NUTRIENT MOBILITY IN CHALAKUDY RIVER, TYPIFIED WITH RIPARIAN BUFFER ZONE AND ITS ADJOINING ESTUARY: SPATIOTEMPORAL MANIFESTATION

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By

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Certificate

This is to certify that the thesis entitled "Nutrient mobility in Chalakudy River, typified with riparian buffer zone and its adjoining estuary: Spatiotemporal manifestation" is an authentic record of the research work carried out by Smt. Padma P under my supervision and guidance in the Department of Chemical Oceanography in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Cochin University of Science and Technology, and no part thereof has been presented for the award of any other degree, diploma or associateship in any University.

Dr S Muraleedharan Nair

DECLARATION

I hereby declare that the thesis entitled "Nutrient mobility in Chalakudy River, typified with riparian buffer zone and its adjoining estuary: Spatiotemporal manifestation" is a genuine record of research work done by me under the supervision and guidance of Dr S Muraleedharan Nair, Department of Chemical Oceanography, School of Marine Sciences, Cochin University of Science and Technology. The work presented in this thesis has not been submitted for any other degree, diploma, associateship, fellowship or any other similar title or recognition.

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Preface

A nutrient element is one which is functionally involved in the production of organic matter by photosynthesis. Nitrogen and phosphorus are considered to be the main limiting nutrients and these react differently once emitted to the aquatic environment. Nutrient pollution in rivers has several undesirable effects, most of which are related to the increased growth of phytoplankton and other aquatic plants, which leads to a shift in the biological structure, and in several cases even to oxygen depletion, production of toxins, and the collapse of entire aquatic ecosystems. This study was aimed at to characterize the spatio-temporal trends in the distributional characteristics of various species of nitrogen and phosphorus as well as to elucidate the factors and processes affecting these nutrients in the dissolved, particulate and sedimentary phases of a river – estuarine system. The main area of study is Chalakudy river in Kerala, which is a fresh water system originating from Anamalai hills and ending at Arabian Sea. Its basin is between 10^0 *05' to* 10^0 *35' North latitude and* 76^0 *15' to* 76^0 *55' East longitude. Being a riparian buffer zone, the dynamics of nutrient mobility tend to be more complex and variable in this river – estuarine system.*

The thesis is encompassed in seven chapters. Chapter I is the Introduction dealing with the significance of rivers and estuaries and appraising its importance with respect to nutrients. Chapter II is the Materials and Methods. A description of the study area, sample collection techniques and the methodology adopted are imparted in this chapter. Chapter III is the Hydrographical parameters and their auxiliary and is stuffed with seasonal and spatial variations of general physical and biogeochemical characteristics inter-related to the Chalakudy river - estuarine system. Chapter IV is the Spatio-temporal variability of dissolved nitrogen and phosphorus comprising the seasonal / spatial modes of speciation of these two imperative nutrients in the fluvial phase. Nutrient loading capacity of suspended solids and its course of transport across the spatial and seasonal diversities are addressed in Chapter V, Nitrogen and phosphorus in suspended particulate matter. Sedimented nitrogen and phosphorus, the VIth Chapter is compiled by incorporating the understanding of speciation, distribution and temporal differences of the nutrient chemistry in the sedimentary environment. Chapter VII is an Integrated GIS water quality model for the assessment of quantitative portrayal of the known linkages of nutrients along the river-estuarine system. Finally, a summary chapter is appended to abridge the overall significance of this doctoral work.

The different species of nitrogen estimated from the filtrate were nitrite-N, nitrate-N, ammonia-N, urea-N, total nitrogen and residual nitrogen. The different forms of phosphorus estimated from the filtrate were phosphate-P, total-P and residual-P. Pre weighed sediments as well as particulate matter were analysed for quantifying nitrite-N, nitrate-N, ammonia-N and urea-N. Total nitrogen was *estimated after digestion with potassium persulfate. Fractionation of phosphorus in sediment/particulate matter was performed by applying sequential extraction procedure. The different forms of phosphorus thus estimated were loosely bound (exchangeable) P, Fe/Al bound P, polyphosphates, Ca bound P and refractory P. Sedimental total P was also measured directly by applying digestion method.*

The analyses carried out in this bimonthly annual survey have revealed specific information on the latent factors influencing the water quality pattern of the river. There was dependence among the chemical components of the river sediment and suspended matter, reflecting the water quality. A period of profound environmental change occurred and changes in various species had been noted in association with seasonal variations in the waterway, especially following enhanced river runoff during the monsoon. The results also successfully represented the distribution trend of nutrients during the rainy as well as dry season. Thus, the information gathered in this work will also be beneficial for those interested or involved in river management, conservation, regulation and policy making in regional and national levels.

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CHAPTER I

INTRODUCTION

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Riverine and estuarine ecosystem

Rivers are flowing bodies of waters. Rivers are an important part of the earth's water cycle and the sculpting of the earth's topography as they carry huge quantities of water from the land to the sea. Rivers frequently constitute the main water resource for inland areas, for irrigation, drinking and industrial activities. The early course of a river is often in steep, mountain areas, with rapidly-flowing cold water. As a river continues along its course (which is always changing), the surrounding terrain flattens out and the river widens. Rivers often meander along their middle course. Tributaries and runoff flow into the river, increasing the river's volume. Most rivers end when they flow into a large body of water like an ocean, sea, or large lake. An estuary is the area where a river meets the sea or ocean, where freshwater from the river meets salt water from the sea. The end of the river is called the mouth. At the source of a river, the water is relatively pure. Rivers and estuaries have less stable natural environmental conditions than inner bays which have high sedimentation rates that allow high-resolution studies (Tsujimoto et al., 2006). As the water flows downstream, it picks up silt and minerals (including mineral salts) from the soil and rock in the river bed and many other chemicals enter river water as it flows downstream, including animal waste, human sewage, agricultural (farm) runoff, urban runoff, and mining/factory effluent. In order to obtain the relationship among sources of nutrients, organic compounds and products of the decomposition, processes must be considered which include different diffusivity, adsorption and/or precipitation processes; selective stripping during mineralization and inputs from inorganic substrates.

River water

The quality of water reflects the combined effects of many processes along water pathways and is greatly influenced by the characteristics of the catchment area including lithology, atmospheric inputs, climatic conditions and anthropogenic inputs. Seasonal variations in precipitation, surface runoff and groundwater flow have a strong influence on flow rate and hence on the level of contaminants in the river water. During exposure to the atmosphere, water loss occurs due to evaporation and drainage (Hou et al., 2005).

The outstanding industrial growth in the world during the past decades has brought dramatically deteriorating changes in water systems. Rivers assimilate and transport waste generated from point sources such as municipal and industrial wastewater discharges and non-point sources such as runoff from agricultural land and urban areas. Nitrogen inputs in intensive-agricultural catchments have been identified as the major causal factor driving trends of increased nitrogen concentrations in surface, ground and coastal waters (Worrall et al., 2003), and thereby, inorganic and organic nutrients may find their way into running water systems. Furthermore, the need to produce more food for a growing population has a link to the quality aspects of the aquatic environment as it results in increased soil erosion, chemical pollution by fertilizers and pesticides, and pollution from animal operations. The need to produce more food means that the annual worldwide nitrogen fertilization which stood at 87 million tonnes in 2000 will increase to 135 million tonnes in the year 2020, whilst phosphorus input will increase from the 2000 estimate of 34.3 million tonnes to 47.6 million tonnes in 2020 (Zehnder et al., 2003). Contaminant loads delivered to surface water bodies are continuously increasing such that water quality is being impaired to the point that drinking water requires more advanced and costly treatment and aquatic ecosystems are greatly damaged (Massoud et al., 2006). The downward shift in water quality, observed in rivers is thus reinforced by the combined effects of natural and anthropogenic processes. Among many undesirable consequences of its rapid growth, marked alterations in eutrophicational status of the aquatic ecosystems occur. Deteriorating water quality threatens human health and the functioning of aquatic ecosystems. Information on temporal and spatial trends of water quality is therefore a necessity.

Suspended particulate matter (SPM)

Characterising the nature and origin of suspended particulate matter (SPM) in waters is a necessary first step in determining the role of these materials in the transport of pollutants. There are three external land-derived sources for particulate matter in aquatic system— riverine, land runoff and atmospheric inputs. Rivers transmit particulates through freshwater into the coastal zone. The relative importance of these inputs varies from place to place and from time to time and the factors influencing this variability are important. Occurrence of SPM in rivers is mainly due to differential weathering of micas and alkali (K) feldspars to form the majority of the particulate (>1 μm) fractions and differential weathering of Na, Ca-feldspars (plagioclase) which decompose to form clay minerals in the colloidal (<1 μm) fractions and release the majority of elements into solution (Beckett, 1986) which may be complexed by the presence of natural organic matter (humic substances) as coatings on the particulate

(>1μm) and colloidal (<1 μm) matter. Obviously, the size range of particles in suspension depends on both the prevailing hydrodynamic and hydrochemical conditions, but generally the grain size of the suspended sediment carried by most rivers is <60 μm i.e. silt and clay. The suspended sediment of many rivers is dominated by particles that have clay to colloidal dimensions. As a consequence, suspended sediments tend to have relatively high specific surface area. This property makes suspended sediment central to the mobility in an environmental context, especially substances that tend to be relatively insoluble and preferentially sorbed to surfaces.

Many sources are known to regulate the SPM concentration in aquatic systems. The most important sources/factors according to Hakanson (2006) are autochthonous production, allochthonous materials, such as the amount of coloured matter (e.g., humic and fulvic substances) and the amount of resuspended material. This is easy to state qualitatively, but more difficult to express quantitatively because these three factors are not independent: high sedimentation leads to high amounts of resuspendable materials; high resuspension leads to high internal loading of nutrients and increased production; a high amount of coloured substances means a smaller photic zone and a lower production; a high input of coloured substances and a high production mean a high sedimentation, etc. Marine waters generally have a higher clarity than rivers, and the variability in suspended particulate matter values is generally significantly smaller in marine systems (Hakanson, 2006).

Particulate matter plays an important role in determining the water quality of rivers by storing nutrients, organic matter and trace metals. Apart from the role of the flow and of residence time of water on nutrient retention, it is difficult to interpret all the 'black-box' input-output differences in composition of suspended matter with internal river processes because of the complexity of the nitrogen and phosphorus cycles. Chemical composition of particulate matter of rivers and estuaries are controlled to some extent by various physico-chemical (pH, temperature, alkalinity, chlorinity, dissolved oxygen, and chemical oxygen demand) and biological processes occurring in the river catchment and within the river. Moreover, the determination of the distribution of SPM and fine sediment provides evidence of the disposition of pollutants, adhered to the particles (Gayer et al., 2006). Estuaries are at the receiving end of the cumulative effects of water abstraction and the urban and/or agricultural runoff owing to their impoundments in the river catchment.

Sediments

Sediments are media-term-integrators for the variations of aquatic ecosystems expressing historical evolution through various biochemical descriptors. Bed river sediments are biogeochemically active zones in reservoirs, rivers and estuaries, playing a key role on the whole river functioning (Battin et al., 2003). Taken as a whole, the physicochemical composition of sediments such as texture, particles' surface area, organic matter and others affect nitrification and the involved organisms and these depend on the step of the process like ammonium oxidation or nitrite oxidation. As the rate of biogeochemical processes is likely to be limited by the availability of organic matter, chemically active zones are often limited to the top layer of sediments (<60 cm) where the exchange rates between the river and the hyporheic zone are the highest. The role of sediment requires evaluation because it exhibits a potential to deliver environmental goods beyond habitat creation; it has the potential to take up particular elements and trap nutrients. This is particularly important where there is eutrophication of water from agriculture and wastewater and also physical degradation of the environmental bed of riverine system.

Sedimentation initiates the permanent removal of material from aquatic systems via sediment burial. Sedimentation can play a role in the community composition of the food web by influencing phytoplankton succession. Sedimentation is important in riverine systems where it plays a role in the global cycling of important elements. One mechanistic reason for the difference between rivers and estuarine systems is related to the fact that the salinity of the system will influence the flocculation/aggregation, and hence also the settling velocity, of the suspended particles: the higher the salinity, the greater the aggregation of suspended particles, the bigger the flocs and the faster the settling velocity. The sedimentation of nutrient elements such as phosphorus and nitrogen that limit production are of particular interest. Phytoplankton community composition also influences sedimenting particles. Periods of overturn can coincide with diatom blooms and subsequent sedimentation events.

Sediment acts like a dynamical buffer representing sources and sinks for nutrients simultaneously. Surface runoff transporting sediment with high phosphorus (P) concentrations has been identified as a major hydrological pathway for sediment associated P delivery to surface waters and is considered a major threat to water quality, due to the ability of P to cause eutrophication in freshwater (Ballantine et al., 2008). Many of the chemical reactions are biologically mediate; their relative importance depends on several factors, such as sediment composition, sedimentation rate, hydrodynamics, bioturbation and irrigation as well as the physical and chemical characteristics of bottom waters. The chemical transformations that take place at the sediment water interface determine the cycling of nutrients between sediment and waters. Porewater migration is an important vehicle for the transport of solutes through the sediments on shorter time scale (Kuwae et al., 2003). Temperature as well as pH alternation has a dramatic effect influencing remineralization of organic matter and nutrients in sediments on very short time scales.

Ecological importance of dams regarding nutrients

Refilling in dams releases nutrients inducing a trophic upsurge. On a general scale, reservoirs have far-reaching effects not only on the hydrology, but also on biochemical and physical characteristics of continental waters. Damming rivers increase residence time and water temperature, decreases the turbidity, modify thermal stratification and enhance in situ primary production. The construction of reservoirs alters the organic carbon cycle, and the oxygen and nutrient balance (Friedl and Wuest, 2002). Reservoirs are of high ecological and economic importance and the assessment of water quality in reservoirs is essential because they are often one of the main sources of water for human consumption and irrigation (Carol et al., 2006).

Significance of nutrients in rivers and estuaries

Nutrient is an element or group of elements that is fully involved in the life processes of living organisms. In aquatic chemistry, the term principally refers to phosphate, nitrate and silicate. Our body transfers nutrients through a network of streams and rivers we call arteries and veins. Rivers feed ecosystem just like arteries and veins feed human cells. Nutrients like nitrogen and phosphorus, occur naturally in water, soil and air. Just as the nitrogen and phosphorus in fertilizer aids the growth of agricultural crops, both nutrients are vital to the growth of plants within rivers, reservoirs and estuaries. Nutrient regeneration is a key process of nutrient cycling which is important for the trophic structure of shallow aquatic ecosystems such as estuaries (Sundback et al. 2003).

The most important effects associated with river are those related to the release of nutrients to the waterbody. The sources of nutrients in surface waters can be broadly divided as *natural* and *anthropogenic* (Figure 1.1). The natural sources come from soils and weathering profiles during initial flooding of the landscape, and from the decomposition of drowned terrestrial vegetation. Natural sources are generally ubiquitous; however, their contribution is usually low because, over the course of time, natural systems have established balances between the production and consumption of nutrients. Nutrient loss from catchments appears to be closely related to the magnitude of human disturbance. Anthropogenic sources arise from many activities and inputs of nitrogen (N), phosphorus

(P) and oxygen-consuming material to riverine and estuarine ecosystems can change nutrient dynamics, deplete oxygen, and change abundance and diversity of aquatic plants and animals. The most tangible impact is an explosive rise in productivity, with both beneficial (e.g., increased fish yields) and deleterious consequences (e.g., spreading of undesirable aquatic plants). In tropical and subtropical freshwater systems, trophic dynamics – relationships between nutrient limitation and phytoplankton biomass is not as simple and linear as in temperate systems (Huszar et al., 2006). In freshwater environments, the presence of dissolved or particulate N often results less from an autochthonous production (N_2 assimilation) than from anthropic inputs such as agricultural fertilizers, nonpoint source pollution, or wastewater discharges (point source pollution) (Montuelle et al., 2003). Industrial establishments with insufficient technologies cause a distinct nutrient pollution in the receiving rivers. The increased concentrations of dissolved nutrients can severely disturb the ecological integrity of rivers. Freshwater replacement time and estuarine circulation are important factors influencing the processing of nutrients specific to estuaries.

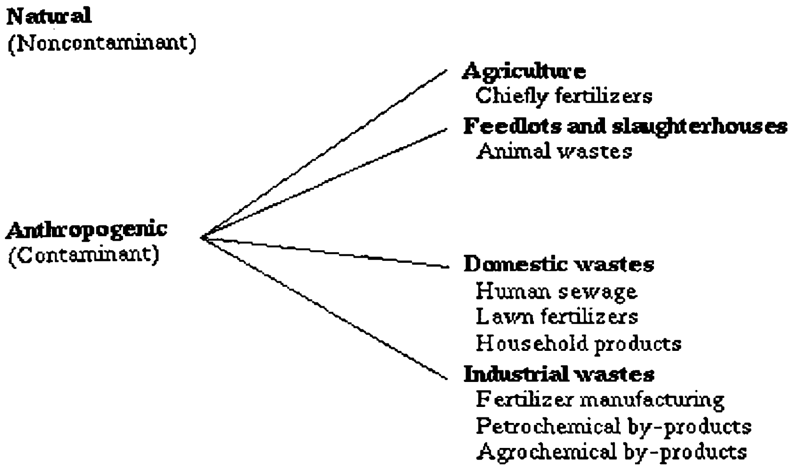

Figure 1.1 Sources of nutrients in surface waters

Eutrophication (as nutrient enrichment) is a serious environmental problem in reservoirs, rivers and estuaries. The processes occurring during eutrophication of a water body is pictured in Figure 1.2. Nutrients are essential for aquatic life, but the excessive build-up of nutrients (mainly phosphorus and nitrogen derived from human activities) can lead to algal blooms and changes to aquatic life. This is known as eutrophication. Higher than natural nutrient levels can cause plant growth, especially the growth of algae. Algae remove oxygen from the water, which makes it difficult for other plants and animals to get enough oxygen to survive. Thus, one of the most common points of aquatic contamination is eutrophication.

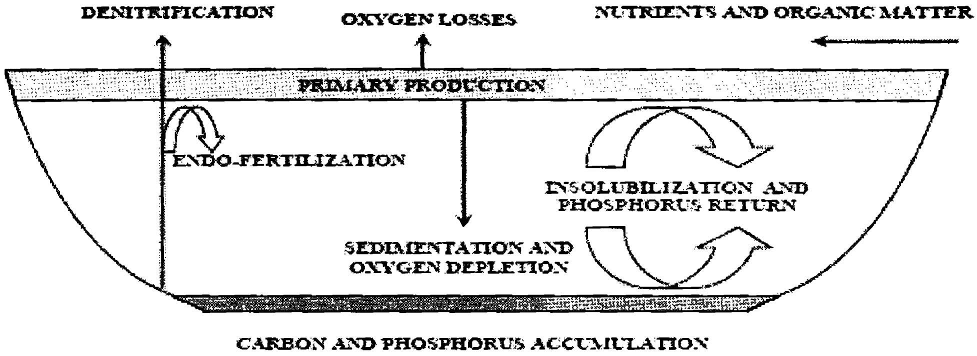

Figure 1.2 Processes occurring during eutrophication of a water body (Niell et al., 2005).

Eutrophication happens naturally. Enrichment of many world's rivers with nutrients has been a direct consequence of social or cultural advances made by growing human populations, accompanied with increased waste water loads, diffuse loads, and run-off from agriculture. The consequences of man-made eutrophication present a growing environmental problem worldwide. Eutrophication is a complex process which involves different time scales and different levels of community structure. The amount of nutrients (N, P, Si) carried to the coastal zone by large river systems, as well as the balance between these elements, are the major determinants of coastal marine eutrophication problems (Billen and Garnier, 2007). The nutrients most likely to influence algal growth in water are phosphate and nitrate. Natural phosphate levels in river waters tend to be low, which limits algal growth. In seas and estuaries, nitrate is more important in limiting plant growth. This is because marine plants have different nutritional needs to freshwater plants. Unnaturally, high levels of either nutrient can lead to eutrophication. Eutrophication can have both temporary and irreversible effects on aquatic ecosystems. Eutrophication caused by excessive inputs of phosphorus and nitrogen is the most common impairment of surface waters and the most widespread pollution problem of estuaries, especially in areas with limited water exchange (Kennish, 2002).

Changes of nutrient in sediment as well as particulate matter are also sometimes linked with the dilution effect on river water. One of the effects of the flooding pulse is an acceleration of the decomposition of detritus and considering that decomposition processes give rise to remineralisation, flooding has a stimulating effect on nutrient release (Palijan and Fuks, 2006). In natural rivers, the rise in primary production may have been further stimulated by increased fluvial discharge due to greater rainfall. Increased fluvial discharge might itself have resulted in an elevated supply of dissolved and particulate nutrients from the catchments. This effect may be particularly significant in the case of phosphorous – often regarded as one of the limiting nutrients for primary production in tropical rivers which can become concentrated in soils and, because it binds strongly to iron oxides, is typically associated with particulate weathering products (Hecky et al., 2003).

The forms and quantity of phosphorus and nitrogen in aquatic ecosystems are a function of not only the external nutrient inputs and outputs but also their interchange between the sediment and the water compartments. Nutrient flux from sediments can thus be one of the important factors controlling the nutrient cycle in aquatic ecosystems. Thus benthic sediments are an important sink for organic matter and sites of nutrient regeneration. Retention can be defined as the capacity of rivers to remove water column P and N through physical, chemical, and biological processes and retain it in sediments in a form not readily released under normal conditions. Retention of nutrients at sediment interfaces decreases the load to downstream aquatic systems such as rivers. River sediments not only store nutrients but also transform nutrients from biologically available forms into non-available forms and vice versa. Thus, it is important to include the contribution of river sediments in retaining nutrients.

Role of chlorophyll and different species of N and P in riverine system

Accelerated eutrophication arising from nutrient enrichment of rivers and estuaries represents one of the most significant water quality problems. The interaction between hydrology and light (turbidity) likely controlled algal biomass in nutrient-rich, agricultural streams (Figueroa-Nieves et al., 2006). Chlorophyll *a* is often a central aspect of water quality and acts as an indicator of algal density to assess the effect of phytoplankton on the elemental composition (N, P) of dissolved as well as suspended materials in the rivers.

Changes in nitrogen and phosphorus concentrations are of particular concern, since they often limit the productivity of aquatic ecosystems and have been identified as contributors to enhanced eutrophication and water quality deterioration. It is well known that the general stoichiometry of phytoplankton cells is $C_{106}H_{263}O_{110}N_{16}P_1$. From these five fundamental elements, carbon (C), hydrogen (H) and oxygen (O) are abundant and readily available in nature. Therefore, availability of the two remaining elements, nitrogen (N) and phosphorus (P) constitute the limiting elements of algal growth. The C:N:P ratio is expressed as 106:16:1, which is the average ratio in marine plankton (Redfield, 1958). Important constituents of aquatic systems are the dissolved nitrogen, phosphorus and silica (Turner et al., 2003). Nutrients released from sediments can influence water column nutrient concentrations and planktonic productivity (Nowlin et al., 2005) and the release rates differed in physical mixing conditions. Leaching of P to the water is considered to be of significance, because of the normally strong P adsorption to particulate matter and sediments. Anoxic sediments at stratified site released soluble reactive P at rates more than an order of magnitude greater than oxic sediments at shallow unstratified site (Nowlin et al., 2005). N can leach to the water in the form of nitrate NO_3^- which may be lost from the aquifer by denitrification.

Nitrogen (N) is essential to the production of plant and animal tissue. It is used primarily by plants and animals to synthesize protein. N enters the ecosystem in several chemical forms and also occurs in other dissolved or particulate forms, such as tissues of living and dead organisms. However, even without anthropogenic inputs nitrogen consuming bacteria can uptake N directly from the atmosphere. Some bacteria and blue-green algae can extract nitrogen gas from the atmosphere and transform it into organic nitrogen compounds. This process, called nitrogen fixation, cycles N between organic and inorganic components. Other bacteria release nitrogen gas back into the atmosphere as part of their normal metabolism in a process called denitrification. Biological nitrogen fixation, the conversion of atmospheric dinitrogen (N_2) to ammonium (NH_4^+), is another important source of new N in the aquatic environment. Ammonia is converted into nitrate through a two-step process with nitrite produced as an intermediate product. Changes in N cycling may be amplified by a switch in the dominant phytoplankton taxa between those dependent upon nitrate and ammonium assimilation and those adapted to N-fixation. Such changes occur seasonally in the river system. In aquatic systems, N can be found in various inorganic forms from the most reduced ammonium to the most oxidised nitrate. Domestic waste waters containing urea and other N components and agricultural fertilizers (ammonium salts) can create very high oxygen demands on receiving water bodies.

Ammonia is one of the most pervasive contaminants in aquatic habitats. Ammonia is contributed to aquatic ecosystems via multiple sources including natural biogenic (e.g., organic matter degradation and animal waste) and anthropogenic (e.g., sewage treatment effluents, agricultural fertilizers, and industrial treatment processes) sources (Fairchild, et al., 2005). Ammonia primarily exists in two forms: NH_3 (un-ionized ammonia) and NH_4^+ (ammonium ion). The relative distribution of the two forms is controlled by pH and temperature. Unionized ammonia is the more toxic form and increases in proportion as pH increases above 8.0 (USEPA 1999). Ammonium regeneration is due to the release of ammonium from nitrogenous organic materials in the process of their decomposition by microorganisms For example, proteins are hydrolyzed by proteinases and peptidases to aminoacids, which, in turn, are deaminated to release ammonium. If the concentration of ammonia nitrogen in river waters is high, the disinfectant effect of chlorine for the production of drinking water will become insufficient because most chlorine would thereby be consumed for decomposition of the ammonia nitrogen (Fukushi et al., 2006). Toxicity of ammonia to the zooplankton community and freshwater amphipods is also of major concern. Moreover, ammonium in drinking water is readily transformed into nitrate, which is toxic for human beings.

Urea is a low molecular weight organic compound, weakly exothermic on hydrolysis and less attractive for ''sensu stricto'' heterotrophic organisms; but as a nitrogen compound, it is easily hydrolysable for autotrophic organisms under limiting conditions (Nair et al., 1994). A considerable amount of urea is found in certain riverine environments. It may originate from freshwater discharge, especially through sewage from densely populated areas, since man and other terrestrial vertebrates represent a primary source of urea. Drainage from agricultural regions, where urea based fertilizers are used, contributes heavily also in the concentration of urea (Remsen, 1971). Urea has been used extensively in studies of microbial N uptake and is considered a suitable dissolved organic nitrogen source because: (1) it is most often the dominant dissolved organic nitrogen type in rivers, estuaries and coastal waters; (2) it is rapidly recycled in the water column and sediment through biological processes. Preference for phytoplankton uptake of the dissolved organic nitrogen forms such as urea, amino acids and DNA over dissolved inorganic nitrogen in some instances has been reported by Berg et al. (2001). Internal regeneration of dissolved organic N supports a large proportion of the phytoplankton primary production and biomass accumulation and N-budgets based on dissolved inorganic N uptake rates alone will seriously under estimate phytoplankton N uptake (Twomey et al, 2005).

Ammonia, nitrite and nitrate have complex toxic effects on aquatic animals. In rivers of southwestern Siberia, Russia, elevated ammonia and nitrite concentrations corresponded to significant reduction in species diversity of mayflies (Beketov, 2004). Although nitrate itself is not toxic, its conversion to nitrite is a concern to public health. Unionized ammonia can induce numerous effects in fish including loss of equilibrium and mortality

The effect of organic loading on nitrification is very important because organic matter removal and nitrification are often carried out within one single reactor. For instance, Hendrickson et al., (2007) found that in blackwater river estuaries, a large portion of external carbon, nitrogen, and phosphorus load are combined in complex organic molecules of varying recalcitrance and determining their lability is essential to establishing the relationship between anthropogenic loads and eutrophication. Organic nutrient re-mineralization is dependent upon the utilization preference of the parent substrate by general microbial heterotrophs (DeBusk et al., 2001). High organic loading in the river water always results in a lower nitrification percentage because of ammonia loss due to assimilation by heterotrophs and the inhibitory effect of the crowded heterotrophic cells on ammonia oxidation. Aquatic humic substances will tend to immobilize the macro-nutrients during decomposition. Also, oxygen consumption during the oxidation of organic matter may reduce nitrification as a result of the reduction in the available oxygen. While inorganic nutrients and some low molecular weight organic compounds are readily assimilated by aquatic primary producers, organic nutrient forms, which must first undergo desorption, hydrolysis, bacterial decomposition or photo-decomposition for inorganic nutrient regeneration and utilization, are less readily available. The presence of dissolved organic nitrogen (DON) in land runoff may affect the quality of the receiving river water in several ways. One probable negative impact of waste water derived DON is its support for bacterial and/or algal growth in the receiving water such as river (Pehlivanoglu-Mantas and Sedlak, 2006). The photochemical reactions in the receiving water may convert wastewater-derived DON into more labile forms.

Phosphorus (P) is the 11th most common element on earth. It exists mostly in phosphate rocks (primarily as calcium phosphate), and the earth's crust contains an average of about 0.1% P. P is primarily obtained to the riverine system from weathering of phosphate rock. But, phosphorus inputs from animal waste, fertilizers and detergents exceed by far the phosphorus generated from rock and mineral weathering. As a result, P is frequently a limiting nutrient in riverine and estuarine systems.

The nutrient P is a vital component in the process of converting sunlight into usable energy forms for the production of food and fiber. It is essential to cellular growth and reproduction for organisms such as phytoplankton and bacteria. Phosphates, the inorganic form are preferred, but organisms will use other forms of phosphorus when phosphates are unavailable. Primary production is found to be P limited in many riverine and estuarine systems. The biological productivity of water is found to be enhancing due to P inputs. Eutrophication is often caused by excessive inputs of phosphate via domestic, industrial, and diffuse agricultural sources. The demand for phosphorus fertilizer increased with growing world's population from 9×10^6metric tons to 40×10^6 metric tons between 1960 and 2000 and was expected to increase further by 20×10^6 metric tons until 2030 (Postel et al., 2001; Vance, 2001). Discharge of sewage and effluents may contain detergents which are rich in polyphosphates. This promotes the nutrient level and causes eutrophication problems. P is unique among the major nutrients (carbon, oxygen, nitrogen, phosphorus) in that it is often assumed to lack a gaseous species for atmospheric transport, though volatile phosphine gas can be detected in the earth's atmosphere at trace levels. The earth's volcanic gases can be rich in P (Obenholzner et al., 2003) and contain traces of methyl phosphine, suggesting that reduced P compounds (phosphorus with oxidation number less than +5) may be present in the earth's crust (Morton and Edwards, 2005).

P is removed by adsorption onto stream bed sediments, sedimentation, and through uptake by algae and aquatic macrophytes. Physical, chemical and biological processes leading to P release to the water column from underlying sediments are numerous, and include the desorption and dissolution of P bound in precipitates and inorganic material, microbial mineralization of organic matter and the diffusion of dissolved P from sediment porewaters. The environmental variables that appear to regulate the release rate of dissolved P from sediments (mostly as phosphate, PO_4^{3-}) are temperature, dissolved oxygen (DO) concentration, pH, nitrate and sulphate concentration and redox potential. P could be taken up from the overlying water to the sediments with high nutrient loading in both anoxic and aerobic conditions leading to transformation between different P fractions in the sediments and water (Jin et al., 2006). In oxygen rich waters, settled P remains permanently buried in the bottom sediments. Under anaerobic conditions, P is released from the sediments into the anaerobic hypolimnion where hydrogen sulfide and ammonia accumulate while nitrate is denitrified. Thus, P enrichment can sometimes be the main cause of eutrophication. Effects of dissolved oxygen on the P distribution at the sediment and overlying water interface were mainly due to the inorganic processes, while effects of light were mainly due to the biological activity. Jin et al. (2006) indicated that oxygen concentration had a predominant control on the distribution and uptake of P in the sediments, and light had obvious effect on the dissolved inorganic P concentration in the overlying water. In eutrophic shallow ecosystems, anoxia and warm hipolimnetic temperature can contribute to increase P releases significantly from the sediment–water interface (Ruley and Rush, 2004).

In contrast to N, P is generally found in its most oxidised state as phosphate (PO_4^{3-}) ion. In most natural aquatic systems, P constitutes the limiting nutrient. Total P is also dependent on biochemical conditions such as the phosphorus cycle and the presence of organisms. Phosphorus enters the rivers in different forms depending on its origin. The sum of immediately available P and P that can be transformed into an available form by naturally occuring processes can be defined as bioavailable P and is responsible for the eutrophication in freshwater systems. Dissolved P, consisting mainly of orthophosphates, is 100% bioavailable to plants, while particulate P and sedimentary P represent a long-term source of P for algae and plants by its existence as various species such as exchangeable P or associated to Al and Fe oxides and hydroxides and Ca minerals or as polyphosphates, refractory (residual inorganic) P and also organic forms which include humic and fulvic complexes, phosphate esters, sugar phosphates, phytate and other compounds (Pardo et al., 2003). Contrary to N, there is no loss of P by atmospheric exchange, so its stock increases continually in the system due to increasingly net input through sewage and agriculture.

About the present investigation

The kind of evaluation of nutrients in the present study entailed two requirements. The first was the necessity of obtaining periodic measurements of the water, suspended impurities and sediment composition with as high as possible a frequency, given the wide variability of the system. The second was to get an insight into the seasonal characteristics.

Kerala is the land of Rivers. 44 Rivers (41 west flowing and 3 east flowing) cut across Kerala with their innumerable tributaries and branches, but these rivers being entirely monsoon-fed, practically turn into revulters in summer, especially in the upper areas. The rainy season in Kerala extends from May till November when there is strong South -West monsoon followed by North-East monsoon. Nearly 75% of the rainfall occurs from late May to September. The season is very hot for the later months of summer. Chalakudy river, one of the longest rivers in Kerala was appropriate for a seasonal geochemical study because of the strong longitudinal gradient of physical and chemical conditions existing in the system.

The aims of the present investigation are to

- elucidate the factors and processes affecting qualities of the long Chalakudy riverine system as well as to characterize the spatiotemporal trends in water quality parameters.
- establish the background levels of nutrients in water, suspended particulates and sediment in the riverine system of Chalakudy river

- evaluate the relative importance of the various sources and sinks of nitrogen and phosphorus during seasonal extremes
- quantify nutrient concentration on a seasonal basis and relate this to various environmental factors to identify the major sources of anthropogenic N and P
- speciate N and P in water, suspended particulates and sediment and
- to clarify the situation through GIS model of the hydrochemical and nutrient data.

The scope of the study covers:

- characterization and prediction of the system responses from accurate estimates followed by realization of a better perceptive of the evolution of the riparian buffer zone and its adjoining estuary
- evaluation of the impacts of modern industry and anthropogenic influences on the system
- functioning as valuable tool in support of the revision of parameters in upcoming investigations.
- Recommendation and accomplishment of better management measures to check degradation of the river quality in future.

An extensive seasonal sampling covering the entire river system, followed by the investigation had been attempted for a better understanding of the biogeochemical processes in this large tropical river of South India. The implications of land-use change on nutrient cycling can be reviewed by contrasting the properties of nitrogen and phosphorus and also of primary production. Summarizing the effects on the environmental aspects at a river-catchment scale demands the integration of complex information collated at the smaller spatial scales. This introduces both complexity and uncertainty into the system because these factors operate over different time periods. ArcGIS is an information system for geographic data developed by the Environmental Systems Research Institute, Redlands, California. Using this programme, surface is derived using the values from the measured locations to predict values for each location in the landscape. This resulted in the development of a chemical framework for organizing data to predict the current ecological state.

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CHAPTER II

MATERIALS AND METHODS

CONTENTS

Description of study area

Chalakudy river in Kerala originates, and continues to flow through much of the Western Ghats—a global biodiversity hotspot before joining the Arabian Sea. Geomorphologically, the stretch of Chalakudy river is characterized by hilly area, highly undulating terrain, moderately undulating terrain, low rolling terrain, transitional plain and floodplain (Raghavan et al., 2008). The river flows through one of the best patches of evergreen forests in the Western Ghats. Deep in the forest, on the way to Valpara are the two dams, Poringalkuthu and Sholayar Dams that generate hydroelectric power to the Kerala state. There are six reservoirs impounded in this basin. The famous waterfalls Athirapally and Vazhachal are situated on this river. Chalakudy river runs through Chalakudy town which is in the Thrissur district of Kerala. The river finally merges with the Periyar river at the village of Puthanvelikkara in Ernakulam district. The Chalakudy river basin is thus a tributary of the Periyar, the largest river in Kerala.

The river has its origin in the Anamalai region of Tamilnadu is actually the collection of the falls from Parambikulam (Parambikulam, Peruvari-ppallam and Thunakadavu originating from Parambikulam region), Kuriyarkutti (originating from Chammanampathy region), Sholayar (originating from Anamalais), Karapara (originating from Nelliyampathy ranges) and Anakayam (a lake with cool and placid waters). The length of the river is 145.5 km. It is the fifth longest river in Kerala and its basin is between 10^0 05' to 10^0 35' North latitude and 76^0 15' to 76^0 55' East longitude. This area is located in Thrissur, Ernakulam and Palakkad disricts of Kerala. The total drainage area of the river is 1704 km^2. Out of this 1404 km^2 lies in Kerala and the rest 300 km^2 in Tamilnadu. Total average annual drainage discharge (1980–2000) is 1421.81 million m^3 near Chalakudy town, as reported by the Irrigation Department, Government of Kerala (Chattopadhyay et al., 2005).

Chalakudy river is one of the very few rivers of Kerala which is having relics of riparian vegetation in substantial level . The riparian forests of Chalakudy river have revealed the existence of a thick riparian vegetation of more than 10 metres width for a distance of 10.5 km downstream from Peringalkuth, covering an area of 58.5 hectares. Out of this, 26.4 hectares lie within the Vazachal area, including three large islands densely covered by riparian forests. The annual report of the National Bureau of Fish Genetic Resources, Lucknow, mentioned that the Chalakudy river is the richest river in fish diversity perhaps in India. 104 species of fish survive in this small river depending on its flowing water. Average annual rainfall in this area is around 3300 mm, varying from a little over 3000 mm in Chalakudy town to 3700 mm in Poringalkuttu (Chattopadhyay et al., 2005).

Chalakudy river basin, is like most river basins in developing countries perturbed by human activities. According to Dr. Sudhirendar Sharma, a water expert and Director of the Delhi-based Ecological Foundation, Chalakudy river has been the biggest victim with 37 per cent reduction in its natural flow and storage, and diversion of waters for irrigation has caused ecological damage as reflected in the salinity intrusions along the coast ("India Together" of 16th November, 2007). The present study on Chalakudy river is limited to the stretch from the Poringalkuttu reservoir to the Azhikodu estuary where the confluence of Chalakudy river with Arabian Sea happens (Figure 2.1).

