically (using UV-Vis Hitachi 150-20) after converting each of the species required coloured substance. Nitrite was converted to an azo dye with sulphanilamide and N- (1-naphthyl) ethylene diamine dihydrochloride (Grasshoff, 1983). Nitrate was reduced to nitrite and estimated as nitrite. (Grasshoff,1983). Ammonia was determined by indophenol blue method using citrate buffer (Koroleff,1983). Urea was estimated by Diacetyl monoxime method (Korroleff,1983). Formation of phospho-molybdate complex using ascorbic acid as reductant was used for phosphate (Koroleff,1983). Sediment urea was determined by Diacetyl monoxime method after leaching the sediment with Milli Q water (Nakas and Litchfield,1977). Extraction with 1 M NaCl solution was used to release the adsorbed nitrite, nitrate and phosphate and the estimations were done using general techniques given above.

d. Speciation of Phosphorus

The main focus of this investigation was the identification of the role played by the sedimentary compartment to the nutrient cycle and so attempts were not made to distinguish between the sedimentary adsorbed and the pore water contributions. The extractions for the speciation were done, so, with the wet sediments only. The data, but, is expressed in terms of the dry weight, using the dry to wet ratio, for effective comparison with earlier works. Dry to wet ratios were determined by drying the samples at 105^0 C for 24 hours and taking the weight before and after drying.

The sequential extraction procedure adopted here for the speciation of phosphorus was taken from Hieltjes and Lijklema (1980) and van Eck (1981) with slight modification to suit to the system of this study. Hieltjes and Lijklema (1980) and van Eck (1981) had suggested 12 hrs extractions for each species but during the trail experiments it was observed that the extraction was all most complete by 4 hrs and the values were reproducible. In this work ,so, all the extractions were limited to 4 hrs. Reported values were the mean of at least duplicate extraction and analyses. The extracted orthophosphate was analysed according to Koroleff (1983)

1.Total phosphorus: Total phosphorus was estimated by perchlolric acid digestion followed by spectrophotometric analyses (Strickland and parson, 1972).

2. Exchangeable and carbonate-associated phosphate: Approximately 1 gm of accurately weighed sample was mixed with 25ml 2 N NH_4Cl solution. After shaking for 4 hours, the solution was centrifuged and the clear liquid was carefully decanted in to a 50 ml volumetric flask. The sediment was then extracted with 15 ml milli-Q water and the extractant was added to the NH_4Cl

extract. The volume of the flask was made up to 50 ml. The analysis of orthophosphate was done spectrophotometrically.

3. Iron and aluminium associated phosphate: The residue of the first extraction after the addition of 25 ml of 0.1 N NaOH and shaking for 4 hours, the solution were centrifuged and decanted in a way similar to that described above. The pH of the extract was adjusted to 7± 0.5 using 0.5N HCl solution. The analysis of ortho- phosphate was done as above.

4. Calcium- associated phosphate: The residue of the second extraction after the addition of 25 ml of 0.5 N HCl and shaking for 4 hours was centrifuged and decanted in a way similar to that described under the former extraction. The pH of the extract was adjusted to 7± 0.5 using 10% ammonia solution. The analysis of ortho-phosphate was done as above.

5. Residual Phosphorus: It is calculated as the difference between the concentration of total phosphorus and inorganic forms.

e. Speciation of Nitrogen

The speciation of nitrogen was done using the scheme proposed by Keeney and Bremner (1966) and Silva and Bremner (1966). As in the case of phosphate here also the extractions were done with the wet sediments for the reasons given earlier. This scheme is not capable of identifying and estimating the nitrate and nitrite species, if any associated with the sediment.

Exchangeable nitrogen (N ex) is defined here as the amount of NH_4^+ extracted by 2 N KCl solution; fixed ammonium (N fix) as the fraction which is not obtained by the extraction with 2 N KCl, but which is liberated with HCl solution after destruction of the organic matter with a hypobromite solution. Organic nitrogen (N org) is defined here as the difference between total nitrogen (N tot) and inorganic nitrogen (N fix + N ex) :

N org = N tot – (N fix +N ex)

Total nitrogen (N tot)

Total nitrogen was estimated using Kjeldhal method and the distilled ammonia was determined by back titration with 0.01 N HCl.

Exchangeable nitrogen (N ex) [Keeney and Bremner. 1966]

After shaking 6 g sediment with 10 ml 2 N KCl solution, 0.1 gm MgO was added followed by flushing with a few ml of Milli-Q water. The extracts were transferred to the Kjeldhal steam distillation unit, 10 ml 10 NKOH were added and the ammonia was distilled by the same methods as those described for N tot.

Fixed nitrogen (N fix) [Silva and Bremner, 1966]

To 2 gm of sample 20 ml of KOBr/KOH (6 ml of Br_2 in 200 ml of 2N KOH, freshly prepared everyday) solution added and mixed. After 2 hour the solution was boiled for 1 min. With 20 ml 0.5 N KCl solution the mixture was flushed into a 50ml centrifuge tube, which was centrifuged for 10 min. The liquid was decanted and the sediment was mixed again with 20 ml 0.5 N KCl solution followed by centrifuging and decanting. Approximately 20 ml of 1 N HCl solution was added to the remaining sediment, which is subsequently shaken for 24 h. The suspension was then transferred in to a Kjeldahl flask and after the addition of 20 ml 10 N KOH solution the ammonia was distilled as described previously for total nitrogen.

Organic nitrogen (N org)

The organic nitrogen content of the sediment is calculated according to:

N org = N tot –N fix-N ex

2.4 Results of hydrographic parameters

The study of the general hydrographic parameters has great importance in characterizing the general features of an estuarine system. The hydrographic conditions in an estuary mainly depend on the intrusion of sea water associated with tides, influx of fresh water from rivers, precipitation and evaporation processes and also weather. The bottom topography and geographical condition of the estuary also contribute to the same. The sedimentary characteristics are more or less governed by the hydrography of the overlying waters.

The hydrography of this Backwater system has been well documented (Qasim and Reddy, 1967; Qasim et al.,1968; Sankaranarayanan and Qasim,1969;Josanto,1971; Shynamma and Balakrishnan,1973; Lakshmanan et al.,1982; Anirudhan,1988;Nair, 1990; Nair,1992; Shibu,1992; Beenamma,1993; Jayasree, 1993; Suresh Kumar, 1998; Harikrishnan,1997).

Temperature

Table 2.1 represent the variations in temperature during the three seasons. During pre monsoon the temperature in zone I, II and III were ranged between 30.9 & 31.9^{0}C, 30.9 & 32.3^{0}C, and 31.0 & 31.6 ^{0}C respectively. During

Table2.1 Stationwise variations of Temperature in water(°C)

Stations	S/B	premonsoon	Monsoon	Postmonoon
1	S	31.9	28.3	29.6
	B	30.9	27.9	29.0
2	S	31.9	28.7	29.6
	B	31.0	28.3	28.8
3	S	31.5	29.0	29.1
	B	30.9	28.6	28.4
4	S	31.6	29.2	29.4
	B	31.2	28.9	28.9
5	S	32.0	28.8	29.1
	B	31.8	28.6	28.7
6	S	32.3	28.6	29.6
	B	32.1	28.5	29.1
7	S	31.3	28.6	28.9
	B	30.9	28.5	28.6
8	S	31.6	28.3	28.8
	B	31.3	28.3	28.6
9	S	31.5	28.3	29.0
	B	31.0	28.3	28.7
zone				
I		31.3	28.6	29.1
II		31.7	28.6	29.0
III		31.3	28.3	28.8

monsoon the highest and lowest temperature observed were 27.9-29.2, 28.5-28.6 and 28.3 in the respective order for zones I, II and III. The maximum values during post monsoon were 29.6, 29.6 and 29.0^{0}C for zones I, II and III respectively. The minimum values were 28.4, 28.6 and 28.7 for zones I, II and III in the respective order.

Salinity

Salinity appeared as the most fluctuating water parameter in this lake and the operation of the salinity barrier at Thanneermukkom plays a major role in the distribution of salinity in the Kuttanad waters. Salinity has been considered as an index of the estuarine mixing processes and the tidal effects. Fig.2.2a&2.2b and table 2.2 shows the variability of salinity at both surface and bottom waters during the three seasons. In general bottom salinity was found to be slightly higher than the surface water.

During pre monsoon the salinity values in zone I varied between 0.28 and 0.84 ppt. In zones II and III the values were in the range 0.78-3.39 ppt and 6.18-10.97 ppt. During monsoon the salinity in zones I, II and III varied between 0.06-0.13, 0.12 & 0.27 and 0.13 and 0.14 ppt respectively. In post monsoon the maximum and minimum salinity values in zone I were 0.15 and 0.06 ppt. In zone II the salinity increased to a maximum of 0.41 ppt from 0.08ppt. In zone III the values were in the range 1.56-1.88 ppt.

A study conducted by Suresh Kumar (1998) revealed that a total change in the pattern of salinity distribution in the lake has taken place since the commissioning of the barrier. An increase in salinity during the dry months when

Stationwise variations of salinity in water (ppt)

Table2.2

Stations	S/B	Pre-Monsoon	Monsoon	Post-Monsoon
1	S	0.67	0.08	0.10
	B	0.67	0.09	0.15
2	S	0.30	0.07	0.07
	B	0.29	0.06	0.07
3	S	0.28	0.07	0.06
	B	0.28	0.06	0.07
4	S	0.84	0.13	0.08
	B	0.84	0.13	0.08
5	S	0.94	0.12	0.08
	B	0.78	0.12	0.08
6	S	1.66	0.19	0.16
	B	1.64	0.22	0.15
7	S	3.39	0.25	0.40
	B	3.29	0.27	0.42
8	S	6.18	0.13	1.88
	B	6.32	0.13	1.87
9	S	10.97	0.14	1.65
	B	10.30	0.14	1.56
zone				
I		0.52	0.09	0.09
II		1.95	0.19	0.22
III		8.44	0.14	1.74

Stationwise variations of salinity in water (ppt)

Fig 2.2a Surface water

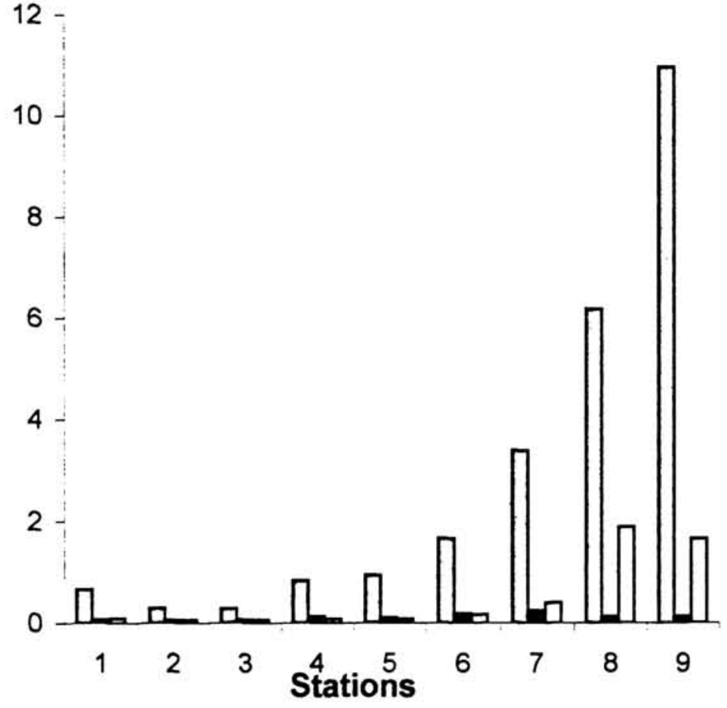
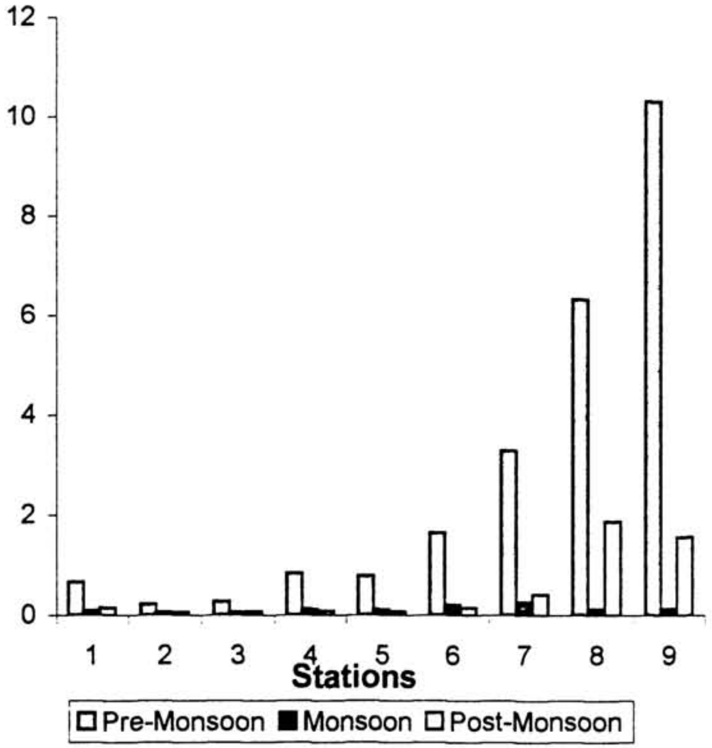


Fig 2.2b Bottom water



the freshwater discharges got reduced and a corresponding decrease in salinity during monsoon when freshwater pushes salt water down the lake are the usual observations (Josanto,1971). Josanto (1971) reported a bottom salinity fluctuations between 18 and 22 ppt prior to the commissioning of the salinity barrier, whereas, in the study of Suresh Kumar (1998) the fluctuation was in a range of 0 to 8ppt. The same trend was observed in the present study. But Kurup and samuel (1987) recorded a salinity fluctuation of 0 to 3 ppt in this region. An increased trend in the salinity recorded may be due to the changes in the operation schedule of salinity barrier.

pH

The pH is an important hydrological feature indicating the level of dissolved carbon dioxide in the water which may in turn reflect the activity of phytoplankton and the level of dissolved oxygen in the sea (Skirrow, 1975). The seasonal distribution of pH is presented in table 2.3 and fig. 2.3a&2.3b.

During pre monsoon, the pH values were in the range 6.43-6.70, 6.33-6.60 and 6.97-7.13 for zones I II and III respectively. During monsoon the values in zone I were in the range 6.45-6.75 and in zone III the values varied between 6.40-6.80. In zone III the maximum pH was 7.05 and minimum was 6.95. During the post monsoon the value of pH in zones I, II and III were between 6.23 & 7.13, 6.40 & 6.93 and 6.73 & 6.90 respectively.

The results obtained are in full agreement with the earlier observations (Harikrishan, 1997; Sureshkumar, 1998). The low pH observed in this system can

Table 2.3 Stationwise variations of pH in water

Stations	S/B	Pre-Monsoon	Monsoon	Post-Monsoon
1	S	6.63	6.70	7.13
	B	6.53	6.75	6.83
2	S	6.70	6.60	7.03
	B	6.50	6.45	6.63
3	S	6.47	6.50	6.63
	B	6.43	6.45	6.37
4	S	6.53	6.50	6.43
	B	6.50	6.50	6.23
5	S	6.60	6.55	6.60
	B	6.53	6.50	6.47
6	S	6.60	6.80	6.63
	B	6.33	6.40	6.40
7	S	6.53	6.80	6.93
	B	6.47	6.55	6.83
8	S	7.07	6.95	6.83
	B	6.97	6.95	6.73
9	S	7.13	7.00	6.97
	B	7.13	7.05	6.90

Stationwise variations of pH in water

Fig 2.3a Surface water

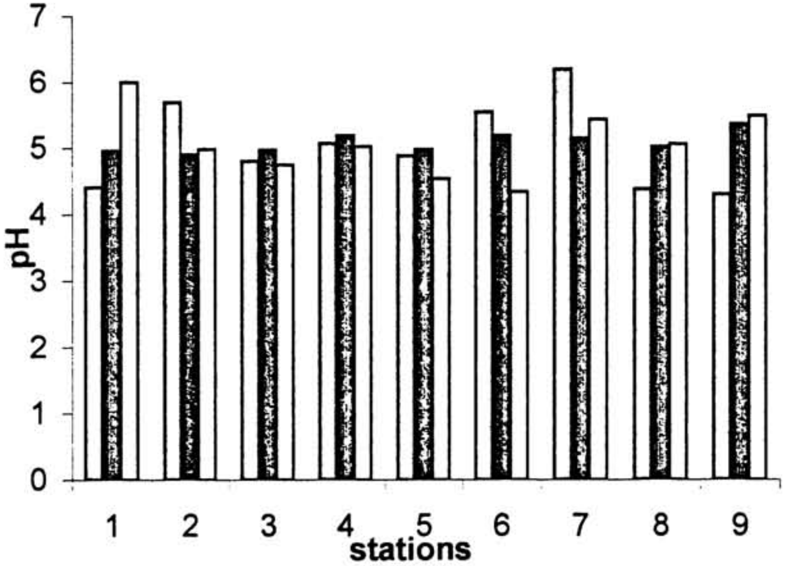
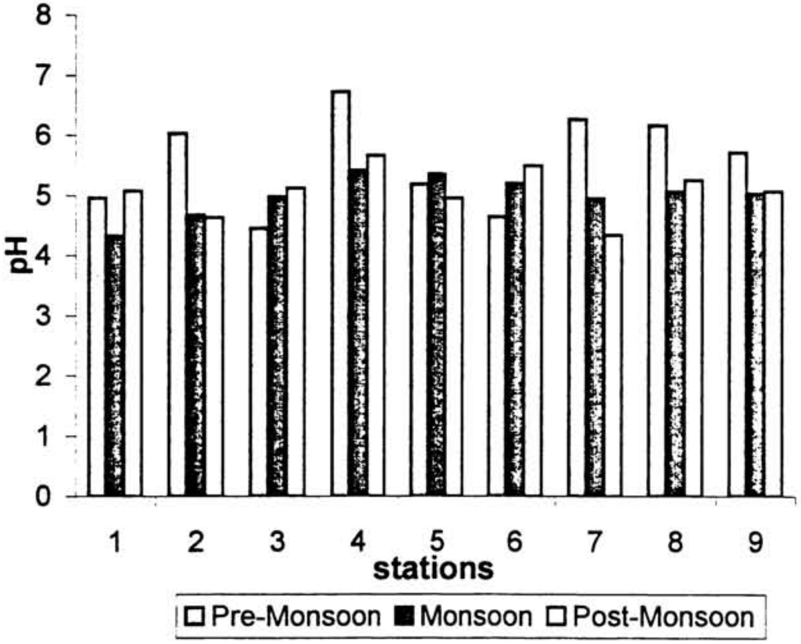


Fig 2.3b Bottom water



be due to the quality of the river water and also due to the significant utilization of dissolved oxygen by organic matter

Dissolved Oxygen

Dissolved oxygen is the most valuable water quality parameter in assessing water pollution. It is also important since the existence of aquatic life is intimately linked with the availability of oxygen for their survival. The amount of dissolved oxygen in natural water depends on various factors such as temperature, partial pressure and salinity. Dissolved oxygen may be helpful to explain the various physical, chemical and biological processes taking place in the estuarine system (Desousa and Sen Gupta, 1986) .

Fig 2.4a&2.4b and table 2.4 shows the distribution of dissolved oxygen during the three seasons. During pre monsoon the dissolved oxygen values in zone I varied between 6.72 and 4.41ml/l. In zone II the values were in the range 4.64-6.27 and 4.31-6.17 ml/l. During monsoon the dissolved oxygen in zones I, II and III varied between 5.41 & 4.32, 4.46 & 5.37 and 5.02 & 5.12 ml/l respectively. In post monsoon the maximum and minimum D.O values in zone I were 6.00and 4.63 ml/l. In zone II the D.O increased to a maximum of 5.49 ml/l from 4.34ml/l. In zone III the values were in the range 5.07-5.50 ml/l.

Estuarine sediment contains high concentration of oxygen demanding materials and when they discharge to the water, a high oxygen demand is exerted.

Grain size analysis

Grain size is one of the basic characteristics of sediments and its determinations are necessary to delineate the sedimentary environments. Table 2.5a, 2.5b , 2.5c, & 2.5d shows the variations in the percentage of grain size during the three seasons.

Zone I

During pre monsoon in zone I the percentage of sand, silt and clay were in the range 6.08-40.50, 24.73-50.31 and 34.75-44.77 respectively. During monsoon the maximum and minimum percentage of sand, silt and clay were in the range 74.84-31.11, 61.66-15.94 and 20.55-9.20% respectively. Post monsoon showed a maximum of 60.16%, 47.38% and 42.40% for sand, silt and clay and a minimum of 10.20%, 25.15% and 9.19% for the same.

Zone II

During pre monsoon the percentage of sand, silt and clay were found to be 36.73 - 72.62, 23.11 - 52.07 and 4.25- 35.82 % respectively of the sediment. During monsoon the observed percentage were 21.86-80.89, 17.78-62.92 and 1.31-15.21% for sand, silt and clay in the respective order. During post monsoon the percentage of sand, silt and clay raised to a maximum of 73.75, 44.22 and 27.81% and a minimum of 32.60, 13.41 and 12.82% respectively.

Zone III

91.05-94.60 %, 79.67-93.16 % and 83.65-89.30 % of sand constituted zone III during pre monsoon, monsoon and post monsoon seasons. During pre monsoon, monsoon and post monsoon the percentage of silt varied between

Grain size analyses

Table 2.5a Sand (%) | Table 2.5b Silt(%)

stations	pre monsoon	monsoon	post monsoon	pre monsoon	monsoon	post monsoon
1	0.06	0.24	0.08	9.91	18.06	5.72
2	0.60	0.22	0.10	8.14	11.63	7.18
3	0.10	0.18	0.09	8.51	25.83	9.10
4	0.07	0.10	0.07	3.64	9.97	11.10
5	0.10	0.19	0.07	10.15	12.82	7.07
6	0.04	0.31	0.05	11.96	25.92	7.62
7	0.07	0.42	0.13	14.85	11.49	9.60
8	0.60	0.53	0.15	15.95	27.35	10.25
9	0.20	0.10	0.10	15.08	37.25	2.72

Table 2.5c Clay (%) | Table 2.5d Nature of the sediment

stations	pre monsoon	monsoon	post monsoon	pre monsoon	monsoon	post monsoon
1	34.75	20.14	28.65	sand, silt, clay	sand, silt, clay	sand, silt, clay
2	44.77	9.20	26.14	clayey silt	silty sand	sand, silt, clay
3	42.28	20.55	9.19	clayey silt	clayey silt	silty sand
4	43.60	15.48	42.40	sand, silt, clay	silty sand	clayey silt
5	35.82	15.21	12.82	sand, silt, clay	sandy silt	sand, silt, clay
6	7.87	12.46	27.81	sandy silt	sandy silt	sand, silt, clay
7	4.25	1.31	23.16	silty sand	silty sand	sand, silt, clay
8	0.63	3.17	8.02	sand	silty sand	sand
9	1.55	1.24	9.26	sand	sand	sand

4.76-7.38, 5.59- 17.15 and 2.67-7.08 respectively. The percentage of clay was very low in this zone. The values were 0.63-1.55% during pre monsoon, 1.24-3.17% during monsoon and 8.02-9.26% during post monsoon.