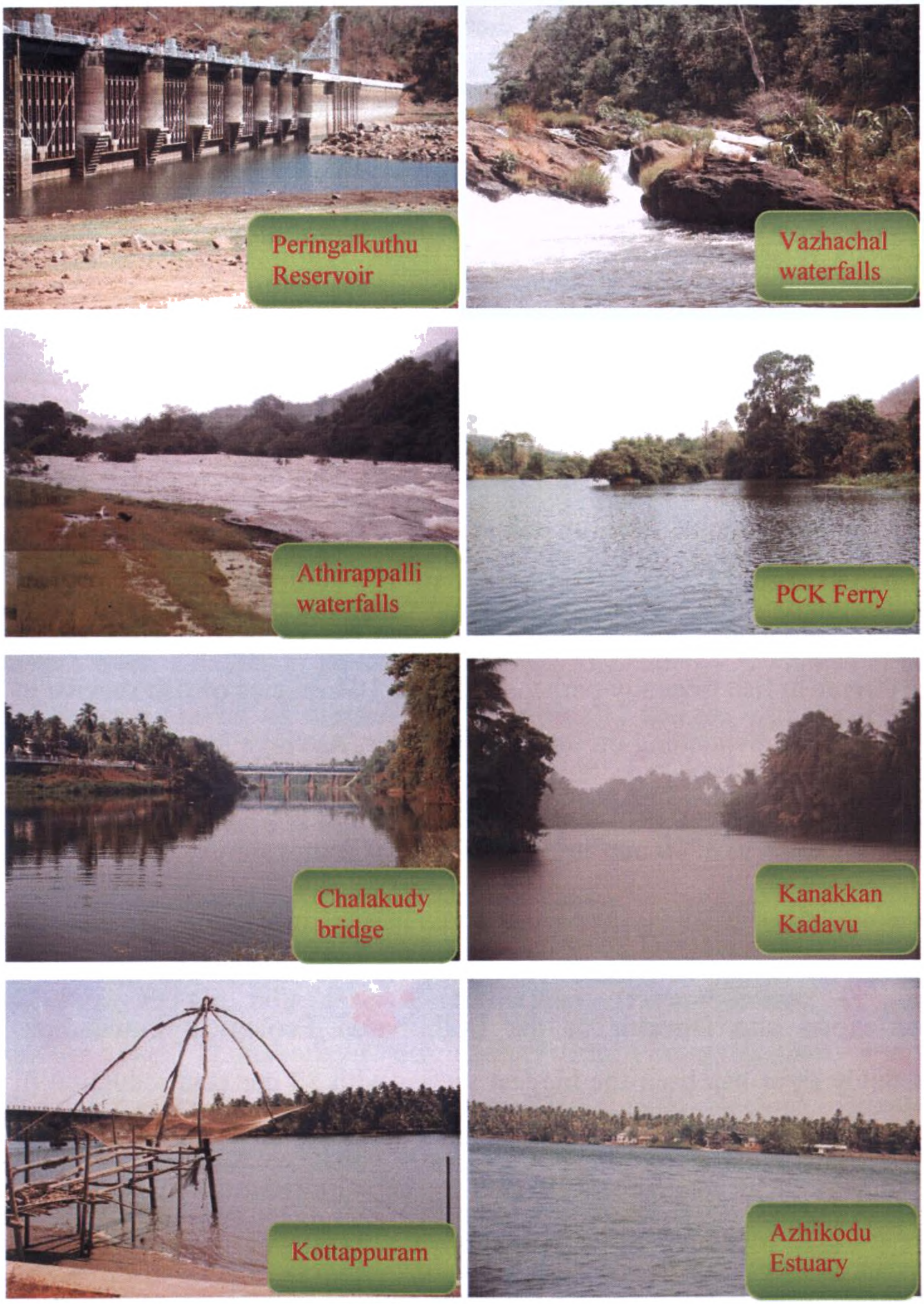

Figure 2.1 Photographs of Sampling Sites

The first station is the reservoir at Poringalkuthu (Peringalkuthu). Downstream, the waterfall region of Vazhachal, is the second station. The Vazhachal waterfall is a scenic and popular waterfall on the edge of the Sholayar forest range in Kerala. Athirappally waterfalls is about 78 kms from Kochi (Cochin). It is located in the forest area at the entrance to Sholayar ranges, and this waterfall is a popular picnic spot, affording to the onlookers, one of the most bewitching sights. Both these waterfalls are a part of Chalakudy river and 5 km apart on the road to hill station (Valparai) which has excellent tea estate and is one of India's highest elephant density habitats and is a crucial corridor between Parambikulam and Malayattur. The Athirapally waterfalls joins Chalakudy river after plummeting a drop of 80 feet. Samples were collected from a location in the river nearby the Athirappalli waterfalls which is presented here as station 3, and the place is slightly affected by human activities. The Plantation Corporation of Kerala (PCK) at Athirappalli, 63 km from Thrissur city, has 2,300 hectares of rubber plantation and is on the bank of Chalakudy river and the fourth river station is the passing through PCK at Ayyampuzha which is a region where there is a ferry service and there are industrial and agricultural activities in the area. The fifth river station is below Chalakudy bridge in Chalakudy town. The sixth station is in a remote area called Kanakkankadavu. Before reaching the next station, the river confluences with Periyar. Station 7 is at Kottappuram where there is intrusion of seawater and here, the river is affected by the intrusion from Arabian sea and waters are seasonally saline in nature. Station 8 is found to be exclusively estuarine as Chalakudy river merges into Arabian sea. Thus, stations 7 and 8 are affected both by Periyar river and Arabian sea.

All the locations that were studied are permanently open to the environment, but differ in the amount of freshwater input and the degree of development in, and utilisation of, their catchment areas. Table 2.1 gives the numbers assigned to the eight different sampling sites of Chalakudy river. Surface samples are denoted by S and bottom samples by B in the analysis of dissolved and particulate components. The locations with their latitude and longitude are depicted in Figure 2.2.

Table 2.1: Sampling sites with station numbers

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

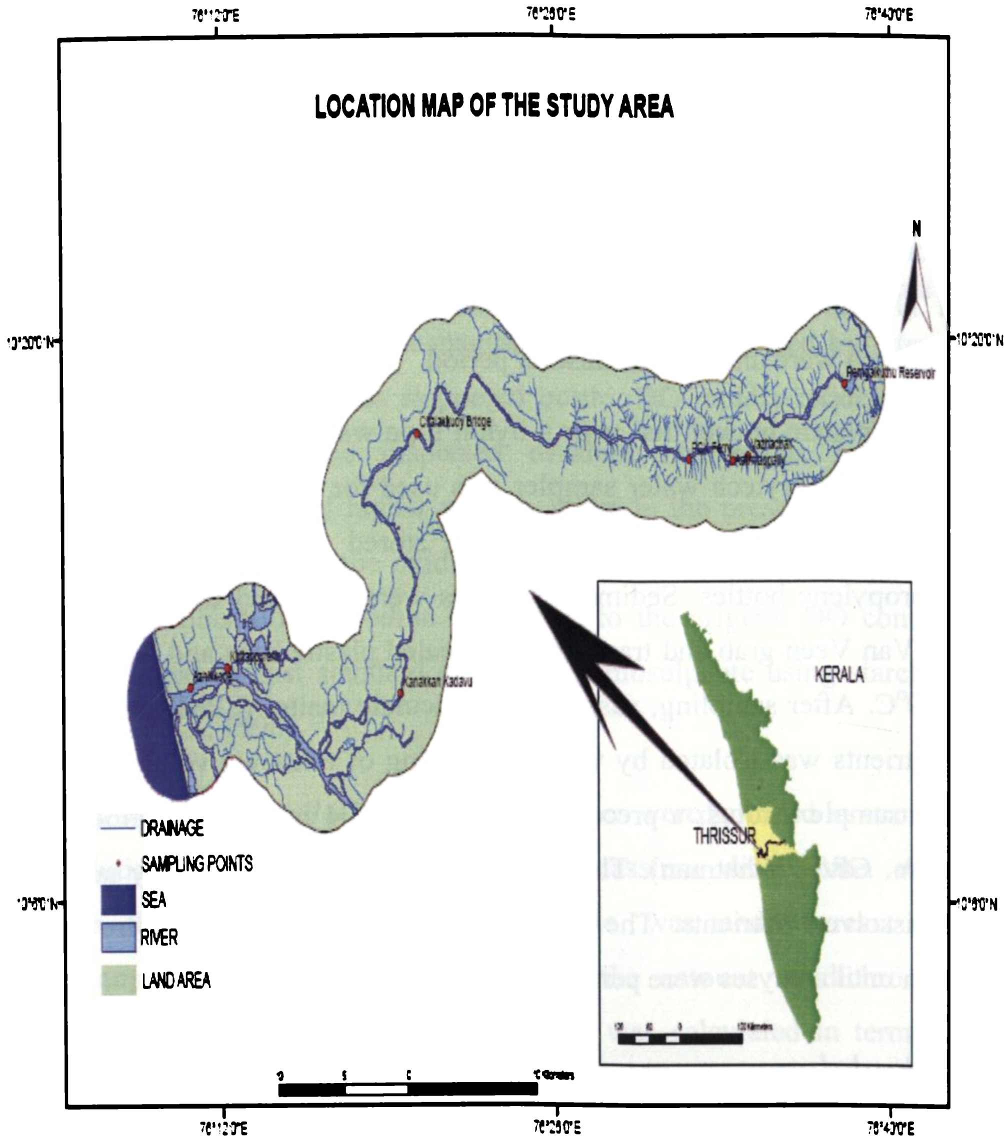

Figure 2.2. Map of Chalakudy river-estuary in Kerala showing the eight sampling sites.

Sampling and storage

Surface and bottom water samples and surficial sediment samples were collected on bimonthly basis from eight stations along Chalakudy river. The bimonthly sampling plan during 2005 – 2006 was divided into two seasons based on the precipitation rate: collections of May, July, September and November months were under monsoon period and those of January and March were under nonmonsoon period.

A clean plastic bucket tied with a nylon rope was used for surface sample collection. A Hytech water sampler was used for the collection of bottom water samples. Water samples were stored in pre-cleaned 5 litre polypropylene bottles. Sediment samples were collected using a stainless steel Van Veen grab and transferred to sealed plastic bags and were frozen at -20°C. After sampling, suspended particulate matter (SPM) for analysis of nutrients was isolated by vacuum filtering of a known volume of each water sample through a precombusted (450°C, 4 hours) glass fiber filter (25 μm. GF/F, Whatman). The water samples were immediately analysed for dissolved nutrients. The filtered suspended particulates were stored frozen until analyses were performed.

Methodology

Analyses of general parameters in river water

Temperature was noted on the spot. Other general parameters such as dissolved oxygen, chemical oxygen demand, pH, chlorophyll content and the chloride content of water samples were carried out. Also moisture content, sediment organic carbon, texture and percentage of CHN (carbon, hydrogen and nitrogen) of the sediment samples were analysed.

pH: pH of each water sample was determined in-situ by using portable pH meter (Merck).

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

Chemical oxygen demand (COD): Water samples were refluxed in strongly acid solution with a known excess of potassium dichromate. After digestion, the remaining unreduced dichromate was made to react with ferrous ammonium sulphate to determine the amount of dichromate consumed and the oxydisable organic matter was calculated in terms of oxygen equivalent (APHA, 1998).

Chlorophyll: The chlorophyll-a content of the extracts were subsequently determined by measuring optical density (APHA, 1998) using spectrophotometer (with a narrow band width of 0.5 to 2.0 nm, since chlorophyll absorption peak is relatively narrow). Water samples were filtered through GF/C glass filters (0.7 µm dia. GF/F, Whatman) and was consequently cut into small pieces and put in a universal tube. Chlorophyll-a was extracted with 96% acetone over 20 h in the dark and then measured using an ultraviolet spectrophotometer in supernatant after centrifugation for 10 min at 3000 rpm. The equation below was used to calculate the Chlorophyll-a concentration

$$\text{Chlorophyll-a: (g/l)} = (Ve*f*A)/\ (Vs*L)$$

Where: Ve = total volume of solvent (ml); Vs = total volume of sample (l); L = light path (1 cm); A = absorbance at 665 nm–absorbance at 750 nm; f = 1/specific extraction coefficient*1000. The specific extraction coefficient for chlorophyll a in the solvent is 83.41 g^{-1} sm^{-1} (Jespersen and Christoffersen, 1987).

Chloride: Chloride was estimated by argentometric method. In a neutral or slightly alkaline solution, potassium chromate can indicate the end point of the silver nitrate titration of chloride. Silver chloride is precipitated quantitatively before red silver chromate is formed (APHA, 1998).

Analyses of general parameters in riverine sediments

Texture analysis: Texture analysis was carried out to study the variations in grain size. A known amount of wet sediment was dispersed overnight in sodiumhexametaphosphate. The sand was separated from the dispersed sediments by wet sieving through a 230 mesh (63 µm) sieve (Carver, 1971). The filtrate containing the silt and clay fractions was subjected to pipette analysis (Krumbein and Pettijohn, 1938).

Sediment organic carbon (SOC): Sediment samples were dried in an oven at 80-90 °C and finely powdered in an agate mortar. Sediment organic carbon (SOC) was determined using the wet oxidation technique by Gaudette et al. (1974), which involved the oxidation of organic matter present in the sample by a known quantity of chromic acid. The amount of the acid consumed was determined by back titration with 0.5 N ferrous ammonium sulphate solution using ferroin as indicator.

Moisture content in sediments: The moisture content in sediments was estimated by drying 10g of homogenized wet sediment sample at 90 °C for 48 hours and finding the difference in weights.

CHN analysis: Approximately, 2 mg of sample is measured into a tin capsule (Elementar Americas, D1034) using a Sartorius M2P microbalance (readability: 0.001 mg, range: 0.1 mg - 55 g). The tin capsule is then carefully folded into a cube approximately 2-3 mm in width with forceps on a pane of glass. The capsule was then loaded into a Perkins Elmer 2400 Series II CHNS/O analyzer for analysis. This analyzer operates by flash combusting the sample encapsulated in a tin cup at 1760 °C. The resulting gases are chemically scrubbed of the halogens and sulfur followed by separation in a gas chromatographic column prior to detection by a thermal conductivity detector.

Analyses of different species of dissolved nitrogen

Nitrite, nitrate, ammonia, urea and total nitrogen were quantitatively estimated from the filtered sample (Figure 2.3). Spectrophotometric analyses using a Genesys 10UV Thermospectronic spectrophotometer were followed.

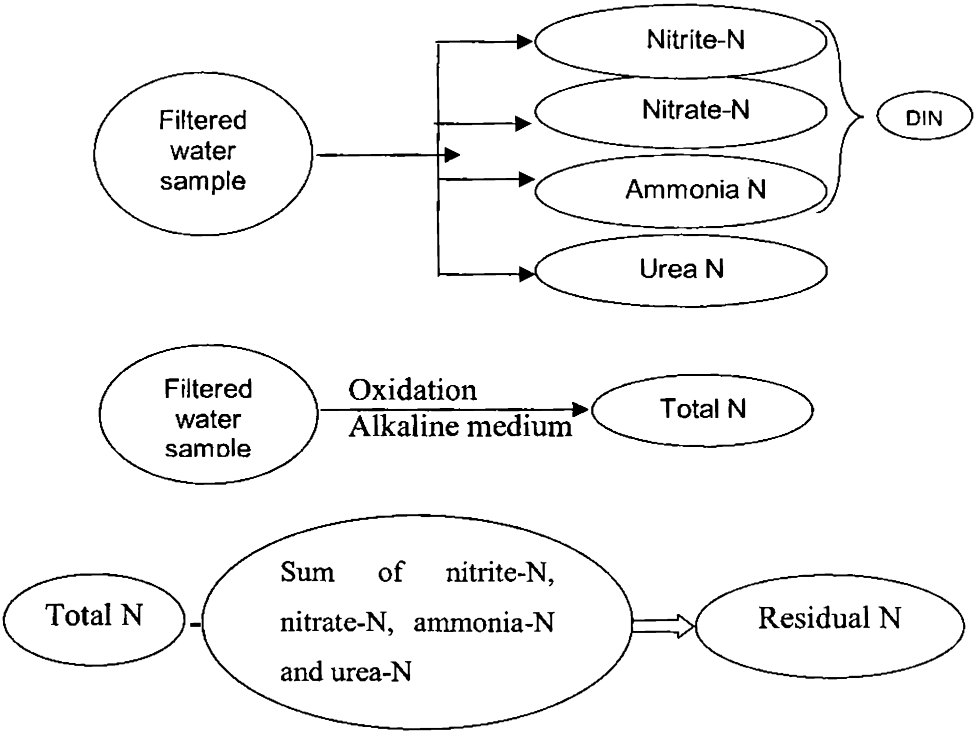

Figure 2.3 Flow chart for the analyses of different nitrogen species in the dissolved state
(DIN : dissolved inorganic nitrogen)

Spectrophotometric determination of nitrite in river water was based on the reaction of nitrite with an aromatic amine, sulphanilamide hydrochloride, leading to the formation of a diazonium compound which, when coupled with a second aromatic amine, N-(1-napthyl)ethylenediamine dihydrochloride, leads to the formation of a pink coloured azo dye (Grasshoff et al., 1999) at a λmax of 540 nm.

The method adopted for nitrate determination was the reduction of nitrate to nitrite by passing through a column containing copper-coated cadmium granules (Grasshoff et al., 1999) and the resulting nitrite was analysed as described above. The reduction efficiency of the column was checked to be 98%.

The principle of the method for estimation of ammonia is that it reacts in moderately alkaline solution with hypochlorite to give monochloramine which, in the presence of phenol, catalytic amounts of nitroprusside ions and excess of hypochlorite, gives indophenol blue (Grasshoff et al., 1999). The formation of monochloramine requires a pH between 8 and 11.5. The absorbances were measured at 630 nm.

Sum of nitrite-N, nitrate-N and ammonia-N is taken as dissolved inorganic nitrogen (DIN).

Urea was determined by the diacetyl monoxime method (Grasshoff, 1983). The principle of this method is that in strongly acidic solution and in the presence of a weak oxidant, urea forms a condensation product with diacetyl monoxime. This product interacts with semicarbazide to form a magenta coloured complex with an absorption maxima at 520 nm.

The total nitrogen was estimated after oxidizing the sample with potassium peroxodisulfate and boric acid in alkaline medium in a sealed bottle (autoclaved for 30 min and cooled to <50°C and decompressed carefully) and obtained quantitative recoveries as nitrate (Grasshoff et al., 1999; Bronk et al., 2000) which was estimated as described before.

The difference between total N and the sum of DIN and urea-N is produced as residual N which is mainly organic N.

Analyses of different species of dissolved phosphorus

Phosphate-P and total phosphorus were estimated from the filtered sample quantitatively by spectrophotometric analyses using a Genesys 10UV Thermospectronic spectrophotometer.The determination of phosphate-P from the filtrate was based on the reaction of the ions with an acidified molybdate reagent forming phosphomolybdic acid, which was then reduced by ascorbic acid to a highly coloured blue compound, heteropoly acid which was then determined spectrophotometrically at 880 nm (Grasshoff, 1983). The total phosphorus was estimated after oxidizing the sample with potassium peroxodisulfate in sulphuric acid where total phosphorus was convertrd to phosphate which was estimated as described before (Grasshoff, 1983). The difference between total P and the phosphate-P is produced as residual P which is mainly organic P.

Analyses of different species of nitrogen in sediments

The different forms of nitrogen analysed and the methods followed are shown in Figure 2.4.

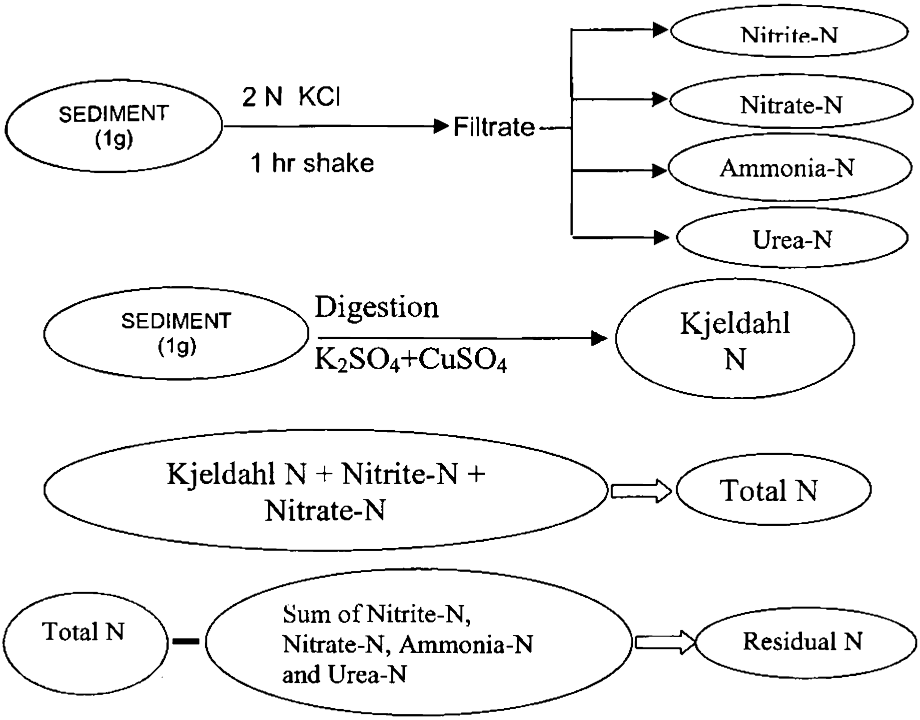

Figure 2.4 Flow chart for the analyses of different nitrogen species in the sediments

The analyses of nitrite, nitrate, ammonia and urea were carried out by the "KCl equilibrium extraction method" (Agemian, 1997) which involves shaking of the sediment sample with a solution of KCl (2N) at room temperature for a period of one hour followed by filtration using standard filtration equipment and Whatman 42 filter paper. The filtrate containing nitrogen in the dissolved state was stored at 4^0C until analysis. From the filtrate the nitrite, nitrate, ammonia and urea were quantitatively estimated by spectrophotometric analyses as described earlier.

Total nitrogen in sediments was determined by the following procedure. Sediment samples were digested in sulphuric acid in the presence of potassium sulphate and copper sulphate catalyst (Agemian, 1997). Organic compounds of nitrogen as well as free inorganic forms, were thus converted to ammonium ions which is determined spectrophotometrically using indophenol blue method. Kjeldahl extraction technique determines the concentrations of nitrogen except nitrate-N and nitrite-N. So, the concentration of nitrate-N and nitrite-N are added to the Kjeldahl N to get the total nitrogen. The difference between the total nitrogen and the sum of nitrate-N, nitrite-N, ammonia-N and urea-N in sediments is expressed as residual N.

Analyses of different species of phosphorus in sediments

Chemical fractionation experiments are designed to separate and quantify specific forms of P using operationally defined extraction schemes. Inorganic phosphorus in sediments can be fractionated by the application of the following scheme, which includes an operationally defined extraction sequence incorporating universally used extraction techniques (Jensen and Thamdrup, 1993; Paludan and Jensen, 1995; Agemian, 1997; Libo et al., 2004; Ladakis et al., 2006).

Extraction step	Form of phosphorus extracted
(A) NaCl	Loosely sorbed exchangeable Phosphorus
(B) Bicarbonate-Dithionate (BD)	Iron/ aluminium-bound phosphorus
(C) NaOH (0.1 M)	Polyphosphates (Note: if the BD step is not performed, NaOH (0.1 M) extracts Iron- aluminium-bound phosphorus plus polyphosphates)
(D) HCl (0.5 M)	Calcium- bound phosphorus
(E) Hot (85^0C) NaOH (1 M)	Refractory phosphorus

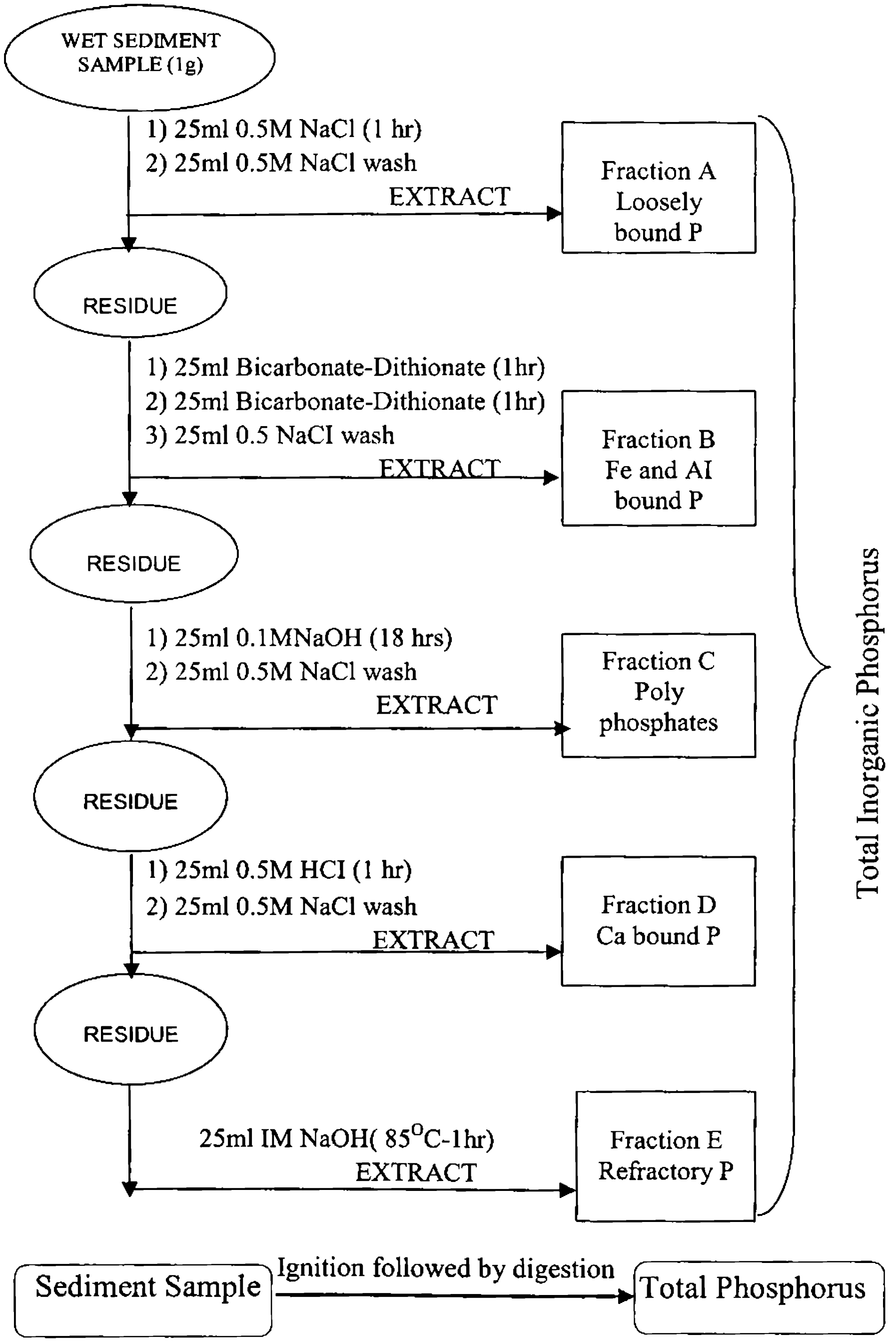

Figure 2.5 Flow chart for the fractionation of phosphorus species in sediments

Sediment was sequentially extracted for phosphorus fractions by the use of a five step extraction scheme (Figure 2.5). One gm of fresh sediment (taken in 100 ml centrifuge tube with lid) was extracted sequentially in solutions of NaCl (0.5 M), bicarbonate dithionite reagent (0.11 M), NaOH (0.1 M), HCl (0.5 M) and NaOH (1 M) and the supernatant was collected after centrifugation at 5000 rpm for 15 min. The first step in the sequence was a dual extraction with 0.5 M NaCl solution that removed loosely adsorbed reactive and nonreactive phosphates as well as porewater dissolved reactive and nonreactive P. The dissolved reactive fraction (NaCl-P) is referred to here as exchangeable P. The next extraction with 0.11 M bicarbonate dithionite (BD) removed phosphate associated with reducible oxides of Fe, Al and Mn, and the dissolved reactive fraction of this extract is referred to hereafter as Fe/Al-P. BD extracts reducible Fe efficiently. The BD reducing reagent is also more efficient in extracting reducible iron than 0.5 M HCl, because BD dissolves crystalline and amorphous Fe oxides, while HCl dissolves only the latter. Further, NaOH is commonly used to dissolve both Fe and Al oxides. Treating the sediment with BD (second step) before NaOH (third step) specifically extracts most Fe (III) and Al (III) oxides. The third step, an extraction with 0.1 M NaOH, removed much of the phosphate adsorbed onto the surfaces of clays and some oxides of Al which can be considered as polyphosphates. The supernatant, often brown because of dissolved organic matter, was acidified to pH 1 to precipitate the humic acids from solution. The fourth extraction sequence with 0.5 M HCl removed phosphate associated with calcium carbonate, and the dissolved reactive fraction of this extraction is denoted as Ca-P. In the final step, the residue was extracted with hot 1.0 M NaOH to determine refractory P (Ref-P).

The pH of the final extracted solutions was adjusted, and the P concentration was determined colorimetrically by the molybdate-ascorbic acid procedure as described in earlier section except for fraction B. For this fraction, the solution must be extracted into an organic phase to remove interference from the reagents. This can be carried out by extracting the phosphomolybdate complex into hexanol / isopropanol with subsequent manual determination. The other fractions provide extracts in the aqueous phase and could be readily analysed. The sum of all these fractions is the total inorganic phosphorus (TIP).

Total phosphorus was determined based on the following method. 2.5 g of sediment was ignited for 2 hr in a furnace at 550 ^{0}C, allowed to cool for 1 hr, digested with 10 ml of 1 N HCl and boiled for 16 hr to convert all the organic P forms to inorganic P forms. The sample was then filtered and made up to 10 ml with distilled water to analyse as orthophosphate using the standard ascorbic acid method (Agemian, 1997). The difference between the total P and total inorganic P is assumed to represent mainly humic and other organic P and is named as residual phosphorus (Res-P).

Analyses of different species of nitrogen and phosphorus in suspended particulate matter (SPM)

The analyses of nitrite, nitrate, ammonia, urea and total N in the suspended particulate matter were done using the same procedures as in the case of speciation of N in sediments mentioned before. Estimations of loosely bound P, iron/aluminium bound P, polyphosphates, calcium bound P, refractory P and total inorganic P in the suspended particulate matter were carried out using the sequential extraction methods as described in fractionation in sediments.

Analytical Reproducibility

All nutrients were quantified by spectrophotometry. Calibration in the context of spectrophotometric analysis meant comparison of the sample absorption after chemical reaction with the absorption of a standard of known concentrations, which had been treated in exactly the same manner. A sequence of standards from zero to a concentration slightly beyond the expected maximum sample concentration were prepared in pure water. Sample aliquots per standard were treated as described for the respective analytical method and the absorbances were measured. Plot of nominal standard concentrations versus absorbances indicates a linear concentration/absorbance relationship. The blank absorbance was determined by measuring a sample volume of pure water plus reagents against a pure water reference without reagents. The calibration and the blank determination yielded the terms required to calculate sample concentrations. The reliability of calibrations decreases with increasing concentration differences between the sample and standard. Consequently, the best calibration and thus the best analytical results were obtained with exactly matched sample and calibration ranges.

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CHAPTER III

HYDROGRAPHICAL PARAMETERS

CONTENTS

Introduction

Materials and methods

Results and discussions

- Chlorophyll
- Temperature
- Salinity
- Dissolved oxygen
- pH
- Sediment Moisture content
- Sediment organic carbon
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- Texture analyses

Inter parameter relationships

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INTRODUCTION

The stability and variability of river quality are known to depend largely on the natural variations in hydrometeorological factors. In rivers, most of the heterotrophic activity depends not only on their physicochemical state but also on the hydrodynamic characteristics of the system. The processes involved i.e. speciation, mobilization, precipitation, bioavailability, metabolism etc of the various constituents in aquatic systems are affected by the combined effects of temperature, dissolved oxygen, salinity, pH and the presence of other chemicals in the overlying waters and sediments. However, the level of these processes may vary by several orders of magnitude within and between streams, and their contribution to whole system metabolism is very important in larger rivers (Fischer and Pusch, 2001). For example the longitudinal development of thermal stratification can lead to the variation in dissolved oxygen concentration in waters above sediments, thus affecting sediment nutrient release rates. Hydrologic forcing (mainly the river flow fluctuations) dominates the upstream as well as up-estuary processes and loosens the coupling among nutrients and phytoplankton. The relation between suspended matter and bottom sediment unravels a direct link between the compositions indulged in them which is hardly dependent on environmental (nature, frequency and amounts of releases in the riverine system) and hydrological conditions as hydrodynamic influence on the variation in concentration and chemical redistribution processes (Montarges-Pelletier et al., 2007). Hydrodynamics as a major factor, controls the fate of suspended materials, themselves influenced by internal parameters of the rivers (section, bank morphology etc) and by external parameters: atmospheric and terrestrial contributions.

The high heterogeneous character of natural aquatic media could be approached through the study of samples collected at different times, different positions, and different compartments of the water system. Furthermore, intense human impact on the environment results in changes in the natural river runoff regime and chemical properties of the river water.

The objective of providing the supplementary specifics in this particular section is to assess the general hydrographical features of the different compartments of the Chalakudy riverine system. Direct and indirect system responses were considered. The temporal and spatial dynamics of a certain biological, physical and chemical parameters were investigated to gain a general insight into the system, and an attempt had also been taken to present the environmental conditions along the river, though contaminants did not always follow the mineralogy, and are strongly influenced by outlets of human facilities.

MATERIALS AND METHODS

Water and sediment samples had been collected bimonthly from the Chalakudy river along the different sampling locations and analyzed for various hydrographical parameters. The methodology for each one is described in Chapter II.

RESULTS AND DISCUSSIONS

The primary data on chlorophyll a and other general hydrographical parameters such as temperature, chloride content, dissolved oxygen and pH, in surface and bottom waters are produced in Tables 3.1 and 3.2, respectively. The sedimental characteristics such as moisture content and sediment organic carbon (SOC) are presented in Table 3.3. The seasonal "CHN" values and textural percentages were also resulted and discussed. Some recent values of hydrographical parameters in rivers, reported on worldwide are presented in Table 3.4.

Table 3.1 Bimonthly distribution of chlorophyll, temperature, chloride content, salinity, dissolved oxygen and pH in the surface waters of Chalakudy river.

Parameters		Stations							
	Months	S1	S2	S3	S4	S5	S6	S7	S8
Chlorophyll (μgl^{-1})	May	3.38	3.35	3.18	8.2	7.15	8.2	2.11	1.13
	Jul	25.17	7.21	8.2	27.14	25.34	27.31	7.14	3.18
	Sep	23.18	9.21	10.19	26.28	24.38	25.25	5.74	2.99
	Nov	14.45	4.17	6.31	19.15	10.16	11.15	5.84	2.98
	Jan	10.05	5.14	6.15	20.12	9.09	12.2	3.09	2.26
	Mar	5.24	4.48	5.39	10.21	8.01	7.28	2.93	1.04
Temperature (°C)	May	28.2	29.6	30.4	30.8	32.6	32	33	32.8
	Jul	25	25.2	25.4	27.2	27.4	28.2	29.4	29.2
	Sep	26	25.8	26.2	27.4	27.2	27.4	31.4	29.2
	Nov	27.6	26.4	27.2	27.4	28.4	27.8	30.2	30.2
	Jan	27.2	26.4	28.2	28.2	30.2	32.2	31.6	31.8
	Mar	27.2	28.2	30.2	29.8	32.2	31.8	33.6	31.6
Chloride (gl^{-1})	May	0.01	0.01	0.01	0.01	0.01	0.05	10.25	16.73
	Jul	0.01	0.01	0.01	0.01	0.01	0.01	0.28	0.19
	Sep	0.01	0.01	0.01	0.01	0.01	0.01	0.10	1.70
	Nov	0.01	0.01	0.01	0.01	0.01	0.02	1.02	2.55
	Jan	0.01	0.01	0.01	0.01	0.02	0.04	15.43	16.15
	Mar	0.01	0.01	0.01	0.01	0.01	0.04	11.44	15.86
Salinity	May	-	-	-	-	-	-	18.51	30.23
	Jul	-	-	-	-	-	-	0.51	0.33
	Sep	-	-	-	-	-	-	0.18	3.07
	Nov	-	-	-	-	-	-	1.85	4.61
	Jan	-	-	-	-	-	-	27.87	29.17
	Mar	-	-	-	-	-	-	20.66	28.65
DO (mgl^{-1})	May	5.33	5.06	6.20	4.64	3.79	4.68	3.16	2.77
	Jul	9.03	8.61	8.07	7.99	6.96	7.15	6.94	5.48
	Sep	8.35	8.35	9.16	8.44	6.62	6.72	6.28	5.54
	Nov	6.07	6.81	7.08	7.36	6.54	6.15	6.22	4.31
	Jan	5.59	6.62	6.71	6.94	6.25	6.71	5.45	4.50
	Mar	4.77	4.37	4.92	4.35	3.91	4.63	3.20	2.77
pH	May	6.85	7.15	7.43	7.25	6.94	6.78	7.25	7.38
	Jul	7.41	7.12	7.15	7.10	7.02	6.67	7.35	6.97
	Sep	7.35	7.45	7.56	7.46	7.34	7.34	7.33	7.41
	Nov	7.23	7.15	7.16	7.00	6.79	6.70	6.84	7.19
	Jan	7.65	7.50	7.53	7.35	7.10	7.08	8.02	8.09
	Mar	7.03	7.10	7.05	7.02	7.03	6.89	7.72	7.90

Table 3.2 Bimonthly distribution of chlorophyll, temperature, chloride content, salinity, DO and pH in the bottom waters of Chalakudy river.