Textural analyses showed a decrease in the percentage of sand in zone II from pre monsoon to monsoon and an increase in the post monsoon seasons. But the clay content showed a reverse trend. The clay fraction of the sediment was increased from 30.87% to 43% during post monsoon to monsoon season. But during post monsoon, the clay content of the sediment was reduced to 26.89 %. The silty nature of the sediment was maximum during pre monsoon seasons.

CHAPTER III

DISTRIBUTION OF NUTRIENTS IN WATER AND SEDIMENT

3.1 Introduction

Supply of inorganic nitrogen and phosphorus is recognised as an important factor regulating the productivity of the sea. Human activities have increased nutrient flows to the coast in many ways, including forest clearing, the destruction of riverine swamps and wetlands, the application of large amounts of synthetic fertilisers, the use of large amounts of nitrogen and phosphorus in various industrial processes, the addition of phosphorus to detergents, the production of large populations of livestock, the high temperature combustion of fossil fuels that has added large amounts of nitrogen to acid rain, and the expansion of human population in coastal areas. The study of nutrients in the dissolved and sedimental form would help in understanding the potential availability of life supporting elements in any particulate region of the aquatic system (Klump and Martens, 1981).

The distribution and dynamics of nutrients especially the processes associated with the sedimentary biogeochemical activities influences the general productivity of the aquatic systems. The estuaries and coastal waters and its sediments are considered to have a significant role in governing the global aquatic production. Though the productivity is restricted to the euphotic zone, the nutrient budget in these waters are more or less influenced by the sedimentary regeneration dynamics (Nixon et al., 1976). In many cases the sediment is considered to be a temporary sink and the influence as a biogeochemical reaction process. In the case of nutrients also, the role of sediments and the sedimentary interactions is observed to be the same.

The chemical forms take part in the dynamics of nitrogen are nitrite, nitrate, ammonium, urea and organic nitrogen. In the aquatic systems, the remineralisation of organic matter can act as a source for these nitrogen species. But in estuaries and coastal waters the land contribution is the main source. The use of artificial nitrogen and phosphorus fertilisers have significantly increased the concentration of these nutrients to the aquatic systems (Neill, 1989). The area of study in the present work, Kuttanad waters, receives significant load of nutrients from the land. The distribution pattern of the various forms of nitrogen and phosphorus in the water and the sediment, forms the content of this chapter.

3.2 Materials and methods

The materials and methods adopted for the analyses of nutrients in water and sediments were given in chapter II

3.3 Results and discussion

a. Nitrate

The surface and bottom distribution and concentrations of nitrate are shown in fig 3.1a &3.1b and table 3.1a. In pre monsoon the highest and lowest values recorded were 19.26 µg at/l and 2.11µg at/l. The maximum and minimum concentrations in the second zone were 7.01µg at/l and 3.07 µg at/l. The concentration in the third zone varied between 2.11 µg at/l – 8.87 µg at/l.

The range of values during monsoon increased to an upper limit of 6.43µg at/l and a lower limit of 4.70 µg at/l. The maximum and minimum concentration of nitrate in the second and third zone varied between 3.60-6.36 µg at/l and 1.69- 4.99 µg at/l respectively. In post monsoon the concentration in the first zone was in the range 2.53 - 14.35 µg at/l. The second and third zone recorded a maximum of 12.21µg at/l and 6.04 µg at/l and a minimum of 4.24 µg-at/l and 1.17µg at/l respectively. During post monsoon season, the concentration range of nitrate decreased steadily from first zone up to the third. A similar trend was observed during monsoon season also.

Table 3.1b and Fig 3.1c shows the distribution of extractable nitrate in the sediments of Kuttanad waters. During pre monsoon the concentration of nitrate in the sediments of the first zone varied between 4.31- 6.94 µg at/g. The maximum and minimum concentration of nitrate in the sediments of second zone ranged 8.37 - 10.10 µg at/g. In the third zone the value lies in between 5.46-4.43µg at/g. During monsoon the highest and the lowest values in the first zone were 6.14 and 4.87 µg at/g respectively. In the second zone the value was in between 5.31 -5.98 µg at/g and in the third zone the concentration ranged from 4.654- 5.83 µg at /g. The highest values were recorded during post monsoon in the first zone in which the mean values ranged from 7.14 to 12.59 µg at/g. The concentration of sediment associated nitrate in the second and third zone varied between 10.40-12.46 and 5.02-6.14 µg at/g.

The general distribution pattern in Cochin backwaters and the estuary is reported to have the nitrate concentrations comparable with the other estuaries (Annexure). The values reported by the earlier workers gave significant variations with the exact geographical location of the water body and ranged between 0-140 µg at/l. In the present study, the observed concentration ranged between 1.17-19.26 µg at/l. Compared to the different segments of Cochin backwaters, the Kuttanad waters, thus, exhibited a lower concentration of nitrate. The zone wise distribution pattern gave lowest concentration for the zone 111 and the highest for zone1. Zone111 being the estuarine zone, it can be implied that the addition of nitrate from the estuarine region to the fresh water region is not a significant process. Fresh water in general and river waters in particular is reported to have high amount of nitrite and is generally considered as a source of nitrate to the coastal and estuarine systems (Neill, 1989).

Nitrate is considered to be the most abundant and the most preferred nutrient. The major sources of nitrogen are land contribution and regeneration. Four rivers, which travels through this agricultural area, drains to the Kuttanad waters. The regeneration of nitrate generally takes place along with the mineralisation of organic matters and the major reaction zone is the subsurface water. As the depth of the water in the study area is low, between 1.5 to 10 meters, the possibility of regeneration in the water column in these water bodies are scarce. The Kuttanad region is well known for its agricultural activity and so the major contribution to the inorganic ions of nitrogen will be the fertilisers applied in the agriculture. Though the sediment can have a nutrient regenerative mineralisation of the organic matter the shallowness of the water makes the oxygen a limiting factor here.

The analysis of the seasonal distribution pattern, indicate a high concentration of nitrate during the post monsoon. The dynamicity of this water body is considered to be maximum during this seasons. The steady flow of fresh water along with the regular tidal activity are the major contributions to this dynamic character. The accumulation of organic matter is comparably low during this season. The agricultural activity during post monsoon is high. All these factors can lead to high nitrate concentration and the observation of the present study is in conformation with it. The monsoon and pre monsoon seasons are reflection of the fresh water discharge and the shallowness of the water body.

The sedimentary nitrate (extractable) levels can be seen to be very low in all the zones. Earlier available reports also indicate low nitrate levels associated with sediment (Annexure). The shallowness of the water column along with the concentration of organic matter will not be favourable for the regeneration of nitrate in the sediments. The anoxic character of the sediment in this backwater system was reported earlier also (Nair, 1992; Beenamma, 1993). The contribution of nitrate from the sediments to the overlying water, so, can be considered as negligible.

b. Nitrite

Fig3.2a&3.2b and table 3.2a shows the variation in the concentration of nitrite in water and the zonal variations during the three seasons. During pre monsoon the concentration range in the first zone lies between 0.23-0.64 µg at/l. In the second zone the highest and the lowest concentrations were 0.22µg at/l and 0.40 µg at/l respectively. During this season the concentration in the third zone was found to be in the range 0.34-0.57 µg at/l. In this season the higher values were observed in the first zone and the lower were in the second zone. During monsoon the concentration in the first zone varied between 0.17-0.41 µg at/l. In the second zone the value ranged between 0.25- 0.52µg at/l and in the third zone the concentration varied between 0.30 - 0.79 µg at/l. In post monsoon the maximum and the minimum values in the first zone were found to be 0.16 and 0.42 µg at/l. During this season the concentration in the second and third zones varied between 0.28 - 0.64 µg at/l and 0.33µg at/l - 0.43 µg at/l

Fig 3.2c and table 3.2b shows the nitrite concentrations in the sediments of Kuttanad aquatic system. The concentration of dissolved and adsorbed forms of nitrite in this region show close similarity. During pre monsoon, where the water show fresh water characteristics, the concentration range in the first zone was found to be 0.23-0.36 µg at/g. In the second zone the value varied between 0.17-0.27 µg at/g. The highest and the lowest concentration in the third zone was found to be 0.14 µg at/g. During monsoon the concentration range in the first zone was found to be 0.13 - 0.62 µg at/g. In the second zone the value lies between 0.14 - 0.23 µg at/g. The third zone showed a concentration which is comparatively lower than that of other two zones, 0.15 - 0.21µg- at/g. In post monsoon the highest and the lowest concentration in the first zone were 0.19 and 0.27 µg at/g. The amount of adsorbed nitrite in the second zone was found to be vary between 0.14 and 0.21 µg at/g. The maximum and minimum concentration in the third zone were 0.26 and 0.21µg at/g.

As in the case of nitrate, nitrite also gave lower concentrations compared to earlier works (Annexure). Nitrite is considered as the intermediate in the regeneration process of nitrogen cycle. Generally the reactivity of nitrite is considerably high and so the concentrations in the aquatic systems are low. As the nitrite concentrations will be near to the possible minimum value, no serious seasonal variation were encountered in any water body. In the present study also no serious variations are observed. The observed concentrations can thus be considered only as the reflections of the aquatic conditions and no anthropogenic additions or removal can be assigned. The sedimentary levels, low but steady values, also suggest such a normal behaviour.

c. Ammonia

The distribution of ammonia during three seasons and in the three zones are shown in the fig3.3a & 3.3b and table 3.3a. In pre monsoon season, the maximum concentration was observed in the station 4 of first zone (2.87 µg-at/l) and the minimum concentration at the bottom water of station 3 (1.37µg at/l). The concentration of ammonia in the second zone in this season ranges between 0.94 -4.17 µg at/l. The third zone behaves purely as estuarine during pre monsoon and the minimum and maximum concentration were 1.31µg at/l and 7.84µg at/l.

In monsoon the three zones behave like fresh water dominated regions. The highest and the lowest values observed in the first zone were 5.11 µg at/l and 2.68. In the second zone the value varied between 1.84 to 6.33 µg at/l respectively. The concentration of ammonia in the third zone ranged between 2.60 and 6.42 µg at/l.

During post monsoon in the first zone the maximum and the minimum were 5.05 and 2.94 µg at/l. The observed maximum value of ammonia in the second zone were 6.38µg at/l and the minimum value were 2.95 µg- at/l. Ammonia concentration in the third zone ranged between 1.52 µg at/l to 3.94 µg at/l.

Generally low concentrations of ammonia nitrogen were observed in the water bodies. Ammonia is the most preferred nutrient and the reactivity is also high. The concentrations are well within the range compared to earlier works (Annexure I). Significant seasonal variations in the ammonium nitrogen level were one of the main observations in the present study. The post monsoon maximum can be considered as reflection of the agricultural activity in this area. The lower values observed in zone 111 during post monsoon confirms this land contribution. The low values during post monsoon in the case of zone111 may have resulted from the higher phytoplankton activity during this seasons. At the same time the pre monsoon high values, indicates a low phytoplankton activity and substantial decomposition of organic matter. The possibility of a break in the decomposition of organic nitrogen to nitrate resulting in a production of ammonia cannot be ruled out. Bacterial remineralisation of organic matter is reported to generate NH_4^+ within the sediments. Reduction of nitrite for the overlying waters also is regarded as an additional source of ammonia in the sediments (Moris et al,1985). In the present study, a low nitrate concentration along with a reducing sediment is available with the system and the operation of above possibilities can not be ruled out. The establishment of this requires a detailed study on the diagenesis of organic matter, which is beyond the scope of the present study.

d. Urea

Though the fertility of the aquatic system was generally defined in terms of availability of inorganic species of nitrogen and phosphorus, the recent studies have indicated that a major portion of dissolved organic substances have a significant role in it. Urea a product of the nitrogen metabolism, which is excreted through urine is observed to be playing a major role in the aquatic productivity. The works on the chemistry of seawater and on the nitrogen and phosphorus requirements of the phytoplankton suggest that urea forms a part of the nitrogen reserve in the coastal waters (Remsen 1971). Along with the excretion, the microbial action on amines, also is found to produce urea in the aquatic system. Generally the concentration observed is very low, except in some specified areas (Remsen, 1971 ; Newell, 1967).

Fig 3.4a & 3.4b and Table 3.4a shows the distribution of urea in water. During pre monsoon the concentration of urea ranged between 3.97 and 6.97µg at/l, 5.02 and 9.84µg at/l and 9.11 and 10.23µg at/l for zones I,II and III respectively. During monsoon the values were in the range 3.43-10.44µg at/l, 4.65-9.55 µg at/l and 3.27-7.76 µg at/l in the respective order. But during post monsoon the concentration of urea were high and the values were in the range 11.25-15.26 µg at/l ,9.59-14.28µg at/l and 10.58-12.70 µg at/l for the zones I, II and III respectively.

Sediment associated urea also showed more or less same trend that of dissolved form (Fig 3.4c and table 3.4b). During pre monsoon the highest and lowest concentration varied between 9.30-5.70 µg at/g, 10.20-2.20 µg at/g and 6.17- 6.57 µg at/g for zones I, II and III respectively. During monsoon the values ranged between 7.73 and 10.03µg at/g, 8.50 and 12.90µg at/g and 8.33 and 9.80 µg at/g for zones I, II and III in the respective order. Comparatively high concentration of urea was observed during post monsoon and the values were in the range 5.80-9.37µg at/g, 7.43-11.33µg at/g and 7.47-8.63 µg at/g for the zone I, II and III respectively.

Reports of the earlier works are given in Annexure . In the present study, the high values of urea observed along with the seasonal variations suggest an anthropogenic input rather than in situ production and conception. The biological population of the higher organism in the Kuttanad waters is unable to build in such high values. Moreover the general fertility and the productivity characteristics does not allow the building up of such high values unless there is a heavy input through the anthropogenic sources. The agricultural practices in Kuttanad waters can be considered as the main sources and the seasonal values clearly points to this. The maximum agricultural activities were observed during post monsoon and the first phase of the pre monsoon. The monsoonal high values also do not support an argument, which attribute the observed urea concentration to the in situ production.

The uniform distribution pattern of urea in the sediment during the three seasons can be considered as the retention of adsorbed urea. In the reducing environment available with the sediment will not favour the oxidative decomposition of urea so the observed concentration can be considered as a reflection of the exchange equilibrium with the overlying waters.

e. Phosphate

Fig 3.5a & 3 5.b and table 3.5a represent the distribution and concentration of phosphate in water during the three seasons. During pre monsoon in zone I the highest and the lowest concentration were varied between 0.75 and 0.43 µg at/l. The range of concentration reported in zones II and III were 0.35-0.92 an 1.87 –0.85 µg at/l. During monsoon in zone I the values were in the range 0.84-1.49 µg at/l. In zones II and III the highest and lowest concentration observed were 3.38 & 0.87 µg at/l. and 1.89 & 0.97 µg at/l. During Post monsoon the values raised to a maximum of 1.01, 0.96 and 1.30 µg at/l for zones I,II and III respectively. The lowest values were 0.81, 0.80 and 0.91µg at/l in the respective order.

The seasonal and zonal distribution of phosphate are given in table 3.5b and fig 3.5c and 3.5b . During pre monsoon the values were ranged between 3.22 - 6.08 µg at/g, 4.33 - 5.34µg at/g and 3.06 - 3.22 µg at/g for zones I, II and III respectively. During monsoon the values in zone I raised to a maximum of 7.15 and a minimum of 3.15. In zones II and III the concentrations were in the range 4.29-4.91 and 3.57-5.55 µg at/g. During post monsoon the concentration of phosphate ranged between 2.45 and 4.60 µg at/g, 3.82 and 5.27 µg at/g and 3.17 and 3.87 µg at/g for zones I, II and III respectively.

The Cochin Backwaters are reported to have the phosphate concentration well within the range observed in different water masses (Annexure). The present study also gave comparably lower values to the phosphate distributions throughout the study area. The significant seasonal variations with a maximum during monsoon is an indicative of contributions from land as well as agricultural operations within the area.

When compared to earlier works the sedimentary phosphate levels also gave lower values. Significant variations were observed in sediments during post

Stationwise distribution of nutrients in surface and bottom waters (µg at/l)

Table3.1a Nitrate

Station	S/B	Pre-Monsoon	Monsoon	Post-Monsoon
1	S	4.59	5.18	4.52
	B	19.26	6.43	12.65
2	S	3.89	5.15	4.47
	B	5.14	4.89	5.82
3	S	2.11	4.94	2.53
	B	11.30	6.21	14.35
4	S	3.04	5.72	4.83
	B	2.67	4.70	6.36
5	S	7.01	6.36	11.78
	B	3.09	3.60	4.38
6	S	5.50	5.31	4.24
	B	6.65	6.27	7.94
7	S	4.94	3.72	8.95
	B	4.81	3.76	12.21
8	S	5.09	4.00	4.85
	B	8.87	4.99	1.17
9	S	3.88	2.47	6.04
	B	2.11	1.69	2.77
Zone				
I		6.50	5.44	6.94
II		5.33	4.84	8.25
III		4.99	3.29	3.71

Table3.2a Nitrite

Station	S/B	Pre-Monsoon	Monsoon	Post-Monsoon
1	S	0.35	0.26	0.42
	B	0.23	0.41	0.32
2	S	0.30	0.21	0.34
	B	0.40	0.28	0.26
3	S	0.64	0.20	0.29
	B	0.34	0.22	0.18
4	S	0.55	0.17	0.31
	B	0.33	0.36	0.16
5	S	0.35	0.29	0.43
	B	0.34	0.25	0.64
6	S	0.40	0.27	0.40
	B	0.34	0.33	0.33
7	S	0.23	0.52	0.37
	B	0.22	0.47	0.28
8	S	0.57	0.37	0.43
	B	0.34	0.31	0.33
9	S	0.47	0.30	0.41
	B	0.37	0.79	0.43
zone				
I		0.39	0.26	0.29
II		0.31	0.36	0.41
III		0.44	0.44	0.40

Table3.3a Ammonia

Stations	S/B	Pre-Monsoon	Monsoon	Post-Monsoon
1	S	1.67	4.79	5.05
	B	1.38	2.68	4.43
2	S	1.58	3.79	3.68
	B	2.15	2.93	5.64
3	S	2.08	3.31	3.86
	B	1.37	2.91	2.94
4	S	2.86	5.11	4.18
	B	2.87	3.71	4.86
5	S	1.37	5.97	4.67
	B	3.46	4.08	2.95
6	S	0.94	1.84	6.38
	B	2.50	6.33	5.92
7	S	4.17	2.58	4.76
	B	3.56	4.64	3.59
8	S	3.46	6.42	3.94
	B	7.84	4.34	3.38
9	S	1.31	3.42	1.52
	B	3.67	2.60	2.38
Zone				
I		2.00	3.65	4.33
II		2.67	4.24	4.71
III		4.07	4.19	2.81

Table3.4a Urea

Stations	S/B	Pre-Monsoon	Monsoon	Post-Monsoon
1	S	3.97	8.80	14.18
	B	6.96	3.43	14.11
2	S	6.13	7.23	13.39
	B	6.97	10.44	13.42
3	S	5.79	5.02	12.75
	B	5.54	5.95	11.25
4	S	5.48	5.21	15.26
	B	5.44	7.50	14.72
5	S	5.02	4.65	9.59
	B	5.22	9.55	13.48
6	S	9.45	5.31	12.38
	B	9.84	5.46	14.28
7	S	5.95	5.68	13.16
	B	8.35	5.79	13.25
8	S	9.11	5.62	12.44
	B	9.90	7.76	12.70
9	S	10.23	4.08	10.58
	B	9.64	3.27	11.36
Zone				
I		5.78	6.70	13.64
II		7.31	6.07	12.69
III		9.72	5.18	11.77

Table3.5a Phosphate

Station	S/B	Pre-Monsoon	Monsoon	Post-Monsoon
1	S	0.75	1.24	0.99
	B	0.62	1.43	1.01
2	S	0.53	1.21	0.84
	B	0.63	1.40	0.91
3	S	0.52	1.49	0.87
	B	0.49	0.84	0.81
4	S	0.43	0.93	0.86
	B	0.50	1.35	0.88
5	S	0.92	2.00	0.94
	B	0.60	1.43	0.85
6	S	0.58	3.38	0.90
	B	0.74	1.01	0.90
7	S	0.35	0.87	0.80
	B	0.57	1.13	0.96
8	S	0.85	1.49	0.91
	B	1.77	1.89	1.30
9	S	1.00	1.20	1.05
	B	1.87	0.97	0.94
zone				
I		0.56	1.27	0.90
I		0.63	1.69	0.89
I		1.37	1.39	1.05

Stationwise variations of nutrients in surface water (µg at/l)

Fig. 3.1a Nitrate

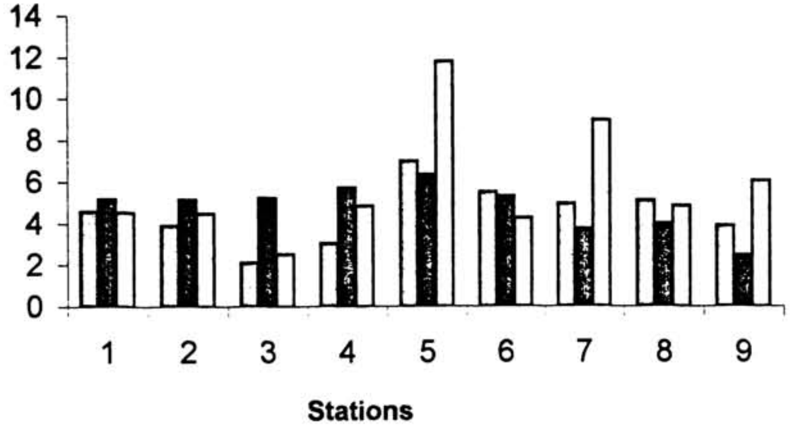


Fig.3.2a Nitrite

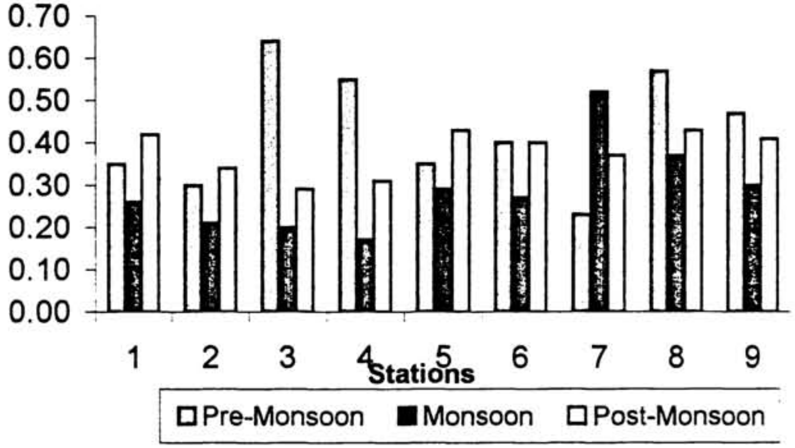


Fig.3.3a Ammonia

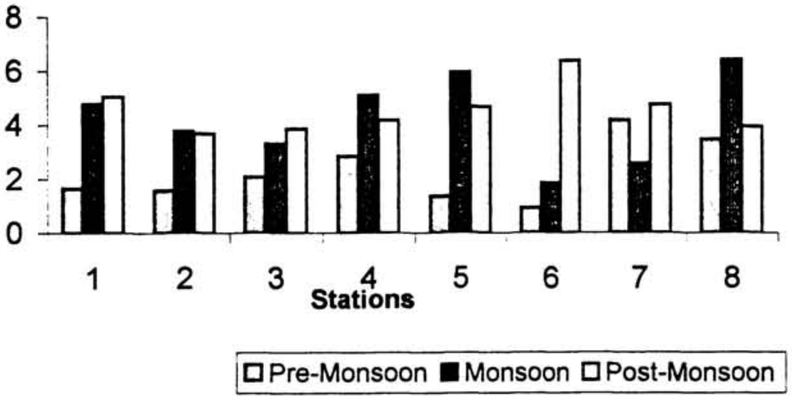
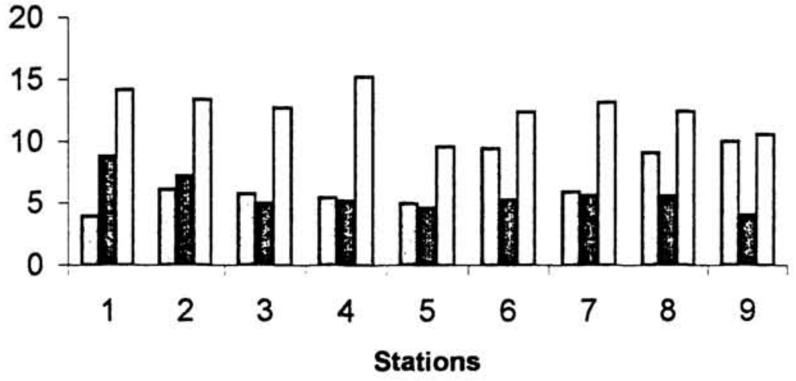