Parameters		Stations							
	Months	B1	B2	B3	B4	B5	B6	B7	B8
Chlorophyll ($\mu g l^{-1}$)	May	3.38	3.35	3.18	9.13	10.27	9.19	2.11	0.92
	Jul	23.26	7.21	8.2	29.27	25.34	9.28	7.14	4.97
	Sep	24.34	9.21	10.19	27.3	16.44	16.34	4.92	3.92
	Nov	13.44	4.17	6.31	18.89	10.16	11.15	5.15	1.29
	Jan	9.02	5.14	6.15	16.14	9.09	11.04	3.09	3.3
	Mar	4.48	4.48	5.39	12.13	7.38	9.15	2.93	2.11
Temperature (°C)	May	28.2	29.6	30.4	31	32.4	31.8	33	32.6
	Jul	25	25.2	25.4	27.2	27.4	28.2	29.4	28.8
	Sep	25.8	25.8	26.2	26.8	26.8	27.4	30.8	28.8
	Nov	28	26.4	27.2	27.4	28.4	27.8	30.2	29.8
	Jan	27.2	26.4	28.2	28.2	30.2	31.8	31.6	31.8
	Mar	28	28.2	30.2	30.2	32	32	33.6	32
Chloride ($g l^{-1}$)	May	0.01	0.01	0.01	0.03	0.10	0.05	10.25	17.52
	Jul	0.01	0.01	0.01	0.02	0.01	0.02	0.28	0.20
	Sep	0.01	0.01	0.01	0.01	0.01	0.01	0.23	0.91
	Nov	0.02	0.01	0.01	0.01	0.01	0.02	1.04	9.41
	Jan	0.19	0.01	0.01	0.01	0.02	0.04	15.43	15.65
	Mar	0.04	0.01	0.01	0.00	0.10	0.05	11.44	16.47
Salinity	May	-	-	-	-	-	-	18.51	31.65
	Jul	-	-	-	-	-	-	0.51	0.36
	Sep	-	-	-	-	-	-	0.42	1.65
	Nov	-	-	-	-	-	-	1.88	17.00
	Jan	-	-	-	-	-	-	27.87	28.28
	Mar	-	-	-	-	-	-	20.66	29.75
DO ($mg l^{-1}$)	May	5.33	5.06	6.20	4.52	4.39	4.36	3.16	2.89
	Jul	8.61	8.61	8.07	8.61	6.96	7.57	6.94	5.46
	Sep	8.35	8.35	9.16	8.35	5.37	6.35	6.28	4.86
	Nov	5.55	6.81	7.08	7.08	6.54	6.15	4.87	4.31
	Jan	5.12	6.62	6.71	6.49	6.25	6.32	5.45	4.50
	Mar	4.07	4.37	4.92	4.49	3.91	4.34	3.20	2.91
pH	May	6.85	7.15	7.43	7.05	7.00	6.83	7.25	7.50
	Jul	7.22	7.12	7.15	7.43	7.02	6.95	7.35	6.97
	Sep	7.35	7.45	7.56	7.63	7.45	7.42	7.40	7.52
	Nov	7.25	7.15	7.16	7.33	6.82	6.70	6.95	7.73
	Jan	7.55	7.50	7.53	7.15	7.10	7.05	8.02	8.03
	Mar	7.13	7.10	7.05	6.79	6.93	6.90	7.72	7.92

Table 3.3 Bimonthly distribution of moisture content and sediment organic carbon in the sediments of Chalakudy river

Parameters	Months	Stations 1	2	3	4	5	6	7	8
Moisture Content (%)	May	49.46	18.86	24.74	21.99	19.88	17.95	60.03	49.98
	Jul	56.78	20.88	16.55	65.31	57.29	44.88	25.69	39.26
	Sep	58.66	17.25	25.74	57.59	55.45	35.26	45.63	47.9
	Nov	39.15	18.61	21.13	34.68	44.03	36.61	50.55	67.29
	Jan	70.13	20.74	23.24	32.42	51.46	42.79	40.16	58.63
	Mar	51.75	20.56	21.29	29.05	39.26	29.59	58.53	51.06
Sediment organic carbon (%)	May	2.60	0.06	0.52	0.10	0.25	0.35	1.14	1.96
	Jul	4.07	0.20	0.19	3.31	3.85	1.88	0.66	1.35
	Sep	5.07	0.07	0.88	4.55	4.71	0.98	1.91	1.69
	Nov	2.62	0.06	0.18	1.14	1.85	0.60	1.53	2.83
	Jan	6.36	0.13	2.62	1.06	3.10	1.22	1.09	2.93
	Mar	3.33	0.12	0.18	0.49	0.85	0.51	2.38	1.48

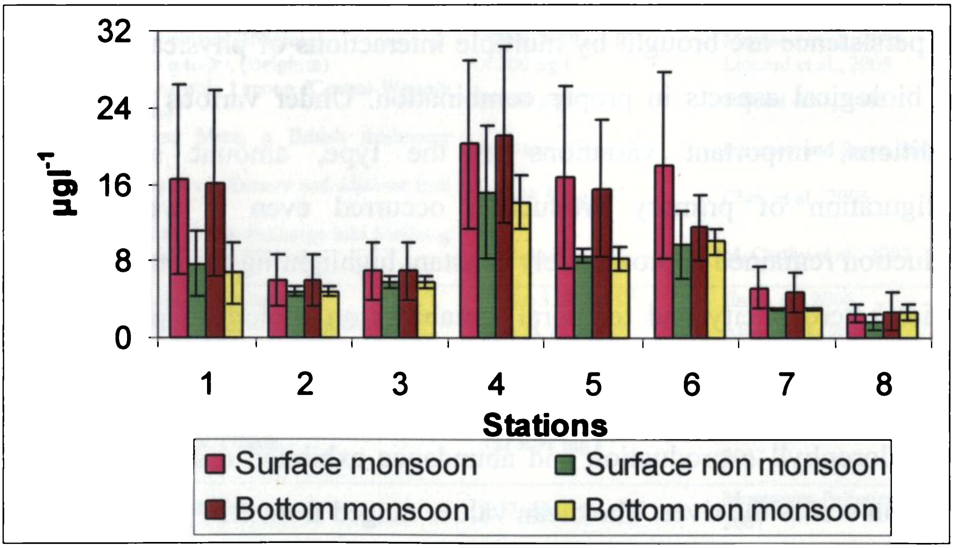
Table 3.4 Recently reported values of hydrographical parameters in rivers on worldwide

Para - meters	Aquatic system	Concentration	Reference
Chlorophyll *a*	Riverine sector of Piratininga Lagoon, Brazil	21.7–123.6	Cunha & Wasserman, 2003
	Tagus estuary, Portugal	1 – 32 $\mu g\ l^{-1}$	Gameiro et al., 2004
	Schelde estuary (Belgium)	<20 – > 60 $\mu g\ l^{-1}$	Muylaert et al., 2005
	Schelde estuary, (Belgium)	> 200 $\mu g\ l^{-1}$	Lionard et al., 2005
	S'Ena Arrubia Lagoon (Central-Western Sardinia)	2–164 $\mu g\ l^{-1}$	Trebini et al., 2005
	Rostherne Mere, a British freshwater lake	0.06 and 206 $\mu g\ l^{-1}$	Krivtsov and Sigee, 2005
	Yangtze River Estuary and adjacent East China Sea	0.3–19.5 mg m^{-3}	Chai, et al., 2006
	Liangxihe River discharge into Meiliang Bay, Lake Taihu (China)	85.4 $\mu g\ l^{-1}$	McCarthy et al., 2007
DO	Wuli Lake in China	7.48 ± 3.08 mg l^{-1}	Jin et. al., 2006
	Surma River, Eastern Bangladesh	5.52 -5.72 mg l^{-1}	Alam et al., 2007
pH	Surma River, Eastern Bangladesh	6.126 -6.093	Alam et al., 2007
	Oukaimeden river (Morocco)	7.6	Oudra et al., 2008
Chloride	Moselle river, France	352 ± 91 mg l^{-1}	Montarges-Pelletier et al., 2007
SOC (%)	Moselle river, France	0.77 -13.01%	Montarges-Pelletier et al., 2007

Chlorophyll

Eutrophication is a complex process of algal blooms which involves different time scales and different levels of community structure, and an indicator of eutrophication is phytoplankton biomass and concentration of chlorophyll *a*. During seaward transport, the phytoplankton disappear from the river water concomitantly with the suspended matter, because of the increased retention of these elements in sediments due to sedimentation. The sedimented particulate matter is decomposed by bacteria into inorganic nutrients, which then influence the primary production in the upper water column. The determination of photosynthetic pigments is fundamental to assess the amount of food available to higher trophic levels and its contribution to organic carbon (Pusceddu et al., 1999). Phytoplankton blooms are often spontaneous and dramatic, however their development and persistence are brought by multiple interactions of physical, chemical and biological aspects in proper combination. Under various water level conditions, important variations in the type, amount and spatial configuration of primary production occurred even if whole-system production remained approximately constant highlighting the importance of spatial heterogeneity and temporal variability on ecological processes in large river ecosystems (Vis et al., 2007).

The chlorophyll *a* production and abundance exhibited a strong seasonal variation across the river. The mean values ranged from 2.57 μgl^{-1} to 21.15 μgl^{-1} during monsoon and 1.65 μgl^{-1} to 15.17 μgl^{-1} during non monsoon (Figure 3.1). The observation confirmed the availability of nutrients necessary for the thriving of plankton communities, through rain water. The rise in chlorophyll *a* concentrations at the estuarine zone during monsoon was less pronounced. Salinity stress alone could not explain the decline in phytoplankton biomass at the salinity gradient (Lionard et al., 2005). Longer water residence times allow phytoplankton accumulation (Gameiro et al., 2004). Chlorophyll could be low down stream presumably because high turbidity and short water residence time precluded phytoplankton community development (Chai, et al., 2006). Strong seasonality in plankton production and abundance has been observed in all river stations and the peak concentrations were seen at stations 1, 4, 5 and 6 in monsoon season. Deviation in mean values were also large at these stations during rainy season. Generally, chlorophyll in surface waters were found to be closer to those in subsurface waters, though exceptions were there as could be seen at station 6 with low bottom values during monsoon.



$\mu g l^{-1}$) in the

surface and bottom waters of Chalakudy river

Temperature

It can be concluded from the observations on temperatures (Figure 3.2) of surface and bottom waters that during non monsoon, the waters were more warmed compared to monsoon season. Also during monsoon as well as non monsoon, the temperature were gradually increased from the hilly reservoir, upstream till the riverine end or better up-estuary, after which the temperature was decreased to the down-estuary where merging with sea water happened. The mean values were generally in the range from 26.7 to 31.0 °C during monsoon and from 27.2 to 32.6 °C during non monsoon period. It never reached lower than 26 °C or higher than 33 °C. This temperature regulation could also be an effect of the tropical climate and anthropogenic discharges in the river.

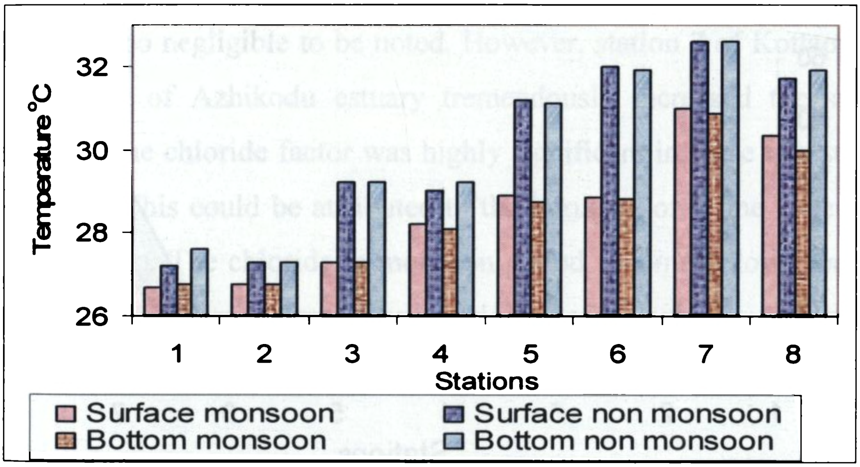


Figure 3.2 Seasonal average concentrations of temperature (°C) in the surface and bottom waters of Chalakudy river.

Salinity

The chloride content plays a dominant role in influencing the nutrient concentrations in water, particulate matter as well as sediments and its distribution depends strongly on sea water intrusion through the barmouth and on the influx of river water in estuaries. Generally, river water has very low chloride content. Chloride could be a useful tracer in the mass balance to distinguish between and assist in separating physical loading and biogeochemical processes in the river (Iwanyshyn et al., 2007). Salinity of estuarine water can be considered as an index of the estuarine mixing processes. Salinity is of paramount importance to a number of species and influences the aggregation of suspended particles (Hakanson, 2006).

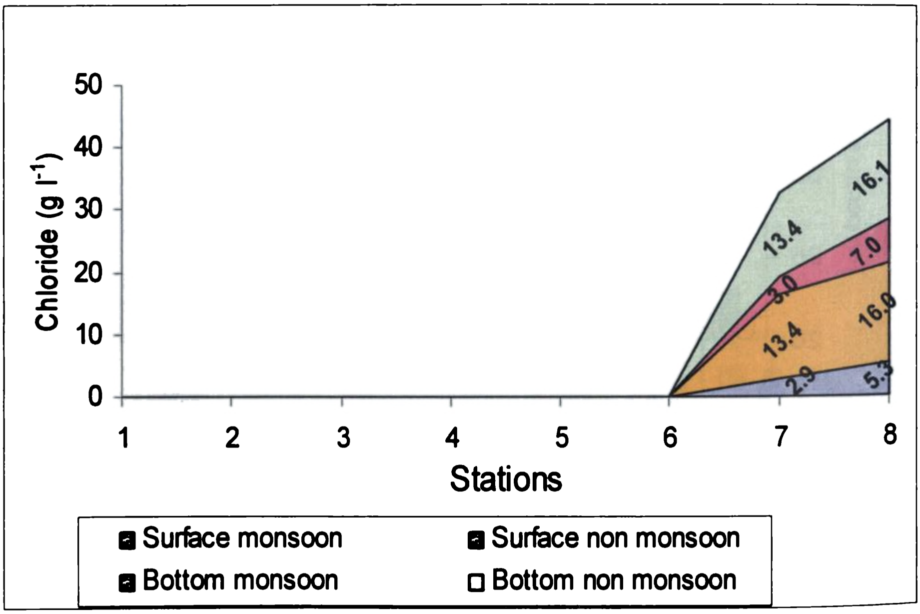


Figure 3.3a Seasonal average concentrations of chloride (g l^{-1}) in the surface and bottom waters of Chalakudy river.

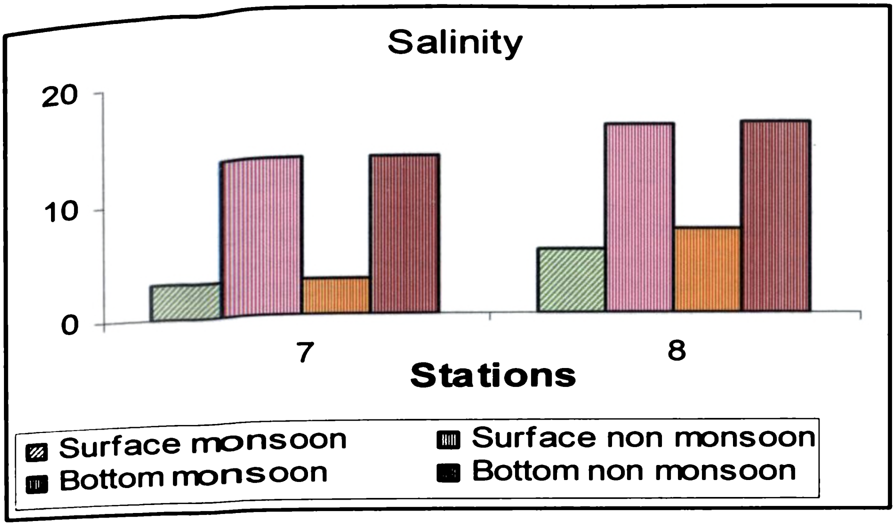


Figure 3.3b Seasonal average concentrations of salinity in the surface and bottom waters of estuarine stations

It was observed that for the exclusively riverine stations 1 to 6, chloride content was too negligible to be noted. However, station 7 of Kottappuram and station 8 of Azhikodu estuary tremendously increased the salinity content, and the chloride factor was highly significant in these two stations (Figure 3.3). This could be attributed to the intrusion of saline water from the Arabian sea. The chloride in monsoon period was much lower because dilution with fresh water from riverine origin predominates in rainy season, thus decreasing the chloride content.

Dissolved oxygen

The amount of dissolved oxygen (DO) in natural waters depends on various factors like phytoplankton content, temperature, salinity, turbulence of water and atmospheric pressure. The depletion of oxygen content in water leads to obnoxious odour under anaerobic conditions and damage aquatic life. Study on the dissolved oxygen concentration thus help to explain the various physical, chemical and biological processes taking place in rivers. The dissolved oxygen requirement varies from organism to organism under different environmental conditions. The decomposition/oxidation of organic and inorganic matter prove harmful to organisms in aquatic environment. The huge oxygen demand is placed on bottom waters by the mineralisation of drowned vegetation and organic matter supplied from surface waters by the increased primary production. As a result, bottom waters as well as sedimentary floor tend to experience at least seasonal anoxia (Talbot et al., 2006). Furthermore, anoxic conditions favour denitrification and loss of molecular nitrogen from the system. Sediment regeneration rates of soluble reactive phosphorus were reported to be low under saturated oxygen conditions, and high under reduced oxygen levels (Swan et al., 2007).

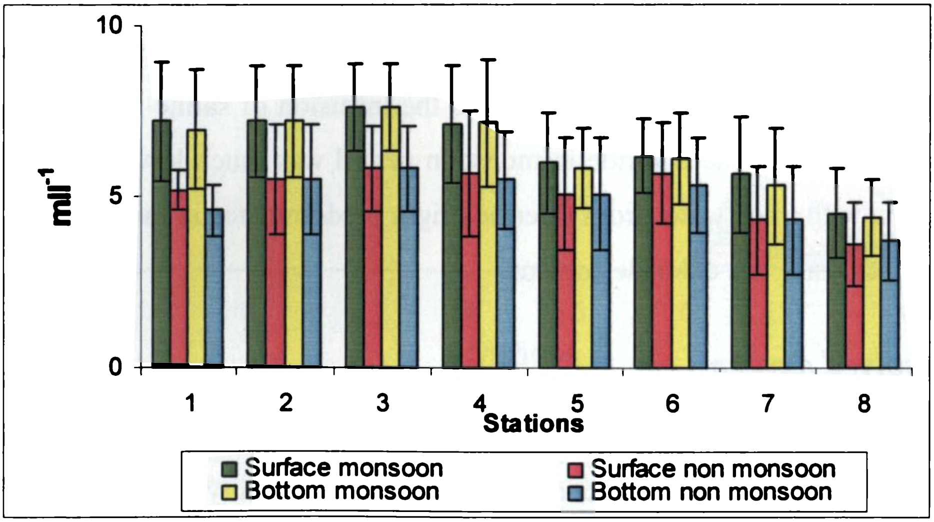


Figure 3.5 Seasonal average concentrations of dissolved oxygen (mll^{-1}) in the surface and bottom waters of Chalakudy river

In the case of dissolved oxygen, the standard recommended for sustaining aquatic life is 4 mgl^{-1}, whereas for drinking purposes it is >5 mgl^{-1} (Alam et al., 2007). The present riverine values of DO were in agreement as shown by the mean DO values for Chalakudy river, lying in between 3.64 mgl^{-1} (non monsoon) to 7.63 mgl^{-1} (monsoon) as shown in Figure 3.5. The dissolved oxygen was high at reservoir and waterfalls and decreasing towards estuary. A large spatial and temporal variability in dissolved oxygen was identified which could probably be related to flow conditions, seasonal effects and anthropogenic impacts (Voutsa et al., 2001). The monsoon values were higher compared to the dry season and the variation was more prominent towards upstream stations till the ferry station 4. Levels of DO exhibited a significant positive correlation with rainfall which could be attributed primarily to the increased flow rate and turbulence (Massoud et al., 2006). Standard deviations were large and the high fluctuations in DO indicated that biological mechanisms were also fast enough to influence DO.

pH

pH is the indicator of acidic or alkaline condition of water status. The mean values for pH ranged from 6.87 – 8.00 (Figure 3.6). The standard for any purpose in terms of pH is 6.5–8.5 (Alam et al., 2007). The values decreased slightly till station 6, where it was less than 7 and afterwards it increased slightly during monsoon and sharply during nonmonsoon periods towards estuary. Surface and bottom pH did not vary much. Majority values were >7, which indicated generally slightly alkaline water. High pH at stations 7 and 8 clearly credits for saline water intrusion.

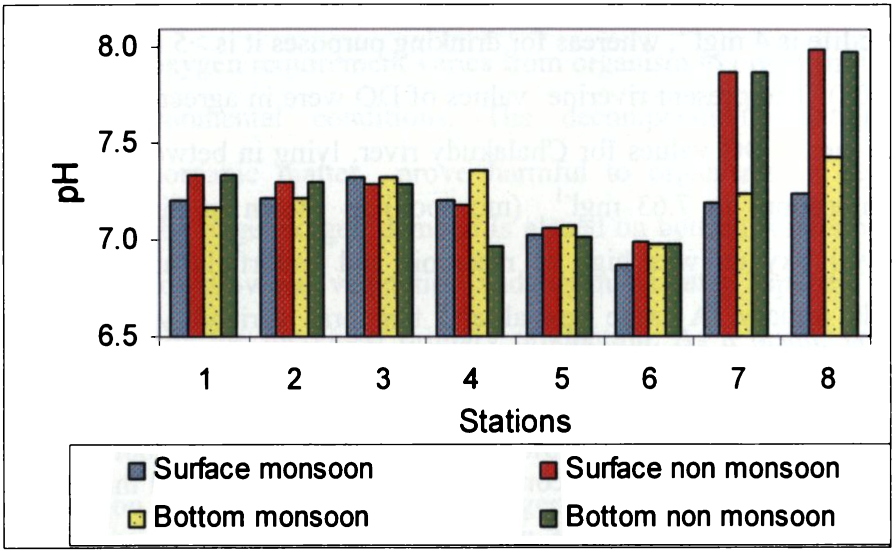


Figure 3.6 Seasonal average concentrations of pH in the surface and bottom waters of Chalakudy river

Sediment moisture content

The sediment quality of Chalakudy river observed in this study with respect to moisture content is summarized in Figure 3.7. The *in situ* sediment moisture content varied in different sediment samples. The highest mean value was at the reservoir station 1 in non monsoon (60.94%) and the lowest value was at the waterfalls station 2 in monsoon (18.90%). Estuarine stations 7 and 8 also retained high moisture. It could be noted that the sediments of waterfalls contained very low percentage of moisture which could be attributed to the sandy nature of the sediments. Stations 2 and 3 did not show wide variations whereas, all other stations changed the moisture content during different periods of collection.

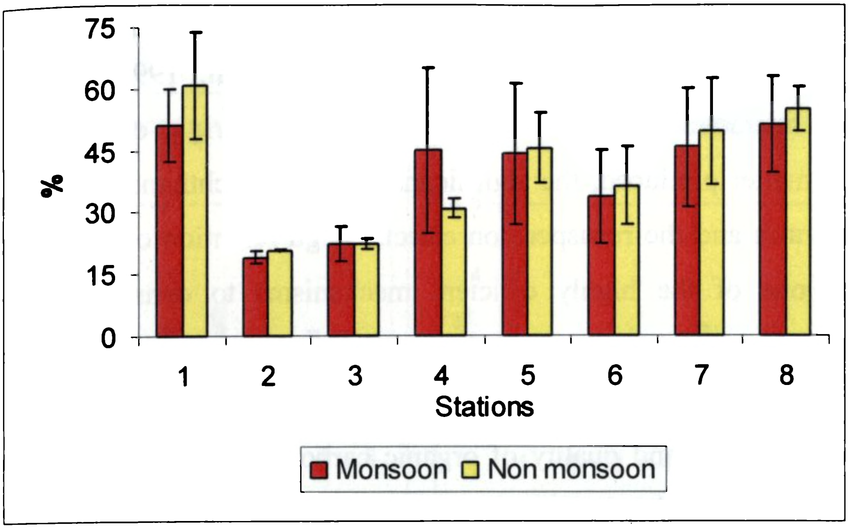


Figure 3.7 Seasonal average moisture contents (%) in the sediments of Chalakudy river

Sediment organic carbon (SOC)

Sediment organic carbon in the sediments of Chalakudy river varied from 0.13% to 3.34% during monsoon and from 0.13% to 4.85% during non monsoon season (Figure 3.8). The waterfall region of station 2 had the lowest, and the reservoir stations pictured the highest peak of SOC during both seasons. The waterfall region 3 had low SOC in monsoon, but gradually enhanced during non monsoon. Generally, non monsoon values were high, though station 4 stood an exception with high monsoon values and also stations 5 as well as 6 had seasonal SOC not widely varying. Sediment organic carbon is an important determinant of the fate of nutrients in aquatic systems. The biopolymeric fraction of the organic carbon, dominant in the suspended matter representing up to 90% of the organic carbon pool, becomes a minor fraction once has reached the sediments (usually ranging from 5 to 15%), so that the carbon pool becomes dominated by a geopolymeric fraction (Danovaro et al., 1998). The extent of such interactions depends on the amount and origin of the primary organic matter produced, the significance of the allochthonous inputs, the sinking rates and the resuspension effects. High retention of fixed carbon can be one of the highly efficient mechanisms to conserve essential nutrients. The resuspension controls the relative amounts of organic carbon and the rates of organic matter degradation in the benthos as well as water column. Quantity and quality of organic carbon in surface sediments are major factors affecting benthic fauna dynamics and metabolism (Pusceddu et al., 1999). Riverine fluxes of organic carbon and nutrients are highly seasonally variable; primarily due to seasonal variations of water discharge and sediment load (Hung and Huang, 2005).

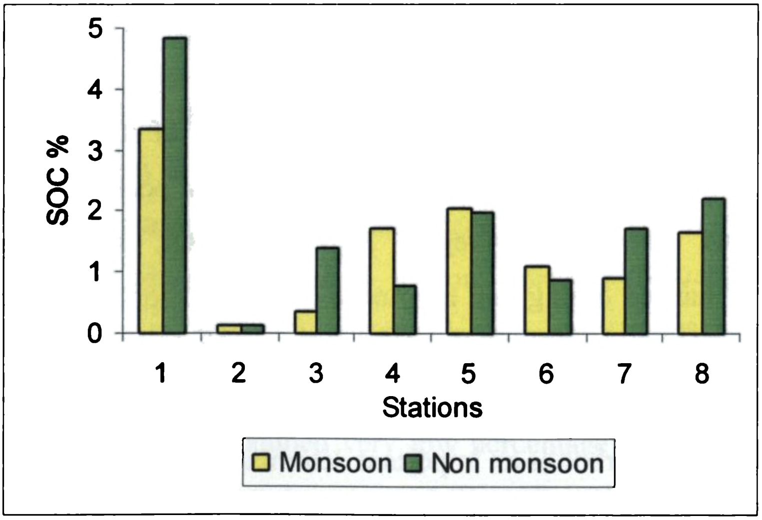


Figure 3.8 Seasonal average SOC contents (%) in the sediments of Chalakudy river.

Carbon, hydrogen, nitrogen (CHN) analyses

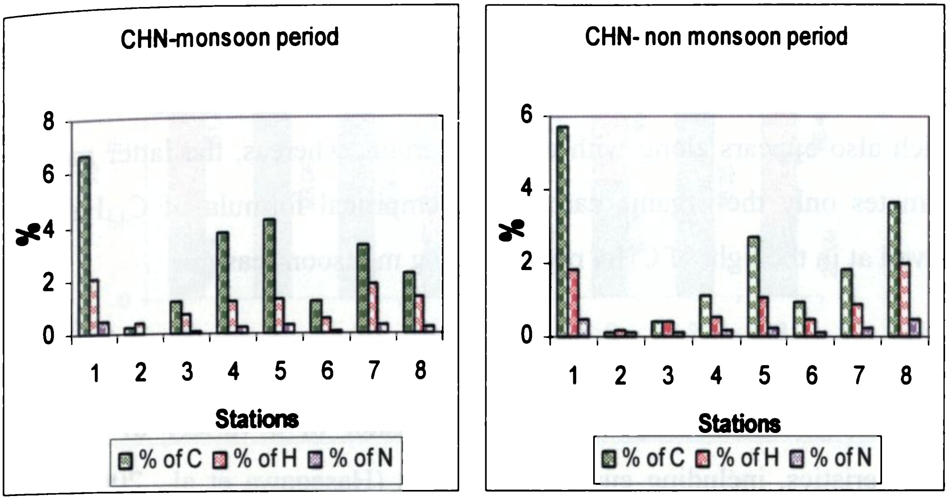


Figure 3.9 Seasonal average CHN contents (%) in the sediments of Chalakudy river

The system is characterized by high spatial and temporal variation in CHN concentrations and the current severity and the extent of carbon are sufficient to alter distributions of organic matter and trophic interactions in the river (Figure 3.9). Carbon ranged from 0.24 to 6.67% in monsoon and 0.12 to 5.71% in non monsoon season. The reservoir had the highest peak of C and the waterfall region, the least. The composition of H ranged from 0.38 to 2.03% and 0.19 to 2.02% during monsoon and non monsoon respectively. The H was shown to be negligibly small by stations 2 and 3. Thus, waterfalls regions had the least H. Monsoon values were higher for C as well as H. The percentage of N was very low in the range of 0.01 to 0.50%.

It is noticeable that the trend of carbon according to CHN analyses is more or less the same as those estimated by the conventional "SOC" method and there occurs only a difference in the absolute values. The slightly higher values of carbon in CHN analyses may be because of the inorganic carbon which also appears along with organic carbon, whereas, the latter method estimates only the organic carbon. An empirical formula of $C_{13}H_4N$ is arrived at in the light of CHN results during monsoon season.

Texture analyses

Sediment grain size may be a good indicator of a variety of physical characteristics, including current conditions (Hasegawa et al., 2008). The grain size distribution was measured using a wet-sieving method and the results were expressed as the percentage of the total dry mass of three size fractions. Figure 3.10 pictured the results of texture analyses performed on freeze-dried sediments. Sand was the predominant form in waterfalls stations 2 and 3 and also up-estuarine station 7 during both seasons. During monsoon, silt was the major portion of texture at the reservoir station 1, but during nonmonsoon, sand dominated in the texture. Stations 4, 5, 6 and 8 had silt as the major constituent and its percentage was higher in nonmonsoon. Clay was generally low at all stations and slight increase could be seen at stations 1, 5 and 8 during monsoon season.

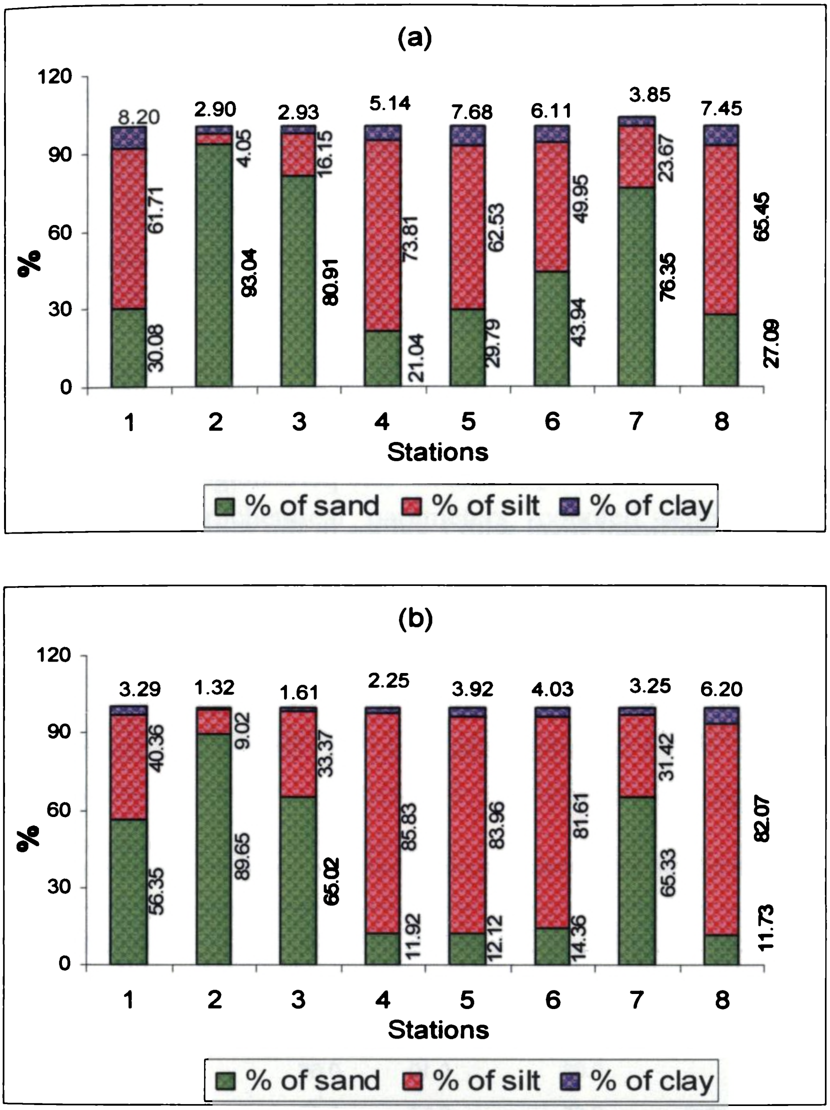


Figure 3.10 Average % of sand, silt and clay in the sediments of Chalakudy river during monsoon (a) and non monsoon (b) seasons.

Inter parameter relationships

On comparing the hydrographical parameters of samples from all sites, several of the hydrochemical data were significantly correlated (Tables 3.5 and 3.6). Chlorophyll was found to be positively related to dissolved oxygen and negatively to temperature. Dissolved oxygen and temperature were negative towards each other with r value -0.79. Chloride was positively significant towards pH and temperature respectively. Moisture content was positive to percentage of C, H, N, SOC, and clay. SOC was significantly interlinked to C, N and H. The percentages of C, H and N are interrelated at significant level with r values in the range 0.89 to 0.93. Clay was found to be highly related with C and H. It is important to note that salinity correlated significantly negative with respect to dissolved oxygen and chlorophyll and positive with respect to temperature and pH as clarified in Figure 3.11, which definitely make way for changes in nutrient pattern at the estuarine end.

Table 3.5 Pearson correlation matrix of hydrochemical parameters in water

	DO	Temperature	Chloride	pH	Chlorophyll
Temp	-0.79				
Chloride	-0.54	0.55			
pH	-0.08	0.10	0.66		
Chlorophyll	0.65	-0.57	-0.45	-0.15	
Salinity	-0.72	0.74	1.00	0.75	-0.76

Table 3.6 Pearson correlation matrix of hydrochemical parameters in sediments

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

The results on hydrochemical parameters, coupled with the nutrient analysis, suggest that the former contributes significantly to the direct transfer of nitrogen and phosphorus biomass, and thus play a prominent role in the turnover of dissolved, sedimentary and particulate nutrients. Developing an integrated approach to hydrochemical situation is inherently diffcult, particularly when it involved multiple issues spread across different geographical and temporal scales.

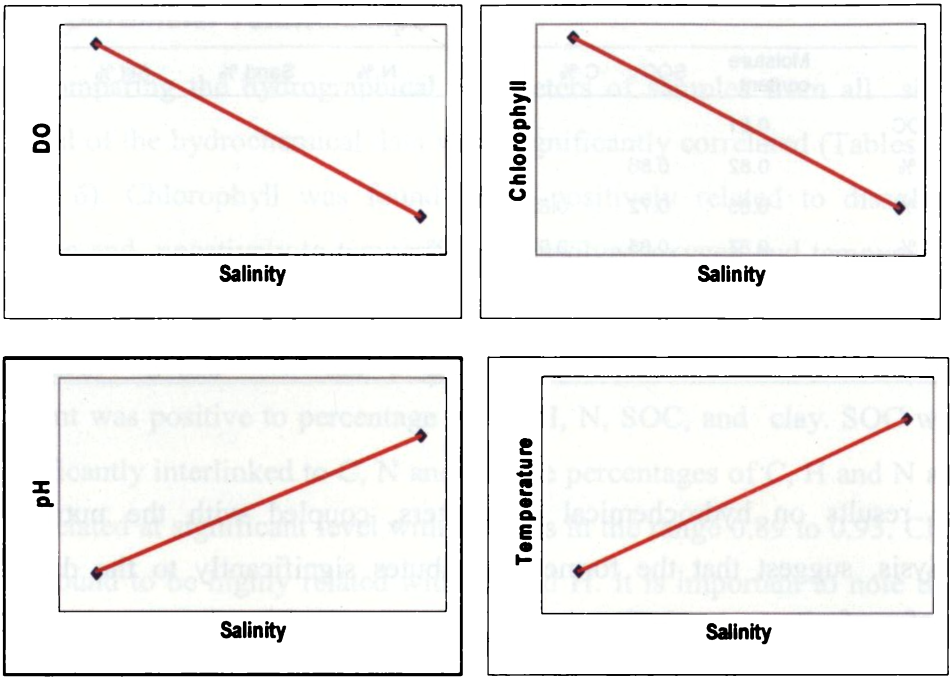


Figure 3.11 Dissolved oxygen, chlorophyll, pH as well as temperature as a function of salinity at the estuarine stations

Conclusion

The studies on chlorophyll and other general hydrographical parameters such as temperature, chloride content, dissolved oxygen, pH, moisture content, sediment organic carbon (SOC) and "CHN" values have documented effects on nutrients. Relationships in regional studies are precise or accurate enough to predict benefits of specific nutrient regulations for rivers throughout a region. In addition, many factors could affect nutrient relationships in rivers within a region and among regions with different climate, geology, water chemistry, and hydrology. Understanding differences in algal–nutrient relationships between very different regions would help establish the range of possibilities that can be expected and the factors that regulate that range (Stevenson et al., 2006).

Assessing ecosystem health of large rivers is often complicated because these ecosystems receive multiple, interacting biogeochemical changes. Confounding factors, such as complicated mixing hydraulics and historical loading effects, can result in equivocal field data that lend weak inference to ecological risk assessments (Cash et al., 2003). Ecological data sets are of upmost importance to describe the changes in response to land management and climatic changes that may occur over several decades in the river system.

In conclusion, efforts to understand and quantify these transport processes from the reservoir across the river through the mouth at estuary had led to an increasing focus on the fluxes of biogeochemical components in water and sediment like algae, dissolved oxygen, 'CHN' and texture. Spatial differences within each habitat arose from interactions between physicochemical factors included in this study. Regulation of the above described fluxes can produce drastic changes in the balance of processes and alter the fluctuations of the physical, biological and chemical characteristics of the river and understanding the effects of biogeochemical processes would be necessary for process interpretations.

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CHAPTER IV

DISSOLVED NITROGEN AND PHOSPHORUS

CONTENTS

INTRODUCTION

A nutrient element is defined as one that is functionally involved in the metabolism of living organisms. Thus, anything besides water and carbon dioxide that is required by plants in the synthesis of organic matter or skeletal materials is regarded as a nutrient. Nitrogen and phosphorus are considered to be the main limiting nutrients. Recent ecosystem level nutrient limitation studies support the evidence that phosphorus is the primary limiting nutrient in fresh waters and nitrogen is the limiting nutrient in marine systems (Conley, 2000; Stevenson et al., 2006; Chambers et al., 2006).

When a body of water has too much nutrients in it, we say that eutrophication has occurred. Excessive amounts of soluble inorganic phosphorous (P) and nitrogen (N) cause eutrophication in water bodies, which may lead to water-quality issues related to riverine ecosystems (Hong and Huang, 2006). Excessive enrichment of rivers with plant nutrients from the catchment area leads to the undesirable growth of algae, which in turn causes a reduction in water clarity and detericrates the quality of water.

Rivers are highly productive systems and the location of critical biogeochemical processes. River waters serve as interfaces between continental and marine environments, and as such they play an essential role in nutrient transfer to the sea. In some environments, phosphate may be the limiting nutrient, in others it may be nitrate. Knowledge of the flow of organic matter and bioavailable nutrients circulating in the food webs is important for our understanding of how river systems function. There are several sources of water pollution which work together to reduce overall river water quality. Industry and agriculture discharge liquid waste products. Rain as it falls through the air, or drains from urban areas and farmland, absorbs contaminants. In lowland rivers, residence time is important in the transfer of nutrients within the food web. So comparison of water chemistry facilitates a better evaluation of the chemical interaction happening across the rivers.

An assessment of nitrogen and phosphorus dynamics of the waters of river Chalakudy is described in this chapter. Enhanced nitrogen and phosphorus input can have a detrimental impact on river ecology since both are linked to problems of eutrophication at local, catchment and regional scales.

MATERIALS AND METHODS

The details of methodology adopted are described in Chapter II. Water samples were collected from Chalakudy river on a bimonthly basis for a period of one year. The nutrient concentrations (various species of nitrogen and phosphorus) were analyzed in the water samples of 8 sampling stations.

RESULTS AND DISCUSSIONS

In this section, the results of measurements on dissolved nitrogen and phosphorus species in the riverine system are presented. Through statistical analysis of these data, attempt is made to characterize the spatio-temporal trends in the distributional characteristics of these nutrient species as well as to elucidate the factors and processes affecting the dissolved nutrients of the riverine system. It is highly wanted as the nutrient status and chemistry of Chalakudy river are not well known till now.

Distributional characteristics of different species of nitrogen

The different species of dissolved nitrogen analysed from the waters of Chalakudy river are nitrite-N, nitrate-N, ammonia-N, dissolved inorganic nitrogen (DIN), urea-N, total-N and residual-N. The spatial and temporal distributional values (in μmoll^{-1}) of all species of N in surface and bottom waters are presented in Tables 4. 1 and 4. 2 respectively.

The mean values of nitrite-N ranged from 0.21 μmoll^{-1} to 0.50 μmoll^{-1} during monsoon (Figure 4.1) and from 0.06 μmoll^{-1} to 0.31 μmoll^{-1} for surface during nonmonsoon. The amount of nitrite-N remained very low during all seasons. The monsoon period showed a slow hike from the reservoir station 1 to the ferry station 4 and descended towards estuarine end. Nonmonscon visualised a slight decrease in nitrite from reservoir towards the waterfalls station 2, then increased through the next waterfalls region to a peak at the ferry and then decreased towards estuary. Staion 3 has almost the same average values during monsoon and nonmonsoon. A distinguishable increase was observed during monsoon for all eight stations as compared to nonmonsoon season. The increase of nitrite was well defined for stations from 4 to 8. The nonmonsoon showed sharp decrease of nitrite for stations after ferry (station 4) towards estuary. Standard deviations were high for 1, 4, 5 and 6 stations during monsoon and for stations 3 and 4 during nonmonsoon.

Table 4.1 Bimonthly distribution of nitrite-N, nitrate-N, ammonia-N, dissolved inorganic nitrogen (DIN), urea-N, total-N and residual-N (in $\mu mol l^{-1}$) in the surface waters of Chalakudy river

		STATIONS							
PARAMETERS	MONTHS	S1	S2	S3	S4	S5	S6	S7	S8
Nitrite-N	May	0.07	0.13	0.10	0.08	0.08	0.12	0.10	0.09
	Jul	0.32	0.25	0.34	0.60	0.53	0.48	0.41	0.44
	Sep	0.20	0.25	0.25	0.73	0.48	0.55	0.49	0.38
	Nov	0.53	0.21	0.36	0.58	0.12	0.13	0.25	0.16
	Jan	0.26	0.16	0.37	0.47	0.13	0.15	0.17	0.08
	Mar	0.16	0.10	0.11	0.16	0.13	0.10	0.11	0.05
Nitrate-N	May	11.87	6.89	15.40	19.79	11.18	8.57	5.13	3.45
	Jul	20.81	5.72	14.75	21.04	17.82	13.87	5.70	6.42
	Sep	19.43	4.90	18.97	23.85	15.46	8.19	6.42	9.11
	Nov	7.01	7.98	15.67	13.57	14.34	7.89	4.61	3.84
	Jan	7.07	6.23	9.49	14.38	10.12	8.61	2.84	2.66
	Mar	7.75	5.32	11.38	11.05	10.09	7.92	2.86	2.41
Ammonia-N	May	1.21	0.85	1.44	1.74	2.20	0.28	1.04	0.37
	Jul	2.07	0.79	2.70	8.10	3.28	3.26	2.03	1.95
	Sep	2.80	0.91	2.22	6.41	0.38	2.18	2.17	1.73
	Nov	2.13	1.07	1.82	1.54	0.62	3.51	1.80	1.26
	Jan	1.91	0.21	0.47	1.96	1.75	0.58	0.94	0.19
	Mar	1.23	0.06	0.22	0.62	2.07	1.19	0.08	0.32
DIN	May	13.15	7.87	16.93	21.61	13.45	8.96	6.27	3.90
	Jul	23.20	6.75	17.79	29.74	21.63	17.61	8.13	8.80
	Sep	22.42	6.06	21.44	30.98	16.31	10.91	9.08	11.21
	Nov	9.67	9.26	17.85	15.68	15.07	11.53	6.66	5.25
	Jan	9.24	6.60	10.33	16.81	11.99	9.34	3.94	2.92
	Mar	9.14	5.48	11.70	11.83	12.28	9.20	3.05	2.77
Urea-N	May	1.22	0.22	0.73	1.30	1.08	1.14	2.00	1.48
	Jul	2.10	0.44	1.73	1.51	1.51	1.32	1.54	2.54
	Sep	1.29	0.75	0.75	1.39	1.48	0.93	1.49	0.31
	Nov	0.98	0.51	0.42	2.00	0.62	0.67	0.87	0.22
	Jan	0.87	0.29	0.39	1.62	1.47	1.02	0.27	0.43
	Mar	0.96	0.36	0.47	1.02	1.32	0.52	0.48	0.47
Total-N	May	16.25	8.12	19.90	25.41	14.66	10.81	8.84	5.92
	Jul	27.71	7.75	21.12	37.40	25.40	19.10	10.77	12.37
	Sep	25.40	8.16	23.25	37.58	21.84	13.07	11.45	12.68
	Nov	11.78	10.43	19.39	20.28	16.58	12.82	8.66	6.57
	Jan	11.69	7.27	11.52	20.37	14.93	11.79	5.25	3.76
	Mar	11.30	5.93	12.98	14.14	14.85	11.75	4.01	3.54
Residual-N	May	1.89	0.03	2.25	2.50	0.13	0.72	0.57	0.55
	Jul	2.41	0.57	1.61	6.16	2.27	0.17	1.10	1.04
	Sep	1.70	1.36	1.06	5.22	4.06	1.23	0.88	1.17
	Nov	1.14	0.67	1.13	2.61	0.89	0.62	1.13	1.11
	Jan	1.59	0.39	0.80	1.95	1.47	1.43	1.04	0.41
	Mar	1.20	0.08	0.81	1.30	1.25	2.04	0.48	0.29

Table 4.2 Bimonthly distribution of nitrite-N, nitrate-N, ammonia-N, dissolved inorganic nitrogen (DIN), urea-N, total-N and residual-N (in µmoll^{-1}) in the bottom waters of Chalakudy river

		STATIONS							
PARAMETERS	MONTHS	**B1**	**B2**	**B3**	**B4**	**B5**	**B6**	**B7**	**B8**
Nitrite-N	May	0.07	0.13	0.10	0.13	0.10	0.13	0.10	0.11
	Jul	0.33	0.25	0.34	0.47	0.53	0.53	0.41	0.41
	Sep	0.23	0.25	0.25	0.52	0.46	0.61	0.55	0.45
	Nov	0.46	0.21	0.36	0.54	0.12	0.13	0.24	0.27
	Jan	0.32	0.16	0.37	0.46	0.13	0.15	0.17	0.10
	Mar	0.14	0.10	0.11	0.12	0.14	0.11	0.11	0.08
Nitrate-N	May	11.87	6.89	15.40	17.64	12.62	9.45	5.13	3.58
	Jul	21.76	5.72	14.75	25.72	17.82	13.03	5.70	5.23
	Sep	20.02	4.90	18.97	23.09	11.28	7.54	4.84	5.53
	Nov	6.40	7.98	15.67	12.80	14.34	7.89	4.97	3.39
	Jan	8.09	6.23	9.49	13.11	10.12	5.74	2.84	2.51
	Mar	7.78	5.32	11.38	10.56	9.44	5.70	2.86	2.93
Ammonia-N	May	1.21	0.85	1.44	1.99	1.96	0.35	1.04	0.33
	Jul	2.00	0.79	2.70	7.50	3.28	2.44	2.03	1.53
	Sep	2.72	0.91	2.22	7.47	0.38	2.77	2.07	1.35
	Nov	1.13	1.07	1.82	1.13	0.62	3.51	1.85	1.57
	Jan	1.66	0.21	0.47	0.33	1.75	1.08	0.94	0.58
	Mar	1.28	0.06	0.22	0.78	2.11	0.97	0.08	0.43
DIN	May	13.15	7.87	16.93	19.75	14.68	9.92	6.27	4.02
	Jul	24.09	6.75	17.79	33.68	21.63	16.00	8.13	7.17
	Sep	22.97	6.06	21.44	31.08	12.12	10.91	7.46	7.32
	Nov	7.99	9.26	17.85	14.46	15.07	11.53	7.06	5.23
	Jan	10.07	6.60	10.33	13.90	11.99	6.96	3.94	3.18
	Mar	9.19	5.48	11.70	11.45	11.68	6.77	3.05	3.43
Urea-N	May	1.22	0.22	0.73	1.26	0.98	1.26	2.00	1.63
	Jul	2.29	0.44	1.73	1.44	1.51	1.44	1.54	3.46
	Sep	1.27	0.75	0.75	1.96	1.49	1.04	1.29	0.45
	Nov	0.94	0.51	0.42	1.54	0.62	0.67	0.93	0.34
	Jan	0.91	0.29	0.39	1.17	1.47	1.27	0.27	0.19
	Mar	0.90	0.36	0.47	1.47	1.26	0.99	0.48	0.25
Total-N	May	16.25	8.12	19.90	23.60	15.78	12.11	8.84	6.18
	Jul	28.44	7.75	21.12	40.65	25.40	18.20	10.77	11.49
	Sep	25.88	8.16	23.25	38.62	13.83	12.63	9.78	8.80
	Nov	10.62	10.43	19.39	19.13	16.58	12.82	8.42	6.86
	Jan	13.35	7.27	11.52	17.77	14.93	9.51	5.25	4.11
	Mar	11.54	5.93	12.98	14.68	14.23	10.78	4.01	3.78
Residual-N	May	1.89	0.03	2.25	2.59	0.12	0.94	0.57	0.53
	Jul	2.07	0.57	1.61	5.54	2.27	0.76	1.10	0.87
	Sep	1.65	1.36	1.06	5.59	0.22	0.69	1.04	1.03
	Nov	1.69	0.67	1.13	3.13	0.89	0.62	0.44	1.29
	Jan	2.37	0.39	0.80	2.70	1.47	1.28	1.04	0.75
	Mar	1.45	0.08	0.81	1.76	1.29	3.03	0.48	0.10

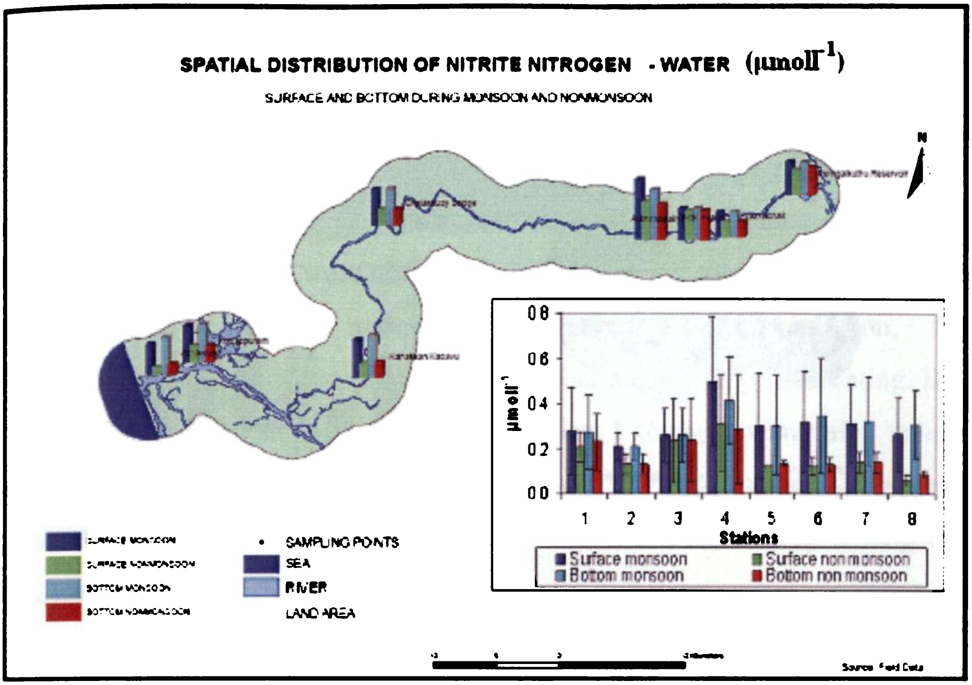

Figure 4.1 Seasonal average concentrations of dissolved nitrite-N during monsoon and nonmonsoon periods in Chalakudy river

The mean values of nitrate-N was found to be appreciably high (Figure 4.2). The range during monsoon was from 4.43 µmoll^{-1} to 19.81 µmoll^{-1}. During nonmonsoon, the minimum value was 2.53 µmoll^{-1} and the maximum was 12.72 µmoll^{-1}. Generally, surface nitrates were higher than bottom values. But exceptions were noticed occasionally, in stations 1 and 8. Stations 2, 6, 7 and 8 were not exhibiting pronounced nitrate as the stations 1, 3, 4 and 5. The trend during both seasons were identical in that there was a decrease from the reservoir towards the waterfalls region, then an increase towards the ferry and again a steady decrease towards the estuarine side.

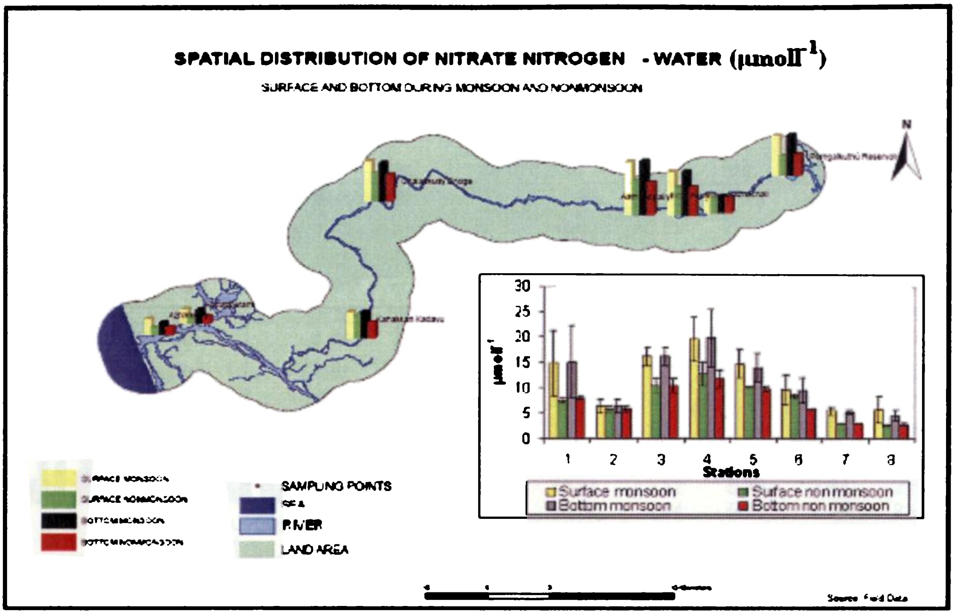

Figure 4.2 Seasonal average concentrations of dissolved nitrate-N during monsoon and nonmonsoon periods in Chalakudy river

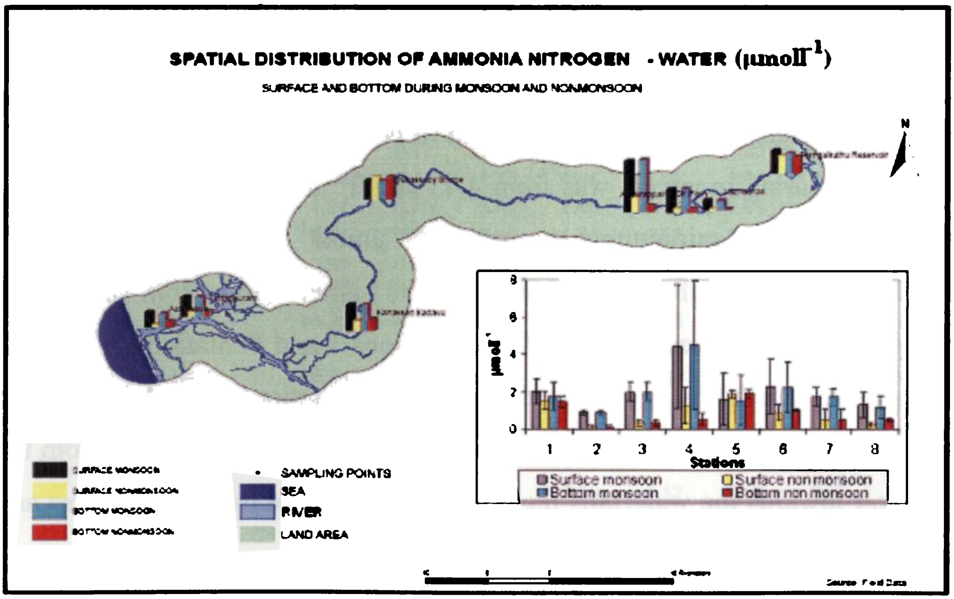

Figure 4.3 Seasonal average concentrations of dissolved ammonia-N during monsoon and nonmonsoon periods in Chalakudy river

The mean values of ammonia-N in water ranged from 0.90 μmoll^{-1} to 4.52 μmoll^{-1} during monsoon and 0.13 μmoll^{-1} to 1.93 μmoll^{-1} during nonmonsoon (Figure 4.3). Ammonia concentration was found to be increasing after the onset of monsoon. It could be seen that in all stations except station 5, lesser ammonia-N was obtained in the nonmonsoon periods. Surface and bottom ammonia concentrations were not significantly different, though stations 1 and 8 occasionally showed noticeable variations. During monsoon, the concentration peak was at station 4, and all other stations kept fluctuating. But nonmonsoon season showed a fall from station 1 towards waterfalls, then a hike towards station 5 and again decreased towards estuary. Ammonia concentrations at station 4 were seemed to be more fluctuating among the study period.

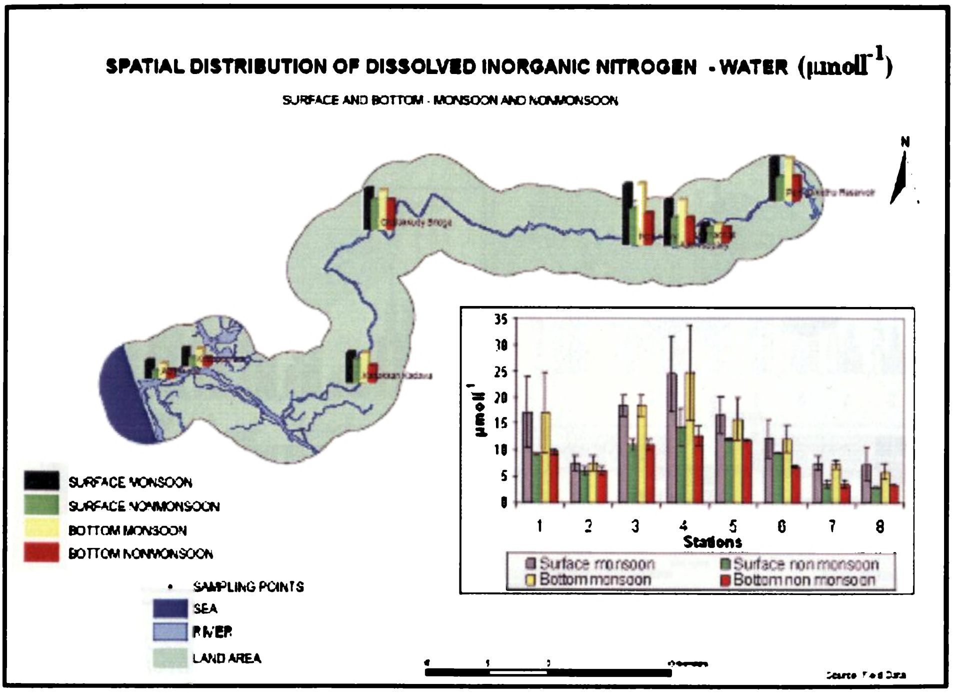

Figure 4.4 Seasonal average concentrations of DIN during monsoon and nonmonsoon periods in Chalakudy river

The trend which the dissolved inorganic nitrogen (DIN) followed was the same for all the seasons. It was high at station 1 and then decreased sharply towards the waterfalls (station 2), then, the concentration got enhanced to a maximum at the ferry station 4 and afterwards a steady decrease occurred stationwise till the estuarine region. The maximum amount recorded during monsoon was 24.74 µmoll^{-1} and the minimum was 5.93 µmoll^{-1}. Nonmonsoon period showed **the highest of** 14.32 µmoll^{-1} and lowest of 2.85 µmoll^{-1} (Figure 4.4). In both cases, the highest DIN was at the ferry area and lowest was at the estuarine region.

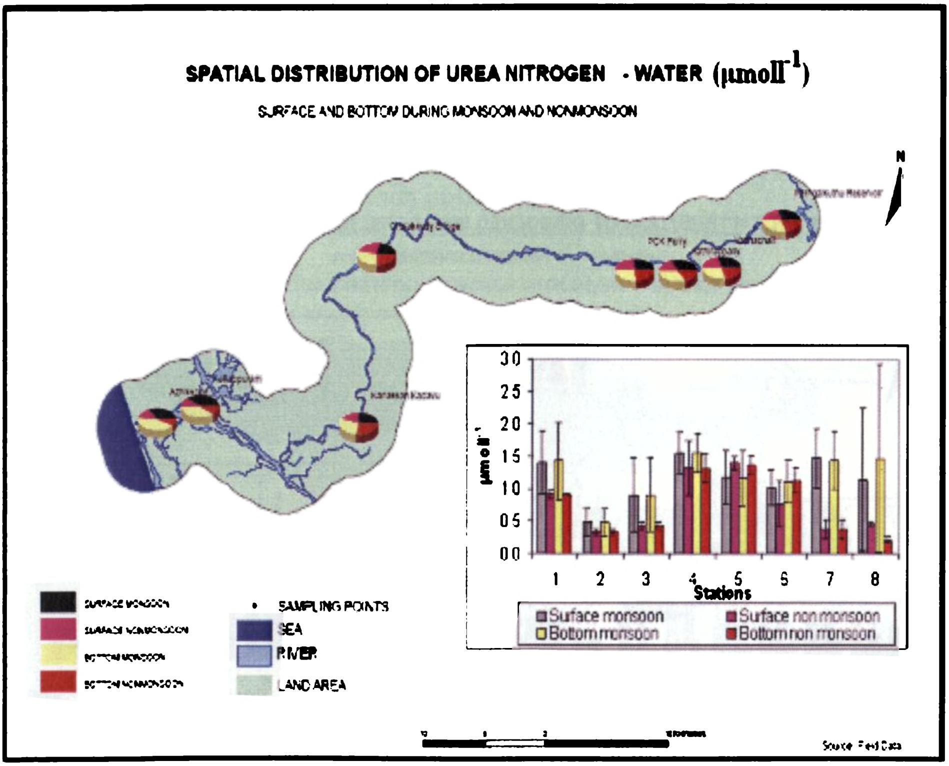

Figure 4.5 Seasonal average concentrations of dissolved urea-N during monsoon and nonmonsoon periods in Chalakudy river

The mean values of urea showed a maximum concentration of 1.55 µmoll^{-1} and a minimum of 0.48 µmoll^{-1} during monsoon period, whereas in nonmonsoon period the maximum was 1.40 µmoll^{-1} and the minimum was 0.32 µmoll^{-1} (Figure 4.5). Stations 1, 4 and 7 had very high urea-N in monsoon, but stations 4, 5 and bottom of station 6 had higher concentrations during nonmonsoon. The waterfalls had comparatively lower urea-N. Generally, surface and bottom concentrations remained closer with the exception of stations 6 and 8.

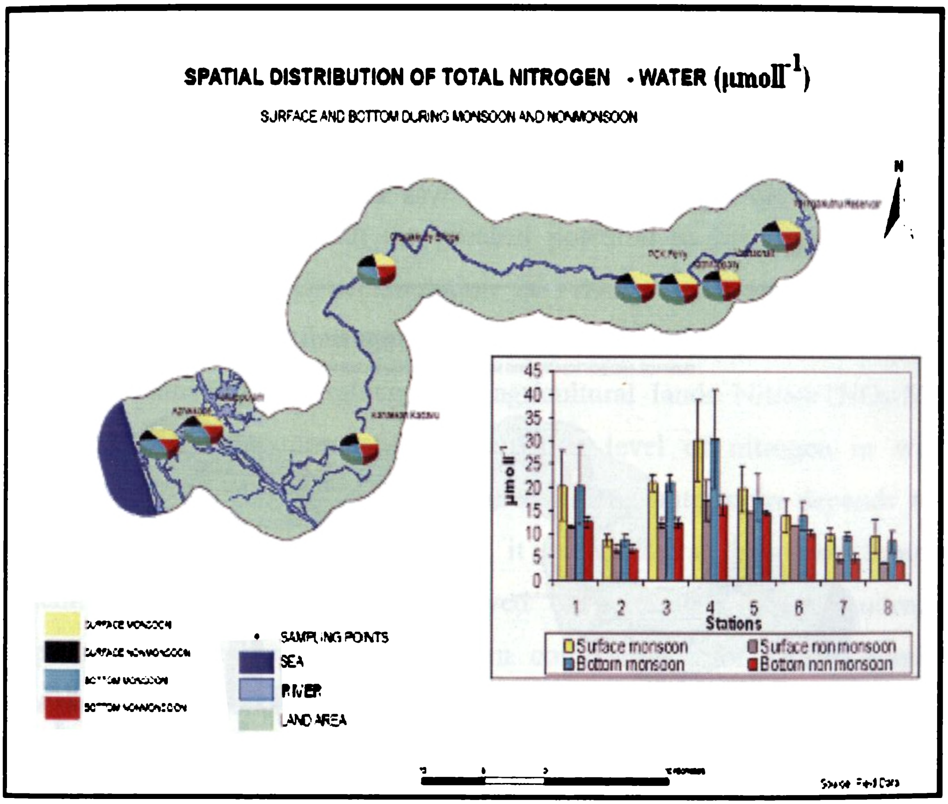

Figure 4.6 Seasonal average concentrations of dissolved Total-N during monsoon and nonmonsoon periods in Chalakudy river

Total nitrogen included all inorganic as well as organic forms of nitrogen in the river water. The distributional trend followed by stations for both seasons by the surface as well as bottom waters appeared as the same (Figure 4.6). Appreciable total N was recorded at the reservoir, and was follwed by a sharp decrease at the waterfalls station 2. Then, a hike occurred through waterfalls station 3 to a peak at the ferry station 4, after that it gradually decreased through the town station 5 to the next riverine station 6. Afterwards also, a steady decrease towards estuarine end was seen which was mild during monsoon and sharp during nonmonsoon season. Monsoon total N was much higher as compared to nonmonsoon values. The mean values for total N ranged from 8.33 μmoll^{-1} (station 8) to 30.50 μmoll^{-1} (station 4) during monsoon and 3.65 μmoll^{-1} (station 8) to 17.26 μmoll^{-1} (station 4) during nonmonsoon (Figure 4.6). No significant variation was observed between surface and bottom waters.

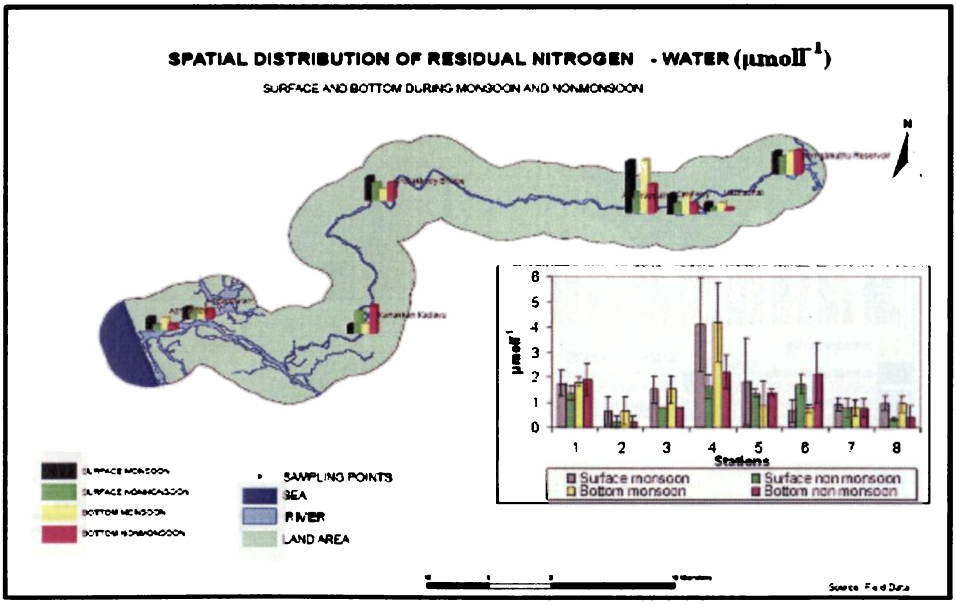

Figure 4.7 Seasonal average concentrations of dissolved residual-N during monsoon and nonmonsoon periods in Chalakudy river

The residual-N was calculated by subtracting the sum of nitrite-N, nitrate-N, ammonia-N and urea-N from the total dissolved N. This mainly consists of organic forms of N other than urea. The waters of Chalakudy river contained a good amount of residual-N. The ferry (station 4), which was extremely rich in residual N compared to other stations, possessed the highest concentration of 4.21 μmoll^{-1} in monsoon, and 2.23 μmoll^{-1} in nonmonsoon season. It was noticeable that the waterfalls station 2 had least amount of residual-N with 0.66 μmoll^{-1} in monsoon and 0.24 μmoll^{-1} in nonmonsoon. Generally, concentrations remained steady for surface as well as sub-surface waters though exceptions were there.

The concentrations of biologically available nitrogen play a key role in determining the ecological status of aquatic systems. Nitrogen (N) is generally regarded as the nutrient with the greatest potential to limit phytoplankton productivity and biomass accumulation in rivers and estuaries. Nitrogen compounds are supplied through river mainly as dissociated nitrate, derived from rock weathering and drainage from agricultural lands. Nitrate (NO_3-N) is considered to be the most stable oxidation level of nitrogen in water (Grasshoff, 1983). Growth of many photosynthetic autotrophs depends to a greater extent on this nitrate. Therefore, it is identified as the growth limiting nutrient. Nitrite, ammonia and dissolved or particulate organic nitrogen compounds are other major nitrogen compounds for biogeochemical processes. The presence of nitrite is usually observed to be very low. The nitrite acts as an intermediate product of microbiological reduction of nitrate or oxidation of ammonia and as an excretory product of plankton. Inorganic nitrogen compounds, thus exist in their oxidized and reduced forms in the aquatic environment which can be represented as $NO_3^- \leftrightarrow NO_2^- \leftrightarrow NH_4^+$. The stage of this equation controls the predominance and occurrence of various living communities especially phytoplankton. Ammonia is toxic to aquatic organisms, and ammonia toxicity is dependent on the pH of the water, since the un-ionized form (NH_3) is more toxic than the ionized form (NH_4^+) (Russo and Lekevicius, 2005). Urea is often chosen to evaluate potential dissolved organic nitrogen (DON) uptake. Urea concentrations in river and estuarine waters can be substantially elevated and represent a large fraction of the total dissolved organic nitrogen pool. Urea is used as a nitrogen substrate by many coastal phytoplankton and is increasingly found to be important in the nitrogenous nutrition of some harmful algal bloom species (Glibert et al., 2006). Studies of urea regeneration in natural systems demonstrate high and consistent microbial mineralization of urea from DON in surface waters and at the sediment–water interface (Berman et al., 1999). Chemical oceanographers and limnologists have shown that anywhere between 2 and 70% of the DON in surface waters is bioavailable (Seitzinger et al., 2002; Stepanauskas et al., 2002). Reviews by Westerhoff and Mash (2002) and Berman and Bronk (2003) gave details about the structure and bioavailability of DON in natural waters. The total N-uptake is defined as the sum of N-incorporation into the particulate matter via NO_3^-, NH_4^+, and urea (Susen et al., 2001). Concentrations of different species of nitrogen ($\mu mol l^{-1}$) in rivers and other aquatic systems from areas subject to extensive human modification are given in Table 4.3.

Nitrogen (N) often limits primary productivity in aquatic systems. Unlike P, dissolved inorganic N (DIN) occurs in different oxidation states. Land-derived N entering rivers and estuaries consists of nitrite, nitrate, ammonia and DON including urea. The fate of these forms of N varies because these compounds differ in biological lability and use. Only a fraction of DON is likely to be labile, and inorganic N forms are much more available for uptake by producers. DIN is assimilated and converted to organic N by phytoplankton, other plants, or bacteria. Organic N can be regenerated as ammonium (NH_4^+) or dissolved organic N (DON) compounds, reassimilated by plants or heterotrophs, or oxidized by bacteria (McCarthy et al., 2007). Water column nitrate and ammonia regeneration and uptake, benthic nutrient fluxes and N sinks (i.e. denitrification), and water column versus benthic N cycling, are important factors related to trophic status and water quality.

The nitrite-N in surface as well as bottom waters was varying only slightly (Figure 4.1). Circulations might possibly lead to a recycling of the nitrite in surface and bottom waters. Station 4 was an exception with the surface waters having more nitrite, which was probably be a reason for high chlorophyll in these surface waters as was clear in Chapter III (Figure 3.1). Nitrites could be brought from land through rain water as was evident from the comparatively higher values in monsoon. At the ferry (Station 4) station, the nitrite-N was comparatively getting greater in monsoon, and decreased towards nonmonsoon. Leaching of fertilizers from farms and other chemicals from factories nearby could be the reason.

According to Meybeck (1982), the average NO_2-N concentration for unpolluted rivers is 1.5 μgL^{-1}. The surface values of nitrite-nitrogen showed a variation of 0.07–0.59 $\mu moll^{-1}$ and the bottom concentrations were higher (Anu et al., 2002) in the waters of Arabian sea. These values are comparable with the values estimated in Chalakudy riverine waters, which finally flows into Arabian sea.

Stations 1, the reservoir exhibited slightly higher nitrate (Figure 4.2) in bottom waters in both seasons, because the exchange of nitrate with the deposited sediments could not be ruled out. Generally stations 1, 3, 4 and 5 had larger values of nitrate which reflected the large run off from land during monsoon. Industrial effluents washed out from nearby factories may be one reason for the enrichment of nitrate in the waters of the ferry station 4. In short, the increasing trends in dissolved nitrate are primarily attributed to both short term river input variability and mixing with bottom enriched waters (Nagy et al., 2002). Nitrate concentration in surface waters of Chalakudy river basin during 2001-2002 was reported to be 0.04 to 4.16 mg l^{-1} (Chattopadhyay et al., 2005).

Table 4.3 Global reference values of different species of dissolved nitrogen

Parameters	Aquatic system	Concentrations	Reference
Nitrite-N	The major river systems of Macedonia	0.01– 0.3 mg l^{-1}	Voutsa et al., 2001
	Pomeranian Bay at the eastern German coast of the Baltic Sea	0.14–1.98 µmol l^{-1}	Estrum-Yousef and Schoor, 2001
	Lake Peipsi	1.5 µg l^{-1}	Kangur et al., 2002
	Surface waters of Arabian sea	0.07–0.59 µmol l^{-1}	Anu et al., 2002
	Mgazana, a warm temperate mangrove estuary in the Transkei, Eastern Cape, South Africa	12.4 µg l^{-1}	Emmerson, 2005
	Rain water samples (yearly volume-weighted average concentration)	<0.5 µM	Kieber et al., 2005
	Rain water samples	0. 1mgl^{-1}	Niedzielski et al., 2006
	Saguaro Lake, Arizona	0 mg l^{-1}	Leenheer et al., 2007
	Liangxihe River discharge into Meiliang Bay, Lake Taihu (China)	13.8 µmol l^{-1}	McCarthy et al., 2007

Parameters	Aquatic system	Concentrations	Reference
Nitrates + Nitrites	Danube River floodplain (Kopac ki Rit, Croatia)	0.82 mg l^{-1}	Palijan and Fuks, 2006
	Ria Formosa coastal lagoon- pore water, S Portugal	46–125 µmol l^{-1}	Serpa et al., 2007
	Ria Formosa coastal lagoon- surface water, S Portugal	0.05 µmol l^{-1}	Serpa et al., 2007
Nitrate-N	Rio de la Plata River Estuary System	25–40 µM d^{-1}	Nagy, 2000
	Pomeranian Bay at the eastern German coast of the Baltic Sea	0.08–16.23 µmol l^{-1}	Estrum-Yousef and Schoor, 2001
	The major river systems of Macedonia, N. Greece	58.4 mg l^{-1}	Voutsa et al., 2001
	Remote South American Rivers	0.13 µmol l^{-1}	Perakis and Hedin, 2002
	Surface waters of Arabian sea	0.79–6.58 µmol l^{-1}	Anu et al., 2002
	North western Adriatic sea (Nitrate-N)	>3 µmol N l^{-1}.	Cozzi et. al. (2002)
	Herrington Lake river impoundment, southeastern United States	89–366 *µ*g l^{-1}	Bukaveckas and Crain, 2002
	Lake Peipsi	58 µg l^{-1}	Kangur et al., 2002
	Acton Lake, OH, U.S.A	20–600 µmol l^{-1}	Nowlin et al., 2005
	Neuse River Estuary (NRE), North Carolina, USA.	<25–248 µg atoms N l^{-1}	Twomey et al, 2005
	Rain water samples (yearly volume-weighted average concentration)	11.1 µM	Kieber et al., 2005
	Chalakudy river basin, Kerala, India	0.04 to 4.16 mg l^{-1}	Chattopadhyay et al., 2005
	Rain water samples	0.05 mg l^{-1}	Niedzielski et al., 2006
	Saguaro Lake, Arizona	0.22 mg l^{-1}	Leenheer et al., 2007
	Liangxihe River discharge into Meiliang Bay, Lake Taihu (China)	73.3 µmol l^{-1}	McCarthy et al., 2007

Parameters	Aquatic system	Concentrations	Reference
Ammonia-N	Mgazana estuary, Transkei, Eastern Cape, South Africa	153 μg l^{-1}	Emmerson, 2005
	Rain water samples (yearly volume-weighted average concentration)	10.1 μM	Kieber et al., 2005
	Acton Lake, OH, U.S.A	50–430 μmol l^{-1}	Nowlin et al., 2005
	Danube River floodplain (Kopac ki Rit, Croatia)	0.32 –.81mg l^{-1}	Palijan and Fuks, 2006
	Saguaro Lake, Arizona	0.05 mg l^{-1}	Leenheer et al., 2007
Ammonium	Major river systems of Macedonia, N. Greece	0.14–4.46mg l^{-1}	Voutsa et al., 2001
	North western Adriatic sea	<0.14 μmolN l^{-1}	Cozzi et. al., 2002
	Lake Peipsi	18 μg l^{-1}	Kangur et al., 2002
	Rio de la Plata River Estuary System	10–20 μM d^{-1}	Nagy,2000
	Neuse River Estuary, NC, USA	0–75.3 μg atoms N l^{-1}	Twomey et al., 2005
	Ria Formosa coastal lagoon S Portugal	0.1–110 μmol l^{-1}	Serpa et al., 2007
	Liangxihe River discharge into Meiliang Bay, Lake Taihu (China)	185 μmol l^{-1}	McCarthy et al., 2007
DIN	Pomeranian Bay at the eastern German coast of the Baltic Sea	0.9–23.8 μmol l^{-1}	Estrum-Yousef and Schoor, 2001
	Piratininga Lagoon - riverine sector	5 –30 μmol l^{-1}	Da Cunha and Wasserman, 2003
	Childs River, Cape Cod, Massachusetts	12.1 ± 2.4 μmol l^{-1}	Valiela et al., 2004
	Quashnet River, Cape Cod, Massachusetts	5.3 ± 2.6 μmol l^{-1}	Valiela et al., 2004
Urea-N	Pomeranian Bay, eastern German coast of the Baltic Sea	0.50–4.17 μmol l^{-1}	Estrum-Yousef and Schoor, 2001
	Arabian Sea	0.04–2.12 μmol l^{-1}	Anu et al., 2002
	Neuse River Estuary, North Carolina, USA.	0 –43 μg atoms N l^{-1}	Twomey et al, 2005

Parameters	Aquatic system	Concentrations	Reference
Total-N	The major river systems of Macedonia	1.3–3 mg l^{-1}	Voutsa et al., 2001
	Lake Peipsi	624 µg l^{-1}	Kangur et al., 2002
	Lake Baikal, Russia	16.8–22.4 mg l^{-1}	Kholodov, 2003
	Mgazana estuary, Transkei, Eastern Cape, South Africa	419.8 µg l^{-1}	Emmerson, 2005
	Rain water samples (yearly volume-weighted average concentration)	24.8 µM	Kieber et al., 2005
	Wuli Lake, China	7.63 ± 2.11 mg l^{-1}	Jin et. al., 2006
	Danube River floodplain (Kopac ki Rit, Croatia)	1.94 –2.92 mg l^{-1}	Palijan and Fuks, 2006
	Saguaro Lake, Arizona	0.41mg l^{-1}	Leenheer et al., 2007
	Fenton River, Connecticut, USA	56–906 µg l^{-1}	Nadim et al., 2007
	Mount Hope River, Connecticut, USA	100–1192 µg l^{-1}	Nadim et al., 2007
	Natchaug Rivers, Connecticut, USA	201–1125 µg l^{-1}	Nadim et al., 2007
	Sahela Reservoir (Morocco)	0.57 – 2.24 mg l^{-1}	Mhamdi et al., 2007
DON	Rain water samples (yearly volume-weighted average concentration)	5.5 µM	Kieber et al., 2005
	Pawcatuck River watershed, southern New England	10 to 34 µM l^{-1}	Fulweiler and Nixon, 2005
	Saguaro Lake, Arizona	0.14 mg l^{-1}	Leenheer et al., 2007

The decrease in ammonia-N during nonmonsoon (Figure 4.3) largely highlighted the absence of constant input from land through rain. The highest concentration of ammonia-N obtained was during monsoon by the ferry station 4, and this certainly corresponded to mixing up of components from humanly interfered land, and pointed to some sort of pollution from the local areas of the ferry. The uniformity in ammonia-N during monsoon by all stations except ferry station 4 could be because of the dilution effect owing to rainfall. The hike observed for station 5 on passing from monsoon to nonmonsoon can be viewed as the impact of anthropogenic perturbation brought by this riverine region on account of its vicinity to Chalakudy town. Higher (0.81mg/l) ammonia determined during low water levels, and lower value (0.32 mg/l) during high water levels in the Danube River floodplain (Kopac ki Rit, Croatia) (Palijan and Fuks, 2006) which is similar to the observation at station 5. Generally, surface concentrations were slightly higher, though exceptions were there. This upward shift in water quality with respect to ammonia must have been reinforced by the combined effects of natural processes such as changes in hydroperiods and in total precipitational inputs, and anthropogenic processes like the disposal of agricultural, municipal and industrial wastes, etc. The maximum permissible concentration of ammonia for drinking water is 0.39 mgl^{-1}, whereas the median value reported for unpolluted waters is 0.015 mgl^{-1} (Meybeck, 1982). So it may be concluded that the waters of Chalakudy river were not at the threat of pollution as far as the concentration of ammonia (0.13$\mu moll^{-1}$ to 4.52 $\mu moll^{-1}$) was concerned.