Fig.3.4 a Urea



Stationwise varaiations of nutrients in bottom water (µg at/l)

Fig 3.1b Nitrate

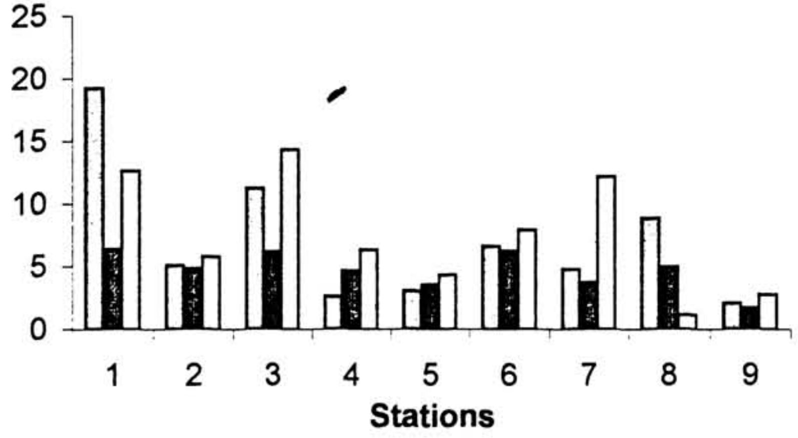


Fig 3.2b Nitrite

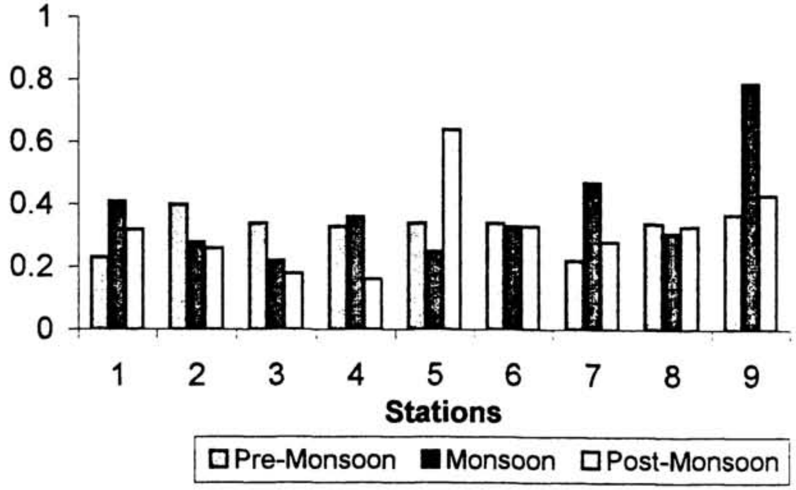


Fig 3.3b Ammonia

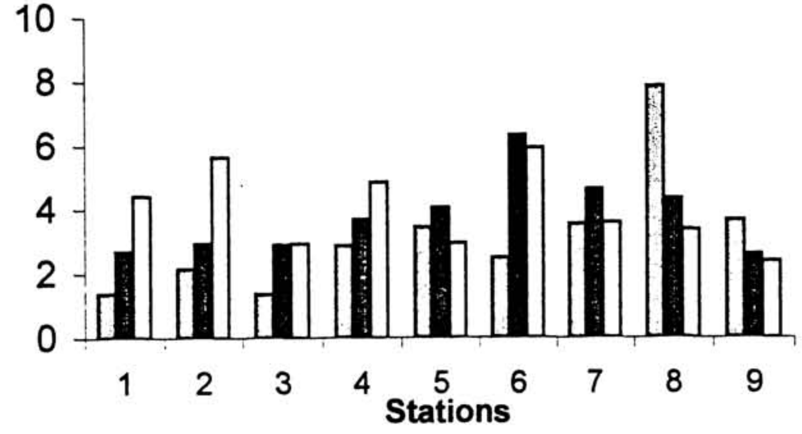
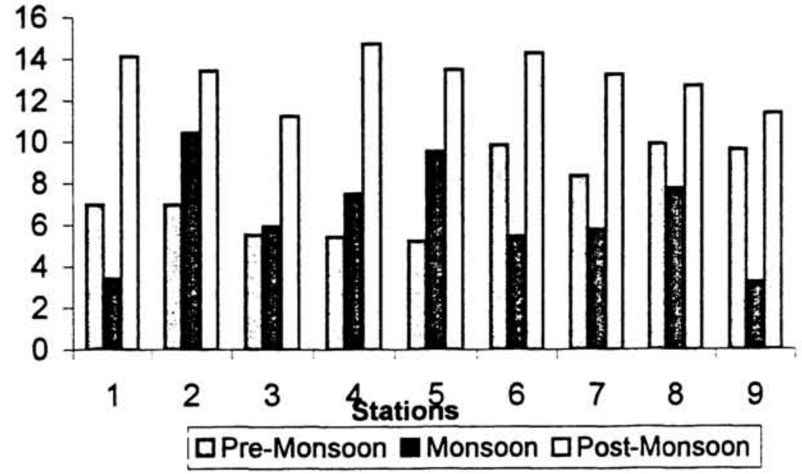


Fig 3.4b Urea



Stationwise variation of phosphate in surface and bottom water(µg at/l)

Fig 3.5a Phosphate (surface)

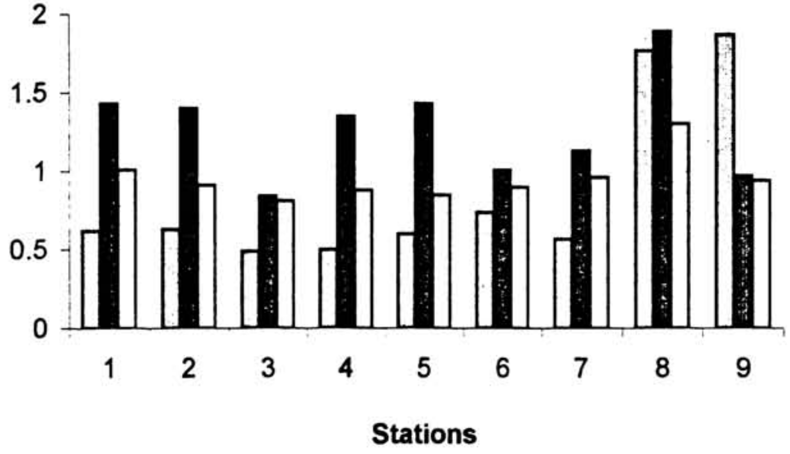


Fig 3.5b Phosphate (bottom)

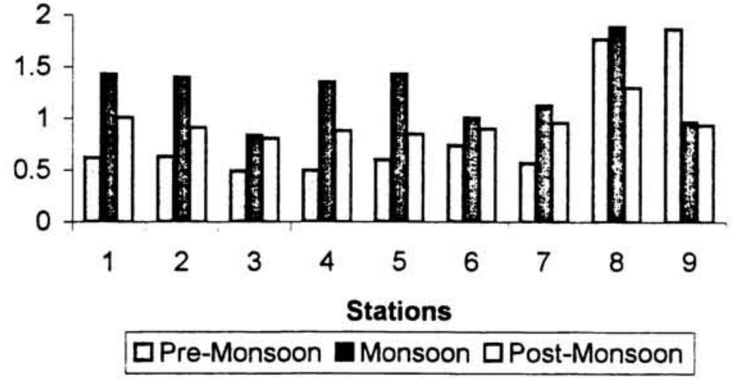


Table3.1bStationwise distribution of Nitrate in sediments (μg at/g)

Stations	Pre-Monsoon	Monsoon	Post-Monsoon
1	5.21	5.41	7.67
2	6.36	4.87	12.59
3	6.94	6.14	7.14
4	4.31	5.19	7.94
5	8.37	5.31	10.40
6	10.10	8.13	12.46
7	10.09	5.98	11.52
8	5.46	5.83	5.02
9	4.43	4.65	6.14
zone			
I	5.71	5.41	8.84
II	9.52	6.48	11.46
III	4.95	5.24	5.58

Fig 3.1c

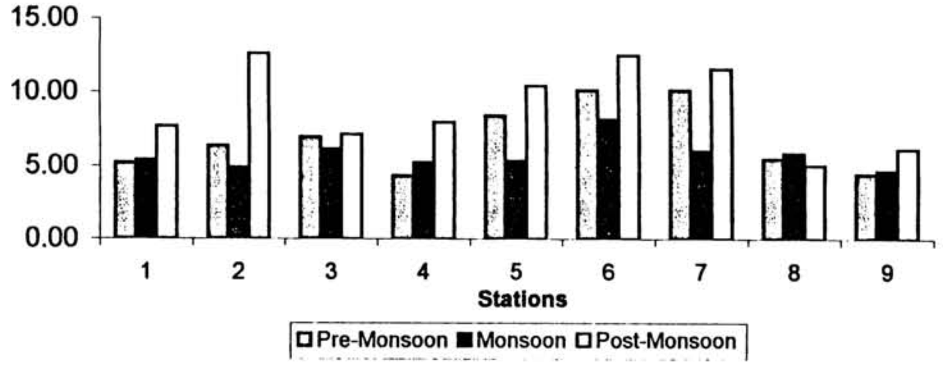


Fig 3.2bStationwise distribution of Nitrite in sediments(µg at/g)

Stations	Pre-Monsoon	Monsoon	Post-Monsoon
1	0.24	0.13	0.23
2	0.24	0.30	0.27
3	0.36	0.19	0.19
4	0.23	0.62	0.23
5	0.20	0.14	0.19
6	0.27	0.23	0.14
7	0.17	0.16	0.21
8	0.14	0.21	0.21
9	0.14	0.15	0.26
zone			
I	0.27	0.31	0.23
II	0.21	0.18	0.18
III	0.14	0.18	0.24

Fig 3.2c

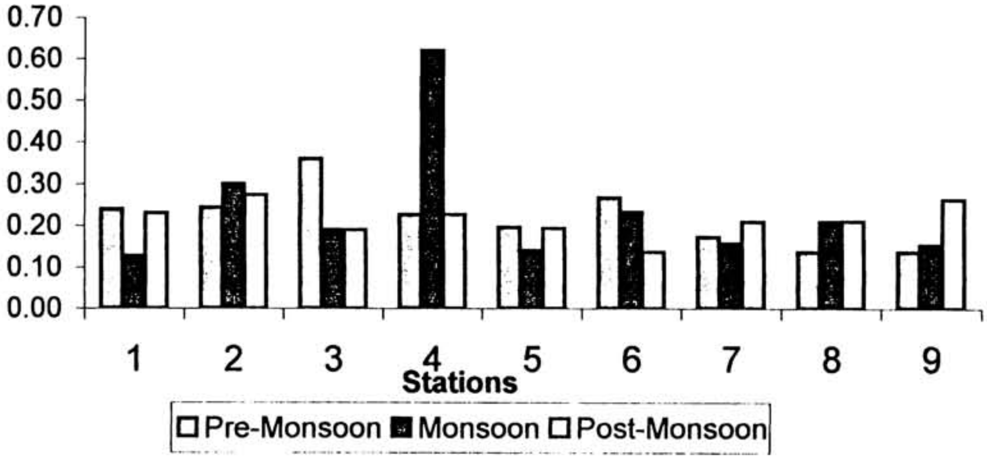


Fig 3.4b Stationwise distribution of Urea in sediments(µg at/g)

Stations	Pre-Monsoon	Monsoon	Post-Monsoon
1	5.70	7.73	5.93
2	9.33	10.03	8.30
3	6.20	8.37	9.37
4	8.30	8.80	5.80
5	7.73	12.90	7.43
6	4.73	9.57	8.30
7	10.20	8.50	11.33
8	6.17	9.80	7.47
9	6.57	8.33	8.63
zone			
I	7.38	8.73	7.35
II	6.95	10.32	9.02
III	6.37	9.07	8.05

Fig 3.4c

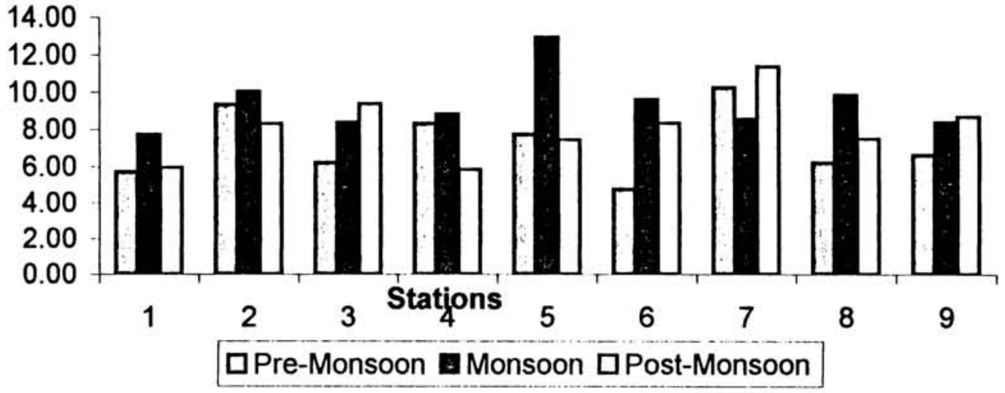


Table 3.5b Stationwise distribution of Phosphate in sediments(µg at/g)

Stations	Pre-Monsoon	Monsoon	Post-Monsoon
1	5.66	3.83	2.45
2	3.22	4.70	2.86
3	4.09	3.15	4.26
4	6.08	7.15	4.60
5	5.34	4.91	5.27
6	5.15	4.29	3.82
7	4.33	4.52	4.74
8	3.06	3.57	3.85
9	3.22	5.55	3.17
zone			
I	4.76	4.90	3.54
II	4.94	4.57	4.61
III	3.14	4.56	3.51

Fig 3.5c

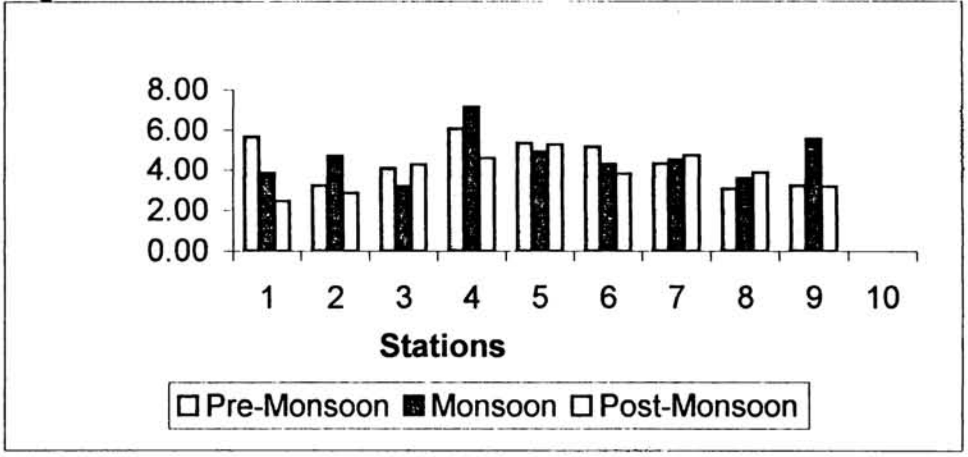


Table3.1bStationwise distribution of Nitrate in sediments (µg at/g)

Stations	Pre-Monsoon	Monsoon	Post-Monsoon
1	5.21	5.41	7.67
2	6.36	4.87	12.59
3	6.94	6.14	7.14
4	4.31	5.19	7.94
5	8.37	5.31	10.40
6	10.10	8.13	12.46
7	10.09	5.98	11.52
8	5.46	5.83	5.02
9	4.43	4.65	6.14
zone			
I	5.71	5.41	8.84
II	9.52	6.48	11.46
III	4.95	5.24	5.58

Fig 3.1c

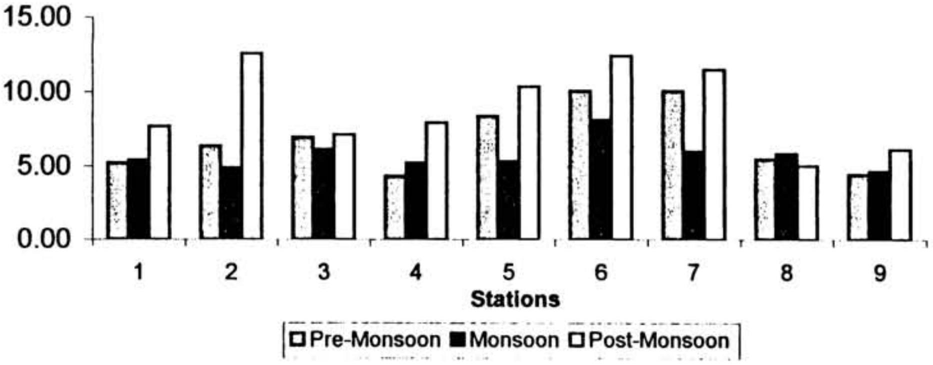


Fig 3.2bStationwise distribution of Nitrite in sediments(μg at/g)

Stations	Pre-Monsoon	Monsoon	Post-Monsoon
1	0.24	0.13	0.23
2	0.24	0.30	0.27
3	0.36	0.19	0.19
4	0.23	0.62	0.23
5	0.20	0.14	0.19
6	0.27	0.23	0.14
7	0.17	0.16	0.21
8	0.14	0.21	0.21
9	0.14	0.15	0.26
zone			
I	0.27	0.31	0.23
II	0.21	0.18	0.18
III	0.14	0.18	0.24

Fig 3.2c

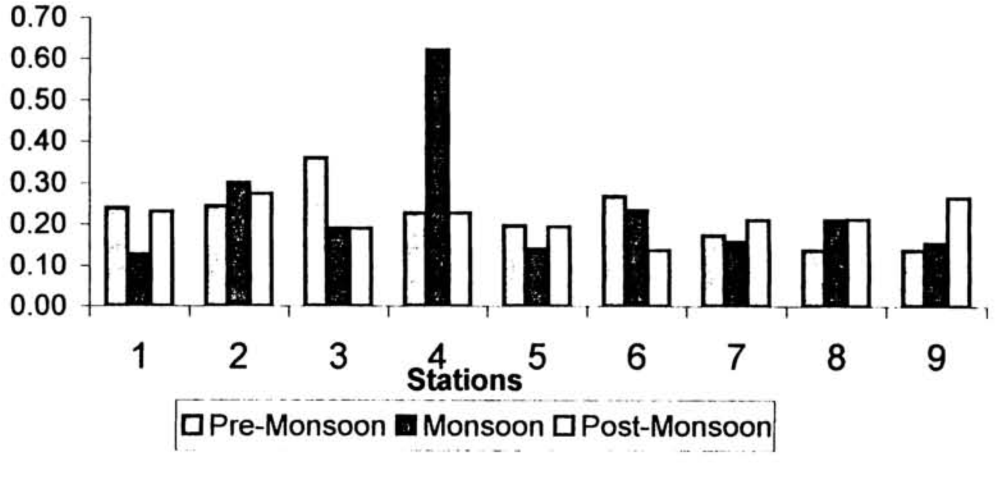


Fig 3.4b Stationwise distribution of Urea in sediments(µg at/g)

Stations	Pre-Monsoon	Monsoon	Post-Monsoon
1	5.70	7.73	5.93
2	9.33	10.03	8.30
3	6.20	8.37	9.37
4	8.30	8.80	5.80
5	7.73	12.90	7.43
6	4.73	9.57	8.30
7	10.20	8.50	11.33
8	6.17	9.80	7.47
9	6.57	8.33	8.63
zone			
I	7.38	8.73	7.35
II	6.95	10.32	9.02
III	6.37	9.07	8.05

Fig 3.4c

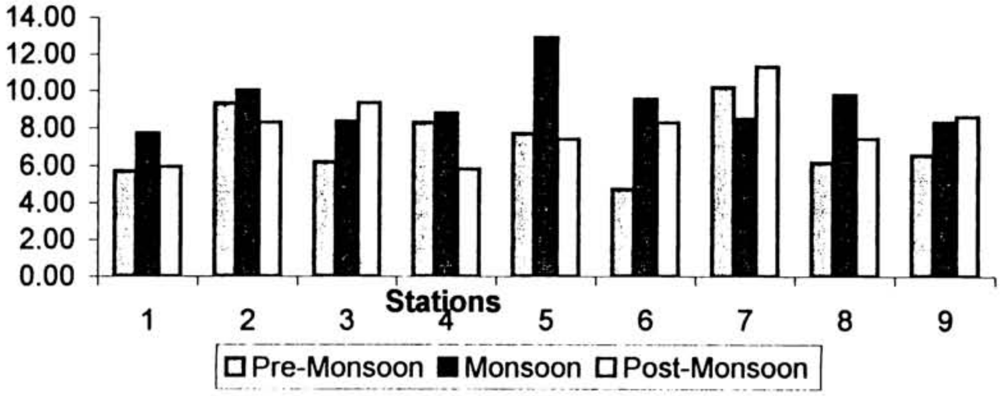
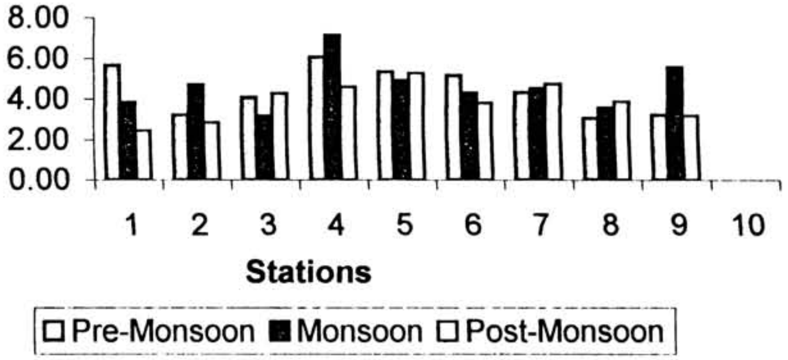


Table 3.5b Stationwise distribution of Phosphate in sediments(µg at/g)

Stations	Pre-Monsoon	Monsoon	Post-Monsoon
1	5.66	3.83	2.45
2	3.22	4.70	2.86
3	4.09	3.15	4.26
4	6.08	7.15	4.60
5	5.34	4.91	5.27
6	5.15	4.29	3.82
7	4.33	4.52	4.74
8	3.06	3.57	3.85
9	3.22	5.55	3.17
zone			
I	4.76	4.90	3.54
II	4.94	4.57	4.61
III	3.14	4.56	3.51

Fig 3.5c



monsoon. The sediments of zone 111 also showed significant variations. In zone 111 maximum values are observed in monsoon due to fresh water discharge.

Comparatively high phosphate concentrations suggest that a small change in water bodies does not reflect the phosphate concentrations. Studies on organic rich marine sediments suggest the formation of dissolved phosphate in pore water. This further gets diffused through the sediments and could get released to the overlying water or remain adsorbed to the sediment (Marten et al, 1978). The net concentration of phosphate available with the sediment was reported to be the result of an equilibrium between the adsorption or release (Krom & Berner, 1980)

3.3 Organic Carbon, Total phosphorus and Total Nitrogen

Seasonal variation in organic carbon at the different stations is presented in fig 3.6 and table 3.6. In general there was an increase in organic carbon during the post monsoon season in zone I and zone III. In zone II pre monsoon showed higher values. During pre monsoon the maximum organic carbon content for zone I, II and III were 32.33 mg/g, 24.35 mg/g and 8.66 mg/g respectively and the minimum observed were 21.78 mg/g, 16.12 mg/g and 8.05 mg/g for the three zones in the respective order. During monsoon all the zones showed low values. The concentration in zone I ranged between 6.50 & 12.97 mg/g. The values in zone II were in the range 3.71 & 13.33 mg/g and in zone III between 5.11& 7.39 mg/g. In post monsoon zone I and II the maximum and minimum values observed were 31.47 & 25.09 and 21.86 & 17.00 mg/g respectively. In zone III the values varied between 3.48 and 29.04 mg/g.

Observed values for total phosphorus are shown in fig 3.7 and table 3.7 Generally phosphorus concentration showed high values in post monsoon and low values in monsoon. During pre monsoon concentration of phosphorus in zone I varied between 0.93 and 1.59 mg/g. In zone II and III the values varied from 0.47 to 1.20 mg/g and from 0.13 to 0.38 mg/g respectively. During monsoon the highest concentration in zone I, II and III were 1.07, 0.76 and 0.22 mg/g . The corresponding lowest values were 0.77, 0.27 and 0.12 mg/g. During post monsoon the highest and lowest concentrations in zone I were 1.83 and 1.45 mg/g. In zone II the values were 0.57 and 2.42 mg/g and in zone III 0.63 and 0.90 mg/g.

During pre monsoon total nitrogen concentration in zones I, II and III were in the range 4.48-6.72, 3.36-7.84 and 3.92-5.04 mg/g respectively. During monsoon the highest and lowest concentrations observed in zone I were 6.72 and 4.48 mg/g. Zone II showed a maximum of 7.84 and a minimum of 7.28 mg/g in the monsoon season. In zone III the values varied between 2.24 and 3.36 mg/g. The observed values in post monsoon season for zone I was in the range 5.62- 7.28 mg/g. In zone II the concentration range was 5.60 and 7.84 mg/g .A maximum of 7.82 and a minimum of 6.72 mg/g were recorded in zone III.

Generally the estuarine sediments are considered to be the storehouse of organic matter which is either brought from the land or generated in the water column or both. So a high organic content in these sediments is a natural feature.

In the sediments of Cochin backwaters also significantly high organic carbon content was reported by several workers (Sankaranarayanan, 1979; Nair, 1992; Beenamma, 1993; Jayasree, 1993). However the riverine zone of the Back water system was found to have only low organic matter which was attributed to the texture of the sediment. The riverine sediments shows more or less sandy character where as the estuarine sediments composes of mainly silt and or clay. In the present study zones I and zone II were found to have significantly high concentration in organic matter compared to zone III. Though zones I and II represent more or less fresh water character, the lake character contributes to the formation of a sediment with a high content of silt and clay. The shallowness of the water body and the restricted character along with the grain size of the sediment can result in an increased settling and accumulation of the organic matter. Zone III continuously gave low organic matter content only. This zone is found to be having estuarine character but the sediment was sandy in texture. The sandy character of the sediment generally exhibits only low organic matter. The case is applicable here also. The contribution from the sediment texture towards the organic carbon content is clearly evident from the values observed for the monsoon season. In all zones the grain size analysis have shown that the sediment in monsoon season is more or less dominated by sand and the concentration of the organic carbon showed the lowest values during monsoon. The flushing of the sediment by the flood water from the rivers can also be a reason for the low organic carbon during the monsoon season.

Though the estuarine sediments generally show a high value of phosphorus and the riverine sediment exhibit a low value, a reverse trend was observed in this study (Fig 3.7 and table 3.7). The riverine zone I and zone II showed high values and the estuarine zone III gave the low values. In the Cochin Backwater system, the earlier studies have indicated that the general trend holds good for this system (Nair, 1990; Nair, 1992; Jayasree, 1993). The observation in the present study can be explained only by analysing the conditions prevailed in Kuttanad waters. The riverine zones are more or less integral parts of the agricultural activities. The shallow watershed character with low flushing promotes a high concentration of phosphorus in the sediments. The discharge of agriculture drains containing substantial remains of the phosphorus fertilisers may be contributing towards the high concentration of the phosphorus in pre monsoon and post monsoon sediments. The flushing of the sediment during monsoon season can lead to the low concentration observed in this season. Zone III though is estuarine in character, the sandy character may be leading to a comparatively low concentration of phosphorus. The post monsoonal maximum is a general observation in estuarine conditions (Sankaranarayanan, 1979; Anirudhan, 1989; Nair, 1992; Jayasree, 1993; Beenamma, 1993)

The behaviour of nitrogen generally runs parallel to the behaviour of phosphorus (Fig 3.8 and table 3.8). In all most all natural systems a definite ratio is always maintained between nitrogen and phosphorus. Though the general trend observed in the present study is also same to that of phosphorus, significant modification in the actual values are observed. The observed values

Table3.6Stationwise variations of Organic Carbon in sediments (mg/g)

station	Pre-Monsoon	Monsoon	Post-Monsoon
1	30.96	8.42	25.09
2	21.79	6.50	31.47
3	32.33	12.97	28.74
4	30.11	8.06	28.33
5	16.12	13.33	21.86
6	24.35	10.97	17.00
7	23.41	3.71	19.02
8	8.05	5.11	29.04
9	8.66	7.39	3.48
zone			
I	28.80	8.99	28.41
II	21.29	9.34	19.29
III	8.35	6.25	16.26

Fig 3.6

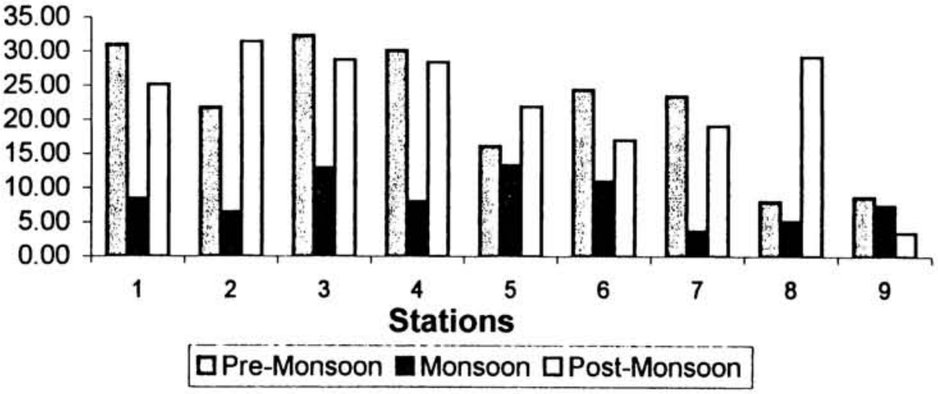


Table 3.7 Seasonal variations of total phosphorus in the sediment(mg/g)

Stations	Pre-Monsoon	Monsoon	Post-Monsoon
1	1.45	0.771	1.784
2	1.59	0.863	1.830
3	1.05	0.875	1.457
4	0.93	1.076	1.637
5	1.20	0.726	2.420
6	1.19	0.763	1.412
7	0.47	0.272	0.578
8	0.13	0.221	0.638
9	0.38	0.119	0.896
zone			
I	1.25	0.896	1.677
II	0.95	0.587	1.470
III	0.26	0.170	0.767

Fig 3.7

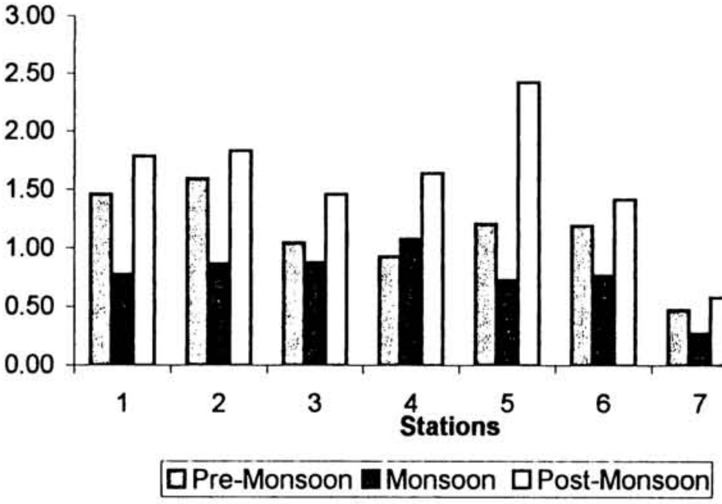
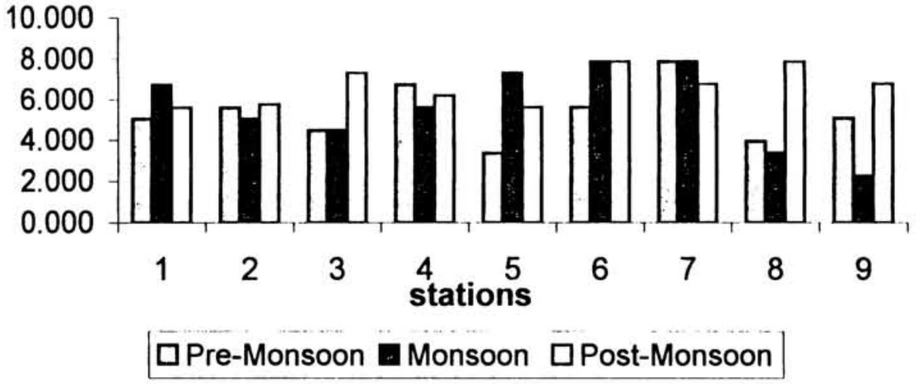


Table 3.8Stationwise distribution of Total Nitrogen in sediments (mg/gm)

Stations	Pre-Monsoon	Monsoon	Post-Monsoon
1	5.04	6.72	5.60
2	5.60	5.04	5.76
3	4.48	4.48	7.28
4	6.72	5.60	6.16
5	3.36	7.28	5.60
6	5.60	7.84	7.84
7	7.84	7.84	6.72
8	3.92	3.36	7.82
9	5.04	2.24	6.72
zone			
I	5.46	5.46	6.20
II	5.60	7.65	7.01
III	4.48	2.80	7.30

Fig 3.8



are significantly higher than that reported by many of the workers (Anirudhan, 1989; Nair, 1990; Nair, 1992; Jayasree, 1993; Beenamma, 1993). Except the reasons sited in the case of phosphorus and carbon no specific reasons are attributed here

3.5 C/N, C/P and N/P ratios

The general chemical characteristics and fertility of the water bodies like Kuttanad waters will have contributions from the land, the agricultural operations and the possible diagenetic processes. The nutrient dynamics thus will be dependent on the anthropogenic input, uptake and regeneration and sedimentary incorporation.. Analyses of C/P, C/N and N/P ratios can throw light in to the nutrient characteristics. The observed values of these ratios are given in table 3.9.

Zones 1 and 11 gave the minimum of C/P in monsoon and the maximum in pre monsoon. Zone 111 but showed maximum in monsoon and minimum in post monsoon. Zones 1 and 11 showed the same trend for C/N and N/P. Zone 111 gave the maximum in monsoon for C/N and pre monsoon for the N/P. C/N and N/P gave the minimum during pre monsoon and post monsoon respectively.

The ratios of carbon, nitrogen and phosphorus reported for other water bodies are given in (Annexure I). Sankaranarayanan et al (1979) have reported a C/P ratio which varies between 2.25:1 and 27.41:1 with an average of 10.67:1 for the sediments of Cochin Backwaters. Qasim & Sankaranarayanan (1972) have reported that the detritus of Cochin

Backwaters is having a C/P of 22.61:1 to 60.4:1 with an average of 41.0:1. The studies on the various constituents of the sediments of Cochin Backwaters by several authors (Qasim & Sankaranarayanan, 1972; Sankaranarayanan et al.,1979; Nair, 1992; Beenamma,1993) have revealed that the surface layers of the sediment comprises of mostly settled detritus. In the present study the C/P ranged between 10.55:1 and 36.77:1 with an average of 21.34:1. Though the aquatic plant material exhibits a high C/P ratio, the sediments, especially the coastal and the estuarine sediments is found to have a lower value. Only. The lower C/P ratio for the coastal and estuarine waters is attributed to the contribution from land to the phosphorus content. The significantly low C/P ratios observed in the present study indicates an anthropogenic input of organic matter which contains substantially high phosphorus.

Analysing the carbon and nitrogen in the sediment of estuaries, lagoons and oceans throughout the world Trask have reported a C/N ratio between 8 and 12. Sankaranarayanan & Panampunayil, (1979) have reported a C/N of 2.52 to 16.9 with an average of 6.4 in the case of Cochin Backwaters. The detritus of Cochin Backwaters exhibited a C/N between 5 and 10.5 with an average of 7.6 (Qasim &Sankaranarayanan, 1972). The studies on the west coast of India during the cruises of *RV Meteor* gave a C/N between 1 and 8 and the shelf sediments of Arabian sea, a value ranging from 2.48 to 37.5 (Bhosle et al., 1977). The high

C/N obtained in the shelf sediments was attributed to the degradation of complex protein. Very low values of C/N 0.2 to 2.0, was reported by Nasnolkar et al., (1996) in the Mandovi estuary along the west coast of India. Generally a high C/N is characteristic of marine organic matter and low that of the fresh water. In the present study the C/N varied between 1.22 to 5.27 with an average of 2.83. The comparison of values with that of the earlier reports for the Cochin Backwaters and other water masses clearly indicates the contribution of terrestrial or fresh water organic matter to the sediment (Annexure). The significant observation in the study is that C/N shows a higher value for the pre monsoon and a lower value to the monsoon. This is contrary to the general observation. The only reasonable argument which can be made to explain, this, is the contribution of nitrogen in the form of fertilisers to the nitrogen content of the sediment. Pre monsoon represent a more shallow condition with a low land discharge. The contribution from the agricultural activities so will be less during pre monsoon. The pre monsoon thus exhibit more or less a general estuarine character.

The C/N and N/P ratios are also low except the C/N values of zone I, during pre monsoon and post monsoon and N/P values of zone 111 during pre monsoon and monsoon. The N/P ratios indicate two possibilities, a decrease in ammoniacal nitrogen or an increase in phosphorus content. In zone 1 during pre monsoon and post monsoon the C/N is more or less near to the values of reported elsewhere. In zone

111 the N/P values during pre monsoon and monsoon are closer to the earlier reported values.

The C/N values when analysed along with N/P values indicate that there is substantial modification in the character of the organic matter as well as the phosphorus content. The low C/N is associated with a normal N/P ratios in the zone III as well as a normal C/N and N/P in the zone 11, all indicate a complex at the same time a dynamic system. Both the phosphorus and the nitrogen are having higher values. The main reason may be the land addition. The variation in the ratios from the normal values also point to such an addition. Moreover the low N/P values suggest substantial addition of inorganic phosphate to the system. The Kuttanad waters, because of the agricultural operations can have such a contribution. The application of bio- manures in the agricultural practices and its transport to the surrounding water masses can also contribute for a high terrestrial organic matter with significantly different nitrogen and phosphorus content. Zone 1 and 11 are having high organic content with low N/P and C/P values.

In conclusion this water body contains substantial contribution from the anthropogenic sources. The shallowness of the water body along with the substantial amount of organic matter may be acting as a limiting factor in the diagenetic processes. The complex nature of ratios supports the above.

Table 3.9 Seasonal variations of C/P,C/N and N/P ratios in sediments

	Zone	C/P	C/N	N/P
Pre monsoon	**1**	22.85	5.27	4.33
	11	22.41	3.80	5.89
	111	32.12	1.86	17.23
Monsoon	**1**	10.55	1.74	6.07
	11	15.82	1.22	12.97
	111	36.77	2.23	16.47
Pre monsoon	**1**	16.91	4.58	3.69
	11	15.31	2.75	5.56
	111	19.39	2.07	9.36

3.6 Interrelations

The correlation matrix observed for the various parameters in water and sediments is given in Annexure. No complete correlations between any of the parameters was but at the same time premonsoon and post monsoon gave the maximum correlation. The influence of the heavy discharge of rain waters on the various biogeochemical processes can be the main reason for the general non-availability of correlation during monsoon seasons. The influence of anthropogenic input may be the reason for the observed structure of the correlations.

CHAPTER IV

Speciation of Phosphorus and Nitrogen

4.1 Phosphorus

a. Introduction

b. Materials and methods

c. Results

d. Discussion

4.2 Nitrogen

a. Introduction

b. Materials and methods

c. Results

d. Discussion

4.1 Phosphorus

a. Introduction

Population growth and concentration in urban settlements have imposed serious threat to the quality of the rivers and coastal regions due to the discharge of wide spectrum of chemical entities through the sewage volumes. One of the main components in these discharges is the artificial or biogenic compounds of nutrient elements which normally gets associated with the sediments. The sedimentary nutrient and the anthropogenic input of nutrient species in estuarine and coastal areas affects the ecological structure of aquatic systems (Stumm and Morgan, 1996) and increases the rates of carbon fixation and storage in the sediments. Recent advancements in agricultural practices generally lead to the input of large quantities of fertilisers, a significant portion of which finally reaches the aquatic system. The quantities used are, however, larger than needed. Recent sediments of estuaries and coastal regions under the influence of man made nitrogen and phosphorus act as a continuous source of nutrients to overlying waters, reinforcing the deleterious effects of fertilisation. An understanding of the chemical factors helping to regulate the biomass and production of the global aquatic ecosystem requires a detailed assessment of the controls on the bioavailability and different forms of the essential nutrients such as nitrogen and phosphorus.

The primary source of phosphorus in the aquatic system is considered to be the leaching of adjacent geological deposits and surface soils and the main regulatory process in the body of the water is the exchange with the sediment. Phosphorus is deposited in the sediment in mineral or organic form. A part of phosphorus accumulating in lake sediments remains potentially mobile and, recycling to the water column, may support high primary production (Ryding, 1981). The relative importance of different environmental factors governing the release and transfer between different forms of sediment phosphorus depends mainly on its fractional composition (Bostrom, 1984). The transport of both particulate and dissolved phosphorus from the sediment to the water is strongly influenced by the hydrodynamical conditions of the lakes system.

Phosphorus may be associated with various components in the sediment. About 40% has been reported to occur as organic matter, another 40% in biogenic carbonate, 10% associated with (hydrothermal) Fe-oxihydroxides, 10% as phosphorite deposits and less than 2% in fish debris (Froelich et al., 1981)

During decomposition of organic matter in oxidising sediments part of the released phosphate adsorbs on iron- oxihydroxides, carbonates and clay minerals (Berner, 1974; Krom and Berner, 1981; De lange, 1986; Lucotte and d'Anglejan, 1985). The high concentration of pore water phosphorus may results in the formation of authigenic minerals. In some estuarine reducing environments the precipitation of vivianite (Fe[11]-phosphate) and of struvite ($MgNH_4$ PO_4) has been reported (Nriagu, 1974; Martens et al., 1978). The capacity of the estuarine sediments to take up and release phosphorus to the water column depends on the chemical form in which the element is present (Vaithiyanathan et al, 1993). Therefore, depending up on the environmental conditions present in the sediment, phosphate may either be released or immobilised. Study of the various forms of phosphorus in the sediment is important to establish the contribution of sediment derived phosphate to the global fluxes of this essential nutrient for biological growth (De Lange,1992). Such study is not easy due to the many geochemical factors that affect the fractionation of phosphorus between the different phases in the sediment and to the generally low concentrations of phosphorus in these phases.

The most promising method for separating and quantifying the various phosphorus reservoirs in sediments are sequential extraction techniques. Such techniques are regularly used in the study of lakes, rivers and soils (e.g. Lucotte and d'Anglejan 1985; Williams et al, 1976). Sequential extraction methods are operationally defined on the basis of reactivity of a particular phase in a given extractant. It take advantage of the fact that different solid phases show dissimilar reactivity toward different solutions (Ruttenberg, 1992).

The present study focuses on the distribution of various phosphorus phases as found by sequential extraction of sediments from Kuttanad waters and its relation to other parameters. The sequential extractions that will be used in this study have been reported to discriminate between the various modes of occurrence of phosphorus in marine and fresh water sediments (Heiltjes and Lijklema, 1980; van Eck,1981). This method is an adaptation of previously published methods, mainly originating from analytical techniques in soil science (Williams et al., 1971,1976; Heiltjes and Lijklema, 1980).

The Cochin estuary is a tropical estuary, rich in aquatic life, in which the estuarine sediment activity influences the distribution of the nutrient pool (Quasim and Sankaranarayanan 1972; Joseph 1974; Nair et al, 1987; Anirudhan 1988; Lakshmanan et al, 1987; Jayasree, 1993; Beenamma, 1993). Physical, chemical and biological factors play a key role in the regeneration of sediment phosphorus within and to the surrounding environments. The actual concentration and transformation processes to different forms are also influenced by these factors (Mortimer, 1971). The study area though is a part of the Cochin backwater system, represents more or less fresh water lake character. The contributions from the rivers, which discharge to this system, is so complex that the seasonal variations are more or less reflections of the seasonal flows of fresh water. The low depth, significant load of organic matter and the shallowness of the water gives an anoxic character to the sediments of these backwater systems (Nair, 1992; Beenamma, 1993).

b. Materials and methods

Sequential chemical extraction schemes used along with the determination techniques of different fractions of phosphorus are given in chapter II

c. Results

The sequential extraction scheme proposed by Hieltjes & Lijklema (1980) and van Eck (1981) was considered as a valuable tool in identifying the nature of phosphorus fractions in these highly productive aquatic systems. Fig 4.1, 4.2 and 4.3 and table 4.2a&b shows the seasonwise distribution of different forms of phosphorus during the three season. The result obtained is reported in percentage of the total phosphorus concentration.