The difference in DIN concentrations (Figure 4.4) at the waterfalls stations 2 and 3 pointed out that the pollutants getting added to the vicinity of station 3 where the sample collection had been made from riverine portion of the waterfalls. Station 2 was actually the waterfalls, and thereby less human interfered and the least polluted. The ferry station 4 was the most contaminated with respect to DIN, probably due to the discharges from the plantations and factories located on its banks. Constant mixing with sea water might be the factor responsible for the low values at the estuary. Also, burial of DIN may take place within estuaries, and rates differ between different estuarine habitats (Valiela et al., 2004).

Urea is a major organic nutrient as far as certain stations of Chalakudy river are concerned and this could be supported by reported studies using labelled urea, which demonstrated preference for strong uptake of the DON forms over DIN in some instances (Tremblay et al., 2000; Berg et al., 2001). There was a distinguished difference among the concentrations with appreciably higher concentrations of urea-N in the reservoir, and riverine points, whereas waterfalls and estuary had minimum amounts (Figure 4.5). The leaching out of urea from agriculture land through runoff and human intrusion was solely responsible for the enhancement of urea. For surface and bottom waters, the concentrations of urea-N apparently remained closer and this can be viewed as the fact that the shallowness of the waterbody largely facilitated a constant recycling. For the estuarine station 8, the bottom concentration was higher during monsoon, but nonmonsoon showed much lesser urea-N for bottom waters. This deviation in concentration between surface and bottom waters of the estuary might be because of the continuous mixing with sea water.

It is prominent from the graphs (Figure 4.6) that the peak amount of total N was observed at the ferry station 4, and the least amount at the estuarine end. The linkage of fertilizer utilization and factory effluents to nitrogen inputs from land to river accounted for the high values, and thus, locality could be solely responsible for the high N at the ferry. More intensive agriculture and animal husbandry led to usually high TN content in rivers (European Communities DG II: 1997). Free intrusion of Arabian sea waters certainly reduced the total N values at estuary. During heavy rains and floods, nutrients enter river system. Station 2 had very low values of total N for both seasons probably because of least pollution in the area and also due to the fact that nutrient load retained during floods could be inversely proportional to flood magnitude in rainy season.

The term residual N primarily consists of dissolved organic nitrogen (DON), which is a growing area of research, especially in drinking water supplies (Westerhoff and Mash, 2002). DON is primarily composed of degraded amino sugars, peptides and porphyrins (Leenheer, 2004: Leenheer et al., 2007). The amino sugar component of DON is considerably larger in molar mass than aquatic fulvic acids (Leenheer et al., 2000). Peptides and amino acids have both amphoteric and amphiphilic properties. The ferry station 4 was quite different in that it had a significantly high DON component (Figure 4.7), just like the DIN. Bottom and surface waters had the concentrations remaining identical, with the exception of station 5 during monsoon and stations 1, 4 and 6 during non monsoon. The difference in concentrations of residual-N of surface and bottom waters of certain stations could be based on the likely chemical and physical properties of DON at different depths. Spatio-temporal variability of residual-N does not show any particular trend, thus pointing to the different point sources of organic matter being introduced into the waterbody.

Stationwise abundance of nitrogen species (in percentage)

During monsoon, it could be seen from the percentage graphs (Figure 4.8a) that nitrite-N was $\leq 3\%$ at all stations. The estuarine regions (7 and 8) recorded comparatively more percentage of nitrite-N, whereas all other non saline stations recorded lesser nitrite-N. The percentage of nitrate-N was found to be between 64% and 78% in all riverine regions, except the estuarine region where it decreased to 55/57%. The estuarine mixing processes were primarily responsible for the comparatively low nitrate values. Ammonia-N was in between 8% and 18% taking all stations into consideration. The percentage concentration of urea was between 4% and 8% for the riverine stations (1 to 6) and it was about 15% for the estuarine stations. The residual- N varied between 5 to 14 %. The ferry station 4 depicted the highest residual-N compared to other stations, substantiating the introduction of more organic fractions mainly of anthropogenic origin into the vicinity of this station.

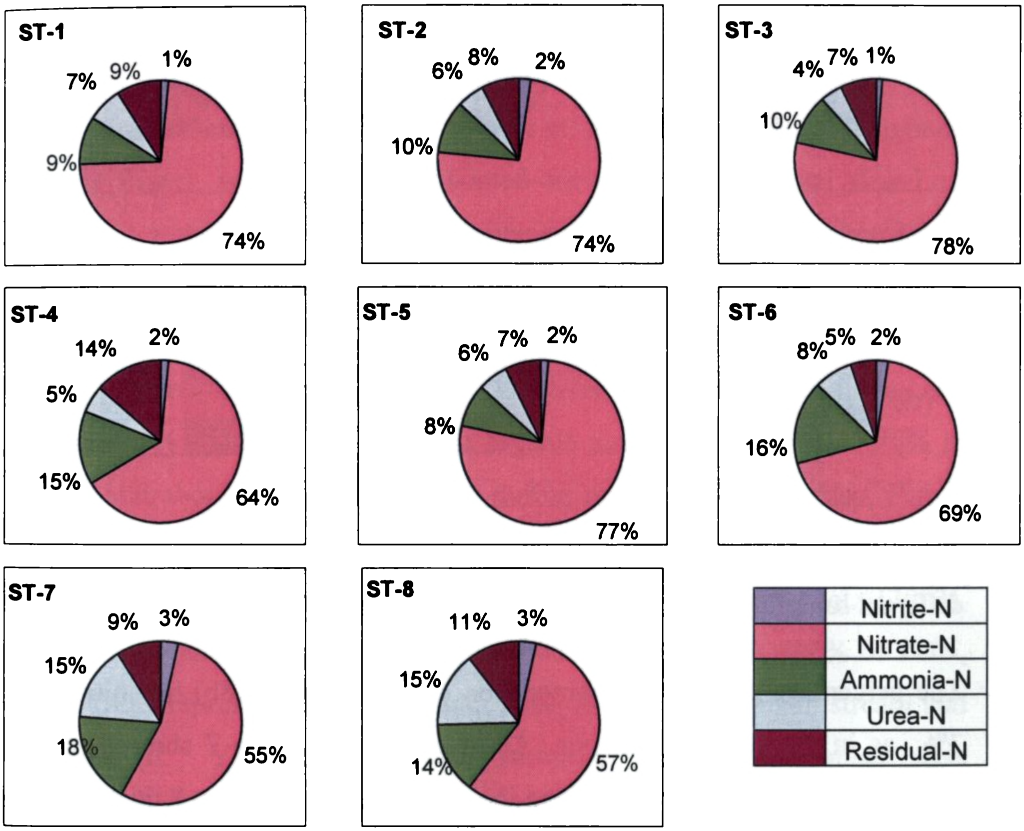

Figure 4.8a Percentage-wise distribution of dissolved nitrogen species in different sampling stations of Chalakudy river during monsoon season.

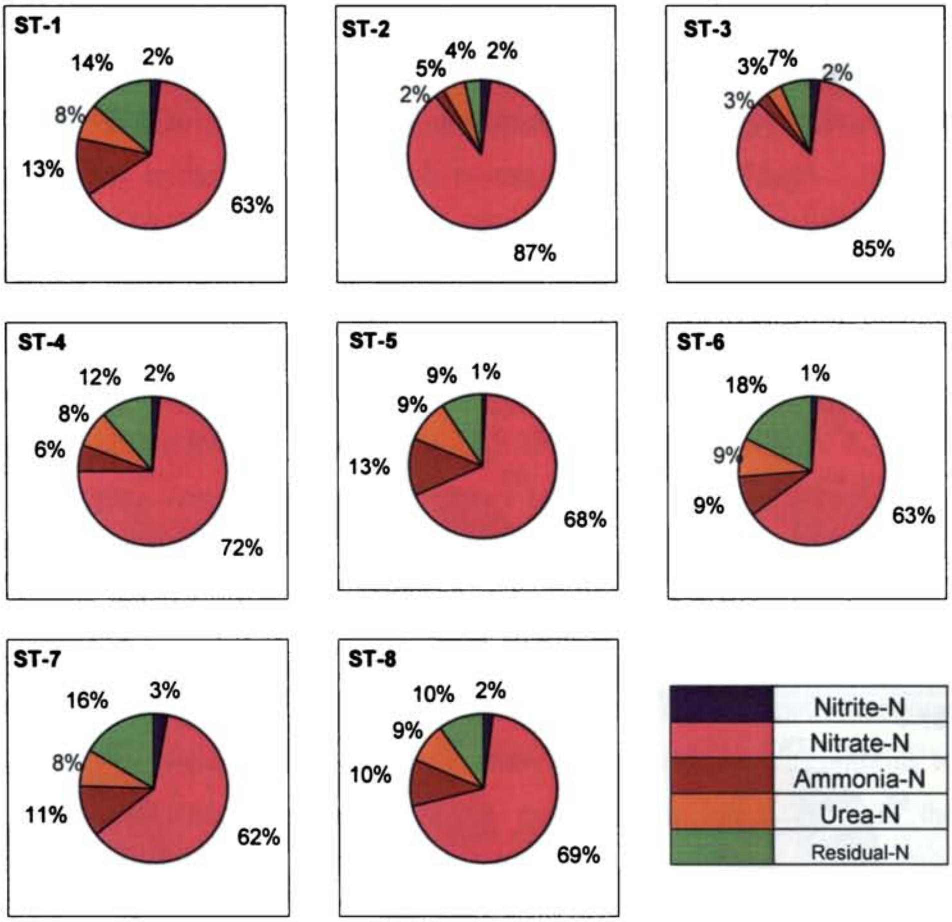

Figure 4.8b Percentage-wise distribution of dissolved nitrogen species in different sampling stations of Chalakudy river during nonmonsoon season.

The percentage graphs of nonmonsoon season (Figure 4.8b) had nitrite-N ≤ 3% as in the case of monsoon. As in monsoon, station 7 showed slightly higher percentage of nitrite-N than the other stations. Station 8 decreased the percentage of nitrite on passing from monsoon to nonmonsoon. The percentage concentration of nitrate-N was in between 62 to 87%. The nitrate was the major contributor of total-N in all the regions, the nitrate in waterfalls stations getting the highest proportion. The percentage concentration of ammonia-N was much lowered during nonmonsoon period especially at the waterfalls stations 2 (2%) and 3 (3%) and the ferry station 4 (6%), and the other stations had it ranging from 9 to 13%. These decrease might be due to the variation in land runoff through rain. The percentage of urea for the riverine as well as estuarine stations ranged from 3 to 9%. Thus, it was decreasing significantly at stations 7 and 8 on entering nonmonsoon season which supports the prevalence of seasonal chemo-estuarine variability. The residual N was ranging from 4 to 18%, and high percentage was obtained from stations 1, 6 and 7.

Similar observations were reported by Liu et. al. (2003) in the Changjiang (Yangtze River), where nitrate accounted for upto 86% of total dissolved nitrogen in a region inland from the river mouth, and ammonia contributed significantly to no more than 20% of total-N towards inland region in Yangtze River. It could be seen from the Figure 4.8a that DIN formed about 81 to 87% in the first 6 riverine stations of Chalakudy river, whereas, the estuarine end had about 75% of it and the dissolved organic nitrogen (DON) was ≤20% in the river and about 25% in the estuary during monsoon season. Also, Figure 4.8b showed DIN to be ranging from 73 to 91% with the DON getting 9 to 27% share during nonmonsoon period. According to Liu et al. (2003), dissolved inorganic nitrogen (DIN) accounted for most, at 80–100% of TDN, and the DON represented no more than 20% of TDN in the main stream and tributaries of Yangtze River. On summing up the percentage wise distributional characteristics of dissolved nitrogen in Chalakudy river, nitrate formed the major contributor to DIN with 72 to 89% during monsoon and 81 to 95% during nonmonsoon period. Ammonia formed 9 to 24% of DIN in monsoon and 2 to 16% of DIN in nonmonsoon period. Nitrite formed the least share to DIN during both seasons with ≤ 2.5% share in the riverine stations 1 to 6, and 3 to 4% towards the estuarine end.

Distributional characteristics of different forms of phosphorus

Phosphorus (P) is a key nutrient in river ecosystem, and is an essential nutrient for living organisms. The external and internal loading of phosphorus are factors of major concern with respect to eutrophication control. Phosphorus occurs in dissolved organic and inorganic forms. Only the forms of phosphorus that may be assimilated by algae, play a direct role in eutrophication. However, some forms of phosphorus (not available directly) may be transformed to bioavailable orthophosphates (Hauer et al., 2007). Phosphorus in different forms as orthophosphate, total-P and residual-P were analysed from waters of Chalakudy river. The bimonthly distributions (in μmoll^{-1}) are produced in Tables 4.4 and 4.5.

Table 4.4 Bimonthly distribution of phosphate-P, total-P and residual-P (in μmoll^{-1}) in the surface waters of Chalakudy river

Parameter	Season	STATIONS							
		S1	S2	S3	S4	S5	S6	S7	S8
Phosphate-P	May	0.35	0.63	0.76	0.82	0.99	0.54	0.71	0.49
	Jul	1.18	1.40	2.00	1.40	1.44	1.30	1.62	1.76
	Sep	1.69	0.81	1.88	1.78	2.00	1.45	0.64	0.54
	Nov	0.66	0.56	0.56	0.73	0.56	0.59	0.71	0.93
	Jan	0.54	0.44	0.47	0.56	0.47	0.59	0.76	1.49
	Mar	0.64	0.71	0.59	0.71	0.61	0.78	0.81	0.83
Total-P	May	0.47	0.66	0.85	0.92	1.10	0.64	0.90	0.65
	Jul	1.31	1.48	2.11	1.52	1.51	1.61	1.64	1.90
	Sep	1.74	0.87	2.03	1.89	2.15	1.61	0.75	0.66
	Nov	0.81	0.62	0.77	0.86	0.73	0.64	1.01	1.05
	Jan	0.69	0.48	0.50	0.69	0.55	0.66	0.92	1.65
	Mar	0.71	0.72	0.62	0.82	0.63	0.85	0.89	0.93
Residual-P	May	0.12	0.03	0.09	0.1	0.11	0.1	0.19	0.16
	Jul	0.13	0.08	0.11	0.12	0.07	0.31	0.02	0.14
	Sep	0.05	0.06	0.15	0.11	0.15	0.16	0.11	0.12
	Nov	0.15	0.06	0.21	0.13	0.17	0.05	0.3	0.12
	Jan	0.15	0.04	0.03	0.13	0.08	0.07	0.16	0.16
	Mar	0.07	0.01	0.03	0.11	0.02	0.07	0.08	0.10

Table 4.5 Bimonthly distribution of phosphate-P, residual-P and total-P (in $\mu moll^{-1}$) in the bottom waters of Chalakudy river

Parameter	Season	STATIONS S1	S2	S3	S4	S5	S6	S7	S8
Phosphate-P	May	0.35	0.63	0.76	0.92	0.71	0.67	0.71	0.70
	Jul	1.37	1.40	2.00	1.40	1.44	1.25	1.62	1.88
	Sep	1.73	0.81	1.88	1.96	2.00	1.88	0.69	0.88
	Nov	0.49	0.56	0.56	0.56	0.56	0.59	1.00	0.86
	Jan	0.42	0.44	0.47	0.44	0.47	0.66	0.76	1.32
	Mar	0.81	0.71	0.59	0.76	0.88	0.88	0.81	1.05
Total-P	May	0.47	0.66	0.85	1.08	0.96	0.72	0.90	0.86
	Jul	1.56	1.48	2.11	1.52	1.51	1.34	1.64	1.95
	Sep	1.92	0.87	2.03	2.09	2.21	1.93	0.71	0.99
	Nov	0.63	0.62	0.77	0.81	0.73	0.64	1.24	0.99
	Jan	0.51	0.48	0.50	0.58	0.55	0.72	0.92	1.50
	Mar	0.89	0.72	0.62	0.84	0.89	0.95	0.89	1.16
Residual-P	May	0.12	0.03	0.09	0.16	0.25	0.05	0.19	0.16
	Jul	0.19	0.08	0.11	0.12	0.07	0.09	0.02	0.07
	Sep	0.19	0.06	0.15	0.13	0.21	0.05	0.02	0.11
	Nov	0.14	0.06	0.21	0.25	0.17	0.05	0.24	0.13
	Jan	0.09	0.04	0.03	0.14	0.08	0.06	0.16	0.18
	Mar	0.08	0.01	0.03	0.08	0.01	0.07	0.08	0.11

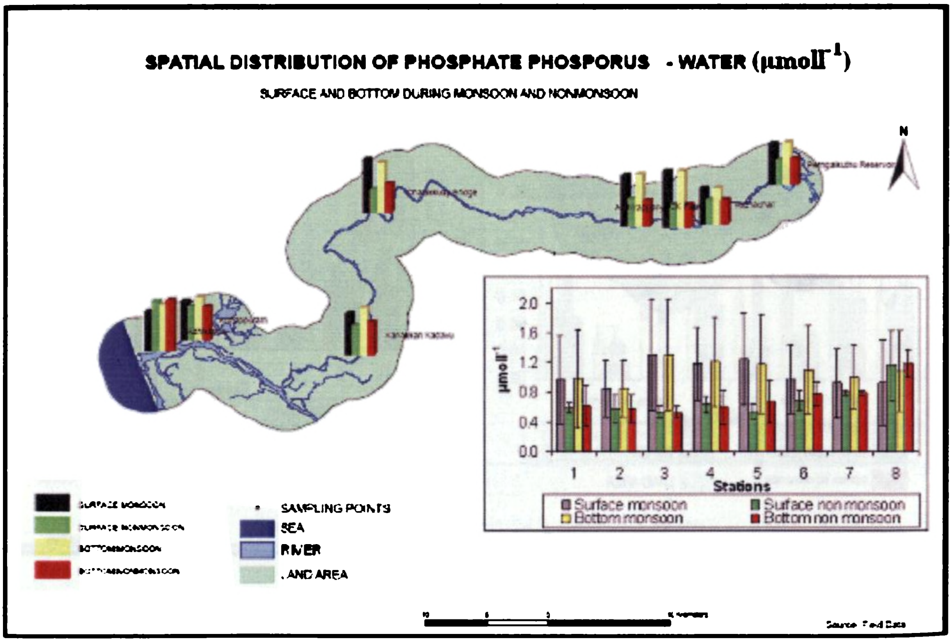

Figure 4.9 Seasonal average concentrations of dissolved phosphate-P during monsoon and nonmonsoon periods in Chalakudy river

It can be seen from Figure 4.9 that phosphate-P was higher for surface waters and lower for bottom waters. Another important point noted was that the surface mean concentrations at all stations were nearer during both seasons. Bottom values were also identical except at station 8 which displayed a hike. Standard deviation was very large for all surface stations, whereas it was lesser for bottom stations during both seasons. Generally, nonmonsoon phosphate-P was lesser compared to monsoon. The highest value obtained was 1.25 μmoll^{-1} and 1.19 μmoll^{-1} and the lowest was 0.85 μmoll^{-1} and 0.53 μmoll^{-1} during monsoon and nonmonsoon seasons respectively.

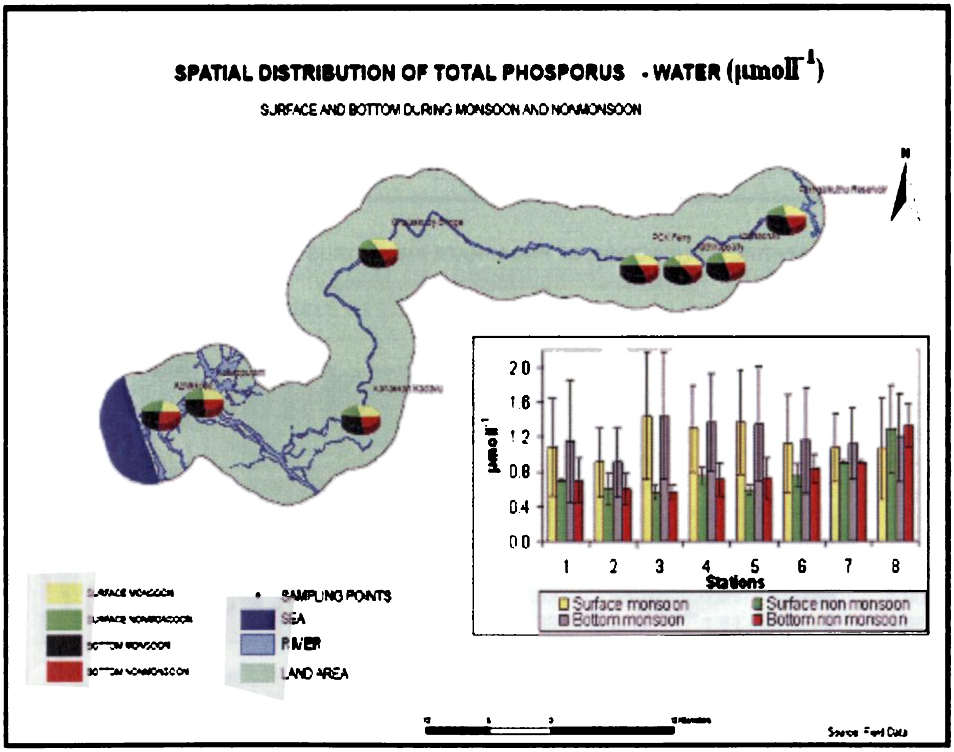

Figure 4.10 Seasonal average concentrations of dissolved total-P during monsoon and nonmonsoon periods in Chalakudy river

The total-P included all inorganic and organic forms of P. Average values ranged from 0.99 μmoll^{-1}(station 2) to 1.44 μmoll^{-1} (station 3) during monsoon and 0.56 μmoll^{-1}(station 3) to 1.33 μmoll^{-1} (station 8) during nonmonsoon (Figure 4.10). Monsoon values were higher for all stations except the estuarine region. During monsoon, station wise mean concentrations were not wildly different. A very slight decrease from reservoir to station 2 was followed by a hike at station 3. Then a steadiness was observable till estuarine end. Nonmonsoonal distributional trends were also identical from reservoir station 1 to town station 5 and afterwards a slight hike towards estuary was noticed. Monsoon showed large standard deviations in all stations, whereas nonmonsoon had notable deviation only for station 8.

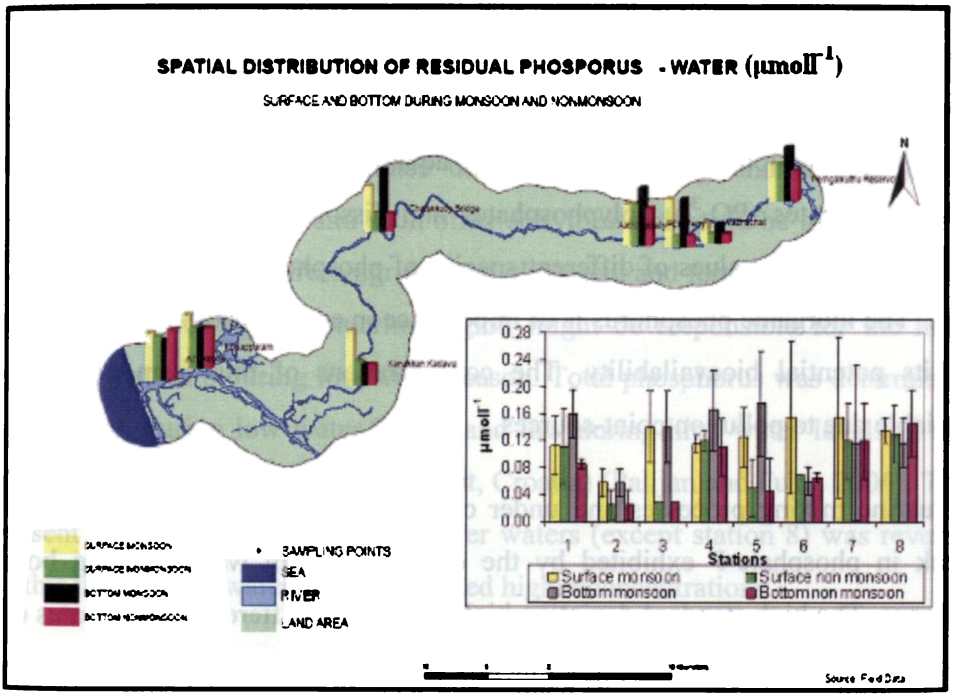

Figure 4.11 -P during

Residual-P included mainly phosphorus associated with dissolved organic compounds. It was calculated by subtracting inorganic phosphate from Total-P. The amount was found to be very low (Figure 4.11) and μmoll^{-1} to 0.18 μmoll^{-1}. Being very low to its absolute values, seasonal difference was not so specific. But still, monsoon values were slightly higher; exception was the estuarine station (8). Surface and bottom waters did not show any significant variations in its residual-P levels.

Phosphorus is the other crucial element for agricultural and numerous industrial activities (Hong et al., 2005). In rivers, soluble reactive phosphorus is derived from both point and diffuse sources, the relative contributions of which are highly variable in space and time (Jarvie et al., 2002). Emissions from point sources (i.e. municipal sewage treatment plants and large animal farms) and internal losses from the river bed play important roles. The dissolved fraction of phosphorus in aquatic systems contains mainly orthophosphates (PO_4^{3-}), polyphosphates and dissolved organic phosphorus. Global reference values of different species of phosphorus are given in Table 4.6. The inorganic phosphorus is of importance in aquatic ecosystems because of its potential bioavailability. The concentrations of this form could be variable due to pollution point-sources.

Estuarine mixing processes and under currents might be responsible for the peak in phosphate-P exhibited by the esuarine bottom waters during both seasons. The high standard deviation highlights to the difference in the rates of biochemical activities and the kinetics of phosphate uptake and release mechanisms in surface and bottom waters. The high values in monsoon is primarily accepted of the fertilizers, detergents and other chemicals being introduced into the riverine system due to land runoff. And the closeness in concentrations demanded attention to the similarity in sources which brought phosphate-P into the whole riverine system except the downstream estuary. Concentrations as low as 0.03 μmoll^{-1} in pristine waters and concentrations as high as 6.667 mmoll^{-1} in some enclosed saline waters were found by Chapman and Kimstach (1996). The dissolved phosphate-P values obtained in the present study was well in agreement with these values. Phosphate concentration in surface waters of Chalakudy river basin during 2001-2002 was reported as 0.17 to 2.66 mgl^{-1} (Chattopadhyay et al., 2005).

It was clear from Figure 4.10 that during monsoon both the minimum and maximum total-P values were recorded at waterfalls stations 2 and 3 respectively. Though, both were waterfalls, they differed entirely in P composition. Station 2 of Vazhachal, a hundred percent waterfall region, was somewhat less polluted. The station 3, just a few metres from Athirappalli waterfalls, seemed to be a place utilized for farming, animal husbandry, washing clothes, bathing and such other activities and could be interpreted as representing influences from agricultural, detergent and fertilizer runoff. Effect of sea water mixing in estuarine region might be responsible for the high values at station 8 during low water season. Total phosphorus was determined to be high during low water levels, and low during high water levels in the Danube River floodplain (Kopac ki Rit, Croatia) (Palijan and Fuks, 2006). The present observation on Chalakudy river waters (except station 8) was reverse to this in that high water levels produced higher concentrations.

Dissolved organic P is of potential importance as a nutrient source to primary producers in aquatic systems (Poder et al., 2003) and algae use dissolved organic phosphorus compounds as a source of phosphorus (Shi et al., 2004).

Organic P diagenesis plays a key role in inorganic nutrient recycling and in the transfer of energy and material to higher trophic levels. Therefore, the impact of organic P might have important consequences both on biogeochemical cycles and on trophodynamics. The very low residual-P, and the very large standard deviation showed the physicochemical changes and differences in the nature of sources of residual P, which primarily consisted of dissolved organic P, getting introduced into the Chalakudy river system.

Table 4.6 Global reference values of different species of phosphorus

Parameter	Aquatic system	Concentration	Reference
DIP	Cromarty Firth river (UK)	0.13 µmol l^{-1}	Balls, 1994
	Gt. Ouse river (UK)	9.3 µmol l^{-1}	Sanders et al., 1997
Phosphate-P	Major river systems of Macedonia	0.01 to 4.67 mg l^{-1}	Voutsa et al., 2001
	Lake Peipsi	10 µg l^{-1}	Kangur et al., 2002
	Herrington Lake river impoundment, United States	11.6 μg l^{-1} to 47 μg l^{-1}	Bukaveckas and Crain, 2002
	S'Ena Arrubia Lagoon, Central-Western Sardinia frequently	28 to to 825 mg Pm^{-3}	Trebini et al., 2005
	Mgazana estuary, Eastern Cape, South Africa	156.6 μg l^{-1}	Emmerson, 2005
	Dam site of Acton Lake, OH, U.S.A	<0.2 to >4 µmoll^{-1}	Nowlin et al., 2005
	River site of Acton Lake , OH, U.S.A	8 to 12.3 µmoll^{-1}	Nowlin et al., 2005
	Chalakudy river basin, Kerala, India	0.17 to 2.66 mg l^{-1}	Chattopadhyay et al., 2005
	Ria Formosa coastal lagoon S Portugal	0.3–16 µmol l^{-1}	Serpa et al., 2007
	Liangxihe River discharge into Meiliang Bay, Lake Taihu (China)	0.18 µmol l^{-1}	McCarthy et al., 2007
	Fenton River, Connecticut, USA	13–89 μg l^{-1}	Nadim et al., 2007
	Mount Hope River, Connecticut, USA	12–211 μg l^{-1}	Nadim et al., 2007
	Natchaug Rivers, Connecticut, USA	11–66 μg l^{-1}	Nadim et al., 2007

Parameter	Aquatic system	Concentration	Reference
Total-P	Nakdong river system, Korea	0.02–1.536 mg l^{-1}	Kim et al,1998
	Pomeranian Bay, German coast of the Baltic Sea	0.96–5.4 µmol l^{-1}	Estrum-Yousef and Schoor, 2001
	Lake Peipsi	40 µg l^{-1}	Kangur et al., 2002
	Seawater - average P content	62 µg l^{-1}	Kholodov, 2003
	S'Ena Arrubia Lagoon , Central-Western Sardinia	89 to 1220 mg Pm^{-3}	Trebini et al., 2005
	Dam site of Acton Lake, OH, U.S.A (Total-P)	<5 µmol l^{-1} to 24 µmol l^{-1}	Nowlin et al., 2005
	Danube River floodplain, Kopac ki Rit, Croatia	0.22 mg l^{-1} to 0.47 mg l^{-1}	Palijan and Fuks, 2006
	Wuli Lake, China	0.17 ± 0.052 mg l^{-1}	Jin et. al., 2006
	Sludge from Lucun Municipal Wastewater Treatment Plant (Wuxi, P.R. China).	79.8 mg l^{-1}	Zou et al., 2006
	Liangxihe River discharge into Meiliang Bay, Lake Taihu (China)	1.5 µmol l^{-1}	McCarthy et al., 2007
	Fenton River, Connecticut, USA	8–188 µg l^{-1}	Nadim et al., 2007
	Mount Hope River, Connecticut, USA	15–235 µg l^{-1}	Nadim et al., 2007
	Natchaug Rivers, Connecticut, USA	9–173 µg l^{-1}	Nadim et al., 2007
	Sahela Reservoir (Morocco)	0.009 – 0.05 mgl^{-1}	Mhamdi et al., 2007
Organic-P	Southern Baltic Sea	2.07– 10.08 µmol l^{-1}	Neddermann and Nausch, 2004
	Pawcatuck River watershed, southern New England (annual fluxes)	0.08 x 10^6 mol y^{-1}	Fulweiler and Nixon, 2005

Stationwise abundance of phosphorus forms (in percentage)

Figure 4.12a depicts the phosphorus forms in their absolute values, whereas, Figure 4.12b presents the distribution in percentage. It can be seen that the percentage composition of inorganic phosphorus was very high as compared to residual phosphorus. The composition ranged from 88 to 94% during monsoon and 84 to 96% during non monsoon. Residual-P ranged from 6 to 12% in monsoon and 4 to 16% in nonmonsoon season. No significant trend was observable since seasonal changes in composition was not prominent. It could be concluded that either the general composition of dissolved P components were not dependant on seasonal changes or land runoff during monsoon brought the P fractions in almost the same ratios.

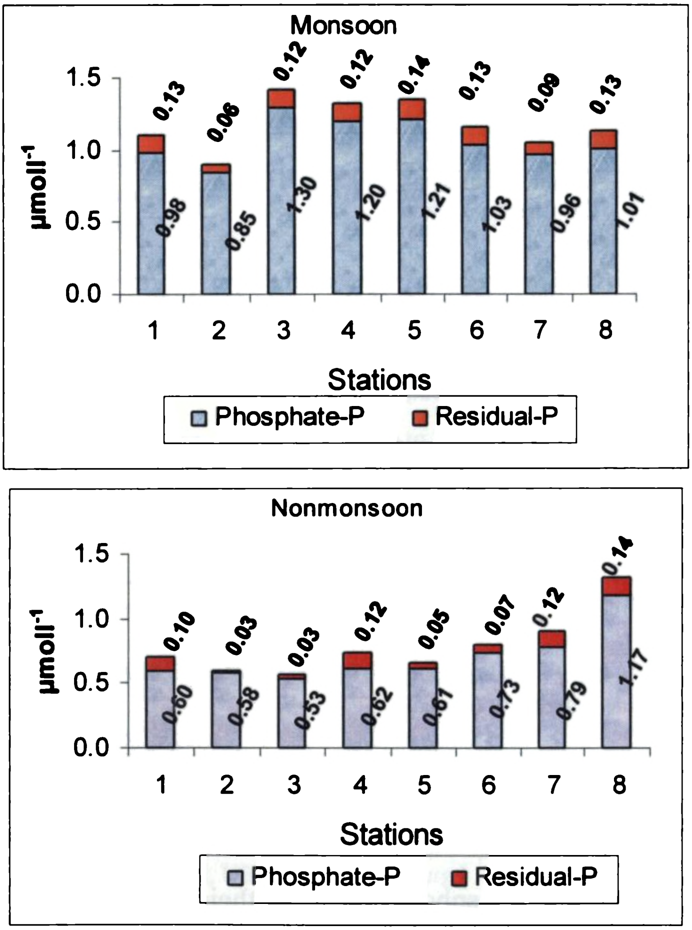

Figure 4.12a Stationwise abundance of different forms of dissolved phosphorus in absolute values during monsoon and nonmonsoon seasons

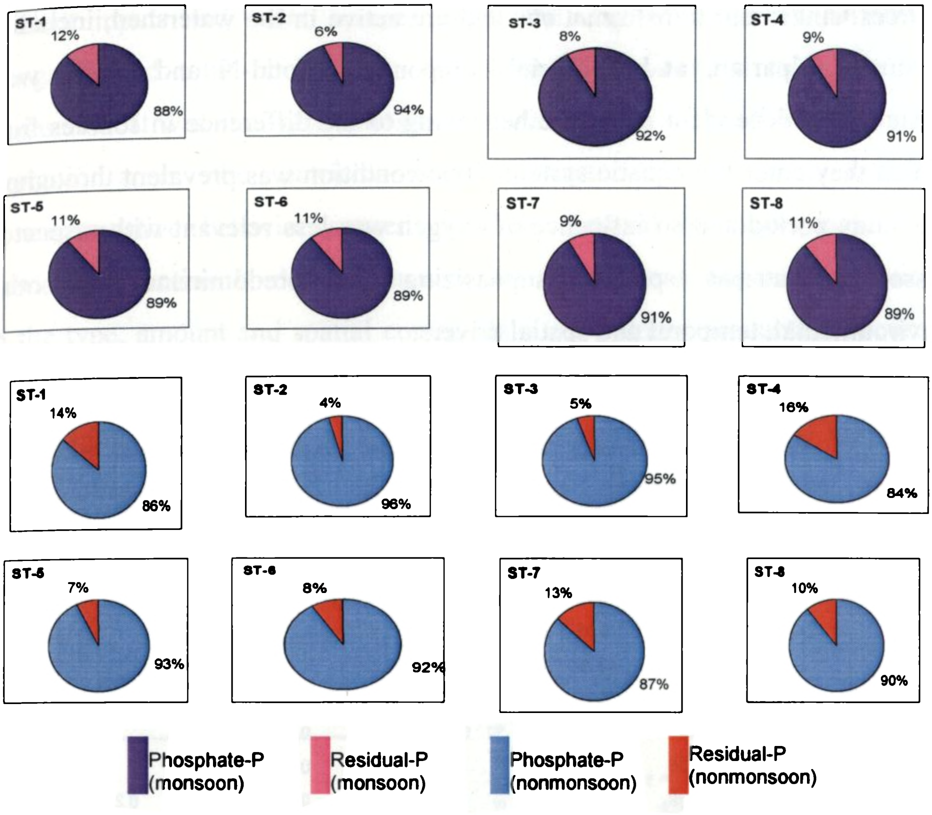

Figure 4.12b Stationwise abundance of different forms of dissolved phosphorus in percentage

Correlation

When a Pearson correlation matrix was run, some interesting significant nutrient inter-relationships were found. Most were, for example between different species of nutrients (Table 4.7). Nitrate-N was 99.9% correlated to total-N, whereas, ammonia-N and residual-N were strongly correlated to total-N . Ammonia-N and nitrate-N were significant towards each other and also to residual-N. Phosphate-P was 99.9% positive to total-P. Strong correlation among these variables confirm that there is a good proxy for nutrient concentrations and provide a highly aggregated view of the net result of sources, sinks, and transformations that are active in the watershed, including in-stream, riparian, and terrestrial components. Total-N and total-P were somewhat independent of each other owing to the difference in sources from which they enter the aquatic system. Oxic condition was prevalent throughout the study period and so influence of oxygen was less relevant with respect to dissolved nutrient species emphasizing the predominance of other environmental, temporal and spatial drivers.

Table 4.7 Pearson correlation matrix for different dissolved species

	Nitrite-N	Nitrate-N	Ammonia-N	DIN	Urea-N	Total-N	Residual-N	Phosphate-P	Total-P	Residual-P
Nitrite-N	0.36									
Nitrate-N	0.54	0.63								
Ammonia-N	0.44	0.98	0.76							
DIN	0.39	0.36	0.36	0.39						
Urea-N	0.48	0.97	0.78	0.99	0.46					
Total-N	0.46	0.66	0.70	0.72	0.37	0.79				
Residual-N	0.44	0.36	0.44	0.41	0.40	0.42	0.27			
Phosphate-P	0.45	0.38	0.45	0.42	0.41	0.43	0.27	0.99		
Total-P	0.16	0.18	0.11	0.18	0.17	0.18	0.08	0.12	0.25	
Residual-P	0.63	0.72	0.64	0.76	0.42	0.77	0.64	0.45	0.47	0.21
DO	0.49	0.50	0.32	0.50	0.13	0.47	0.21	0.39	0.38	0.01
Salinity	-0.85	-0.77	-0.88	-0.86	-0.38	-0.85	-0.60	-0.29	-0.26	0.23

On relating the knowledge of the fluxes of basic nutrients, delivered by rivers and estuaries, to the primary production is a powerful tool in the study of biochemical processes. Spatial and temporal variations of nutrient species were associated with variations in chlorophyll-a (Zvalinsky et al., 2005). The positive correlations towards chlorophyll-a were more pronounced for total-N, nitrate-N, nitrite-N, ammonia-N and residual-N (Figure 4.13). Large amounts of rainfall and water runoff have the potential to increase the levels of non point source nutrient loadings from the watersheds they affect, thus enhancing the productivity. The scatter plots showed a combination of the relative nutrient inputs and point sources along the way of the river. Dissolved inorganic and total phosphorus, did show slight decrease with plankton production. It was shown (Zvalinsky et al., 2005) that within the limits of the euphotic zone, the nutrients were characterized by a pronounced nonconservative behavior caused by their removal by phytoplankton in primary production. Under various water level conditions, important variations in the type, amount and spatial configuration of primary production occurred even if whole-system production remained approximately constant, highlighting the importance of spatial heterogeneity and temporal variability on ecological processes in large river ecosystems (Vis et al., 2007).