During pre monsoon the percentage of exchangeable and carbonate bound phosphorus in zone I was ranged between 0.06-0.60 and Fe and Al bound phosphorus constituted 3.64 to 9.91% of the total. During this season the observed values of residual phosphorus was 85.22-88.83% of the total amount of phosphorus. In zone II the percentage of inorganic form was comparatively higher than the zone I with an average of 23.16%. Residual phosphorus constituted about 76.84% of the total concentration of phosphorus. The percentage of exchangeable & carbonate , Fe and Al bound and Ca bound phosphorus ranged between 0.04-0.10, 10.15-14.85 and 1.21-18.79 % respectively of the total phosphorus. In zone III the value for exchangeable phosphorus was in the range 0.20-0.60% and for Fe and Al phosphorus in the range 15.08-16.0 %. Ca bound phosphorus constituted about 11.69 to 33.50% of the total. The percentage of residual phosphorus was low compared to the other two zones (49.95%-73.03%).

During monsoon percentage of inorganic form was comparably higher than pre monsoon. In zone I the percentage of exchangeable phosphorus varied between 0.10 and 0.24 % of the total phosphorus and the Fe and Al bound phosphorus between 9.97 and 25.85%. The concentration of Ca bound phosphorus ranged from 2.25% to 14.29% of the total. The percentage of residual phosphorus was in between

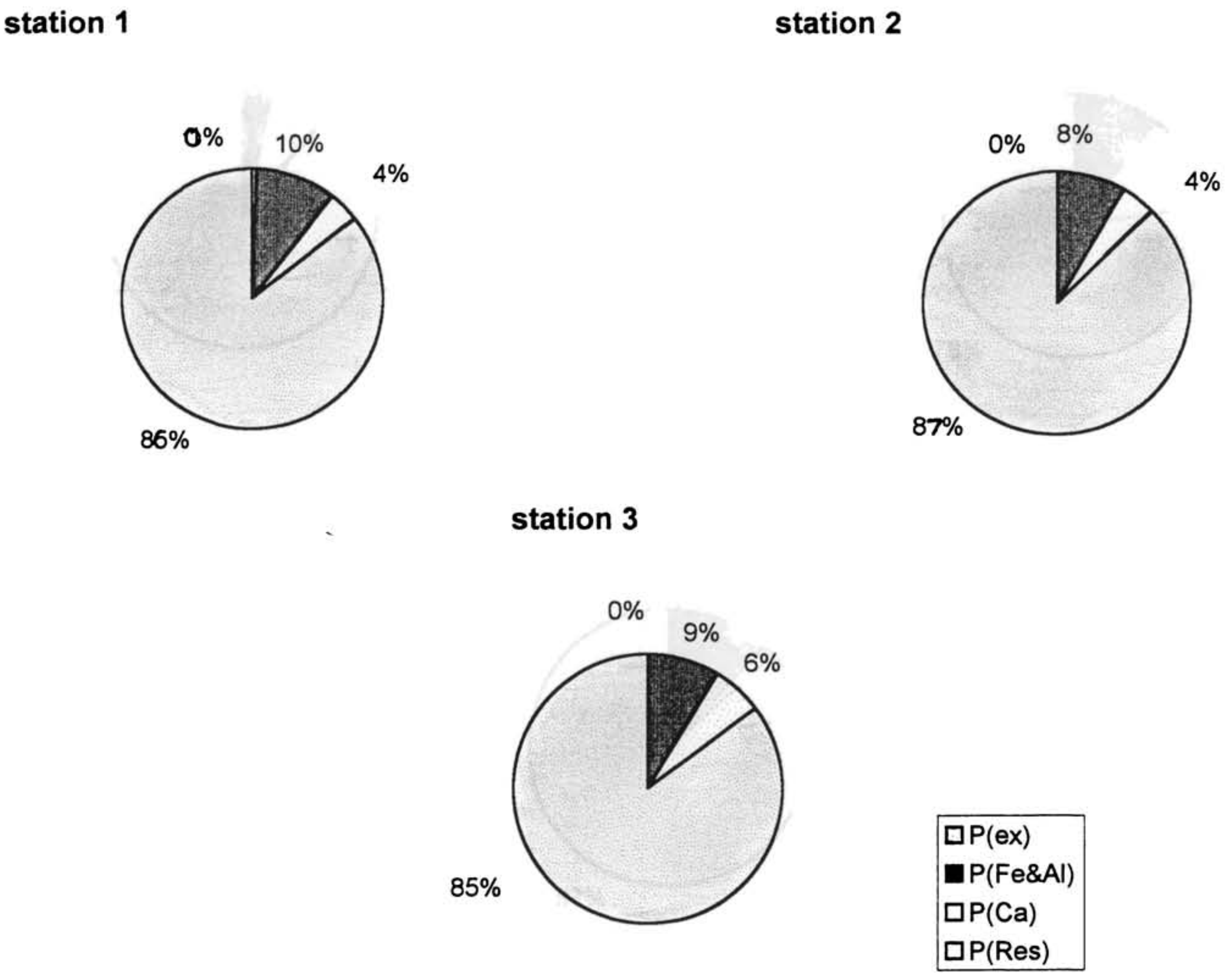
67.63% and 87.68%. In zone II Fe and Al bound phosphorus were in the rang 11.49-25.92 % respectively. The concentration of Ca bound phosphorus constituted 8.33-33.05% of the total phosphorus. Residual phosphorus accounts for 40.06 to 54.72% of the total.

During post monsoon the percentage of exchangeable phosphorus in zone I ranged between 0.07 and 0.10% of the total phosphorus. Among the inorganic forms of phosphorus Fe and Al bound phosphorus showed higher percentage (5.72-11.10%) than Ca bound phosphorus (2.19. to 5.30%). The residual phosphorus in zone I was in the range 83.53-91.65% of the total. In zone II the maximum values of exchangeable, Fe and Al and Ca bound and residual phosphorus were 0.13%, 9.60%, 8.48% and 91.38% respectively and the lower values were 0.05%, 7.07%, 1.49% and 81.79% in the respective order. In zone III exchangeable phosphorus was in the range of 0.10-0.15% and Fe and Al bound phosphorus showed high values of 10.25% and a low value of 2.72% in zone III. The percentage of Ca bound phosphorus was in between 6.26 and 9.48% during this season. Here also residual phosphorus showed high percentage, 8012-90.19% of the total phosphorus.

Discussion

The bioavailability of nutrients determines the fertility of the aquatic systems. The aquatic levels of the various forms of any chemical element is always governed by the sedimentary exchange. Though

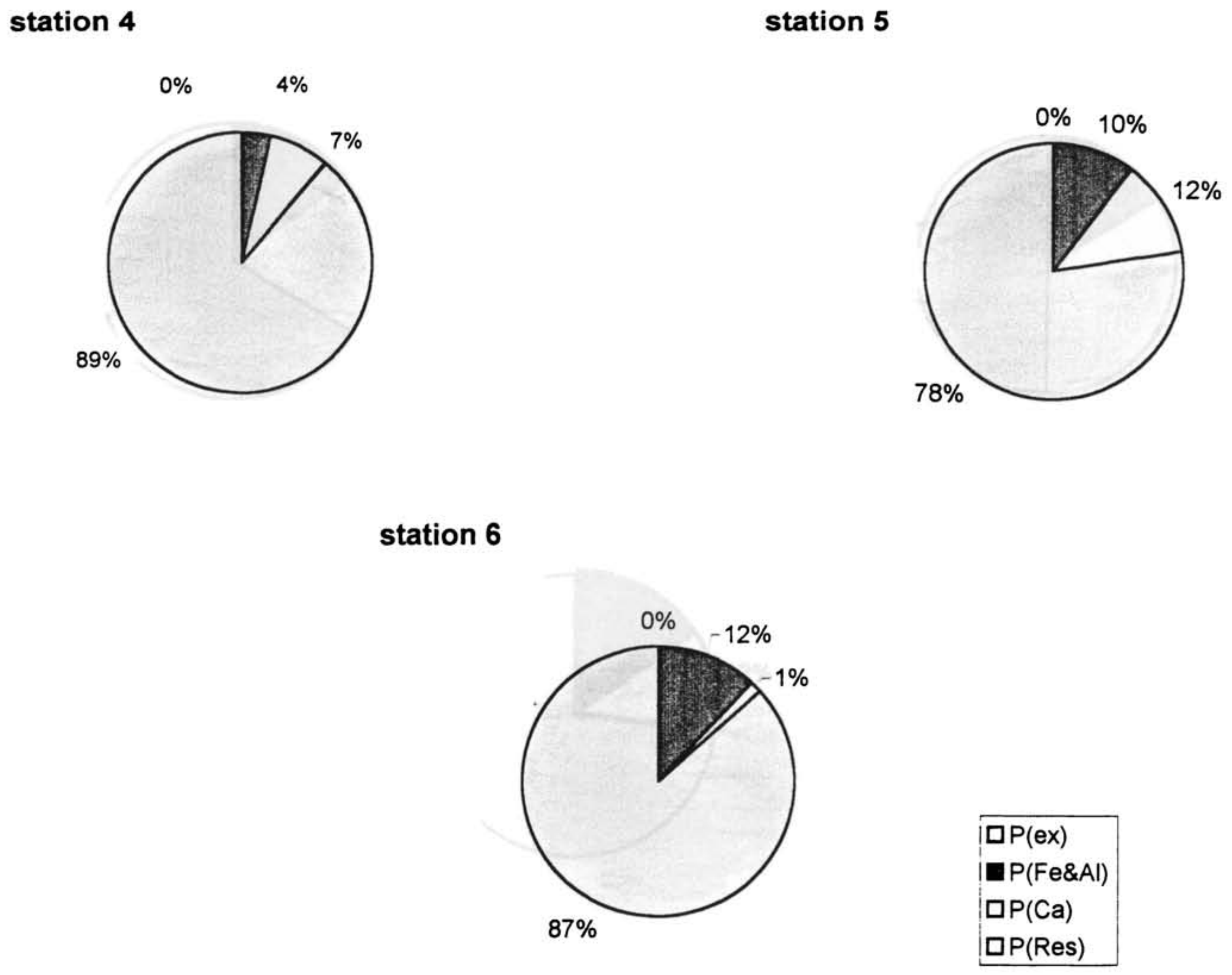
Fig 4.1 Distribution of Phosphorus fractions during pre monsoon



station 1

station 2

station 3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4%
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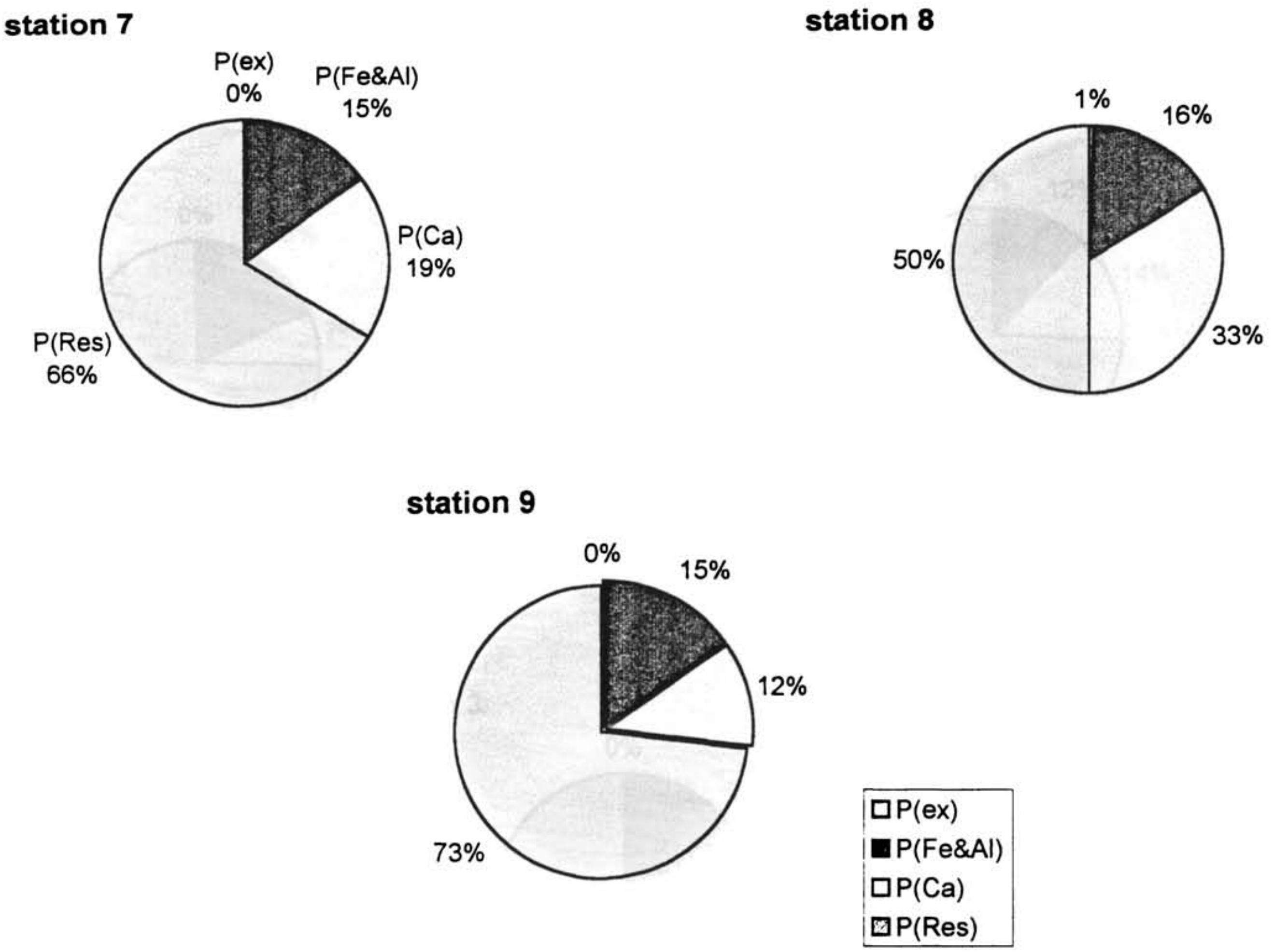
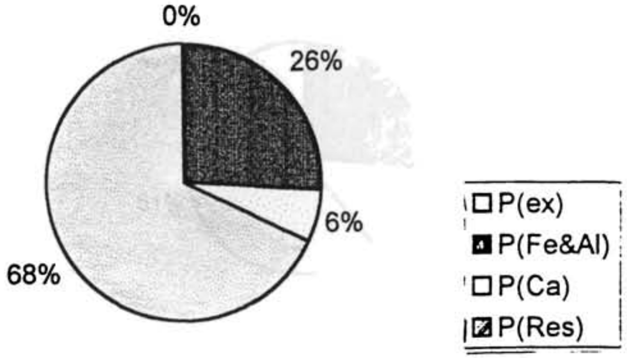

station 7
P(ex)
0%
P(Fe&Al)
15%
P(Ca)
19%
P(Res)
66%
station 8
1%
16%
33%
50%
station 9
0%
15%
12%
73%
☐ P(ex)
■ P(Fe&Al)
☐ P(Ca)
▨ P(Res)

Fig 4.2 Distribution of Phosphorus fractions during monsoon


Station-1

Station-2

Station 3



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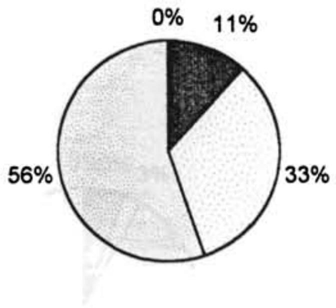

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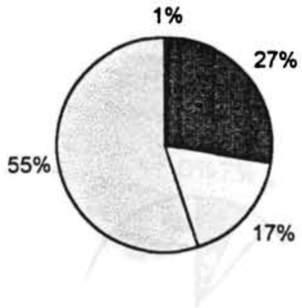

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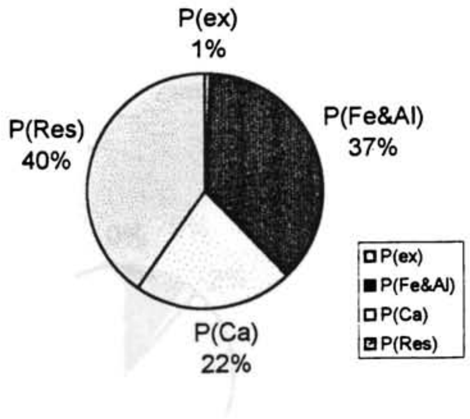
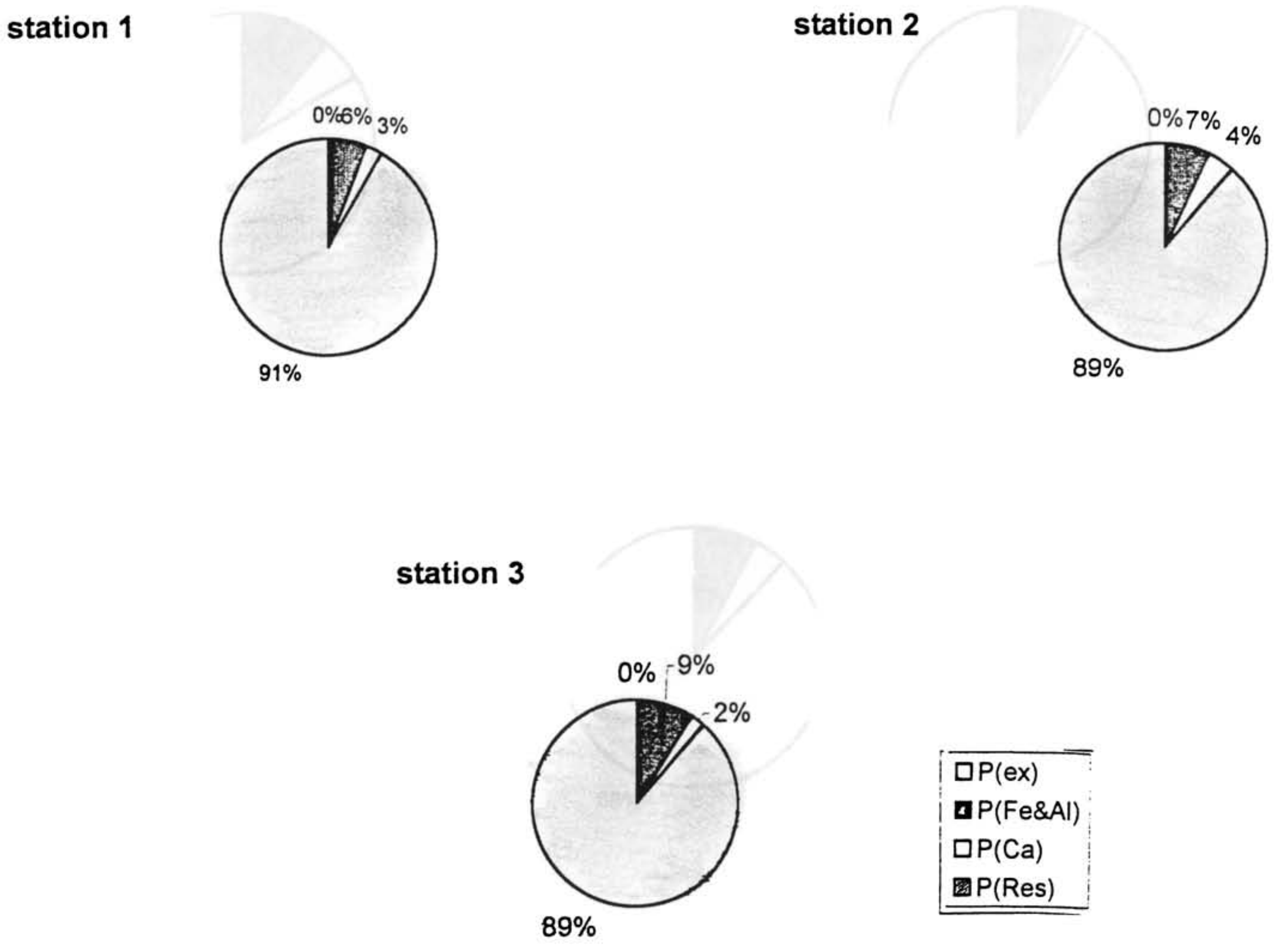
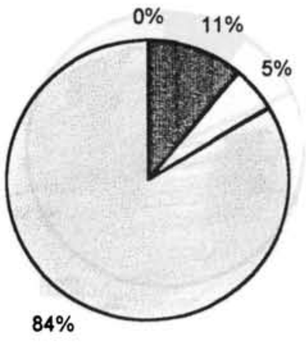


station 6

Fig4.3
Stationwise distribution of phosphorus during post monsoon season



station 4



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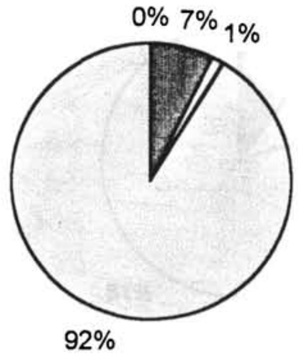

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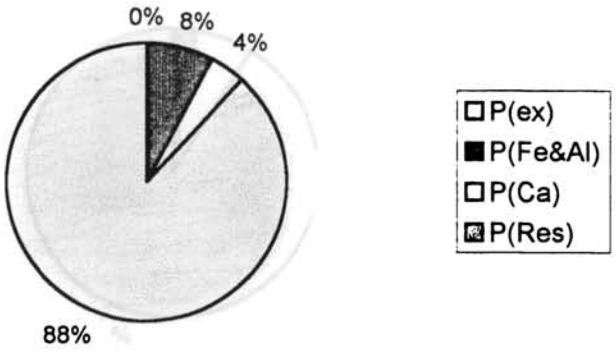

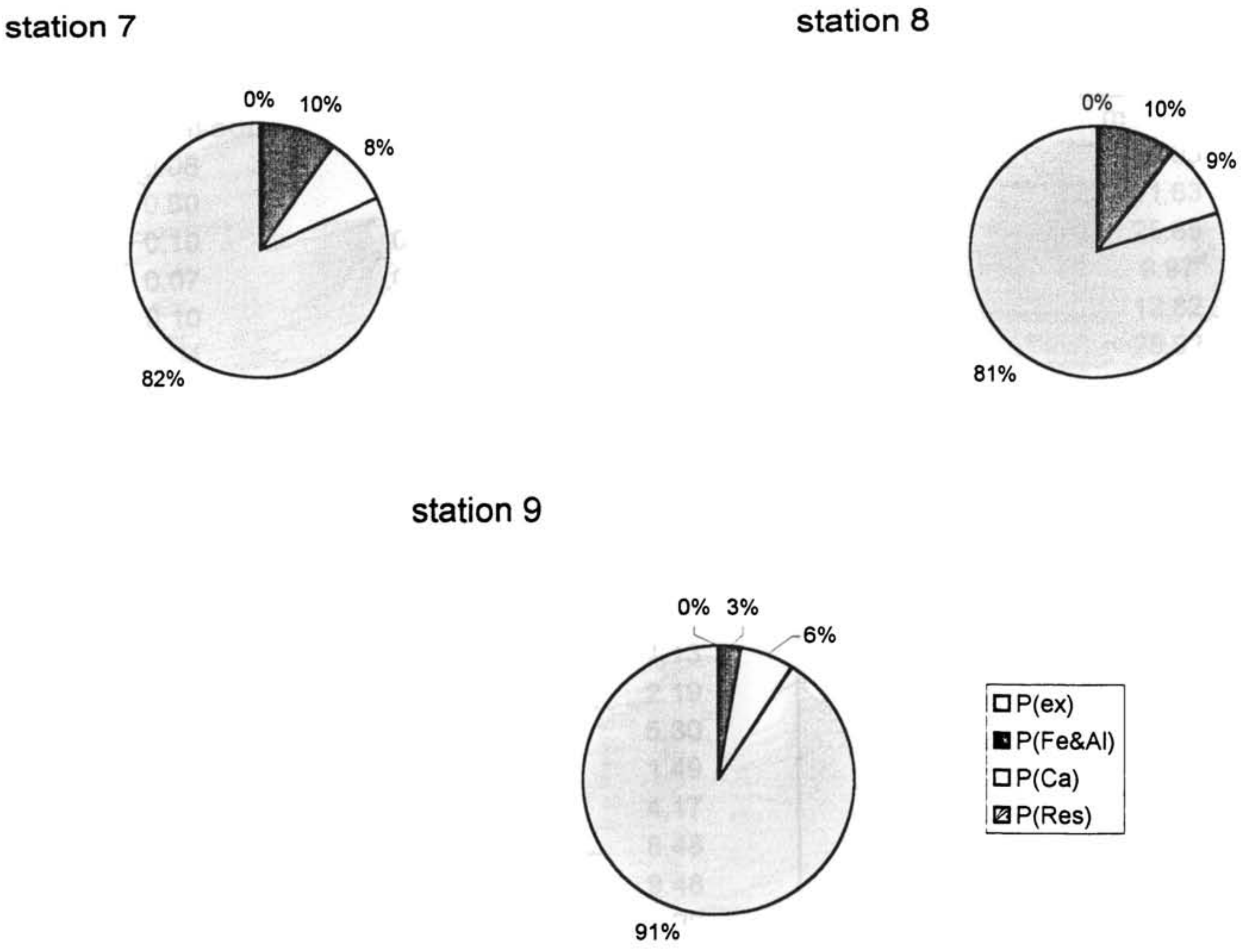
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station 9