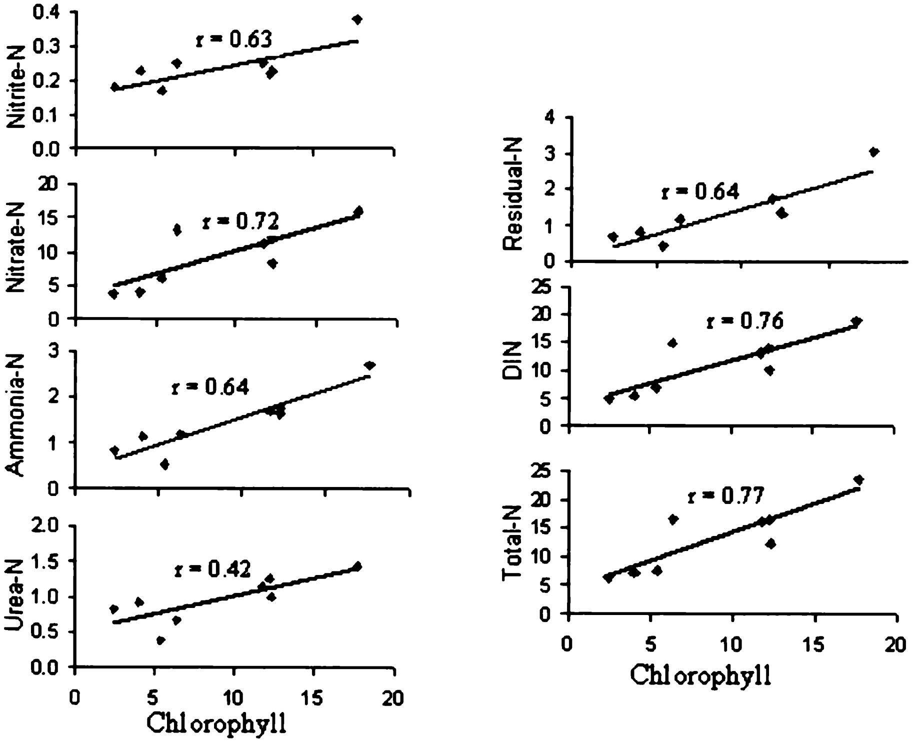

Figure 4.13 Dissolved N compositions ($\mu mol l^{-1}$) as a function of chlorophyll-a ($\mu g l^{-1}$)

Influence of salinity in estuary

Variability in water quality parameters in the estuarine end, wherein the riverine water spread into the sea was shown to be closely related to the fluctuations in the salinity, and hence nitrogen and phosphorus species behaved differently (Figure 4.14). As salinity enhanced from station 7 to station 8, concentrations of nitrogen species were found to decrease. The dependence of the concentration of nitrates, nitrites and phosphates on salinity

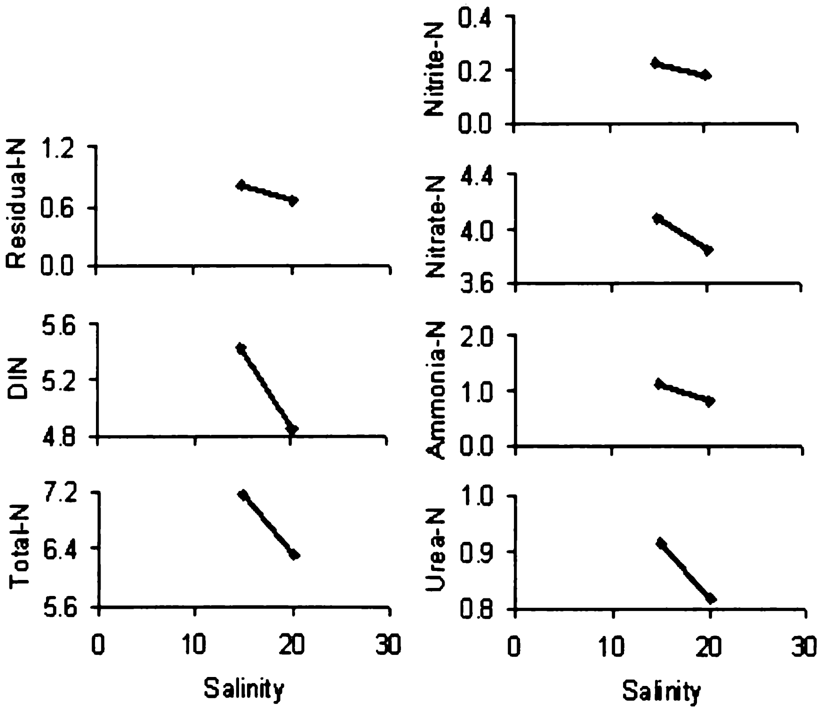

Figure 4.14 Dissolved N compositions as a function of salinity at the estuarine stations

in the estuary of Razdol'naya river declined with a linear dependence on the dilution in the first survey, whereas the dependence was pronouncedly nonlinear in the second survey which evidenced a nonconservative behavior and removal of the nutrients from the environment (Zvalinsky et al., 2005). The correlation matrix between salinity and nutrient parameters (Table 4.7) showed significant negative relation for nitrite-N, nitrate-N, ammonia-N and total-N. A common perception is that primary production in marine systems is N limited, while in freshwater systems is P limited. In freshwater systems, P limitation of production is common, partially driven by the tendency for P to form insoluble complexes and become unavailable for biological uptake, whereas in salt systems, N limitation is partially attributed to cation competition for uptake sites, sulfide toxicity- that inhibits N uptake, and N requirements for osmoregulation (Crain, 2007).

N:P ratios

Nitrate:Phosphate (N:P) ratio can be taken as an index of the extent of extraneous influence on a productive system. An indicator of coastal eutrophication potential (ICEP) of riverine nutrient inputs is proposed as their N:P:Si ratios and this represents the carbon biomass potentially produced (kg C km^{-2} day^{-1}) in the receiving coastal water body through new production sustained by the flux of nitrogen and phosphorus (according to which one is limiting with respect to the other) delivered in excess over silica (Billen and Garnier, 2007). This remains negative for most (sub-)tropical river systems.

To evaluate the eutrophication status, the N:P ratios were calculated. The concentrations of nitrate and phosphate as well as the ratio in which these two occur in the aquatic environment has become the subject of much research, since this ratio may influence the types of organisms occuring and whether or not individual species or whole communities are likely to be N- or P-limited.

Some global references from aquatic systems for N:P ratios are presented in Table 4.8.

Table 4.8 Global references for N:P ratios

Aquatic system	N:P	Reference
Major river systems of Macedonia, N. Greece	<8 to 79.7	Voutsa et al., 2001
Waters of north western Adriatic sea	30 to 83	Cozzi et. al., 2002
Rio de la Plata River Estuary System	>25	Nagy et al., 2002
Mgazana estuary, Eastern Cape, South Africa	27	Emmerson, 2005
Razdol'naya river-estuary (Amur Bay, Sea of Japan) Riverine waters Estuary	17–22 9	Zvalinsky et al., 2005

The seasonal N:P ratios were in the range from 8.83 to 21.23 for stations 1 to 6 where as the ratio remained 2.34 to 6.25 for stations 7 and 8 (Figure 4.15). The estuarine end had relatively low ratio which was much lowered towards nonmonsoon. Similar observation had been reported by Nagy et al., 2002, that nonconservative behaviour of nitrogen in estuarine system of Rio de la Plata River lead to a low N:P ratio (<3) because of both phytoplankton assimilation of nitrogen and denitrification, and benthic flux of phosphate. Also riverine waters of Razdol'naya river-estuary (Amur Bay, Sea of Japan) were specified with depleted phosphorus and high N : P ratio of 17–22, as compared to estuarine waters with low N: P ratio of 9 in estuary (Zvalinsky et al., 2005). It should be noticed that the N:P ratio simply showed the likelihood for either P or N-limitation conditions, however it was not indicative of the nutrient concentration levels (Jarvie *et al.*, 2002). Thus, ratio values >25 were reported for very clean rivers having very low N and P concentrations, and also for rivers with much higher nutrient contents, and ratio values <16 have been found in many rivers characterized as polluted, but also in rivers which have relatively low mean dissolved inorganic nitrogen and phosphate concentrations (Meybeck 1982; Jarvie *et al.*, 2002 and the references therein). N:P ratios are used as a tool for assessing nutrient limitation with low N:P ratios (<14) indicating N limitation and high N:P ratios (>16) indicating P limitation (Crain, 2007). It could be concluded that nitrogen levels were comparatively higher and phosphorus levels comparatively lower at the riverine locations 1 to 6, whereas nitrogen levels were comparatively lower and phosphorus levels comparatively higher at the estuarine end of stations 7 and 8.

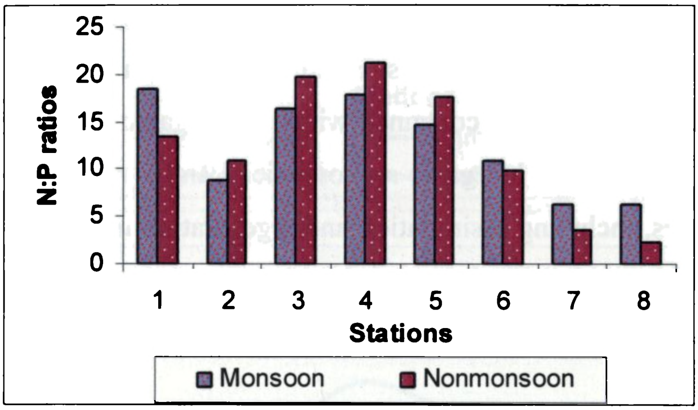

Figure 4.15. Seasonal N:P ratios in the waters of Chalakudy river

Overall summary

In rivers and estuaries, nutrients are generally the major factors that regulate primary production. Anthropogenic loading of nitrogen (N) and phosphorus (P) from industrial, municipal and agricultural sources has increased nutrient concentrations in rivers worldwide, increased production of aquatic plants, caused changes in the abundance and composition of consumers, and contributed to declines in dissolved oxygen (Smith *et al.*, 1999). The outstanding industrial growth during the past decades has brought dramatically deteriorating changes in our natural ecosystems. The discharge of municipal waste water effluent and rainwater runoff from urbanized areas are important anthropogenic nitrogen and phosphorus sources. Overall, it has been estimated that wastewater-derived nitrogen accounts for 12 to 33% of the nitrogen pollution in the rivers worldwide, while agriculture and fertilizer runoff accounts for the remainder of the anthropogenic nitrogen released to rivers (Howarth, 2004). In rivers, nitrate is derived predominantly from diffuse (agricultural) sources. The total phosphorus and nitrogen also include organically bound molecules, that is transported by rivers (Hauer et al., 2007). For blackwater rivers of the southeast U.S. coastal plain, a large portion of the nitrogen and phosphorus are contained within the organic fraction (Graves et al., 2004). The dissolved inorganic and organic N and P reflect the effects of many processes, including assimilation and regeneration in the water column, nutrient exchange with the sediments, advection processes and mixing between freshwater and seawater (Cozzi et al., 2002).

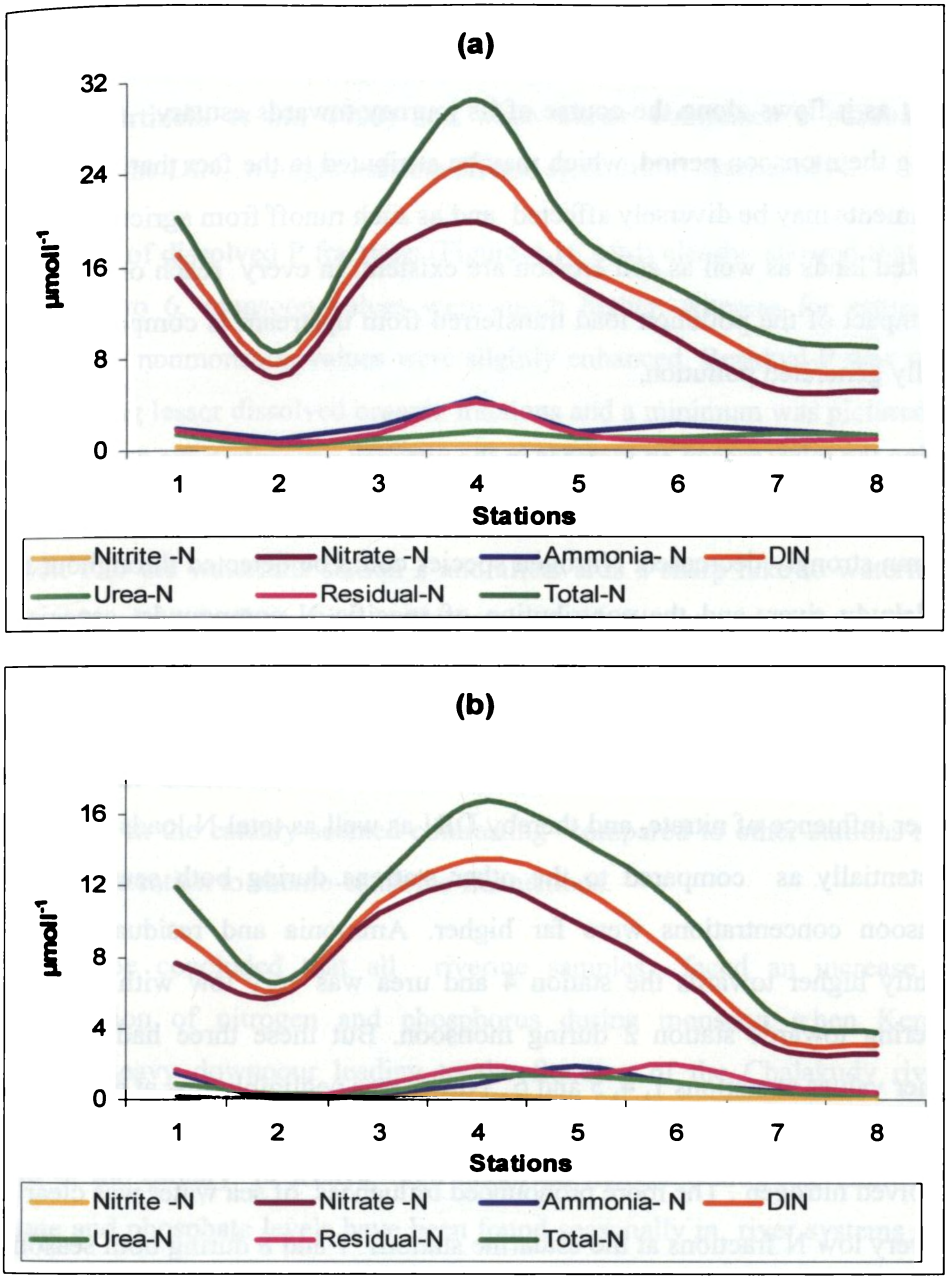

Figure 4.16(a,b). Trends of various nitrogen species in Chalakudy river during monsoon (a) and non monsoon (b) seasons.

The results of the seasonal and spatial assessments conducted on dissolved nitrogen revealed that water quality of Chalakudy river degraded to some extent as it flows along the course of its journey towards estuary, especially, during the monsoon period, which may be attributed to the fact that these sub-catchments may be diversely affected and as such runoff from agricultural and forested lands as well as soil erosion are existent. In every reach of the river, the impact of the pollution load transferred from upstream is compounded by locally generated pollution.

During the rainy season an increase in the nitrogen concentrations due to larger river inputs was encountered, while afterwards, DIN concentration in the water column strongly decreased. Nitrogen species could be detected throughout the Chalakudy river, and the contribution of specific N compounds, especially nitrate to DIN and Total-N suggests a seasonal dependency with comparatively lower values during nonmonsoon (Figure 4.16 a&b). The first, fourth and fifth stations (and stations 3 and 6 to some extent) reflected the higher influence of nitrate, and thereby DIN as well as total-N loads increased substantially as compared to the other stations during both seasons. The monsoon concentrations were far higher. Ammonia and residual-N were slightly higher towards the station 4 and urea was very low with a further lowering towards station 2 during monsoon. But these three had slightly higher values at stations 1, 4, 5 and 6 . Nitrite was negligibly low at all stations during both seasons. The waterfall station was specific in having lesser dissolved nitrogen . The more pronounced influences of sea water was clear in the very low N fractions at the estuarine stations 7 and 8 during both seasons. Also, the Periyar river is confluencing with Chalakudy river in between station 6 (Kanakkankadavu) and station 7 (Kottappuram) at Puthenvelikkara. This mixing might tremendously influence the relatively significant different nature of the waters of stations 7 and 8. The highest total-N, DIN and nitrate-N concentrations in waters could be attributed to the influence of sewage inputs (Martinelli *et al.*, 1999) and when nitrate comprised a substantial fraction of the DIN, it might indicate diffuse agricultural sources of N.

The trends of dissolved P fractions (Figure 4.16 c&d) clearly showed that for stations 1 to 6, monsoon values were much higher, whereas for estuarine stations the nonmonsoon values were slightly enhanced. Residual-P was very low showing lesser dissolved organic fractions and a minimum was pictured at station 2. The phosphate-P as well as total-P followed almost the same trend during both seasons. During monsoon, there occurred a decrease from the dam station 1 to the waterfalls station 2 and afterwards a sharp hike to waterfalls station 3, where a fluctuation could be observed till station 5 and then there was a gradual decrease to the estuarine end. But during nonmonsoon, a steadiness could be seen till station 5 (with a slight hike at stations 1 and 4) and then an enhancement towards estuary. The slightly high nonmonsoon value of P in the estuary seemed contrasting compared to other stations and focus the attention to chemo-estuarine fluctuations.

It could be concluded that all riverine samples faced an increase in concentration of nitrogen and phosphorus during monsoon when Kerala received heavy downpour leading to the flooding of the Chalakudy river. Various nitrogen forms were found to decrease slightly upstream towards the head of the estuary. In Kenya, high dissolved inorganic nitrogen, ammonia, nitrate and phosphate levels have been found seasonally in river systems and mangrove systems following rain or groundwater runoff (Kitheka et al., 1999;

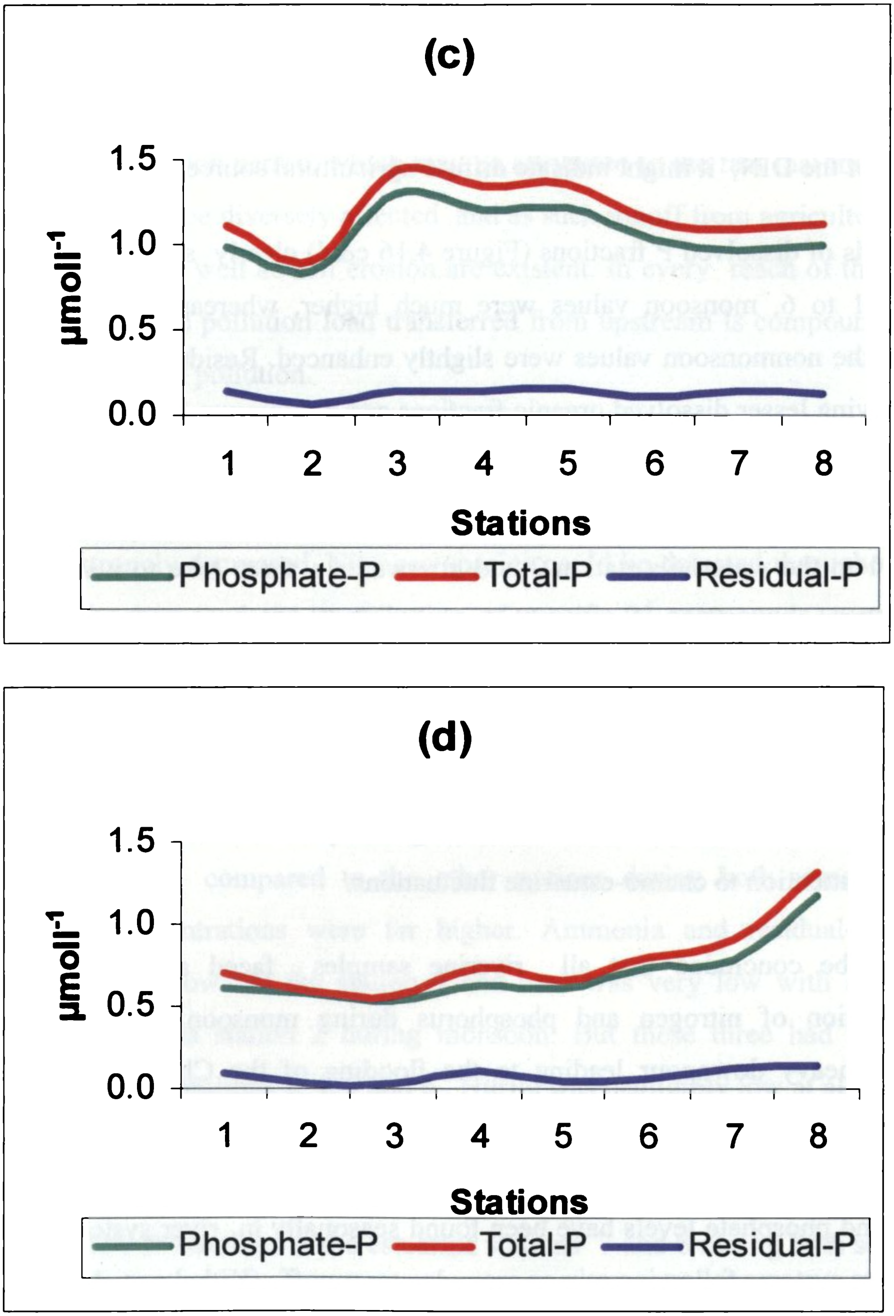

Figure 4.16(c,d). Trends of various phosphorus species in Chalakudy river during monsoon (c) and non monsoon (d) seasons.

Lara and Dittmar 1999). Changes of DIN concentration in the riverine sector were mainly related to nutrient input fluctuations from the rivers (Da Cunha and Wasserman, 2003). During floods the estuarine basin could be completely flushed of brackish water and the majority of the nutrient loads passed directly through the estuary. Estuaries mediate a large part of the nutrient flux from the land to the sea. As nutrients enter estuaries through the tributary rivers, concentrations could often be maximal in the freshwater regions, since riverine freshwater was not diluted by relatively nutrient-poor seawater (Muylaert et al., 2005).

Thus, a substantial input of nutrients was observed in Chalakudy river water. Within various locations, geographical and human activities have produced effects on the nitrogen and phosphorus loading capacity which reveals pronounced ample variability in the spatial and temporal distributions.

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CHAPTER V

NITROGEN AND PHOSPHORUS IN SUSPENDED PARTICULATE MATTER

CONTENTS

INTRODUCTION

Suspended particulate matter (SPM) in natural waters is a heterogenous, often aggregated mixture of inorganic (e.g. clays, quartz, Fe oxyhydroxides) and natural organic matter (humic) components (Beckett, 1986) spanning the particulate ($>1 \mu m$) and colloidal ($<1\ \mu m$) size ranges. It is generally a complex mix of substances of different origins with different properties (size, form, density, specific surface area, capacity to bind pollutants, etc). The suspended impurities include suspended silt and clay grains, algae and other plankton, microbes, organic matter and other fine, insoluble particulate substances. According to Hakanson (2006), suspended particulate matter seems to vary in a systematic way among and within marine/brackish systems, rivers and lakes. Turbidity due to SPM is an important water quality variable, through its relation to light suppression, biological oxygen demand impact, sediment-associated contaminant transport, and suspended sediment effects on organisms and habitats (Lawler, 2006). SPM concentrations in the water column regulate the penetration depth of light and, therefore, is an important parameter influencing the primary production of plankton. Particles other than plankton cells are also important factors.

Suspended particles are well known as a principal carrier of nutrients in the riverine and estuarine waters. Many factors are responsible for the variation in nutrient export. In addition to the geographical location of the basins, they involve different land use and climate, comprise a large range of basin sizes, and water quality can be studied under high variable sampling protocols (Salvia-Castellvi et al., 2005). External inputs that arise from land are subject to human interference (Krogerus and Ekholm, 2003). This inputs from offshore are little impacted by human activity directly, and the key determinants on the size of this input are physical exchange process. These vary with large-scale ocean circulation in estuaries and well influenced by climate change processes as wind and rain in the aquatic system as a whole, and hence are indirectly impacted by human activity.

The transport of material from rivers to the sea is part of the global cycle of nutrients. Nutrient over-enrichment of fresh and coastal waters is of concern because it can alter the competitive balance of aquatic species, sometimes leading to potentially toxic and unsightly algal blooms (Whitehead et al., 2006). An important aspect which determines the concentration of nutrients in the SPM of rivers and estuaries involves vertical exchange processes and horizontal advection, due to currents and waves as the diffusion of SPM in the water column, sedimentation, resuspension, and erosion at the bottom interface, sinking of particles as well as processes of consumption and bioturbation in the water column (Gayer et al., 2006). Identification of the nutrient export through SPM is therefore necessary to understand and categorize nutrient origins and transport mechanisms and assess effective conservation/remediation measures to improve water quality. It is unclear, however, whether resuspended N and P are important in terms of eutrophication, i.e. is it available to algae. Appropriate spatial and temporal scale resolutions are required to correctly identify the principal nutrient sources and the principal factors involved in nutrient transport. Nutrient concentrations as well as physiological characteristics of the vegetation (e.g. NH_4^+ preference, NO_3^-storage), usually regulate the rate of N-uptake into the particulate pool (Schulz and Gucker, 2005). An endeavor is made in this chapter to get an insight into the species of nutrients in the suspended particulate matter of Chalakudy river. The goal of the present study is to examine and quantify the forms of nitrogen and phosphorus in suspended solids.

MATERIALS AND METHODS

The details of methodology adopted for analyses and speciation of particulate nutrients are described in Chapter II. Particulate matter were isolated by vacuum filtering a 500 ml of each river water sample (Section 2.2) through a precombusted (450^{0}C, 4 hours) glass fiber filter (25 µm. GF/F, Whatman). The nutrient concentrations (various species of inorganic nitrogen and phosphorus) were analyzed. Speciation of nitrogen is done as nitrite-N, nitrate-N, ammonia-N and urea-N, and the total N is also determined. Difference between total N and the other four species (NO_2^--N, NO_3^--N, NH_3-N and urea-N) determined is presented as residual-N, which contains mainly organic forms of N other than particulate urea. Fractionation of P in its inorganic forms was studied by applying the sequential chemical extraction procedure mentioned in Chapter II. The major forms of inorganic phosphorus analysed were loosely bound P, Fe/Al bound P, polyphosphates, Ca bound P and refractory P. Schematic representation of the speciation is also given in Chapter II. Sum of these five forms is presented as total inorganic P.

RESULTS AND DISCUSSIONS

The river water is characterized by comparatively high concentrations of suspended solids, and particulate loads of nitrogen and phosphorus. The external inputs of nutrients in the form of particulate matter, and their contribution to the nutrient status of the Chalakudy riverine segment are addressed in this section. The objectives of the present study are to

- investigate the occurrence of different particulate N and P forms in suspended particulate samples identified by recognized sequential extraction procedures
- evaluate and compare the seasonal and stationwise contributions of the different forms of nitrogen and phosphorus in SPM
- discuss mechanisms which may explain the changing concentrations of different forms of N and P in particulate phase
- assess the contribution of suspended sediment transport and other suspended impurities during runoff to the annual bioavailable N and P loads of River Chalakudy

Spatiotemporal dependence: Nitrogen

Nitrogen dynamics in the suspended particulate matter of the waters of Chalakudy river is described below. The primary data for the quantitative determination of different species of nitrogen in SPM for surface and bottom waters (in μmoll^{-1}) are presented in Tables 5.1 and 5.2 respectively. Seasonal trends concerning each species are pictured graphically (Figure 5.1). The nitrogen distribution in particulate matter occurred in different forms, and nitrite-N, nitrate-N, ammonia-N and urea-N (in μmoll^{-1}) were determined quantitatively from KCl extractions. Total-N was also determined after digesting the filtered particulate matter. Residual-N was calculated as the difference of total-N and sum of the other four forms.

Table 5.1 Bimonthly distribution of nitrite-N, nitrate-N, ammonia-N, urea-N, residual N and total N (in μmoll^{-1}) in the particulate matter of surface waters of Chalakudy river

		Stations							
Parameter	Period	S1	S2	S3	S4	S5	S6	S7	S8
Nitrite-N	May	0.104	0.077	0.011	0.088	0.079	0.015	0.048	0.009
	Jul	0.032	0.009	0.012	0.028	0.023	0.031	0.034	0.028
	Sep	0.014	0.012	0.003	0.016	0.005	0.044	0.029	0.02
	Nov	0.05	0.046	0.041	0.043	0.036	0.077	0.039	0.077
	Jan	0.012	0.011	0.023	0.004	0.011	0.052	0.032	0.023
	Mar	0.037	0.027	0.01	0.007	0.01	0.03	0.011	0.012
Nitrate-N	May	0.44	0.57	0.65	0.67	0.68	0.37	0.35	0.34
	Jul	0.89	1.26	0.66	0.88	0.74	0.74	1.24	1.22
	Sep	0.77	0.57	0.38	0.49	1.09	0.98	0.64	0.47
	Nov	0.77	0.6	0.69	0.67	0.7	0.77	2.42	0.83
	Jan	0.43	0.34	0.35	0.21	0.53	0.55	0.55	0.59
	Mar	0.41	0.31	0.44	0.27	0.34	0.36	0.44	0.36
Ammonia-N	May	0.12	0.12	0.18	0.13	0.15	0.02	0.19	0.15
	Jul	0.24	0.13	0.15	0.1	0.23	0.13	0.11	0.19
	Sep	0.25	0.15	0.16	0.11	0.24	0.17	0.18	0.15
	Nov	0.07	0.24	0.12	0.12	0.28	0.18	0.14	0.1
	Jan	0.02	0.06	0.04	0.02	0.07	0.11	0.04	0.13
	Mar	0.1	0.07	0.16	0.06	0.05	0.09	0.03	0.1
Urea-N	May	0.11	0.03	0.11	0.09	0.31	0.16	0.23	0.09
	Jul	0.17	0.12	0.14	0.13	0.27	0.09	0.5	0.14
	Sep	0.13	0.18	0.2	0.19	0.16	0.3	0.26	0.16
	Nov	0.05	0.08	0.05	0.06	0.23	0.15	0.11	0.15
	Jan	0.15	0.07	0.12	0.05	0.11	0.07	0.18	0.05
	Mar	0.06	0.01	0.02	0.03	0.05	0.04	0.03	0.06
Total-N	May	0.99	0.87	1.02	1.16	1.27	0.78	1.18	0.77
	Jul	1.58	1.61	1.01	1.33	1.52	1.31	2.11	1.86
	Sep	1.35	1.02	0.78	1.02	1.81	1.70	1.37	1.09
	Nov	0.98	0.99	1.03	1.16	1.37	1.29	3.03	1.42
	Jan	0.79	0.55	0.65	0.44	0.81	1.07	0.92	0.92
	Mar	0.90	0.49	0.74	0.51	0.55	0.77	0.65	0.79
Residual-N	May	0.22	0.07	0.07	0.18	0.05	0.22	0.36	0.18
	Jul	0.25	0.09	0.05	0.19	0.26	0.32	0.23	0.28
	Sep	0.19	0.11	0.04	0.21	0.32	0.21	0.26	0.29
	Nov	0.04	0.02	0.13	0.27	0.12	0.11	0.32	0.26
	Jan	0.18	0.07	0.12	0.16	0.09	0.29	0.12	0.13
	Mar	0.29	0.07	0.11	0.14	0.10	0.25	0.14	0.26

Table 5.2 Bimonthly distribution of nitrite-N, nitrate-N, ammonia-N, urea-N, residual N and total N (in $\mu moll^{-1}$) in the particulate matter of bottom waters of Chalakudy river

		Stations							
Parameter	Period	B1	B2	B3	B4	B5	B6	B7	B8
Nitrite-N	May	0.104	0.077	0.011	0.075	0.074	0.042	0.048	0.019
	Jul	0.03	0.009	0.012	0.028	0.023	0.045	0.034	0.014
	Sep	0.013	0.012	0.003	0.03	0.025	0.029	0.03	0.013
	Nov	0.04	0.046	0.041	0.05	0.036	0.077	0.043	0.057
	Jan	0.016	0.011	0.023	0.018	0.011	0.036	0.032	0.012
	Mar	0.077	0.027	0.01	0.012	0.003	0.007	0.011	0.037
Nitrate-N	May	0.44	0.57	0.65	0.56	0.68	0.33	0.35	0.34
	Jul	0.77	1.26	0.66	2.04	0.74	1.1	1.24	1.38
	Sep	0.75	0.57	0.38	0.62	1.46	0.86	1.79	0.58
	Nov	0.67	0.6	0.69	0.67	0.7	0.77	3.34	0.45
	Jan	0.73	0.34	0.35	0.42	0.53	1.25	0.55	0.67
	Mar	0.98	0.31	0.44	0.35	0.76	1.28	0.44	0.36
Ammonia-N	May	0.12	0.12	0.18	0.16	0.18	0.03	0.19	0.17
	Jul	0.35	0.13	0.15	0.14	0.23	0.16	0.11	0.26
	Sep	0.28	0.15	0.16	0.18	0.27	0.22	0.24	0.26
	Nov	0.12	0.24	0.12	0.18	0.28	0.18	0.26	0.19
	Jan	0.07	0.06	0.04	0.09	0.07	0.16	0.04	0.13
	Mar	0.18	0.07	0.16	0.08	0.08	0.11	0.03	0.17
Urea-N	May	0.11	0.03	0.11	0.18	0.38	0.26	0.23	0.17
	Jul	0.2	0.12	0.14	0.16	0.27	0.12	0.5	0.18
	Sep	0.15	0.18	0.2	0.24	0.31	0.16	0.11	0.18
	Nov	0.13	0.08	0.05	0.15	0.23	0.15	0.19	0.22
	Jan	0.12	0.07	0.12	0.07	0.11	0.13	0.18	0.19
	Mar	0.09	0.01	0.02	0.09	0.07	0.15	0.03	0.12
Total-N	May	0.99	0.87	1.02	1.47	1.38	0.78	1.18	0.79
	Jul	1.55	1.61	1.01	2.62	1.52	1.58	2.11	2.15
	Sep	1.41	1.02	0.78	1.33	2.21	1.48	2.24	1.19
	Nov	1.04	0.99	1.03	1.23	1.37	1.29	3.95	1.02
	Jan	1.17	0.55	0.65	0.79	0.81	1.80	0.92	1.11
	Mar	1.59	0.49	0.74	0.72	1.02	1.79	0.65	0.89
Residual-N	May	0.22	0.07	0.07	0.50	0.07	0.12	0.36	0.09
	Jul	0.20	0.09	0.05	0.25	0.26	0.16	0.23	0.32
	Sep	0.22	0.11	0.04	0.26	0.15	0.21	0.07	0.16
	Nov	0.08	0.02	0.13	0.18	0.12	0.11	0.12	0.10
	Jan	0.23	0.07	0.12	0.19	0.09	0.22	0.12	0.11
	Mar	0.26	0.07	0.11	0.19	0.11	0.24	0.14	0.20

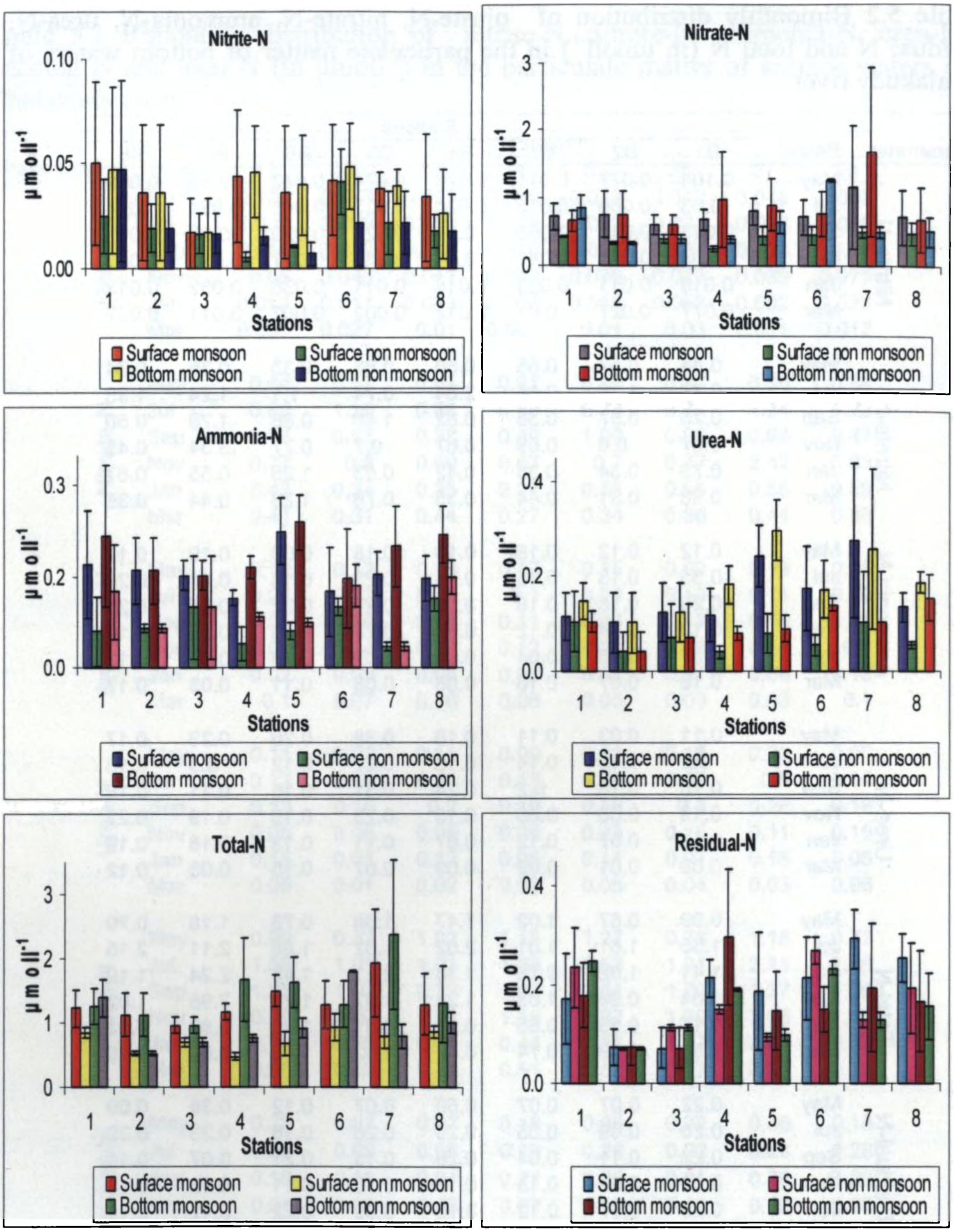


Figure 5.1 Seasonal average concentrations of nitrite-N, nitrate-N, ammonia-N, urea-N, total N and residual N in the SPM of Chalakudy river

Figure 5.1 depicted the seasonal average concentrations of nitrite-N, nitrate-N, ammonia-N, urea-N, total N and residual N in the SPM of Chalakudy river. The concentrations of nitrite-N of the particulate matter (in μmoll^{-1}) were found to be negligibly small. The surface and bottom SPM recorded concentrations between 0.01 to 0.05 μmoll^{-1} during both seasons. Since particulate nitrite values are very low, it would not be appropriate to draw any conclusive statements for its seasonal / depth variables, based on the results presented in the figure. Nonmonsoon season showed a general decrease at all stations. A decrease happened for surface particulate from station 1 to station 4 where it was minimum, and then enhanced sharply at station 6 and afterwards, a decrease occurred towards estuary. But, the bottom particulate had a high value at reservoir, decreased to a minimum at station 5 and then slightly increased at the estuarine end.