Fractions of Phosphorus extracted (%)

Table 4.2a Exchangeable P				Fe & Al bound P		
stations	pre monsoon	monsoon	post monsoon	pre monsoon	monsoon	post monsoon
1	0.06	0.24	0.08	9.91	18.06	5.72
2	0.60	0.22	0.10	8.14	11.63	7.18
3	0.10	0.18	0.09	8.51	25.85	9.10
4	0.07	0.10	0.07	3.64	9.97	11.10
5	0.10	0.19	0.07	10.15	12.82	7.07
6	0.04	0.31	0.05	11.96	25.92	7.62
7	0.07	0.42	0.13	14.85	11.49	9.60
8	0.60	0.53	0.15	15.95	27.35	10.25
9	0.20	0.10	0.10	15.08	37.25	2.72

Table 4.2b Ca bound P				Residual P		
stations	pre monsoon	monsoon	post monsoon	pre monsoon	monsoon	post monsoon
1	3.94	7.28	2.55	86.09	74.43	91.65
2	4.27	14.29	4.13	86.99	73.86	88.58
3	6.17	6.34	2.19	85.22	67.63	88.61
4	7.46	2.25	5.30	88.83	87.68	83.53
5	12.31	8.33	1.49	77.44	78.66	91.38
6	1.21	12.27	4.17	86.78	61.50	88.16
7	18.79	33.05	8.48	66.29	55.04	81.79
8	33.50	17.39	9.48	49.95	54.72	80.12
9	11.69	21.62	6.26	73.03	40.06	90.91

inorganic phosphorus is more or less totally in the form of orthophosphate, the solubility and the stability of the various phosphates containing compounds will lead to a different exchange phenomenon. The identification and assessment of the binding character of the phosphate in the sediment thus is essential to define the contribution of phosphate to the fertility of the water column. This subject has been in the priority of investigators in this field of study for the last few decades. Accordingly a number of extraction schemes for the determination of fractional composition of sedimentary phosphorus is available. Each of them has its own merits and demerits. Table4.1a&b gives a brief account of the schemes available

In the present study the extraction scheme used is close to Hieltjes and Lijklema (1980) and van Eck (1981). The general sedimentary character and the available data on the chemical composition of the sediment in the study area are the reasons for the selection of these schemes. In the present scheme the sequential extraction identifies four major fractions. The exchangeable phosphate obtained from NH_4Cl extraction, Fe & AL bound phosphate from NaOH extraction, Ca bound phosphate by HCl extraction and residual fractions which can not be quantified by any extraction procedure. The detailed examination indicated that the exchangeable fraction includes the carbonate bound phosphate also.

The earlier works indicate a significant concentration of the exchangeable phosphorus in the sediments of various water bodies (Table 4.1a&b). Eventhough the extractant and the scheme are different for each of the work, the percentage of exchangeable which is obtained by more or less neutral extraction is in the range of 2-8%. In the present study the independent extraction with NaCl, gave a phosphate concentration of 0.065-0.83% of total phosphorus (1.68-3.9 mg/g). The NH_4Cl extraction but gave a percentage in the range0.04-1.07 towards the exchangeable phosphate. The aquatic system in this study is all most fresh water and the sediment is having contribution from the anthropogenic activities. The mild variation in the level of exchangeable phosphate for the NH_4Cl extraction can be due to the behaviour of the sediment towards the extractant. NH_4Cl though neutral have preferential for an alkaline character. Moreover the ionic size, which is a determining factor in the formation of ion pairs which assist extraction, is higher than the NaCl. Thus can restrict the transfer of phosphate from the sediment to the extraction media. However the NH_4Cl extraction will give a better definition to the exchangeable phosphate as this will include only smaller fractions of the ion pair phosphate.

The general comparison indicate considerably lower percentage of the exchangeable phosphate in this system. Zone I and II exhibit only insignificant amount of exchangeable phosphate. The absence of diagenetic processes, which will result in the formation of exchangeable

Table 4.1aSequential extraction schemes for the speciation of phosphorus

Scheme	Forms of phosphorus extracted	References
1. a	Exchangeable and carbonate bound	Hieltjes & Lijklema,1980
b	Fe- and Al- bound	
c	Ca- bound	
2. a	Exchangeable	Engler et al., 1977
b	Carbonate bound	
c	Organic bound	
d	Fe- and Al- bound	
3. a	Exchangeable	Williams et al.,1971 modified by Li, 1973
b	Fe- and Al-bound	
c	Ca- bound	
4	Exchangeable, organic, carbonate and Fe- and Al- bound	Duinker et al, 1974
5	Exchangeable, organic, carbonate and Fe- and Al- bound	Sorensen et al, 1971
6. a	Exchangeable, carbonate and Fe- and Al- bound	Shukla, 1973
7. a	Exchangeable, organic, carbonate and Fe- and Al- bound	Spear, 1970
b	Exchangeable, organic, carbonate and Fe- and Al- bound	
c	Exchangeable, carbonate and Fe- and Al- bound	
8. a	Exchangeable, organic, carbonate and Fe- and Al- bound	Cowen, 1974
b	Exchangeable, organic, carbonate and Fe- and Al- bound	
c	Exchangeable	
9. a	Fe- bound	Golterman, 1982
b	Ca- bound	
10.a	Water soluble	Psenner et al, 1984
b	reductant soluble	
c	Fe- and Al- bound	
d	Ca- bound	
e	refractory phosphorus	
11.a	Fe(OOH) P Fe(OOH) P+Organic P~Fe	Golterman,1996 (modified)
b	CaCO3~P CaCO3~P+OrganicP~Ca	
d	Organic-P acidic	
e	Organic-P alkaline	
f	Reactive organic phosphorus	
12.a	Loosely sorbed phosphorus	Ruttenburgh, 1992
b	Fe-bound	
c	CFAP+biogenic hydroxyapatite Carbonate bound	
d	FAP	
e	Organic bound	

Table 4.1b Earlier reported values of Phosphorus fractions under different schemes

No	Scheme adopted	Fractions extracted	Reference
1.	**a** Hieltjes& Lijklema,1980	Pex+carbonate -6-12%(MB) - 7-8% (NMB) Fe+Al bound-11-12%(MB) -15-20%(NMB) Ca bound-1-3%(MB) -1-3%(NMB)	Nair et al., 1993.
	b Engler et al.,1977	Pex ->20% Fe+Co3 bound P -70-90% organic P -30% (for MB&NMB sediments)	
	c Golterman,1982	Fe(OOH)~P -30% CaCO3~P- 35-40% (for MB&NMB sediments)	
11	Golterman&Booman,1988 Golterman,1996 (modified)	Fe(OOH)'P- 34.6-61.2% CaCO3~P- 9.3-19.6% Organic~P- 13.6-45.9%	Fabre et al., 1999
111	Golterman,1996 (modified)	Fe(OOH)' P- 23.6-38.1% Org~P- 61.9-79%	Di'az-Espejo et al., 1999
1V	Olsen et al 1982	Organic~P- 10% InorganicP-80-95% I Inorganic forms are a. non-occluded P- 6% b. ocluded P- 24% c. Ca bound P- 70%	Vaithiyanathan et al., 1993
V	Hieltjes& Lijklema 1980	Exchangeable-6.5% NaOH-RP-14.5% NaOH-nRP-15.6% HCl-RP-37.8 res-P- 41.05	Vera Istvanovics 1988
V1	Psenner et al., 1984	Organic bound P-58.6-63.6% H2O-P-3.2-5.8% reductant solubleP-22.9-29.9% Fe and Al bound-22.0-25.0% apatite P-11.1-15.5% refractory P-12.3-14.2%	Andreas et al., 1997
V11	Ruttenberg,1992 (modified)	Exchangeable P- 2% Easily reducible or reactive Fe bound P- 20-60% NaOH -5- 30% Apatite P->10% Organic P- 5-15%	Darren 1996

MB- mud bank ; NMB- non mud bank

phosphorus, may be a reason. This explanation has to be read along with the other fractions of phosphate. From the studies on the speciation of phosphate in the Cochin estuarine system by Nair, et al (1993) have reported less than 10% of exchangeable phosphate. In his study slight estuarine character was shown by zone III, and this zone gives the maximum percentage of exchangeable phosphate. The observed data thus indicate a significant contribution from the saline water.

Fe and Al bound Phosphorus

The second fraction obtained in the extraction scheme, Fe and Al bound phosphate is considered to be the major inorganic fraction available in sediments. The reported concentration ranges between 15-60% for the different aquatic systems. The speciation of phosphate in the Cochin estuarine system by Nair et al (1993) gave a value in the range 15-20% of the total phosphorus for this fraction. In the present study the post monsoon season indicated considerably low percentage of this fraction. The dissolved phosphate also gave low values during the post monsoon. The post monsoon season is considered to be a season of high agricultural activity and considerably high concentration of phosphate was the normal expectation. The marginal changes in the definition of the past monsoon with reference to the climatic conditions and the agricultural activity may be the complicating factor here. In the present study October to January is considered as the post monsoon, but the post monsoonal agricultural activity starts only by November. So the contribution from the agricultural activity to the post monsoonal values of the phosphate may not be a significant factor. Moreover the maximum percentage of Fe and Al bound phosphate was observed during monsoon season. The contribution of land towards this fractions may be the reason. The low level of the fraction in pre monsoon and post monsoon suggest two possibilities

1. The diagenetic activity, which leads to the regeneration of phosphate to the sediments, is not favourable either for a regeneration of phosphate or does not favour binding of phosphate to Fe and Al bound.
2. The major source of Fe and Al bound phosphate fractions is the land contributions and the post monsoon represents a season where either the retention of Fe and Al bound phosphorus is low or its actual concentration that reaches the water body is low. The identification and characterisation in the micro level is required to explain this observation which is beyond the scope of the present study. The observed trend at any cost does not reflect on a normal behaviour of an aquatic system. A significant feature of this water mass to be considered here, is the consistent low pH (less than 7) which will generally not be favourable for the retention of Fe and Al bound and similar fractions of phosphate.

Ca bound phosphorus

The studies on the bioavailability of sedimentary phosphorus have indicated that the unavailable fraction of the inorganic phosphate is constituted by Ca bound phosphorus (Engler and Sarnelle 1990).The nature of the phosphorus in this fraction is still not quite clear.

1. In estuarine systems it is reported that phosphate adsorbed on calcite plays a key role in controlling the phosphorus concentrations (De Jonge & Velerius, 1989).
2. But generally phosphorus is considered as bound to calcium as $CaPO_4$ as in the case of apatite. Such association of phosphorus to form apatite is observed in nutrient rich upwelling areas (Lucas & Pervert, 1984) and the phosphorus was observed to be stable in this form both in the oxic and anoxic conditions.

In the first case the concentration of calcium bound phosphorus should be dependent on the availability of dissolved phosphate and the dynamicity of the sediment water interface. But in the second case the concentration should reflect the variation observed in the concentration of calcifying organisms. In estuarine and fresh water systems it is reported that the $CaCO_3$ adsorption of phosphorus plays a key role in the phosphorus concentration and in the reducing environment available with the sediment leads to a decrease in pH and will assist the desorption of phosphorus. Therefore though the $CaCO_3$ adsorption have an edge over the Fe and Al bound phosphorus, the relative retention of phosphorus will lead to a higher percentage of Fe and Al bound phosphorus. In short the concentration of Ca bound phosphorus in estuaries and fresh water will generally exhibit low values compared to

Fe and Al bound phosphorus. In the present study the observed percentage is lower than the Fe and Al bound Phosphorus in zone I and zone II. This supports the views expressed above. In zone III the Ca bound phosphorus is high in pre monsoon and post monsoon. The increased concentration of dissolved phosphate observed in the zone III and the relatively higher pH favours for an increased adsorption. The presence of significantly high percentage of Fe and Al bound phosphorus observed in zone III, but, does not favour such an explanation. The overall high percentage of the inorganic phosphorus observed in zone III along with the lower values of the total phosphorus in the zone III suggest either an enhanced mineralisation or enhanced anthropogenic input of inorganic phosphorus. The high concentration of dissolved phosphate and the lower concentration of sedimentary organic carbon indicate the operation of one or other or both of the above processes.

Residual P

The residual phosphorus, which can be considered as the immobile fraction of phosphorus, is generally constituted by organic phosphorus. In the marine sediments, it is reported that organic phosphorus holds a definite relation with organic carbon (Mach et al., 1987). At the same time, in poor sediment, it is suggested that the organic phosphorus is independent of organic carbon content. In many cases the relation between organic phosphorus and organic carbon is not clearly obtained due to the difficulties in precise and accurate measurements of organic phosphorus. A main source of error will be inclusion of some immobile inorganic phosphorus during the determination (Hartman et al.,1976). In this study the residual fraction is named so because of this difficulty in identifying the organic phosphorus from the total immobile fraction.

In the present study the residual phosphorus constitute the major position of the total phosphorus. A definite correlation between the residual phosphorus and the organic carbon is observed for the pre monsoon and monsoon seasons. At the same time no correlation was observed during the post monsoon. The various possibilities for such an observation are

1. The residual phosphorus during the pre monsoon and monsoon are clearly linked with the diagenetic processes or even can be considered as the remains of the remineralisation of organic carbon.
2. The post monsoon season contains high ratio of the immobile inorganic phosphorus, which will modify the relation with the organic carbon.
3. The high percentage of residual phosphorus when considered along with the actual values of total phosphorus and organic carbon indicate considerable addition of terrestrial phosphorus poor organic matter to the system. The observed correlation also points to such a situation

4. The discharge pattern of the fresh water and the shallowness of the water body along with the reducing conditions of the sediment does not lead to an effective diagenesis of the organic matter. Generally a release of Fe and Al bound phosphorus is observed in reducing conditions. The decrease in the remineralisation of the organic carbon and the decrease in the percentage of mobile inorganic phosphorus by the release of phosphorus from the Fe bound phosphorus can lead to such a high percentage of residual phosphorus.

5. The Kuttanad waters due to the agricultural activities is expected to receive significant contribution from inorganic fertilisers during the post monsoon season. The conditions of the water column are favourable for the precipitation of phosphate. This can lead to a high percentage in the residual phosphorus.

4.3 Speciation of Nitrogen

a. Introduction

Though sediments are considered to be an active media in the diagenesis of organic matter, its actual contribution towards the N cycle is still not completely clear. The significant differences between the properties of phosphorus species and nitrogen species resulted in diverting more attention towards the phosphorus cycles. The inorganic phosphorus species, which acts as the primary source of the phosphorus to the biota, is the ions of ortho- phosphoric acid. These are capable of forming a wide variety of soluble and insoluble salts, leading to considerable dynamicity to the system. In the case of nitrogen the inorganic species nitrite, nitrate and NH_4^+ ions which are considered as the major sources of nitrogen to the biota, gives only soluble inorganic nitrogen compounds. This restricts the contribution of sedimentary bound inorganic nitrogen species in the N cycle. Generally the reducing environment available with the sediment will favour for the decomposition of the organic nitrogen to NH_4^+, but is not favourable for the formation of nitrite or nitrate. In many cases the situation may even lead to the denitrification of any available nitrite or nitrate (Kemp et al 1990, Vanderborght, 1977). In many cases the tendency of inorganic nitrogen species either generated or available by some other processes will tend to get transferred or dissolved in the bulk waters. The actual transfer from the sediment to the water takes place through sediment water interface, but in actual practice the formed inorganic nitrogen species first get dissolved in the pore water and then get diffused through the boundary to the overlying water. In any case a reverse movement of inorganic nitrogen species from water to the sediment is not possible. The sediment so can have only three forms of the nitrogen, exchangeable ammonia, fixed ammonia and organic nitrogen. As the movement of inorganic nitrogen species can takes place only in a direction towards the water column, the amount of exchangeable ammonia present in the sediment will be considerably very low.

In the present study the speciation of sedimentary nitrogen is done from the wet samples because of the reasons stated in the case of phosphorus.

b. Materials and methods

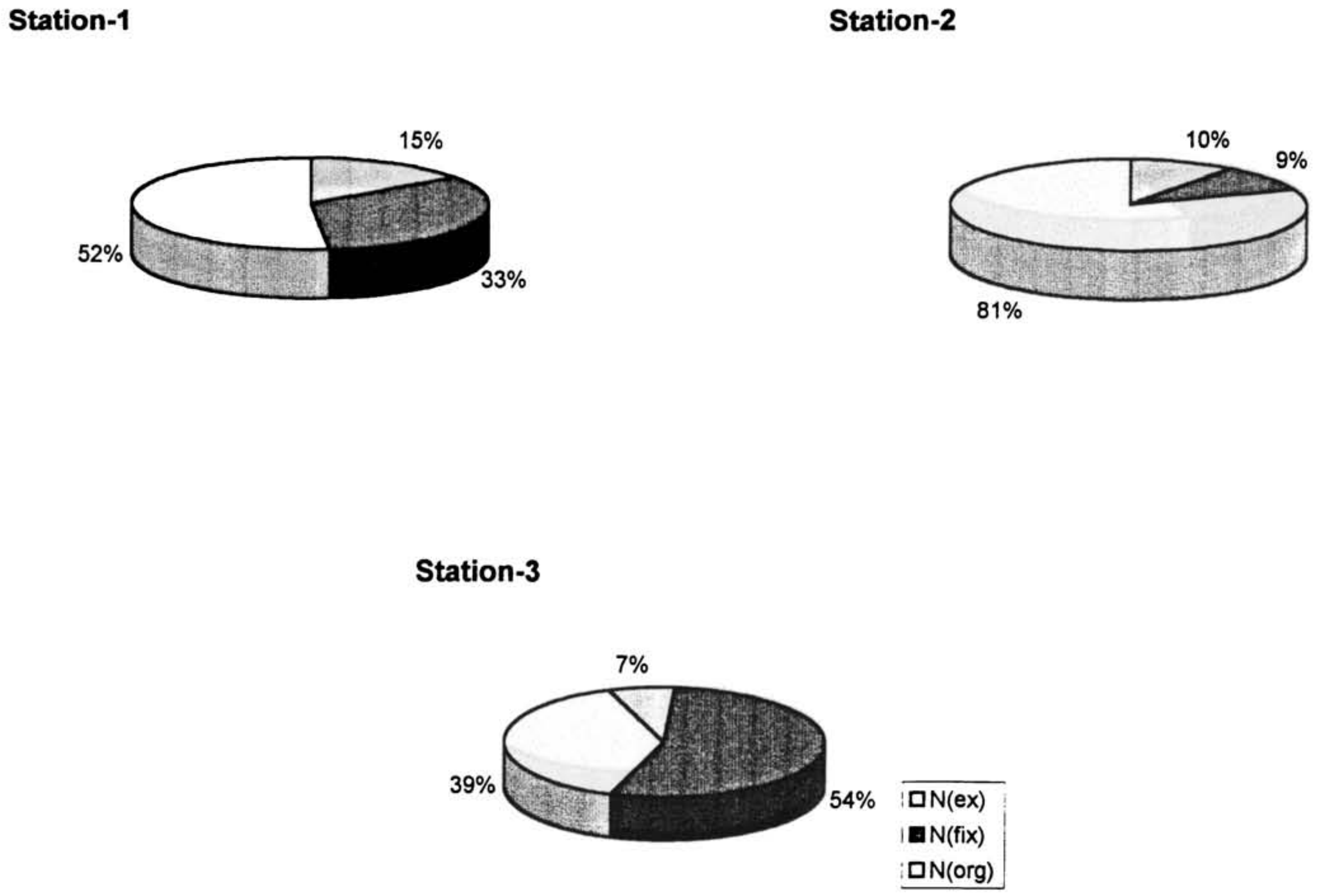
The materials and methods for the speciation of nitrogen is given in chapter II

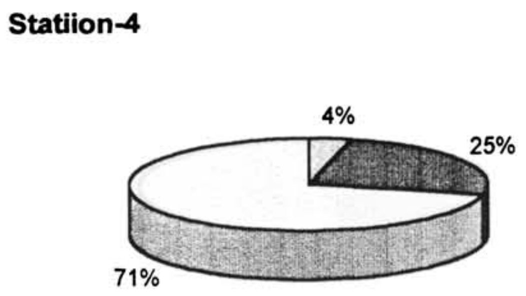
c. Results

The speciation scheme applied here distinguishes three forms of ammoniacal nitrogen species, exchangeable, fixed and organic ammoniacal nitrogen. The percentage of different forms of nitrogen to the total nitrogen is given in fig 4.4,4.5 and 4.6 and table 4.5 a and b

In zone I the percentage of exchangeable nitrogen varied between 3.99 to 16.16 of the total nitrogen during pre monsoon whereas the same during monsoon and post monsoon were in the range of 0.66-8.07 and 2.96-11.02 respectively. In zone II the maxima and minima for pre monsoon, monsoon and post monsoon were19.84 & 3.89, 7.07 & 1.55 and 14.19 & 5.93 respectively. In zone III the corresponding ranges were 7.31-9.54, 14.78-20.23 and 4.84-5.38 in the respective order of the seasons.

The percentage composition of fixed nitrogen to the total nitrogen content was found to be in the ranges 7.27-54.84 for pre monsoon, 20.70-36.26 for monsoon and 26.12-31.46 for post monsoon seasons in zone I. In zone II a maximum of 40.25 and minimum of 14.94 was fig 4.4 Distribution of Nitrogen fractions during pre monsoon

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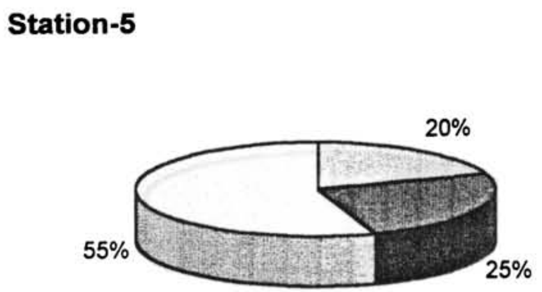
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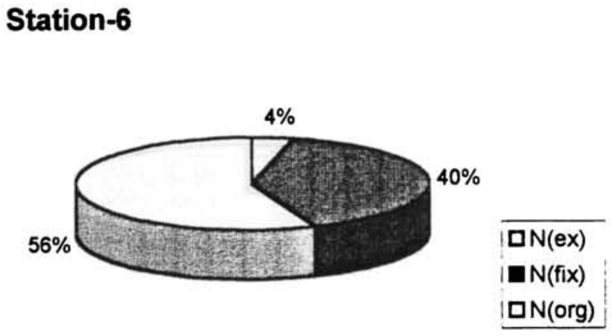
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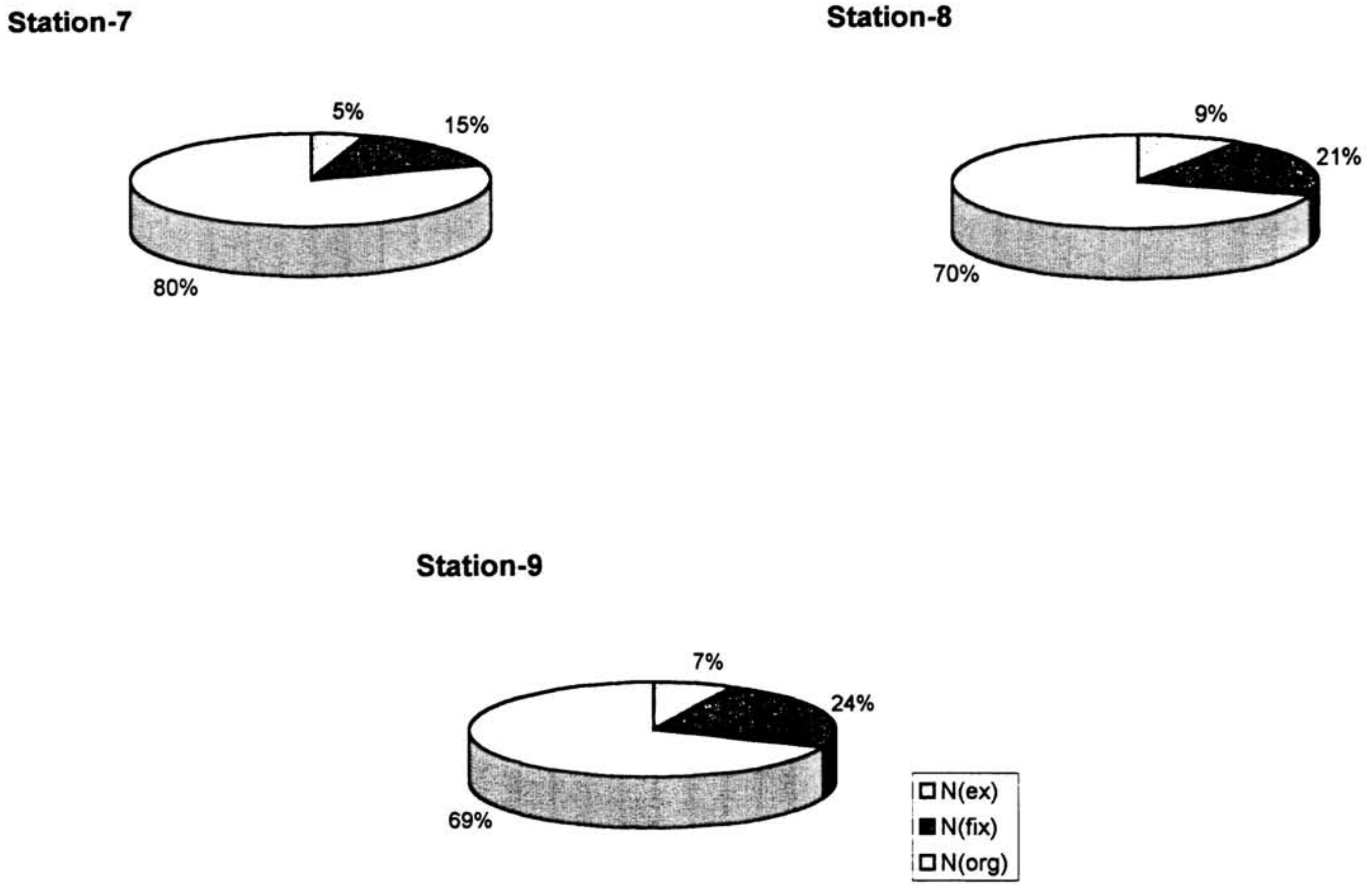
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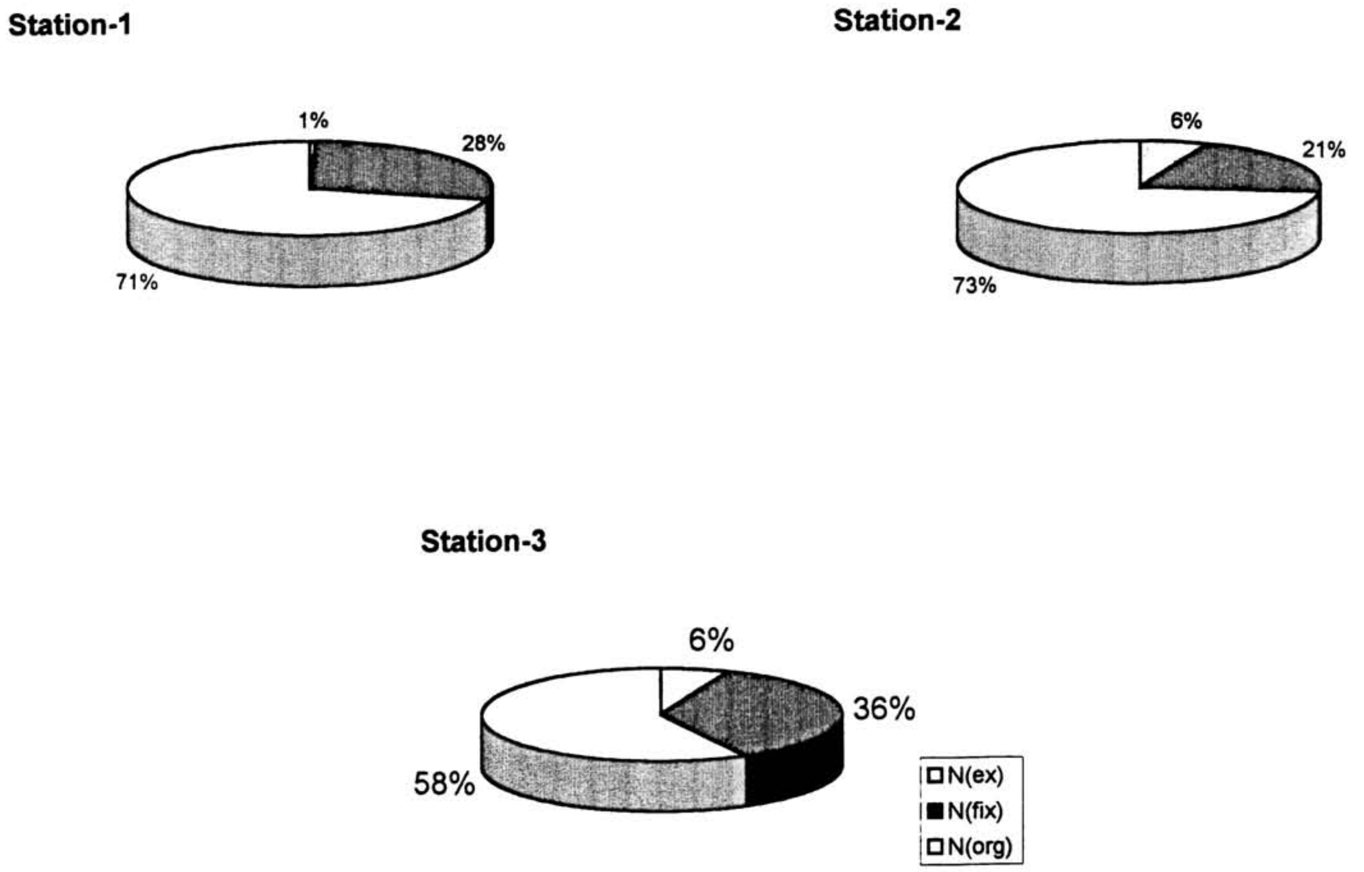
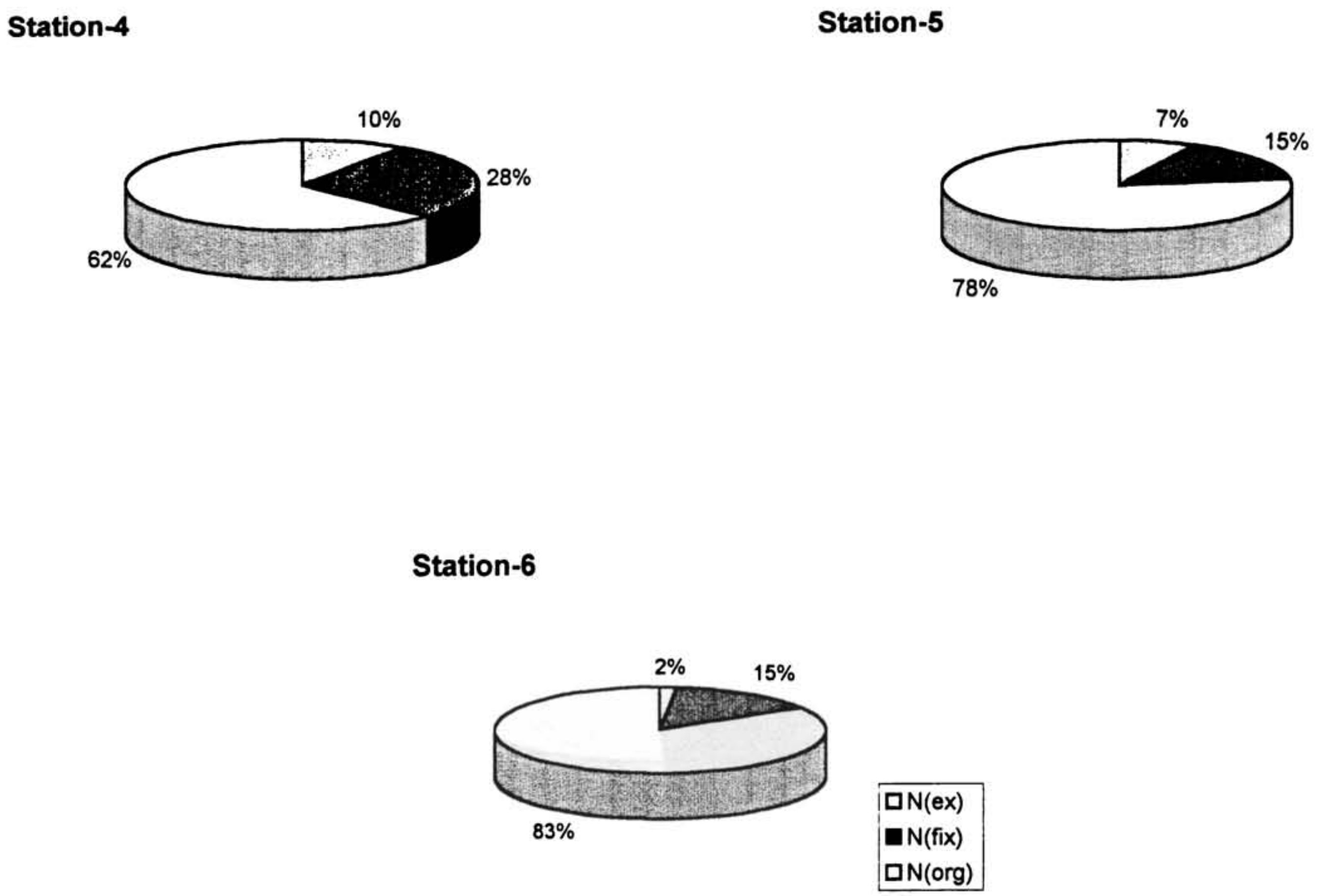
Fig 4.5 Distribution of Nitrogen fractions during monsoon

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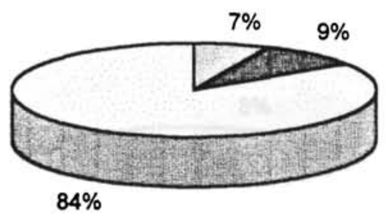

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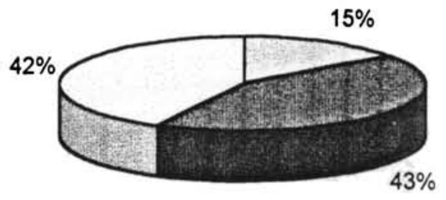

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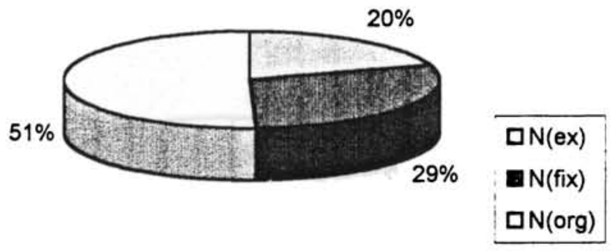
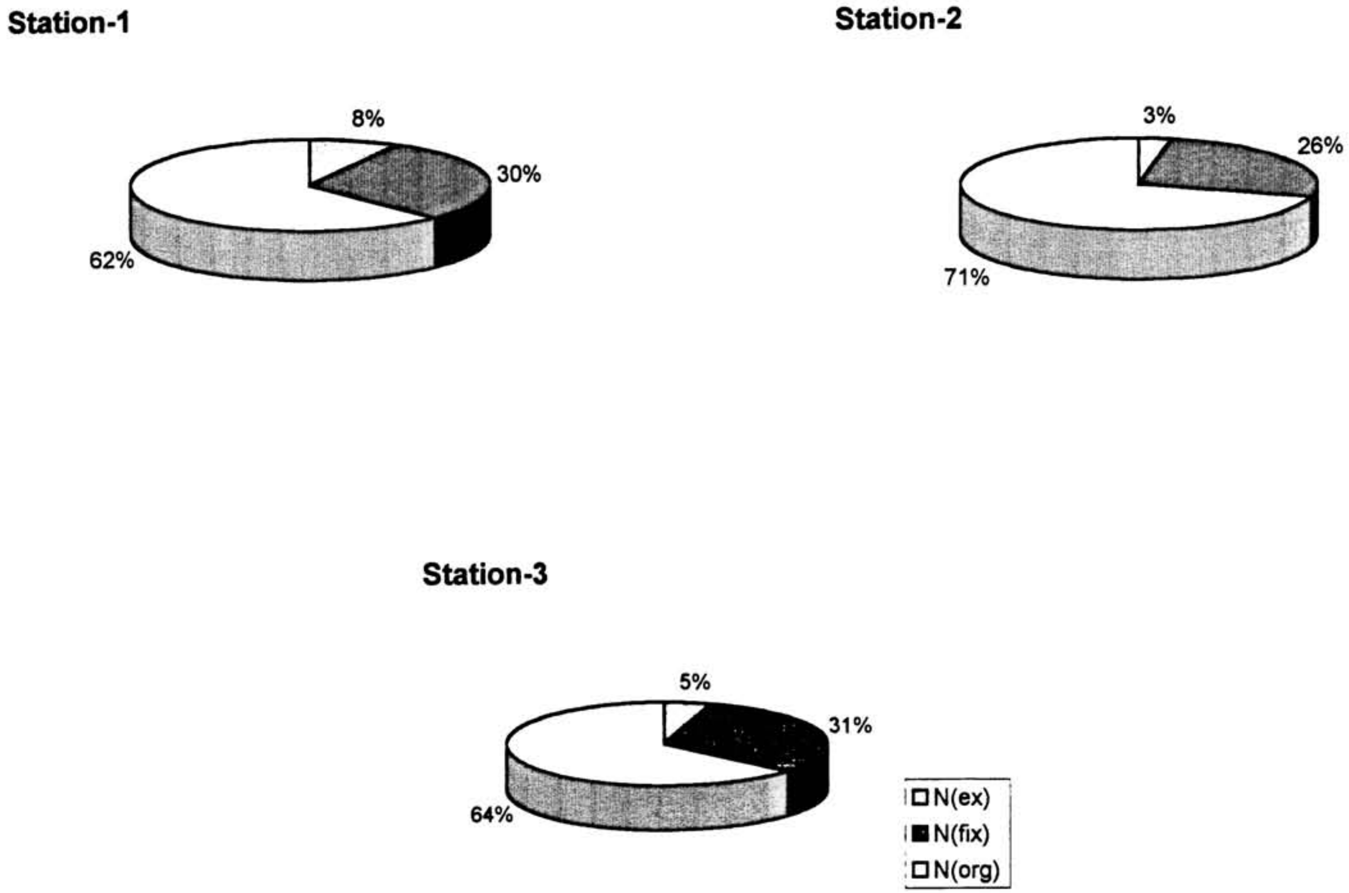


Fig 4.6 Distribution of Nitrogen fractions during post monsoon



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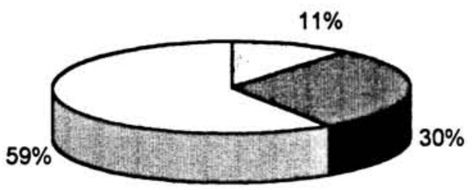

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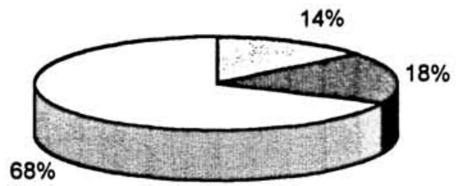

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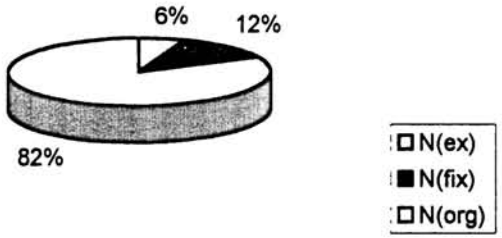

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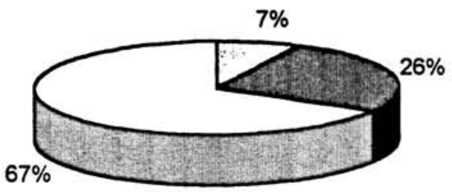

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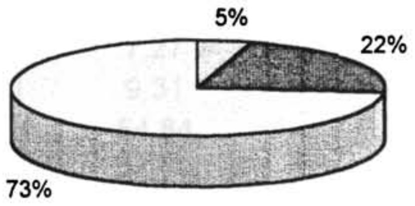

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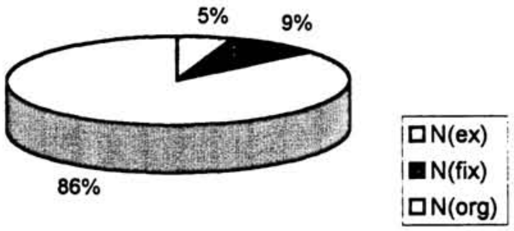


Fractions of Nitrogen extracted (%)

Table 4.5a

	Exchangeable N			Fixed N		
stations	pre monsoon	monsoon	post monsoon	pre monsoon	monsoon	post monsoon
1	16.16	0.66	7.99	7.27	28.47	29.66
2	9.65	6.19	2.96	9.31	20.70	26.12
3	6.50	6.11	4.80	54.84	36.26	31.46
4	3.99	8.07	11.02	24.79	22.87	29.68
5	19.84	7.07	14.19	24.75	15.29	17.66
6	3.89	1.55	5.93	40.25	14.80	12.31
7	5.10	6.73	7.37	14.94	9.29	26.24
8	9.54	14.78	4.84	20.57	43.07	21.71
9	7.31	20.23	5.38	23.78	29.41	8.84

Table 4.5b Organic N

stations	pre monsoon	monsoon	post monsoon
1	76.57	70.87	62.34
2	81.04	73.11	70.92
3	38.66	57.63	63.74
4	71.21	51.21	59.31
5	55.36	77.65	68.15
6	55.86	83.65	81.75
7	79.96	83.98	66.39
8	69.89	42.15	73.45
9	68.91	50.36	85.78

Table 4.6a Earlier reported values of nitrogen fractions

Scheme	Forms of nitrogen extracted	Values(µg/g)	Reference
1	Exchangeable nitrogen	0-38	De Lange, 1992
	Fixed nitrogen	25-200	
	Organic nitrogen	0-1500	
2	Exchangeable nitrogen	4.0-9.0	Kemp& Mudrochova, 1972
	Fixed nitrogen	48-324	
	Organic nitrogen	0.0-5542	

reported during pre monsoon. For monsoon and post monsoon seasons the percentage of the above was in the range 9.29-15.29 and 12.31-26.24 respectively. In zone III a maximum of 23.78, 43.07 and 21.71 and a minimum of 20.57, 29.41 and 8.84 were corresponding to pre monsoon, monsoon and post monsoon seasons respectively.

From the recorded values it is evident that the organic nitrogen constitute the major share of the total nitrogen content. During pre monsoon the percentage of organic nitrogen to the total nitrogen rose up to a maximum of 81.04 while the minimum is 38.66 in zone I. The same was found to vary between 51.21 and 73.11 during monsoon and between 59.31 to 70.92 during post monsoon. In zone II organic nitrogen contributes to the total nitrogen a maximum of 79.96% and a minimum of 55.36 % during pre monsoon. During monsoon and post monsoon this ranged between 77.65-83.98 and 66.39-81.75 respectively. In zone III the range of percentage contribution of organic nitrogen to the total nitrogen were 68.91-69.89, 42.15-50.36 and 73.45-85.78 for pre monsoon, monsoon and post monsoon respectively.

d. Discussion

A significant concentration of exchangeable ammonia was observed in this study, which is quiet unexpected. It is to be stated that the speciation is done on the wet samples, which contains pore water also. As described above the NH_4^+ formed by the mineralisation of the organic matter in the sediments gets rapidly dissolved in the pore waters. In the pore water this ammonia will be available until it gets diffused to the water column (Kemp et al.,1990). So it can be considered that the concentration observed is a reflection of the formation and residence time of NH_4^+ in the pore water. The contribution of pore water towards the estimated exchangeable ammonium is not worked out here mainly because the intention of the study was to quantify the availability of different nitrogen species in the sedimentary compartment. But trends given by the sedimentary nitrate that estimated from the dry sediment (Chapter III) is indicative of the absence of any major retention character of sediment towards the inorganic nitrogen species. The present observation indicates significant contribution from the sediment towards NH_4^+ concentration in the water column. It is reported that in most of the coastal environments the vast majority of recycled nitrogen released to the water from sediments is in the form of NH_4^+ (Nixon, 1981). Further it is suggested that this NH_4^+ is regenerated by the decomposition and deamination of organic matter with subsequent diffusion to the overlying water. It is also observed that the relative influence of sediment nitrogen cycling on water column processes tends to decrease with increasing depth (Harrison, 1980). The amount of NH_4^+ can also be influenced by the nitrification process and it is suggested that nitrification rates are regulated generally by availabilities of oxygen or NH_4^+ (Henriksen and Kemp, 1988). Anoxic metabolism in sediments is observed to build up dissolved ammonia in the interstitial waters of near shore sediments (Berner, 1974; Suess, 1971).