Appreciable concentrations of nitrate–N were determined in the particulates of Chalakudy river. The monsoon values were high and ranged from 0.60 to 1.68 μmoll^{-1}. The low nonmonsoon values ranged from 0.24 to 1.27 μmoll^{-1}. The surface and bottom particulates during monsoon exhibited almost a steady value except at station 7 which had a hike. The values of particulate nitrates in surface waters during nonmonsoon exhibited a consistent and increasing trend towards the estuary with a sink low only at station 4. The bottom particulate nitrates had higher values at stations 1 and 6, and all other stations had lesser values.

The concentrations of ammonia–N were low in the SPM of Chalakudy river. The values were much lowered in nonmonsoon and the trend was different for surface and bottom suspensates. The ammonia concentration in particulate matter was too low to draw a relevant trend. Heavy rainfall events could sometimes result in increased runoff which increases the SPM, and thereby ammonia-N during monsoon season. The lowest concentration of 0.12 μmoll^{-1} was depicted at station 4 and the highest was recorded to be 0.24 μmoll^{-1} at station 5 during the monsoon season. The nonmonsoon season showed the lowest ammonia-N concentration of 0.04 μmoll^{-1} (stations 4 and 7) and the highest was 0.14 μmoll^{-1} (station 6).

The particulate levels of urea-N exhibited a fluctuating trend with a slight increase at certain stations. The mean values of particulate urea-N ranged from 0.10 μmoll^{-1} to 0.30 μmoll^{-1} during monsoon and 0.04 μmoll^{-1} to 0.16 μmoll^{-1} during nonmonsoon. The bottom particulate matter had slightly higher urea-N though exceptions were there with almost identical surface and bottom values. Stations 5 and 7 exhibited slightly high values during the monsoon season. During monsoon, the mean urea-N values of both surface and bottom SPM maintained a steadiness from reservoir to ferry, then alternately increased and decreased towards the estuarine region. High fluctuations were noticeable in the mean values at station 7. The surface and bottom particulate urea behaved differently in nonmonsoon season. The surface urea-N had zig-zag values among the stations from reservoir to estuary. But the bottom particulate urea distribution exhibited a decrease from station 1 to 2, then gradually increased till station 6, followed by more or less high values at the estuarine boundary.

The lowest values reported for total-N in SPM were 0.96 and 0.52 μmoll^{-1} and the highest values were 2.37 and 1.80 μmoll^{-1} for monsoon and nonmonsoon seasons respectively. No significant trend was observable. High values were observable at stations 7 during monsoon. Bottom SPM had slightly higher Total-N. During monsoon period, higher values at the

the reservoir were gradually decreased to station 3 and then varied intermittently, for both surface and bottom SPM. Wide deviations in mean values were observed for SPM of station 7. Station 1 had high value of particulate N load in nonmonsoon of surface SPM which sporadically changed till station 5, which followed a fluctuating trend towards the estuarine limit. The N– enriched bottom particulate of the reservoir station is noteworthy to mention, and also the estuarine stations, apart from the ferry station 4.

Residual-N in SPM was calculated as the difference of Total-N and the sum of other four forms of N and mainly comprises organic forms, other than urea. Low residual-N values were observed in the particulate of Chalakudy river (Figure 5.1). The concentrations were ranging from 0.07 to 0.30 $\mu moll^{-1}$. During monsoon, there was a decrease from the reservoir to waterfalls and then an increase at the ferry after which the residual-N in the surface particulate was fluctuating and increasing towards estuary whereas the bottom SPM had a low residual-N. The trend of residual-N in surface and bottom SPM was similar in nonmonsoon season. The trend was a sharp decrease from the reservoir to the first waterfalls and then a slow increase till ferry station after which there occurred an intermittent variation towards the estuarine end. The highest residual-N was recorded at the ferry during monsoon, and at the riverine station 6 (Kanakkankadavu) during nonmonsoon.

To predict the impacts of nutrients and pollutants discharged by river inflow on the ecosystem, it is essential to quantify the sedimentation, resuspension and transport processes of fine particulate matter (Kuhrts et al., 2006) and then to speciate the components in the SPM.

The concentrations of nitrite-N in SPM being negligible, the observed variations were too insignificant for an explanation. But nitrate-N was appreciable and the surface and bottom values were not wildly varying, pointing to the identical nature of particulate matter. An exception was at station 6 during nonmonsoon, probably due to the replenishment of bottom waters of the station 6 with particulate matter. The high monsoonal nitrate values are associated with the increased loads of SPM transported to the river during rainy periods and which in turn enhanced the availability of sources of nitrate-N to particulate material. Variations of particulate nitrate concentrations in the stations which are limited to the mainstream / periphery of estuarine environments should be appraised as a resultant effect of runoff from land / habitats and the intrusion of sea water. This resultant effect was projected as some of the peculiar features in the distributional characteristics of particulate matter.

Fertilizers and biocides, leakage from overloaded sewage networks, irrigation of agricultural land, and deteriorating septic treatment system are sources of nitrite, nitrate and ammonium pollution (Elhatip and Gullu, 2005). Through nitrification in the presence of oxygen, ammonium is transformed into nitrates as result of the following reaction:

$$2O_2 + NH_4^+ = NO_3^- + 2H^+ + H_2O$$

The very low ammonia-N in the SPM implies either because of this process of nitrification or less pollution due to particulates. The wild variations in distributional pattern of ammonia-N in SPM might be due to the differences in the availability, presence and nature of chemicals involved in particulate material. This seemed to be completely locality dependant.

Urea was the organic species of N identified. Where the river was subject to a particularly wide variety of perturbations including domestic wastewater discharge, agricultural practices and recreational activities, all these combined result play a great role in determining the concentrations of urea in suspended impurities of rivers. Lack of an observed trend or occurrence of an oscillating trend in particulate urea-N might mean that a specific distribution pattern was not present. Uptake of urea fraction contributed least to the total pool of nitrogen in the surface SPM, but augmented its importance in the bottom SPM as could be observed from Figure 5.1, where bottom values were higher in majority of stations.

Results of analysis on total-N showed that a periodical uniformity in chemical composition exists, especially during the rainy periods, due to the source and rate of recharge. The mean concentrations revealed a clear seasonal variation. Monsoon values of total-N were much higher because rainfall and increased discharge could have possibly enhanced the river water contaminants in the form of SPM. The fluctuating concentrations of surface SPM during nonmonsoon season is partially attributed to geological reasons as rainfall events cause increased runoff and soil erosion. Changes in land-use or management practices also might affect SPM in water outflow and thereby total-N. Particulate total nitrogen should be of great importance in the biogeochemical cycles of the river because significant quantities of various species of N are transported and circulated as solid materials within the water body (Estrum-Yousef and Schoor, 2001; Schulz and Gucker 2005).

Residual-N though generally low, could not be neglected at certain stations which suggested the dominance of particulate organic matter over certain inorganic N species. Particulate organic nitrogen represents a major reactive reservoirs of organic N and exploring their transport and transformations help in understanding the global biogeochemical cycling of these elements (Kaiser et al., 2004). The considerable variability among nutrients and various forms of particulate organic matter implies that a variety of processes acting on shorter time scales influenced the composition of suspended matter (Verity, 2002). Fine particles from the clay minerals, montmorillonites sometimes present as part of particulate and are known to sorb certain basic amino acids like arginine, histidine, ornithine and lysine (Balakrishna and Probst, 2005). The particulate organic N in the water column is a metabolically active component of aquatic ecosystems. The nitrogen content of SPM is crucial at low trophic levels as a source of energy for phytoplankton. A variety of environmental changes may result in the increased or decreased accumulation of particulate residual organic nitrogen in a riverine system. These are in detrital and small fragments. Human controlled inputs are derived from the increase in populations and their activities mainly agricultural in origin. These organic fraction will be subject to bacterial decomposition and will influence the oxygen concentration, thereby affecting the ecosystem. There is also a chance for the labile organics to be disintegrated/destroyed by the high velocity currents by wear and tear with the sediments it interacts (Balakrishna and Probst, 2005). It was demonstrated by Verity, 2002, that enhanced loading of dissolved inorganic and organic N species was associated with increased concentrations of particulate organic forms of these nutrients. Some global values related to studies on particulate nitrogen are presented in Table 5.3.

Table 5.3 Global values related to particulate nitrogen

Parameters	Aquatic system	Concentrations	Reference
Total Particulate N	Pomeranian Bay at the eastern German coast of the Baltic Sea	2.69–41.01 µmoll^{-1}	Estrum-Yousef and Schoor, 2001
	US Geological Hydrologic Benchmark Network watersheds	103–112 µg l^{-1}	Lewis, 2002
	Adriatic coastal zone	8.0–115.1 µg l^{-1}	Turchetto et al., 2002
	Piracicaba River basin, Southeast Brazil	<0.5 mg l^{-1}	Filoso et al., 2003
	Weiße Elster (Central Germany)	1.18 to 3.39%	Junge et al., 2005
Particulate Nitrate-N	Rostherne Mere, a British freshwater lake	0 to 2.25 mg l^{-1}	Krivtsov and Sigee, 2005
Particulate Ammonia-N	Rostherne Mere, a British freshwater lake	1.2 ppm	Krivtsov and Sigee, 2005
Particulate organic N	Skidaway River estuary	148 µg l^{-1} to 170 µg l^{-1}	Verity, 2002

Spatial abundance (percentagewise): Nitrogen

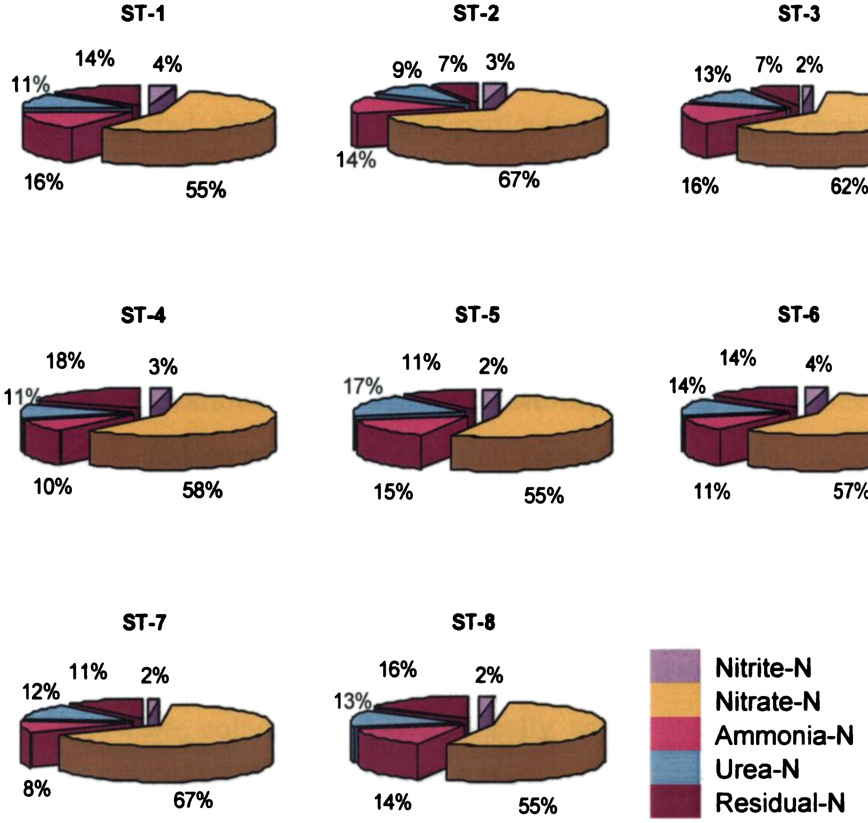


Figure 5.2a Percentage-wise distribution of nitrogen species (nitrite-N, nitrate-N, ammonia-N, urea-N and residual N) in the SPM of the different sampling stations of Chalakudy river during monsoon season

Figure 5.2a shows the stationwise abundance of nitrogen species (in percentage) in the SPM during monsoon period. Results from all the eight stations indicated that nitrite-N was very low in percent (2 to 4%) and nitrate-N was the predominant form which ranged in composition from 55% to 67%. It could be noted that the waterfall regions 2 and 4 and the station 7 had the maximum percentage of nitrate-N. The percentage of ammonia-N in SPM was in the range from 8% to 16% and station 7 had the lowest value. Urea-N was also substantial in composition ranging from 9 to 17%. The particulates of station 5, the town region had the highest percentage composition of urea. Residual-N accounted for 7 to 16% which obviously encompasses organically bound N compounds such as basic amino acids and sugars excluding urea. The proportion of residual-N in particulate matter was comparatively higher at the reservoir (station 1), ferry (station 4), Kanakkankadavu (station 6) and estuary (station 8).

The percentage fractions of nitrogen species during nonmonsoon period is pictured in Figure 5.2b. The percentage of nitrate-N in particulates during nonmonsoon was almost comparable to the corresponding monsoon value (50 to 68%). Waterfalls regions, ferry and estuarine end faced a decrease in percentage of nitrate towards nonmonsoon, whereas the reservoir (station 1), and stations 5 and 6 enhanced it. Nitrite-N composition was 1 to 4%. Ammonia-N ranged from 4 to 14% which is lesser compared to the monsoon values. Waterfalls regions and estuary recorded the highest ammonia values. Station 7 had the least as in the case of monsoon period. Contribution of urea-N decreased during nonmonsoon season, ranging from 7 to 13%. The percentage of residual-N was found to be sharply increasing during the non rainy season and occurred in the range, 12 to 28%.

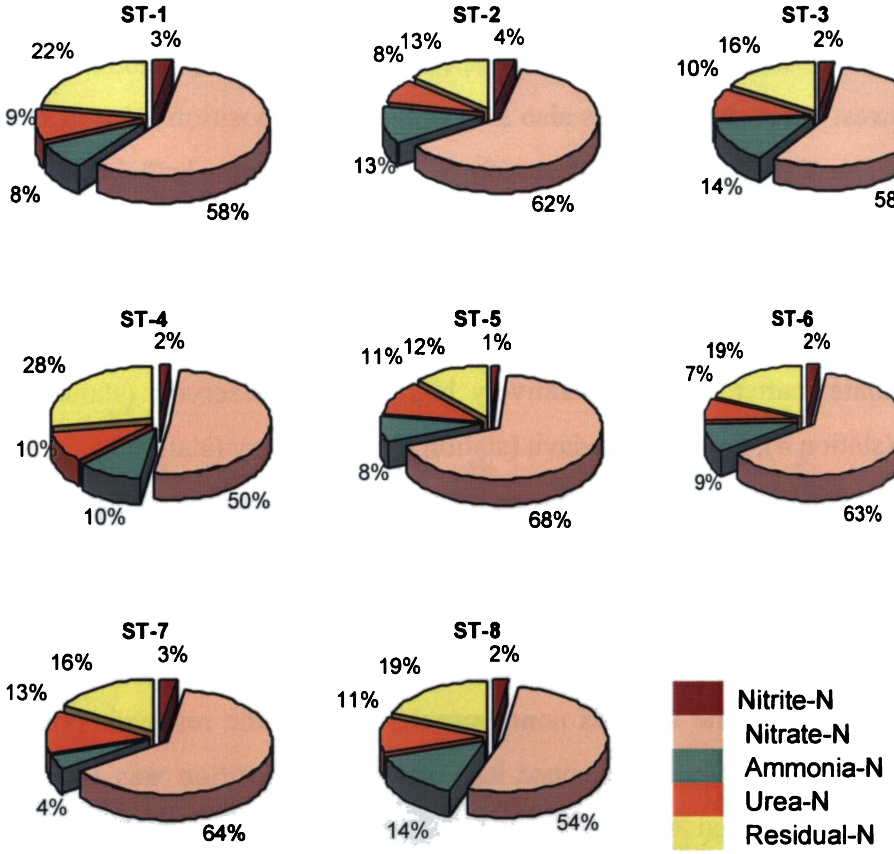


Figure 5.2b Percentage-wise distribution of nitrogen species (nitrite-N, nitrate- N, ammonia-N, urea-N and residual N) in the SPM of the different sampling stations of Chalakudy river during nonmonsoon season

The results are of particular interest in understanding how composition of SPM varies within Chalakudy river-estuarine system and also points to the many roles that SPM plays in influencing important structural and functional aspects of this aquatic system. Generally, it can be concluded that nitrate had the major share and nitrite, the least among the various nitrogen fractions in the suspended particulate matter during both seasons.

Spatiotemporal dependence: phosphorus

Suspended particulate matter during both seasons was also analysed to assess the potential bioavailability of particulate phosphorus. The various species were fractionated based on flow chart Figure 2.5 in Chapter II. Physical (separation by filtration) and chemical (sequential extraction) fractionation techniques were applied. The distribution of phosphorus in particulate matter occurred in the forms such as loosely bound P, iron/aluminium bound P, polyphosphates, calcium bound P and refractory P. The temporal and spatial variabilities were also investigated. Sum of all the five P components analyzed is presented as total inorganic P. The primary data for the quantitative determination of different species of phosphorus in the SPM for surface and bottom waters (in μmoll^{-1}) are presented in Tables 5.4 and 5.5 respectively. Seasonal trend concerning each species is pictured graphically in Figure 5.3. NaCl-extractable P was an estimate of the immediately available P ('labile P'). Buffered dithionite extractable P is assumed to originate mainly from Fe hydroxyhydroxide ('FeOOH~P'). Mild NaOH (0.1M) extractable P represented polyphosphates. HCl-extractable P represented P bound to carbonates. NaOH (1M) extractable P represented refractory P, the inorganic forms not easily extractable.

Table 5.4 Bimonthly distribution of loosely bound P, iron/aluminium bound P, polyphosphates, calcium bound P, refractory P and total inorganic P (in $\mu mol l^{-1}$) in the SPM of surface waters of Chalakudy river

Parameter	Months	S1	S2	S3	S4	S5	S6	S7	S8
Loosely bound P	May	0.019	0.009	0.009	0.013	0.015	0.006	0.004	0.004
	Jul	0.007	0.005	0.002	0.012	0.002	0.001	0.001	0.002
	Sep	0.006	0.009	0.003	0.018	0.002	0.003	0.005	0.005
	Nov	0.005	0.001	0.002	0.017	0.012	0.001	0.007	0.005
	Jan	0.003	0.002	0.002	0.012	0.013	0.005	0.004	0.003
	Mar	0.009	0.005	0.005	0.006	0.003	0.006	0.006	0.004
Fe/Al bound P	May	0.145	0.062	0.061	0.085	0.081	0.079	0.082	0.093
	Jul	0.109	0.071	0.069	0.094	0.074	0.080	0.074	0.083
	Sep	0.095	0.070	0.071	0.074	0.072	0.083	0.079	0.081
	Nov	0.102	0.082	0.079	0.079	0.078	0.073	0.072	0.074
	Jan	0.076	0.059	0.042	0.059	0.063	0.046	0.066	0.061
	Mar	0.073	0.031	0.039	0.063	0.062	0.061	0.042	0.062
Poly phosphates	May	0.042	0.029	0.027	0.060	0.046	0.026	0.035	0.027
	Jul	0.036	0.031	0.032	0.050	0.041	0.031	0.032	0.033
	Sep	0.036	0.037	0.035	0.042	0.047	0.035	0.039	0.036
	Nov	0.029	0.028	0.029	0.042	0.039	0.028	0.037	0.029
	Jan	0.027	0.027	0.018	0.033	0.037	0.017	0.029	0.031
	Mar	0.028	0.027	0.027	0.052	0.028	0.026	0.036	0.026
Ca bound P	May	0.026	0.025	0.025	0.036	0.030	0.031	0.145	0.193
	Jul	0.026	0.030	0.028	0.031	0.029	0.028	0.107	0.115
	Sep	0.029	0.029	0.027	0.036	0.035	0.030	0.092	0.147
	Nov	0.025	0.022	0.022	0.054	0.025	0.025	0.115	0.148
	Jan	0.022	0.020	0.042	0.024	0.022	0.022	0.058	0.194
	Mar	0.023	0.023	0.024	0.033	0.024	0.022	0.028	0.115
Refractory P	May	0.011	0.012	0.011	0.012	0.011	0.011	0.011	0.011
	Jul	0.018	0.013	0.012	0.014	0.011	0.015	0.014	0.014
	Sep	0.017	0.012	0.012	0.012	0.012	0.014	0.015	0.013
	Nov	0.016	0.014	0.012	0.010	0.019	0.007	0.015	0.015
	Jan	0.012	0.005	0.006	0.007	0.005	0.016	0.012	0.014
	Mar	0.013	0.001	0.001	0.002	0.010	0.004	0.011	0.020
Total inorganic P	May	0.243	0.136	0.132	0.205	0.184	0.152	0.276	0.327
	Jul	0.196	0.150	0.143	0.201	0.157	0.155	0.228	0.246
	Sep	0.183	0.158	0.147	0.183	0.169	0.164	0.230	0.282
	Nov	0.176	0.147	0.144	0.202	0.173	0.134	0.246	0.271
	Jan	0.141	0.113	0.110	0.135	0.140	0.106	0.170	0.303
	Mar	0.145	0.087	0.095	0.156	0.127	0.118	0.123	0.227

Table 5.5 Bimonthly distribution of loosely bound P, iron/aluminium bound P, polyphosphates, calcium bound P, refractory P and total inorganic P (in µmoll^{-1}) in the SPM of bottom waters of Chalakudy river

Parameter	Months	B1	B2	B3	B4	B5	B6	B7	B8
Loosely bound P	May	0.019	0.009	0.009	0.015	0.020	0.011	0.004	0.012
	Jul	0.012	0.005	0.002	0.017	0.002	0.012	0.001	0.013
	Sep	0.014	0.009	0.003	0.026	0.015	0.014	0.013	0.015
	Nov	0.018	0.001	0.002	0.024	0.012	0.001	0.016	0.020
	Jan	0.010	0.002	0.002	0.015	0.013	0.015	0.004	0.010
	Mar	0.012	0.005	0.005	0.012	0.008	0.019	0.006	0.009
Fe/Al bound P	May	0.145	0.062	0.061	0.119	0.097	0.095	0.082	0.012
	Jul	0.123	0.071	0.069	0.114	0.074	0.102	0.074	0.124
	Sep	0.117	0.070	0.071	0.101	0.083	0.093	0.088	0.084
	Nov	0.114	0.082	0.079	0.128	0.078	0.073	0.091	0.077
	Jan	0.084	0.059	0.042	0.070	0.063	0.053	0.066	0.075
	Mar	0.076	0.031	0.039	0.063	0.072	0.069	0.042	0.069
Poly phosphates	May	0.042	0.029	0.027	0.081	0.068	0.045	0.035	0.054
	Jul	0.070	0.031	0.032	0.062	0.041	0.047	0.032	0.078
	Sep	0.056	0.037	0.035	0.057	0.066	0.051	0.043	0.097
	Nov	0.063	0.028	0.029	0.071	0.039	0.028	0.034	0.050
	Jan	0.037	0.027	0.018	0.043	0.037	0.027	0.054	0.032
	Mar	0.031	0.027	0.027	0.068	0.039	0.026	0.036	0.039
Ca bound P	May	0.026	0.025	0.025	0.054	0.033	0.038	0.145	0.253
	Jul	0.070	0.030	0.028	0.091	0.029	0.046	0.107	0.210
	Sep	0.039	0.029	0.027	0.043	0.058	0.042	0.131	0.155
	Nov	0.044	0.022	0.022	0.102	0.025	0.025	0.123	0.187
	Jan	0.022	0.020	0.042	0.033	0.022	0.032	0.062	0.197
	Mar	0.026	0.023	0.024	0.032	0.041	0.038	0.003	0.135
Refractory P	May	0.011	0.012	0.011	0.013	0.012	0.021	0.011	0.011
	Jul	0.025	0.013	0.012	0.026	0.011	0.015	0.014	0.016
	Sep	0.026	0.012	0.012	0.021	0.018	0.016	0.016	0.005
	Nov	0.029	0.014	0.012	0.016	0.019	0.007	0.005	0.014
	Jan	0.015	0.005	0.006	0.014	0.005	0.014	0.012	0.009
	Mar	0.011	0.001	0.001	0.012	0.009	0.006	0.014	0.014
Total inorganic P	May	0.243	0.136	0.132	0.282	0.230	0.210	0.277	0.342
	Jul	0.299	0.150	0.143	0.310	0.157	0.222	0.228	0.441
	Sep	0.252	0.158	0.147	0.248	0.240	0.216	0.291	0.356
	Nov	0.268	0.147	0.144	0.341	0.173	0.134	0.269	0.348
	Jan	0.168	0.113	0.110	0.175	0.140	0.141	0.199	0.323
	Mar	0.156	0.087	0.095	0.187	0.169	0.158	0.101	0.266

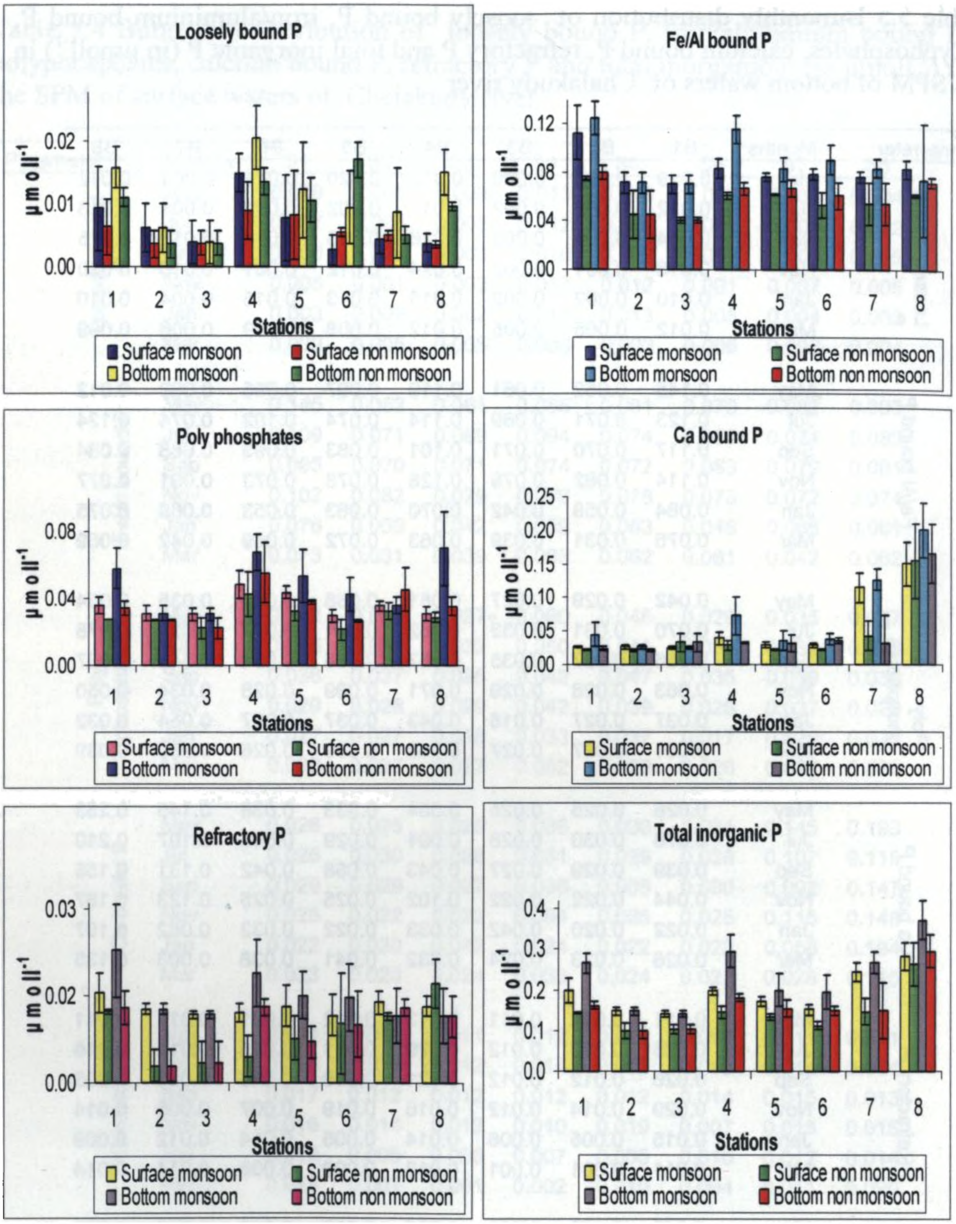


Figure 5.3 Seasonal average concentrations of loosely bound P, iron/aluminium bound P, poly phosphates, calcium bound P, refractory P and total inorganic P (in µmoll^{-1}) in the SPM of Chalakudy river.

Seasonal average concentrations of loosely bound P, iron/aluminium bound P, polyphosphates, calcium bound P, refractory P and total inorganic P (in μmoll^{-1}) in the SPM of Chalakudy river are presented in (Figure 5.3). The concentrations of loosely bound phosphorus (labile P) in particulate matter displayed very low values during both seasons. The values were in the range from 0.003 to 0.021 μmoll^{-1}. The values during both seasons for surface SPM presented a hike towards stations 1, 4 and 5 and decreased towards waterfalls and estuarine regions. But the bottom particulate had an increase of labile P at stations 1, 4 and 8 during monsoon with lesser values at other stations, and during nonmonsoon, stations 5 and 6 also had higher values.

The concentration of Fe/Al bound phosphorus in particulate matter was the highest among all fractions. The highest value obtained was 0.12 μmoll^{-1} and the lowest was 0.04 μmoll^{-1}. Monsoon values were slightly higher. The reservoir station had slightly high Fe/Al bound P during monsoon and all other stations had more or less a steady value for surface SPM, whereas for bottom SPM, there occurred a slight hike at the ferry station 4. The nonmonsoon showed a slight depletion of Fe/ Al bound P from reservoir to waterfalls particulate and then an increase which remained erratically towards estuary.

Concentrations of polyphosphates were also very low as could be seen from the Figure 5.3. The maximum concentration reported was 0.07 μmoll^{-1} and the minimum was 0.02 μmoll^{-1}. But, the range was too narrow for extracting a pertinent comparison. Still, the noticeable feature was that bottom values were same or slightly higher for all riverine stations till the estuarine end. Also, the nonmonsoon values were slightly lower compared to monsoon period. Comparative abundance of polyphosphates in the ferry regionwas marked.

Analysis of samples revealed that the suspended particulates of river water stations were depleting with calcium bound phosphorus, whereas the mainstream estuarine stations (7 and 8) were enriched, with the maximum values during monsoon. As compared to all other stations (except station 7), the Ca bound P was seen to be doubled in the suspensates of the estuarine mouth, where seawater merges with riverine system. During monsoon season, station 4 had a slight increase. The concentration of Ca bound P ranged from 0.02 to 0.20 μmoll^{-1}.

The fractions of P which were not easily extractable are labeled as refractory P. Generally, very low refractory phosphorus was detected in SPM of river Chalakudy (Figure 5.3). The levels of refractory P of surface as well as bottom suspensates exhibited an inconsistent trend towards monsoon. The maximum values of refractory P recorded were 0.023 and 0.017 μmoll^{-1} and the minimum values were 0.012 and 0.003 μmoll^{-1} for monsoon and nonmonsoon seasons respectively.

Total inorganic P (the sum of the five components described), in SPM, is depicted in Figure 5.3. The average total P concentration was comparatively higher for the saline stations 7 and 8 during monsoon as well as nonmonsoon. Deviations in mean values were limited. Generally, the mean concentrations of all stations showed a gradual decreasing trend. The trend was as follows. During monsoon, for surface particulates there was a hike in total P at the estuarine end, but the bottom SPM had higher values at the reservoir station 1 and the ferry station 4 and the peak concentration was observable at the estuarine region. The total inorganic P was lowered during nonmonsoon and the surface as well as bottom particulates followed the same trend with slight deviations. The monsoon values ranged from 0.14 to 0.37 μmoll^{-1} and the nonmonsoon values from 0.1o to 0.29 μmoll^{-1}. While NaCl extractable particulate P represents a fully exchangeable and therefore bioavailable phase, the bioavailability of other phases will depend on geochemical transformations and on the time allowed for diagenesis. P may be bound to iron and aluminium oxides and it may exist in carbonates, apatite and organic matter. Inorganic P compounds are associated with amorphous and crystalline forms of Fe, Al, Ca, and other elements and organic P forms are generally associated with living organisms. Some of the P-forms (e.g. primary mineral apatite) are practically inert, whereas others may be potentially available to algae, by desorption. At low redox potentials (<200 mV), Fe (III) in the particulate matter might be reduced to Fe (II), leading to the release of PO_4^{3-} and Fe (II) (Nowlin et al., 2005). The total P concentration and the relative concentration of various P fractions (i.e. Fe-bound P, Al-bound P, organic-bound P) in particulate matter also influence P release rates. Suspended nutrients and discharge are positively correlated in the rivers entering modern Lake Malawi, Africa, (Hecky et al., 2003). Global reference values for studies on various forms of particulate phosphorus are presented in Table 5.6.

Table 5.6 Global values for various forms of particulate phosphorus

Aquatic system	Parameters	Concentrations	Reference
Northern and Central Adriatic	Particulate total P	0.106–0.207 μmol l^{-1}	Gismondi et. al., 2002
Drains from agricultural land between Lake Vattern and Lake Vanern, Southwest 5	Particulate phosphorus on filters with a pore diameter of 0.2 μm	0.066 – 0.082 mg l^{-1}	Ulen, 2004
	Fine colloidal phosphorus	0.003 – 0.019 mg l^{-1}	
Rostherne Mere, a British freshwater lake5	Particulate N/particulate P ratio	1.6 – 9.6	Krivtsov and Sigee, 2005
	Particulate P	15 and 160 μg l^{-1}	
	Particulate Orthophosphate P	0 – 0.4 mg l^{-1}	
Danish rivers (% in Particulate Total P)	Loosely adsorbed phosphate	1.6–12.7%	Jensen et al., 2006
	Iron-bound P (major fraction)	38–79%	
	Phosphate adsorbed onto aluminum oxides and clay	4.3–36%	
	Calcium-bound P	2.2–5.3%	
	Humic-bound P	2.4–4.4%	
	Extractable organic P	4.5–9.8%	
	Refractory organic P	2.7–6.6%	

The concentrations of loosely bound P were very low. No consistent trend was noticeable. This suggested intermittent removal and redeposition of labile P on suspended particles and also other physico chemical effect. Generally, the estuary (station 8) exhibited very low concentration of loosely bound P during monsoon, indicating the dilution effects and the high value in nonmonsoon could be associated with chemoestuarine variations. Bottom particulate of station 6 had comparatively higher values during nonmonsoon which can be extrapolated over to the geochemical processes prevailing locally.

Fe/Al bound P was introduced much towards the SPM of the riverine region since it accounted for the high values. The release of Fe/ Al bound P (bicarbonate dithionate extracted P) is likely to occur when the decomposition of the primary production products becomes intense and deep waters in the fresh water system become anoxic (Hupfer et al., 1995). So the high concentrations in SPM could also be attributed to higher rate of decomposition.

P-stress has been associated with the development of toxicity in flagellates (Flynn, 2002). Large quantities of polyphosphates occur in green algae and flagellates and the polyphosphates usually disappear when ambient phosphate is depleted (Miyata and Hattori, 1986). The reserved phosphorus in the natural populations of phytoplankton is usually composed of polyphosphates. The very low polyphosphates in the SPM, therefore could be due to the utilization by algal species.

Ca-bound P can be orthophosphate adsorbed onto $CaCO_3$ (which are the labile forms of P), or to different forms of apatite (calcium phosphate) which are considered to be unavailable, although they are pH sensitive. So, calcium can be relevant for the removal of phosphorus from the water column (Pardo et al., 2003) and can contribute to the permanent removal of P to particulates and sediments. The results of the seasonal and spatial assessments conducted on Ca bound P revealed that water quality due to

SPM degrades as it flows along the course of the river to estuary with the highest concentrations detected at sites close to the ocean. The particulate compositions of Ca bound P for stations 1 to 6 in monsoon and stations 1 to 7 in nonmonsoon periods were very small and almost constant, reflecting the same predominant nutrient source. The high estuarine values for Ca bound P in the particulates of estuarine region might be due to the high amount of Ca bound P in saline sea waters. The water quality as related to particulate matter of a river depends on different factors. One important factor is the mixing of sea water of different quality. Intrusion of saline water affects concentration of major elements such as Ca (Hoz et al., 2003).

Refractory P includes practically inert and unavailable inorganic forms of P. Rivers transport various P fractions and transform it through chemical, physical, and biological reworking and the origin and presence of the refractory P are of particular interest since it greatly determines specific transformation pathways under certain physicochemical conditions. Lack of an observed trend or a fluctuating trend may mean that a trend was not present with regard to refractory P during monsoon season. But the gradual increase from waterfalls to estuary during nonmonsoon pointed to river flow influences which brought refractory P into the SPM.

The sum of all species of P in SPM accounted as total inorganic P was appreciable owing to Fe/Al bound P, polyphosphates and Ca bound P. The high total inorganic P towards estuarine end could be the consequence of very high Ca bound P in the estuarine stations. The other fractions such as easily exchangeable P and Fe/Al bound P might be responsible for the slightly enhanced total P at the reservoir and ferry. But, generally the concentrations varied only in lesser amounts and the overall constancy in total inorganic P pointed to some sort of uniformity in the nature of suspended matter in surface and bottom waters of all stations.

Spatial abundance (percentagewise): Phosphorus

Not all forms of phosphate are likely to be released, and it is important to know which part of the stock can be mobilized (Ruban and Demare, 1998). Figure 5.4a depicts the percentage composition of loosely bound P, Fe/Al bound P, polyphosphates, Ca bound P and refractory P during monsoon in the particulates of the river. The percentage composition of exchangeable P was ranging from 3 to 7%. The composition was found to be the highest at station 4, which could be attributed to the influence local pollutants. The percentage composition of Fe/Al bound P in particulates was the highest for stations 1 to 6 ranging from 40 to 49% and the estuarine stations had shares of 31% and 24% respectively. The presence of Fe/Al bound P was therefore a major partner or contributor as far as the fractions of P were concerned. Polyphosphates of stations 1 to 6 have a composition ranging between 20 to 26% whereas stations 7 and 8 had low compositions of 14%

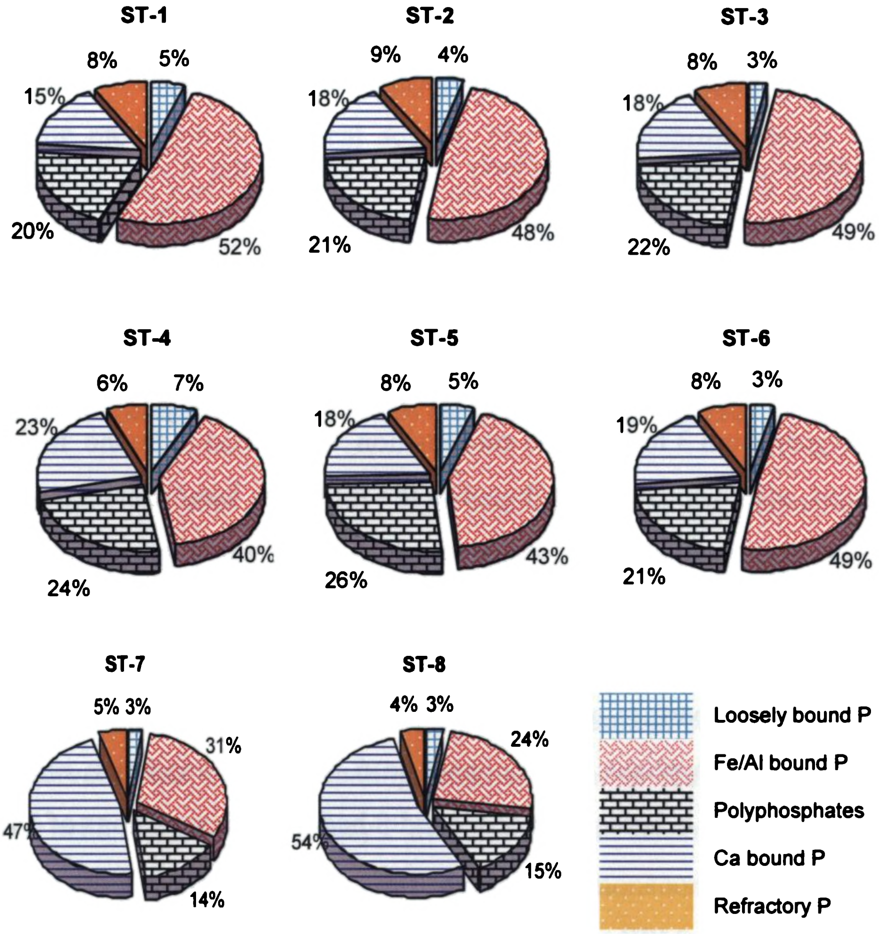


Figure 5.4a Percentage-wise distribution of phosphorus forms (loosely bound P, Fe/Al bound P, poly phosphates, Ca bound P and refractory P) in the SPM of the different sampling stations of Chalakudy river during monsoon season

and 18% respectively. The percentage of Ca bound P was widely ranging from 15% to 23% for stations 1 to 6. A drastic shooting up can be observed for the saline station 7 (47%) and the station 8 was highly specific during monsoon with a 54% species of Ca bound P. The estuarine station 8, thus increases the Ca bound P composition to a highly significant level. Mixing with seawater might be a factor definitely affecting these high compositions of Ca bound P in estuarine suspensates. The percentage of refractory P during monsoon was within the range of 6 to 9% for riverine stations 1 to 6, and was 5% and 4% respectively for stations 7 and 8. So an overall variation in the composition of forms of P at the estuarine end was a noticeable phenomenon during monsoon.