Considerable controversy exist on the possible contributions by the pore water during the estimation of exchangeable nitrogen and most of the workers preferred estimation from dried samples to avoid any such controversy. De Lange (1992) but has reported that no detectable differences in the various nitrogen fractions between wet, freeze-dried and oven-dried samples were observed. He has also observed that the pore water ammonium concentration is also considerably low and so its contribution is considered as insignificant. This is a sharp contrast with the observation of many other workers as well as theoretical possibilities of the system. No comment except the reporting of the observation of Lange is intended.

Fixed Nitrog

The fixed nitrogen represent the $NH_4{}^+$-N fixed to the clay minerals and so its percentage depends on the sediment characteristics. It is reported that the clay minerals, illite and kaolinite etc are capable of fixing ammoniacal nitrogen. Stevensan (1959) and Kemp and Mudroch, (1972) have observed that this fixation is more or less governed by the depth of the sediment. Lange (1992) pointed out that the fixed nitrogen has a definite correlation with aluminium.

In the present study the fixed N ranged between 7.27- 54.84 %. The observed range is in tune with the earlier reports (Annexure). The sediments of the Kuttanad have showed silty clay characteristics in zone I and II. The studies on the chemical characteristic of the sediments of this back water systems have showed that the clayey fraction contains significantly high Al. The reducing environment prevailing in the sedimentary compartment restricts the nitrification processes and the significant by high NH_4^+-N in the pore waters, along with the sedimentary composition leads to a markedly high fixed NH4-N. The sediment nitrification rates are observed to be governed by the availabilities of oxygen or NH_4^+ (Henriksen and Kemp, 1988). The observed NH_4^+ concentration can also be due to the decrease in the oxygen availability at the sediments. Anoxic sediments are observed to contribute NH_4^+ significantly to the overlying water (Kemp et al, 1990).

Organic nitrogen

Generally the organic nitrogen is the major constituent in the total nitrogen in the sediments which may even represent more than 90 % of the total nitrogen. In the sediment were the organic matter is less, a lower percentage organic nitrogen is observed. In the present study the observed percentage of organic nitrogen which varies between 38.66-85.78 indicate a significantly low percentage in these sediments. The possibilities for such a low organic N content can be

1. High mineralisation or deamination of organic nitrogen can substantially decrease the percentage of organic nitrogen. The sedimentary environment plays a significant role here. The population of the deaminating bacteria

and the redox conditions are the contributing factors. In shallow waters like Cochin backwaters the sediments are more or less at a reducing environment (Nair, 1992; Beenamma,1993). This will have a restrictive influence on the population of the deaminating bacteria and the deamination. The deamination and remineralisation so can not be considered as significant contributors to the low percentage of organic nitrogen.

2. Significant input of anthropogenic organic matter with low nitrogen content can be another reason. The C/N ratios indicated higher nitrogen content in the sediments.

The presence of high exchangeable ammoniacal nitrogen and comparable fixed NH_4 -N in the sedimentary compartment suggests mixed possibilities. The actual values of organic nitrogen are comparably high, at the same time the values of exchangeable and fixed NH4-N are also high. The texture of the sediment supports the retention of percentage of organic matter.

The distribution of exchangeable, fixed and organic nitrogen in the sedimentary compartment is indicative of significant contribution from the sediment to the nitrogen cycle in the system. Zone III, because of the slight estuarine character, behaved in a different way. The sediment in this zone was having considerably high sandy character and the amount of organic carbon is significantly low. It is reported that in sediments having low organic carbon content the percentage of organic nitrogen is also less. The relatively high percentage of fixed ammoniacal nitrogen may be the reason.

CHAPTER V

Conceptual Model for Sedimentary Nutrient Dynamics

5.1Introduction

Coastal and estuarine waters, the aquatic systems adjacent to landmasses, receive most of the anthropogenic wastes of the land. As a result of these discharges a wide spectrum of labile and refractory organic and inorganic compounds are introduced to the aquatic system. Most of the remineralisation of organic carbon and nutrients takes place in water, but in relatively shallow environments, sediments play the key role in the regeneration process (Fisher et al., 1982). Some of these compounds will be inert to the remineralisation process and others decompose and the products will be released to the pore water. The decomposition of organo phosphorus compounds leads to the production of orthophosphate. The regenerated phosphate from the pore water may get released to the overlying water or reprecipitated within the sediments as an authigenic phase or adsorbed by the other constituents of the sediment. Adsorption to metal oxides are considered as one of the principal reactions involving phosphate (Froelich, 1988).

Reports suggest that iron is involved in the removal of phosphate from the pore waters and the sediment water interface (Ishikawa&Nishimma,1989).The increase of phosphate concentration in the liquid phase was observed to be accompanied by a decrease of iron bound phosphate in the solid phase(Hosomi et al,1982,Joh,1983). Similarly the formation of apatite with calcium is considered as removal mechanism of phosphate from the reactive phase.

5.2 Modelling of Nutrient Regeneration

Considering the significance in modelling of the system for better management, several models were suggested to explain and predict the nutrient diagenesis and dynamics (Vanderbought et al., 1977; Ishikawa and Nishmma, 1989; Krom & Berner, 1981, Koop et al., 1990, Sundby et al., 1992;). Almost all of the models suggested recognise the role played by the sediments and pore water in the release of nutrients to the overlying water. The model proposed in this study is not significantly different from the general concepts considered by the earlier workers. No mathematical interpretation to the model is employed here for want of some kinetic data, which could not be collected, in this investigation due to unavoidable technical reasons.

The present model is based on the following assumptions,

1. In shallow estuarine and lake waters, the remineralisation of the organic matter will be restricted to the sediment phase.

2. The inorganic soluble species of the nutrients formed will get associated with the pore water .

3. The release of inorganic nutrients to the overlying water takes place by diffusion through the sediment water interface.

4. In most of the sediments of shallow waters where there is substantial input of organic matter, oxygen will be a limiting factor in the remineralisation process and very often the process will either get broken at some stage or take alternate process.

5.In the mineralisation of organic nitrogen in sediments, the process usually will get broken with the deamination, the result being the release of NH_4-N to the pore water. The solubility of NH_4-N is so high that the adsorption to the sediments is negligible

6. Phosphate released to the porewater undergoes three main processes of removal;

a. Reprecipitation with some other compound/ element (eg. Apatite).

b. Adsorption to Fe and Al minerals.

c. Diffusion to the overlying water.

7.Though the remineralisation process is irreversible but the regular addition of organic matter will always maintain a steady state. The steady state will lead to constancy in the composition in the sediment.

8.The surface sediments are always subjected to significant effects from the turbulent character of overlying water and so the concentration of the chemical constituents will be dependent on the porosity and surface conditions of the sediment.

5.3 The system

The sedimentary compartment in this model is considered as a complex reducing biogeochemical reaction vessel and is always in a reducing condition. Continuous addition of organic matter from the overlying water followed by microbial anoxic remineralisation leads to regular discharge of inorganic nutrients to the pore water. The pore water thus, behaves as a store of the inorganic nutrients, which, as and when required, will be available for the overlying water as well as to the sediment. The processes are so regular and continuous in character, that no building up of any from of the nutrient elements takes place. In other words system can be assumed to be in a steady state.

The Processes that are expected in the present system, Kuttanad waters, and the observations lead to two major activities,

a. Sedimentation and mineralization of the organic matter.

The contributing parameters to the sedimentation are the input sources and character of the overlying water. Generally the main input source is land or river discharges. In the present study, the estimation of organic matter indicated significant seasonal and zonal variations. With in the season and zone, but, the sedimentary organic carbon, total N and total P showed comparably high degree of constancy, indicating a steady state.

b. The exchange processes by pore water

The exchange processes that can contribute to the inorganic nutrient levels in the pore water are limited to the diffusion of the species to the overlying water. A steady state in the exchange processes of nutrients in the pore water, thus, means to the steady state between the mineralisation and diffusion through the sediment water interface and only low concentration of the nutrient will be available with the pore water. This was found to be true with nitrogen where the concentration of exchangeable nitrate, nitrite and NH_4-N were found to be significantly low. In the case of phosphorus, the tendency of phosphate to form Fe and Al bound phosphate and Calcium bound phosphate add two additional parameters to the exchange processes. The significant concentration and the constancy observed in the actual values of these species, but confirms the presence of a steady state.

5.4 The Model

The system contains basically three compartments, the sediment, pore water and the overlying water. Depending on the nature of the species, the sedimentary compartment may behave as a multi compartment system, for example each of the adsorbing species may act as individual compartment. Though the general character of the system will be same for the regenerative dynamics of phosphorus and nitrogen, the sediment will have difference in the compartmentalization. Thus nitrogen will have two sedimentary compartments- one for the residual and the second for the fixed. But phosphorus will have three compartments- one for the residual, the second for immobilized phosphorus species and the third for iron and aluminium bound phosphorus.

5.5 Phosphorus

In the release of inorganic phosphorus from the sediment to the overlying water, pore water plays a key role. The transfer is considered to be by the diffusion of phosphate from the pore water to the overlying water through a boundary layer (Santschi et al., 1983; sundby et al., 1992). The reactions that release phosphate to the pore water are desorption of phosphate from surface sites on sediment particles, mineralisation of organic matter and reduction of iron oxides in the anoxic zone of the sediment (Krom and Berner, 1981). Sundby et al (1992) argues that the release of phosphate to the pore water when iron oxides undergo reduction controls the flux of phosphate out of the sediment. This, but, depends on the buffering capacity of the sediment. The transport of phosphorus from the sediments to the water can be explained by the stagnant flux model of Santschi et al (1983), where the flux of phosphorus out of sediments is given as

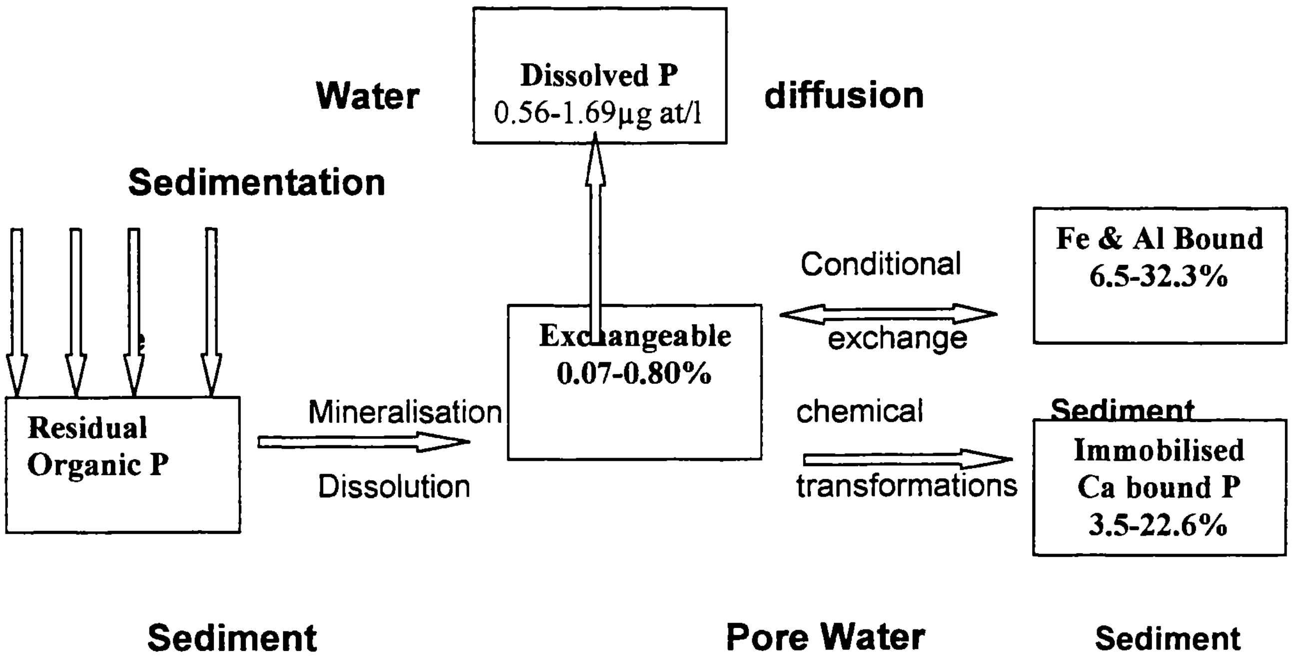
$$J = D_m (C_s - C_w)/Z$$

J is the flux of phosphate, Dm is the molecular diffusion coefficient of phosphate in sea water at 45^0 C, C_s is the concentration of phosphate at the bottom of the diffusive sub layer (concentration in the pore water corrected for the presence of solid particles, i.e. concentration in a volume of whole sediment with porosity 90%), C_w is the concentration of phosphate in the bottom water on top of the diffusive sublayer, and Z the thickness of the sublayer.

The dynamics of phosphorus in the sedimentary compartment thus depends on the buffering capacity of the sediment and the thickness of the boundary layer. A net conversion of the dissolved phosphate in the pore water to adsorbed phosphate in the sediment will, so, takes place only if the buffering capacity favours for an increased production and the boundary layer thickness of the interface offers significantly high resistance to the diffusion of the phosphate (Sundby et al 1992). The system can be represented in fig 5.1

In this study the residual organic phosphorus was found to have a substantial contribution to the total phosphorus, indicative of a low mineralisation rate. Generally a low organic phosphorus was observed to be present in the sediments. The comparable levels of iron and aluminium bound phosphorus and calcium bound phosphorus also are indications of such a low mineralisation. The texture and the moisture content of the sediment indicate the presence of considerable porosity which can support a faster transfer of flux to water. The water is shallow and the

Fig 5.1


Water
Dissolved P
0.56-1.69μg at/l
diffusion
Sedimentation
Residual
Organic P
Mineralisation
Dissolution
Exchangeable
0.07-0.80%
Conditional
exchange
Fe & Al Bound
6.5-32.3%
chemical
transformations
Sediment
Immobilised
Ca bound P
3.5-22.6%
Sediment
Pore Water
Sediment

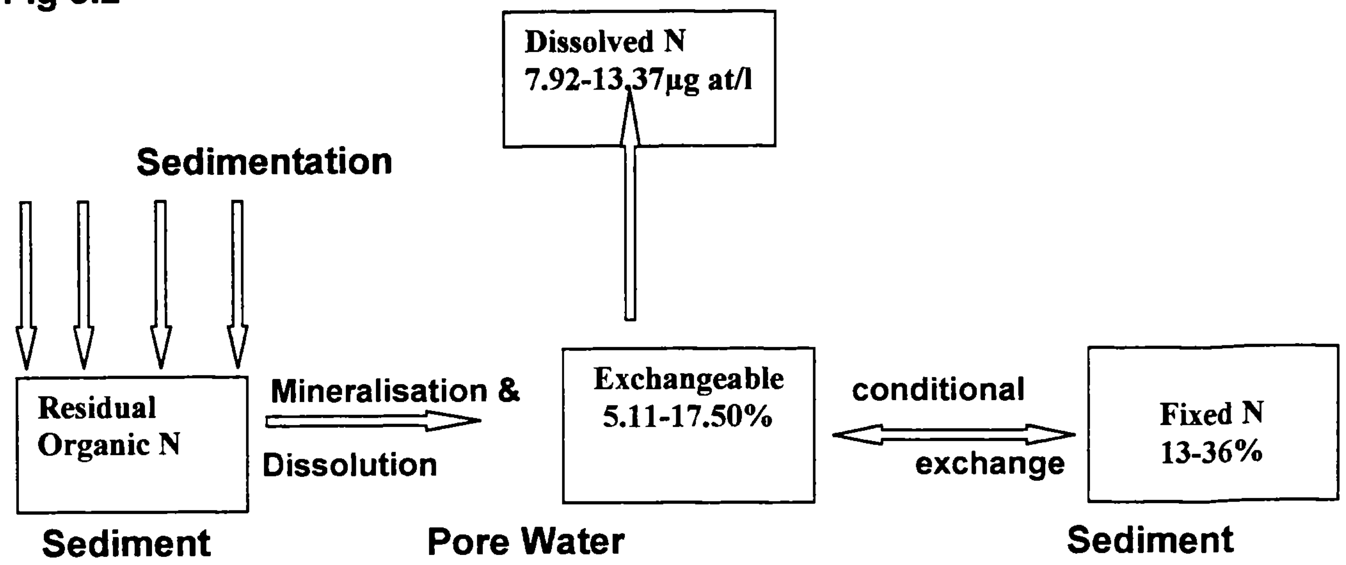
thickness of the boundary,so, will have the maximum value. (The exact calculation of the flux and the thickness could not be done due to technical reasons). Significant correlation observed between the PO_4 ($_{dissolved}$) & salinity, Total P(S) & salinity and Total P(S) and $PO_{4\ (dissolved)}$, indicate intimate relation between the P(S) and $PO_{4\ (dissolved)}$ and eliminate any restriction to the release of PO_4 to the water from the sediment by the boundary.

5.6 Nitrogen

The system can be represented in Fig 5.2

Though in the beginning of the definition of the processes, nitrogen was designated as different from phosphorus because of the absence of the transformations leading to the immobile ammonia, the observed percentage of the different fractions indicate a same behaviour to that of the phosphorus. The pore water acts as the distributor of nitrogen from sediment by diffusion to the overlying water or for the formation of conditional exchangeable fixed ammonia. The observed percentage does not indicate a higher rate of mineralisation. The contribution of nitrification and denitrification are not considered here as serious contributors to the overall diagenesis because of the anoxic character of the sediment. An increased role of mineralisation would have resulted in a high concentration of fixed ammonia and a lower concentration of organic nitrogen. This would have been the case especially when we consider the

Fig 5.2


Dissolved N
7.92-13.37µg at/l
Sedimentation
Residual
Organic N
Mineralisation &
Dissolution
Exchangeable
5.11-17.50%
conditional
exchange
Fixed N
13-36%
Sediment
Pore Water
Sediment

resistance to the diffusion due to the increased thickness of the boundary in the shallow water conditions.

Conclusion

The conceptual model proposed on evaluation with the available data on the distribution was found to be in confirmation with the flux concept proposed earlier. The exchange of nutrients between the sediment and water depends on the mineralisation of organic matter, the diffusion characteristics of the nutrients, the secondary chemical transformation of the sediment and the surface conditions, which determine the resistivity of the boundary to the diffusion. The system studied in this investigation, Kuttanad waters, was found to exhibit a slow mineralisation and the amount of nutrients which can be made available to the overlying water by the diffusion process is found to be considerably low. The exact picture can be obtained only by undertaking a detailed examination of the flux of the nutrients in the various compartments of the sediment including the deep sediments. The work is in progress in these lines.

SUMMARY

The fertility of the coastal and estuarine waters are of great concern in the scientific scenario because of its contribution to the total productivity of the aquatic realm. The concentration and dynamics of the inorganic nutrients is more or less controlled by the sedimentary exchange. Quantitative and qualitative studies of Nitrogen and Phosphorus in sediments are important for understanding the basic processes governing the distribution and biogeochemical cycling of nutrients. Inorganic phosphorus, the species generally utilised by plants, is almost completely present in the form of orthophosphate. The organic phosphorus, the biogenic phosphorus, gets remineralised in the aquatic system and orthophosphate is regenerated. Remineralisation and thereby regeneration mostly take place in sediments and phosphate will be released to the system through the exchange between sediment and water.

Estuarine sediments have a significant influence in the regulation of phosphate concentration in overlying water column by virtue of the capacity for uptake and release of phosphorus under changing environmental conditions. The ability of sediments to adsorb the phosphate will be largely governed by the chemistry of the sediment and by the concentration of the sedimentary phosphate.

In the sedimentary compartment, the inorganic fraction of phosphorus consists of exchangeable and metal bound and residual fraction consists of organic forms. The inorganic phosphorus is more or less totally in the form of orthophosphate and its contribution to the fertility of the water body is found to be significant.

The Kuttanad region is well known for its agricultural activity and so the major contribution to the inorganic ions of nitrogen will be from fertilisers applied in the agriculture. The dynamicity of this water body is considered to be maximum during post monsoon season. The analysis of the seasonal variation of nitrate indicated a high concentration during this season. Generally the reactivity of the nitrite is considerably high and so its concentration in the aquatic system is low. Same trend was observed in the present investigation also. The observed concentrations can thus be considered as the reflections of the aquatic conditions and no anthropogenic additions or removal can be assigned. The concentrations of ammonia were well within the range, compared to earlier works. The concentration of ammonia was high in post monsoon season except in zone III. The main reason is the higher phytoplankton activity during this season. In the present study high values of urea was observed along with seasonal variations suggests an anthropogernic input rather than in situ production.

The shallowness of the water body along with the considerable input of organic matter will not be favourable for the regeneration of nitrate in the sediment. Compared to earlier works the sedimentary phosphate gave lower values. But significant variations are observed during post monsoon season. The net concentration of phosphate available with the sediment was generally assigned to the result of an equilibrium between the adsorption on sediment and its release to the overlying water.

In the speciation scheme the main phosphorus fractions identified were exchangeable and carbonate bound, iron and aluminium bound, calcium bound and residual phosphorus. The comparison with available literature indicate the presence of considerably lower percentage of the exchangeable phosphorus. The observation in the present study showed a similar trend. Zone III gave maximum amount of exchangeable phosphorus, can be due to a significant contributions from the saline waters. The second fraction identified was Fe and Al bound phosphorus. The maximum value was observed during monsoon season. The low level of this fraction in premonsoon and post monsoon suggest two possibilities.

1.The diagenetic activity which leads to the regeneration of phosphate in the sediment is not favourable either for a regeneration of phosphate or does not favour binding of phosphate to Fe and Al bound

2. The major source of Fe and Al bound phosphate fractions is the land contribution and the post monsoon represents a season where either the retention of Fe and Al bound phosphorus is low or its actual concentration that reaches the water body is low.

In the present study the observed calcium bound phosphorus percentage is lower than the Fe and Al bound phosphorus in zone I and II. The presence of significantly high percentage of calcium bound phosphorus in zone III suggest either an enhanced mineralisation or anthropogenic input of inorganic phosphorus. The residual phosphorus, which can be considered as the immobile fraction of phosphorus, is generally constituted by organic phosphorus.In the present study the residual phosphorus constituted the major portion of the total phosphorus.

In the case of nitrogen, the inorganic species nitrite, nitrate and NH_4^+ ions are considered as the major sources of nitrogen to the biota. Major portion of the recycled nitrogen released to the water from sediments is in the form of NH_4^+. Availability of NO_2^- and NO_3^- depends on the concentration of dissolved oxygen and so generally in estuarine sediments because of the reducing conditions NH_4^+ is the major product. Ammonia is regenerated by the decomposition and deamination of organic matter in the reducing environment present in the sediments of this aquatic system and a significant amount of exchangeable ammonia in the pore water was observed. The observed values of fixed nitrogen is in tune with the earlier reports. The reducing environment prevailing in the sedimentary compartment restricts the nitrification processes and the significantly high NH_4-N in the pore waters, along with the sedimentary composition leads to a significantly high fixed NH_4-N.Generally organic nitrogen is the major constituent in the total nitrogen in the sediments. In the present study the observed percentage of organic nitrogen varied between 38.66-85.98. The lower values may be due to high mineralisation or deamination of organic nitrogen and or significantly high input of anthropogenic organic matter with low nitrogen content.

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