Figure 5.4b presents the percentage composition of loosely bound P, Fe/Al bound P, poly phosphates, Ca bound P and refractory P in the suspended impurities of the river during nonmonsoon season. Percentage composition of exchangeable P was found to be 4 to 9% for stations 1 to 6, whereas stations 7 and 8 had 3% and 2% respectively. The percentage composition during nonmonsoon of Fe/Al bound P was also very high as in monsoon. Their contributions ranged from 39 to 51% for stations 1 to 6. The least composition of 24% was observed at station 8 and at station 7, Fe/Al bound P was 38%. Therefore, during nonmonsoon period also Fe/Al bound P seemed to be a prominent fraction in SPM. Polyphosphates of stations 1 to 7 compiled an appreciable proportion of total P ranging from 18 to 30% whereas at station 8 it decreased to 11%. The percentage of Ca bound P during nonmonsoon was 15 to 32% for stations 1 to 7 and was 58% for station 8. For station 8, there occurred a slight increase from monsoon to nonmonsoon period, whereas the station 7 showed a tremendous decrease. Various chemoestuarine processes like desorption, sedimentation etc might be responsible for the spatiotemporal behaviour of particulate Ca bound P at stations 7 and 8. Refractory P was very low with a range in between 3 and 8%, the lowest being at waterfalls regions.

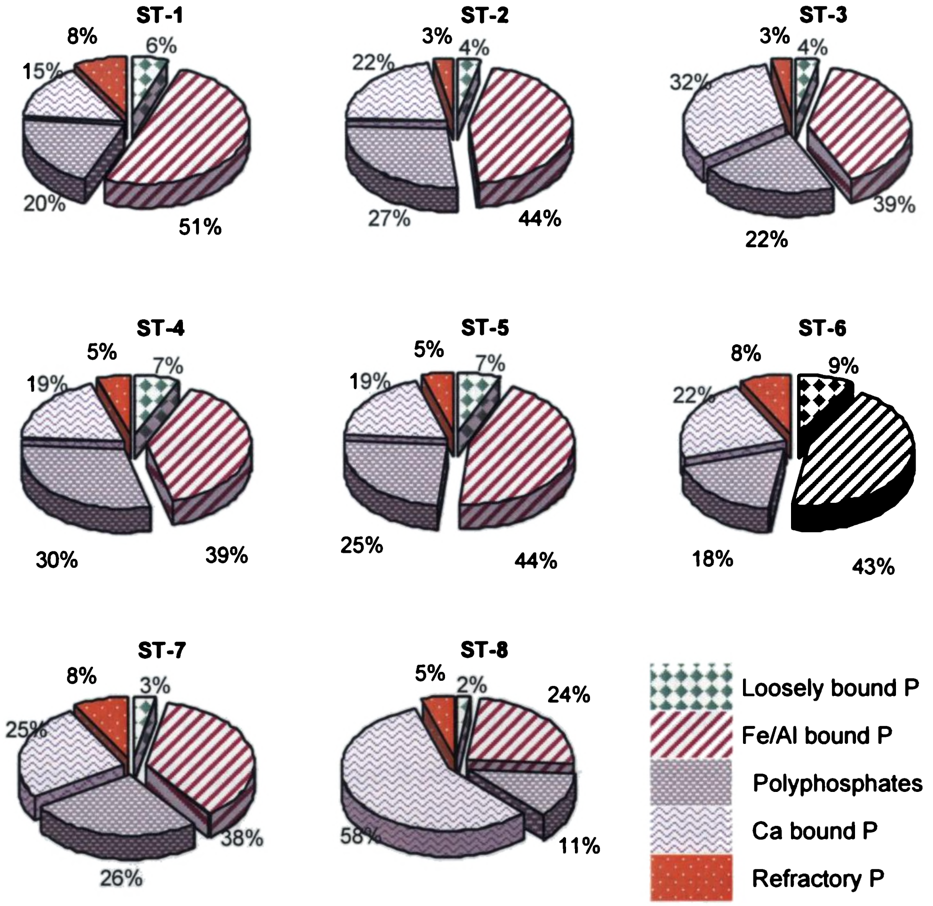


Figure 5.4b Percentage-wise distribution of phosphorus forms (loosely bound P, Fe/Al bound P, poly phosphates, Ca bound P and refractory P) in the SPM of the different sampling stations of Chalakudy river during nonmonsoon season

Particulate phosphorus has two origins, i.e., external and internal. External P originates from point (industrial and domestic effluents) or diffuse sources (weathering, agricultural runoff), but it is also released by sediments, which act as an internal source contributing phosphate to the overlying waters and particulates at levels comparable to the external source. Sedimentation and filtering of suspended solid particles are commonly suggested as removal mechanisms for particle-borne nutrients such as phosphorus (Ulen, 2004).

It was reported by Jensen et al.(2006), that Fe-bound P amounted to 38–79% and phosphate adsorbed onto aluminium oxides and clay to 4.3–36% of particulate total P in the Danish rivers and it was also pointed that loosely adsorbed phosphate accounted for 1.6–12.7% and calcium-bound P to 2.2–5.3%. All these are in agreement with the presently investigated values of species of P in SPM. Other studies related to percentagewise distribution of P in suspensates are also tabulated on Table 5.6.

Correlation

The various correlation matrices of N and P forms in the particulate matter are depicted in Tables 5.7 and 5.8 respectively. Among nitrogen components, the most significant positive correlation observed was between total-N and nitrate-N, the r value being 0.95. Correlation analysis identified two other environmental variables calcium bound P and total inorganic P with very strong correlation (r value 0.87). Ammonia-N also had significant positive relation with total-N. Also, loosely bound phosphorus exhibited positive correlation with polyphosphates. Only weak correlations were observed among other phosphorus containing fractions. The poor correlations among all other measured nutrients and quantity of particulate matter, suggest that biological processes and rainfall–mediated nutrient injections overwhelmed upstream sources over interannual time scales.

Table 5.7 Pearson correlation matrix of N fractions

	NO_2^--N	NO_3^--N	NH_3-N	Urea-N	Total-N	Residual N
NO_3^--N	0.06					
NH_3-N	0.12	0.38				
Urea-N	0.14	0.24	0.34			
Total N	0.15	0.95	0.53	0.44		
Residual N	-0.15	-0.04	0.20	0.23	0.02	
Mass of SPM	0.07	0.21	0.13	-0.02	0.20	-0.04
Chlorophyll	-0.14	0.14	0.25	0.16	0.20	0.12
D O	-0.14	0.16	0.35	0.11	0.17	0.06
Salinity	-0.25	-0.60	-0.46	-0.42	-0.70	0.24

Table 5.8 Pearson correlation matrix of P fractions

	Total-N	Loosely bound P	Fe/Al~P	Poly-phosphates	Ca~P	Refractory P	Total Inorganic P
Loosely bound P	0.17						
Fe/Al~P	0.34	0.45					
Polyphosphates	0.19	0.58	0.49				
Ca~P	0.24	0.04	0.03	0.22			
Refractory P	0.27	0.23	0.50	0.31	0.09		
Total Inorganic P	0.37	0.40	0.52	0.60	0.84	0.38	
Mass of SPM	0.20	0.21	0.08	0.27	0.62	0.08	0.58
Chlorophyll	0.20	0.19	0.31	0.25	-0.38	0.37	-0.10
D O	0.17	-0.03	0.29	0.06	-0.36	0.27	-0.15
Salinity	-0.70	-0.10	-0.52	-0.24	0.10	-0.04	-0.13

When the amount of particulate matter increases, Ca bound P and total inorganic P also increases as viewed from the scatter plots (Figure 5.5a). Total N exhibited no significant relation with total inorganic P (Figure 5.5b). Also total N decreased with salinity (Figure 5.5c) in the estuarine region.

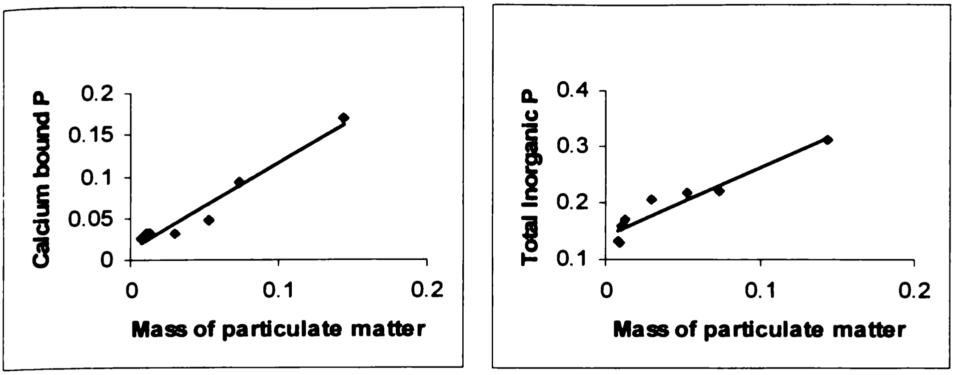


Figure 5.5a Relation of Ca bound P and total P (μmoll^{-1}) to the mass of particulate matter in the Chalakudy riverine system

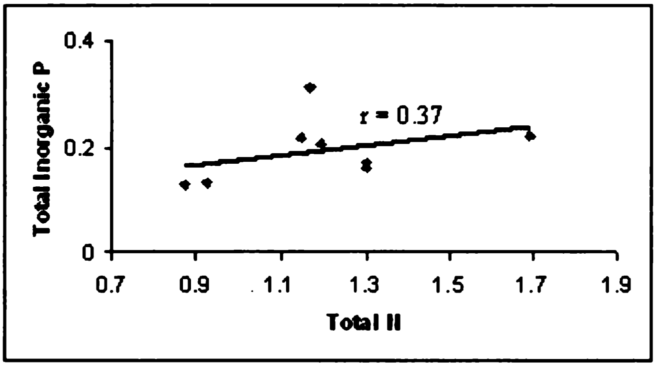


Figure 5.5b Total N Vs total inorganic P in the Chalakudy riverine system

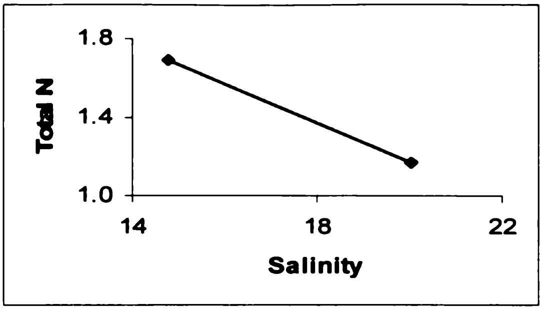


Figure 5.5c Total N Vs salinity in the estuarine region

N:P Ratios

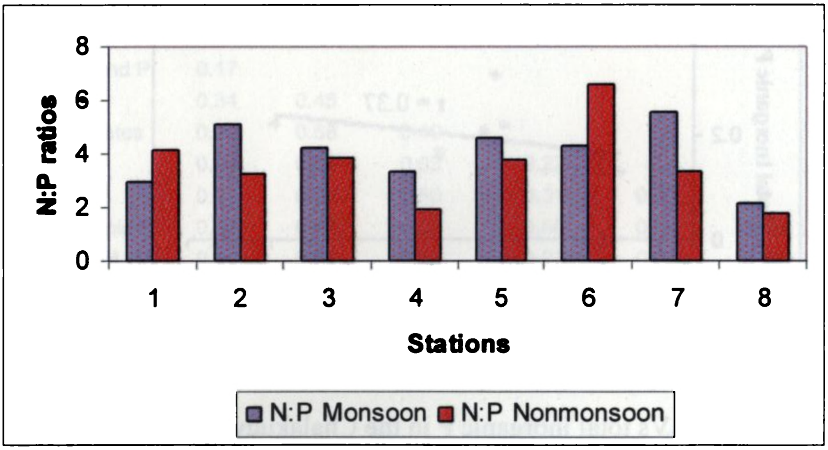


Figure 5.6 N:P ratios of SPM of Chalakudy river

Determination of the N:P ratio and its lability is essential to establish the relationship among particulate matter, anthropogenic loads and eutrophication. There is a general consensus that P is most often limiting in freshwaters, whereas N is most often limiting in marine waters (Conley, 2000). The most biologically active nutrient is phosphorus P, with nitrogen N coming second (Berner and Berner, 1996). The particulate matter should be efficient in conserving the nutrients incorporated by various sources. There is, therefore, a need to test the changes in the partitioning of nutrients and finding out the N:P ratio among suspended impurities of different locations of the riverine system.

The N:P ratios of suspended impurities ranged from 2.15 to 5.56 during monsoon and from 1.77 to 6.57 during nonmonsoon season (Figure 5.6). It was recorded that the particulate matter in the Adriatic offshore waters was characterized by N:P ratios higher than the Redfield ratio (Giani et al., 2003). The N/P mass ratios in the sedimenting particulates were generally low in the range of 0.55 to a constant at about 3 in Sahela Reservoir (Morocco) (Mhamdi et al., 2007). The Particulate N/P ratio for most of the year at Rostherne Mere, a British freshwater lake fluctuated between extreme values of 1.6 and 9.6 (Krivtsov and Sigee, 2005). Kamp-Nielsen et al. (2002) reported that water, organic matter, particulate N, particulate P, and particulate Fe-content were all correlated positively with mud content. Decomposition of labile aquatic organic matter in the aquatic environment tends to the regeneration of inorganic N and P (Sun et al., 1997). Also, in highly productive areas of the river, under conditions of limited or high water circulation, surficial bottom sediments may constitute an internal source of bioavailable nitrogen and phosphorus to SPM. Increase of particulate P relative to N might have accounted for the low N:P ratios.

Overall summary

During monsoon, both nitrate-N and thereby total-N in SPM were decreasing from reservoir towards station 3, then increasing towards station 5, again lowering at station 6 (Figure 5.7a). Afterwards, a maximum could be seen around station 7. Thus, the nitrate-N as well as total-N followed the same trend, whereas other N fractions were very low. The low ammonia-N and urea-N exhibited only slight increase around stations 5 and 7. Residual-N decreased from dam to waterfalls and there it decreased to near to non detectable level concentration and afterwards it slightly enhanced through station 4 towards estuary. Nitrite-N in SPM remained insignificantly low through out the whole river.

Comparatively, the concentrations were low in nonmonsoon period (Figure 5.7b), but the trend was identical with respect to nitrate-N and total-N. A very sharp decrease could be seen from the reservoir station 1 to waterfalls station 2, then a slight increase at waterfalls station 3 followed by a decrease at station 4. Then, the concentration slowly increased to a peak at station 6 followed by a sharp fall at station 7 and a mild increase to estuarine station 8. The other fractions of N in SPM were very low as in monsoon season. Residual-N exhibited slightly higher values at stations 1, 4, 6 and 8. Urea-N very slowly increased towards estuary. Nitrite-N was insignificantly low. Ammonia-N had a constancy for stations 1 to 8, except at station 7 where it neared to non detectable level.

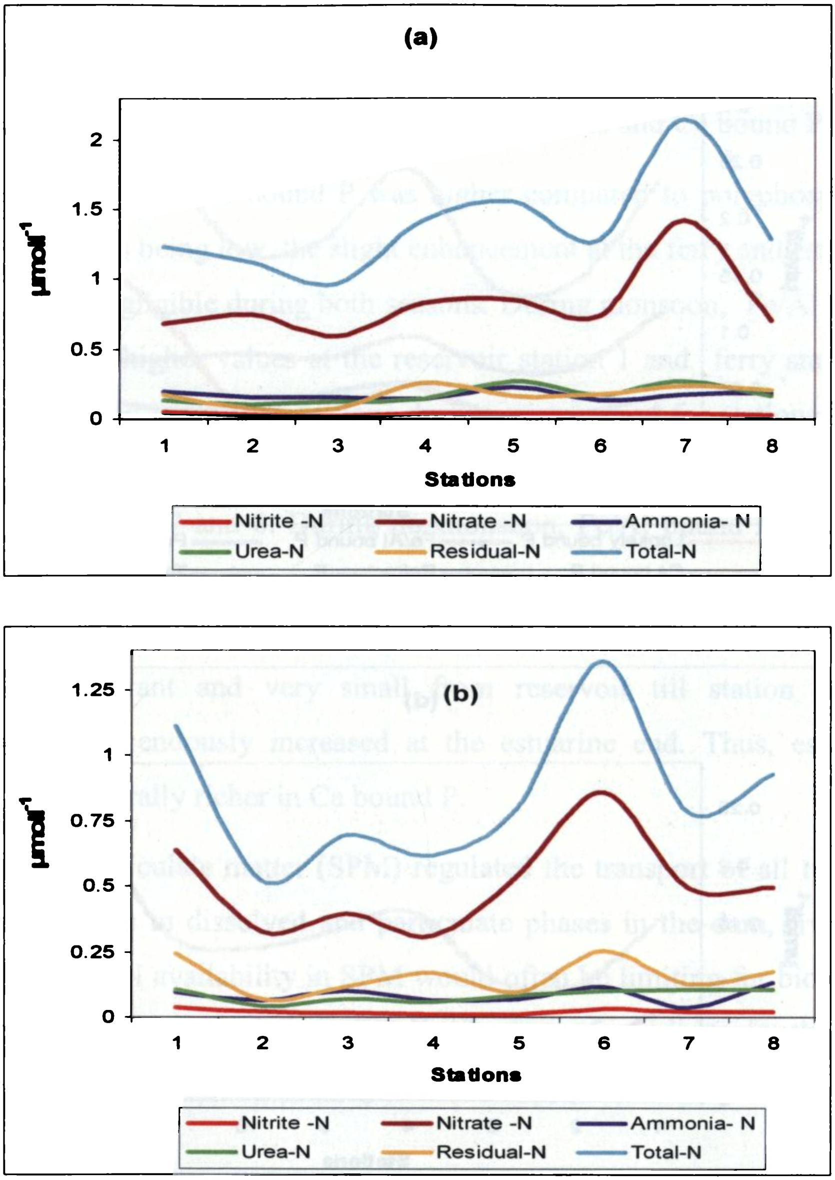


Figure 5.7(a,b) Trends of various nitrogen species in SPM during monsoon (a) and nonmonsoon (b) periods

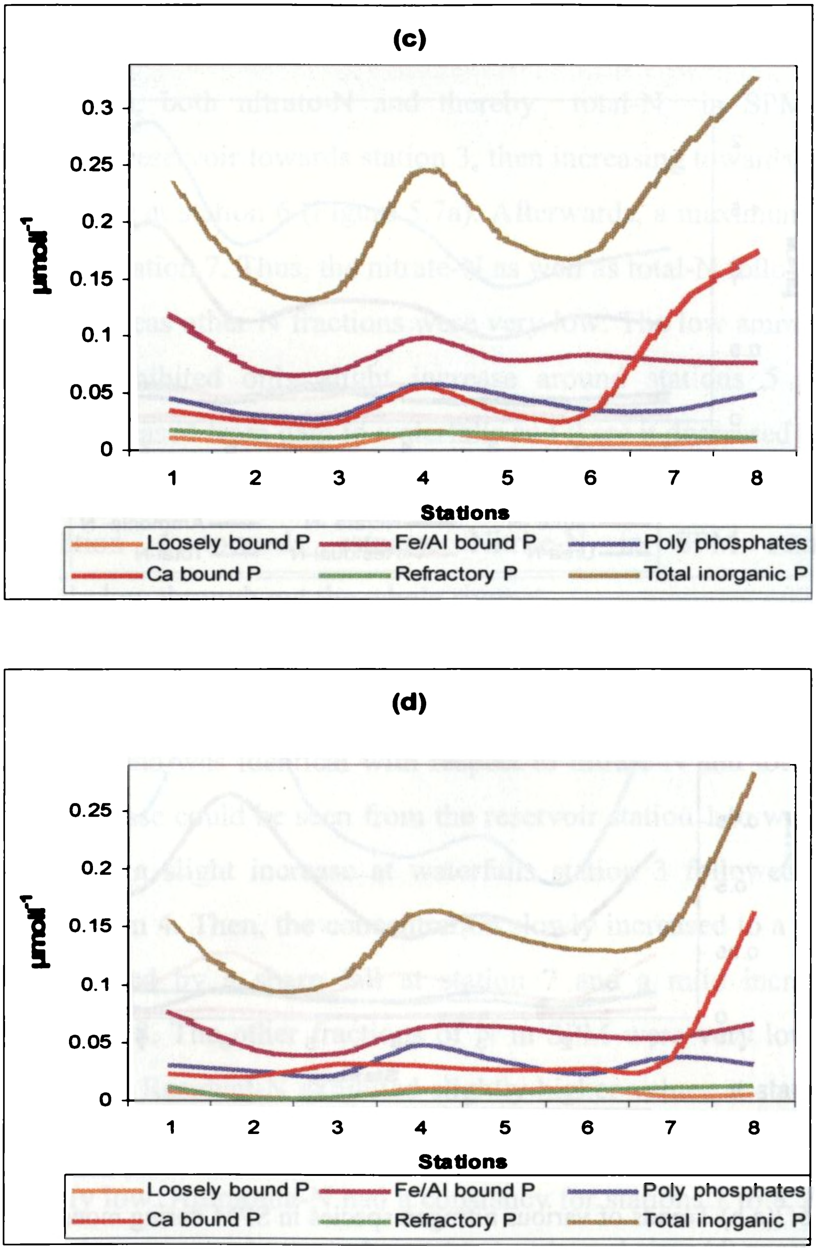
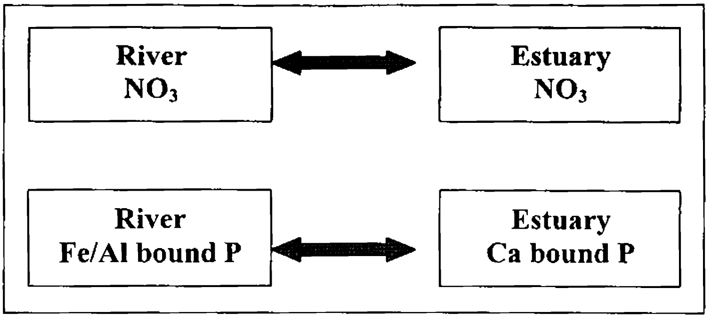


Figure 5.7 (c,d) Trends of various phosphorus species in SPM during monsoon (c) and nonmonsoon (d) periods

Generally, loosely bound P and refractory P in SPM (Figure 5.7(c,d)) were too small to be significant during both seasons. The total inorganic P was appreciable owing to Fe/Al bound P, polyphosphates and Ca bound P.

Concentration of Fe/Al bound P was higher compared to polyphosphates. Polyphosphates being low. the slight enhancement at the ferry and estuarine end seemed negligible during both seasons. During monsoon, Fe/Al bound P had slightly higher values at the reservoir station 1 and ferry station 4. Ca bound P had low concentrations during rainy period for stations 1 to 6 with a slight hike at station 4, and afterwards it sharply enhanced at the estuarine stations 7 and 8. During nonmonsoon, Fe/Al bound P gradually decreased from reservoir to waterfalls and again increased to more or less a steady value from ferry to estuary. Ca bound P in nonmonsoon season remained constant and very small from reservoir till station 6, and afterwards tremendously increased at the estuarine end. Thus, estuarine SPM was generally richer in Ca bound P.

Suspended particulate matter (SPM) regulated the transport of all types of water pollutants in dissolved and particulate phases in the dam, river and estuary. P and N availability in SPM would often be limiting for biological activity. Results showed that the distribution of nutrients in the total suspended matter was rather complicated during periods of normal as well as high flow.



Nitrate was the dominant form of N taken up during both the study periods, contributing greater than half of the total measured N uptake throughout the river and estuary. But the behaviour was different in the two seasons. Fe/Al bound P was the dominant form of P in river, whereas Ca bound P dominated in estuary.

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CHAPTER VI

SEDIMENTED NITROGEN AND PHOSPHORUS

CONTENTS

INTRODUCTION

Rivers throughout the world have varied hydrologic and biogeochemical characteristics. Intensive anthropogenic activities such as industrialization, urbanization and agricultural runoff have placed a tremendous ecological stress on the receiving water bodies as well as sediments. Most of the riverine and estuarine sediments around the world have increased levels of nutrients, and other ecologically harmful chemical compounds. The problem is further complicated by the fact that most of these pollutants, dissolved or particulate, tend to adhere to suspended organic and inorganic particles which eventually end up in bottom sediments. Thus, changes in land-use or management practices affect sediment nutrients. At the same time, contaminants are continuously released from the sediments by diffusion or during bottom sediments resuspension events. As a result there is a continuous recycling of pollutants between the ambient water and bottom sediments. Sediment is the source of nutrient minerals for macrophytes (Jin et al., 2006). Nutrient recycling complex mechanisms, including nutrient release from the sediment–water interface are suggested as the main nutrient pathway when shallowness, at the same time as mineralization, increases (Sanchez-Carrillo et al., 2006).

The present chapter aims at analyses of nutrients in sediments of Chalakudy river beginning from the Poringalkuthu reservoir, then passing through waterfall regions, entering into a riverine stage and ending up in estuary. Thus, there is a wide variation in the ecosystem of each station of sediments. Nitrogen (N) and phosphorus (P) are the primary nutrients that affect sediment and water quality in rivers worldwide. N and P reach these rivers via subterranean tiles that discharge shallow ground water and associated solutes directly into the streams (McIsaac and Hu, 2004). Surface runoff can also contribute nutrients, particularly P. This may be due to the application of fertilizers in agricultural fields. Sewage effluent is also another source of N and P in rivers. N and P are the two elements that react completely differently once emitted to the terrestrial and aquatic environment. The fate of P in the soil is dominated by chemical processes like adsorption-desorption and dissolution-precipitation, whereas the fate of N is dominated mainly by biological processes such as mineralisation, nitrification, and denitrification (Edwards and Withers, 1998). Nutrients limiting the primary production in riverine ecosystems may vary locally. N is the most common limiting element of primary production in most marine ecosystems (Mortimer et al., 1999). P can be a limiting nutrient in coastal systems (Thingstad et al., 1998) due to eutrophication resulting from increased population, urbanization and industrialization. N and P exchange at the water–sediment interface is controlled by many complex physico-chemical factors, as well as by biological processes. Zoobenthos can influence nutrient dynamics at the water–sediment interface through excretion of nutrient compounds, and through continuous release of nutrients from sediments through channels created by bioturbation activity (Risnoveanu et al., 2004)). Biological nitrogen fixation, the conversion of atmospheric dinitrogen to ammonium, is an important source of new nitrogen in the sedimentary environment. Organic nitrogen mineralization in sediments can be a significant source of ammonia- N to the overlying water. Ammonia is the main form of inorganic nitrogen in anaerobic soils because nitrification of organic nitrogen stops at ammonium due to lack of oxygen to oxidize it. Nitrate N predominates in aerobic soils.

The residual matter obtained after determination of major inorganic forms of nitrogen and phosphorus contains mainly organic N and P. The content of organic matter (OM) has been proposed as a major determinant of heterotrophic activities in sediments (Findlay and Sobczak, 2000). For rivers of the southeast U.S. coastal plain, where a large portion of the nitrogen and phosphorus are contained within the organic fraction (Graves et al., 2004), the failure to account for differences in organic nutrient and carbon lability in the external load seriously compromises the assessment of anthropogenic eutrophication effects (Hendrickson et al., 2007). Sediment OM content, thus, can be the limiting factor and an important indicator for nutrients and production in both aerobic and anaerobic sediments.

The composition of sediments may vary along the longitudinal axis of a reservoir through a river towards estuary. For example, sediments near inflows possibly contain a larger proportion of allochthonous material and sediments near a dam may contain a larger proportion of autochthonous material and sediment of estuaries may be of different constitution. Spatial heterogeneity of sediment characteristics within a reservoir, waterfall region, riverine system and estuary potentially affecting the N and P-binding capacity of sediments and release rates. As organic pollutants and nutrient salts are accumulated, the stability and density of the sediment surface layer decrease sharply, becoming semifluid sapropel (Jin et. al., 2006).

Sediment P inputs (internal P loading) can be a significant term in the annual P budget of many rivers. Further, in fresh water systems, sediment nutrient release may represent a more ecologically important process than inputs from external nutrient sources because P released from sediments often contains a larger portion of immediately bioavailable P (Pardo et al., 2003). Therefore, it is critical to characterise sources of P, both external and internal, to rivers and reservoirs in order to manage nutrient inputs to freshwater systems. To study the bioavailability/mobility of sediment phosphorus several methods can be used, such as algae bioassays, chemical fractionation, exchange with anion resin, electrodialysis and isotopic exchange. Among these, chemical fractionation, involving extraction procedures, has been widely used and is presently used in this section. The main problem of such procedures is that they lead to operationally defined fractions, i.e., that depend on the experimental conditions and the reagents used for the separation (Pardo et al., 2003).

Biogeochemical reactions in the hyporheic zone are often limited to the top few decimetres of sediments below the water–sediment interface (Mermillod-Blondin et al., 2005). Since an important fraction of the chemicals present in the aquatic environment is reversibly associated with surficial sediments, the study of nutrient dynamics in surficial sediments as done in this study is prerequisite to the understanding of their behaviour in the riverine system.

In this Chapter, an exertion is made to speciate the different forms in which N and P are existing in the sediments of Chalakudy river. The work aims to estimate the benthic nutrient fluxes and the extent to which they have an effect on the riverine ecosystem.

MATERIALS AND METHODS

The details of methodology adopted for analyses of sediment nutrients are described in Chapter II. Sediment samples were collected from the river Chalakudy.on a bimonthly basis. The nutrient concentrations (various species of inorganic nitrogen and phosphorus and also total nitrogen and phosphorus) were analyzed in the surficial sediments of 8 sampling stations. The analyses could be a complementary tool to assess the sediment quality of the river. Speciation of nitrogen is done as nitrite-N, nitrate-N, ammonia-N and urea-N, and the total N is also determined. The sum of the nitrite-N, nitrate-N and ammonia-N is considered as sedimentary inorganic nitrogen. Difference between total N and the other four species determined is presented as residual N which contains mainly organic forms of N, excluding urea. Fractionation of P in its inorganic forms was studied by applying the sequential chemical extraction procedure described in Chapter II. The major forms of inorganic phosphorus analysed were loosely bound P, Fe/Al bound P, polyphosphates, Ca bound P and refractory P. Schematic representation of the speciation is given in Figure 2.5 of Chapter II. Total P is also estimated. The difference of total-P and total inorganic P is pictured as residual P, which may possibly be richer in organically bound P.

RESULTS AND DISCUSSION

The results of the quantitative determination of different species of nitrogen and phosphorus (in $\mu molg^{-1}$) in the sediments during the investigation period are presented in (Table 6.1) this section. Seasonal trend concerning each species during the investigation period is also focussed. Conclusion in all cases is finally addressed in comparison of the results found with more spatially and temporally extensive observations.

Nitrogen species: Distribution profiles

Nutrients are chemical elements and compounds in the environment from which organisms synthesize living matter: their body cells and tissues, their genetic material, their energy-bearing molecules, and their reproductive cells. In the discussion of sediment nutrient quality of Chalakudy River, four species of nitrogen compounds are described: nitrite [NO_2^-], nitrate [NO_3^-], ammonia [NH_3] and urea [$CO(NH_2)_2$]. The first three are the most significant inorganic forms and urea is a significant organic form of the element, nitrogen, that commonly limit the productivity. Total-N as well as residual nitrogen [subtracting sum of nitrite, nitrate, ammonia, and urea from Total-N] are also discussed. Bimonthly values of all species of nitrogen analysed are given in Table 6.1.

The concentrations of nitrite-N in the sediment ($\mu molg^{-1}$) were found to be insignificantly small, and the mean values were ranging from 0.003 to 0.043 $\mu molg^{-1}$ during monsoon and from 0.002 to 0.011 $\mu molg^{-1}$ during nonmonsoon (Figure 6.1). During monsoon period, the concentration of nitrite-N decreased from the dam towards waterfall regions, then sharply rose at the ferry and was found to decrease towards station 6 and finally increased on its path to estuary. But nonmonsoon period depicted comparatively low nitrite concentration in almost all stations. Stationwise variability during nonmonsoon period is insignificant to project any spatial features.

Table 6.1 Bimonthly distribution of nitrite-N, nitrate-N, ammonia-N, urea-N, total N and residual N (in μmolg^{-1}) in the sediments of Chalakudy river

Para Meters	Months	Stations							
		S1	S2	S3	S4	S5	S6	S7	S8
Nitrite-N	May	0.011	0.008	0.007	0.039	0.033	0.046	0.033	0.040
	Jul	0.021	0.010	0.003	0.033	0.016	0.026	0.021	0.027
	Sep	0.018	0.003	0.003	0.056	0.024	0.010	0.023	0.047
	Nov	0.011	0.002	0.001	0.044	0.032	0.007	0.037	0.015
	Jan	0.008	0.002	0.004	0.011	0.008	0.006	0.011	0.007
	Mar	0.007	0.001	0.008	0.010	0.009	0.016	0.006	0.008
Nitrate-N	May	0.612	0.078	0.288	0.317	0.812	0.357	0.392	0.261
	Jul	0.624	0.211	0.734	0.909	1.035	0.631	0.627	0.742
	Sep	1.453	0.853	0.846	1.434	0.978	1.283	1.161	0.867
	Nov	0.697	0.332	0.627	0.664	0.752	1.477	0.783	1.125
	Jan	0.641	0.098	0.372	0.390	0.373	0.332	0.281	0.289
	Mar	0.454	0.015	0.275	0.186	0.328	0.195	0.377	0.156
Ammonia-N	May	0.111	0.024	0.026	0.109	0.083	0.091	0.059	0.097
	Jul	0.351	0.123	0.243	0.204	0.167	0.233	0.245	0.232
	Sep	0.217	0.103	0.146	0.294	0.221	0.356	0.311	0.227
	Nov	0.145	0.063	0.057	0.163	0.205	0.132	0.244	0.075
	Jan	0.131	0.017	0.044	0.035	0.061	0.031	0.077	0.063
	Mar	0.064	0.026	0.092	0.076	0.034	0.112	0.026	0.041
Urea-N	May	0.043	0.013	0.051	0.053	0.106	0.069	0.047	0.038
	Jul	0.086	0.031	0.042	0.117	0.088	0.079	0.098	0.079
	Sep	0.078	0.047	0.048	0.093	0.120	0.106	0.072	0.053
	Nov	0.072	0.034	0.077	0.093	0.074	0.086	0.081	0.042
	Jan	0.038	0.004	0.017	0.029	0.013	0.038	0.028	0.050
	Mar	0.034	0.005	0.009	0.038	0.018	0.057	0.013	0.024
Total-N	May	1.299	0.137	0.402	1.118	1.452	0.791	0.789	0.697
	Jul	1.488	0.394	1.057	1.573	1.607	1.132	1.313	1.289
	Sep	1.949	1.029	1.098	2.228	1.723	1.782	1.803	1.629
	Nov	1.309	0.498	0.844	1.658	1.499	1.810	1.298	1.605
	Jan	1.041	0.126	0.493	0.495	0.527	0.524	0.489	0.455
	Mar	0.853	0.054	0.412	0.416	0.450	0.433	0.550	0.335
Residual-N	May	0.523	0.014	0.031	0.600	0.419	0.228	0.259	0.262
	Jul	0.407	0.019	0.036	0.311	0.301	0.164	0.322	0.209
	Sep	0.183	0.024	0.055	0.351	0.381	0.027	0.236	0.436
	Nov	0.384	0.067	0.083	0.695	0.436	0.108	0.153	0.349
	Jan	0.223	0.005	0.056	0.030	0.072	0.118	0.092	0.046
	Mar	0.295	0.007	0.028	0.107	0.062	0.053	0.128	0.106

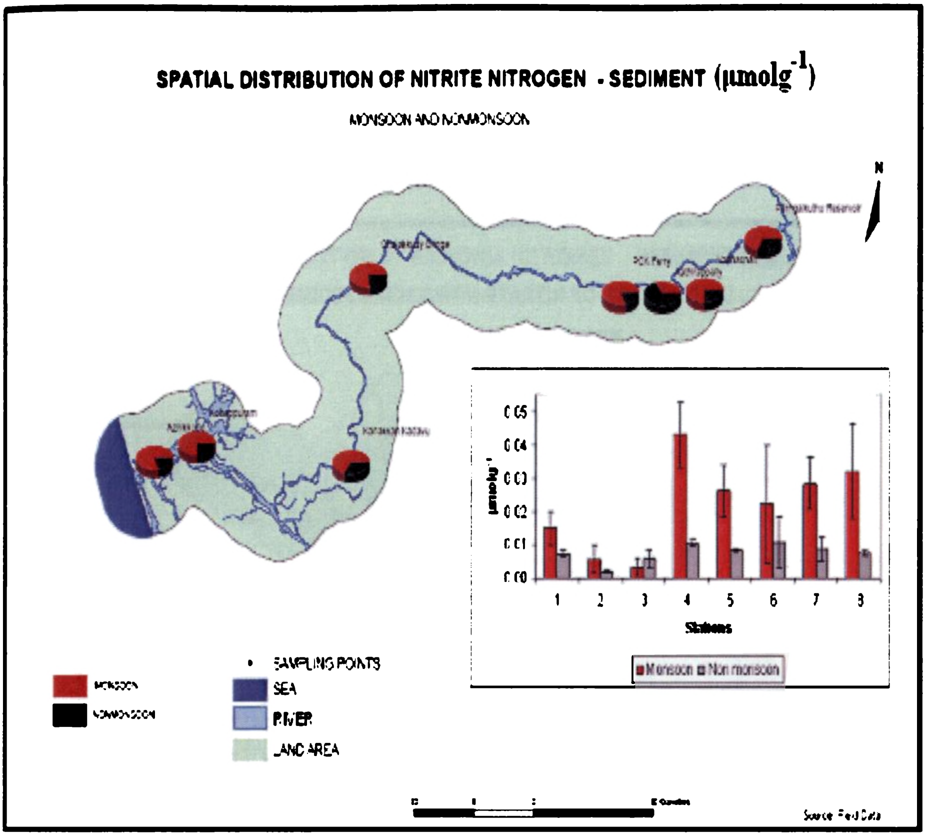

Figure 6.1 Seasonal average concentrations of nitrite-N (µmolg^{-1}) during monsoon and nonmonsoon periods in sediments of Chalakudy river.

Appreciable concentrations of NO_3-N were found in the sediments of the riverine system. The values of nitrate in sediment exhibited a consistent and increasing trend during the onset of monsoon (Figure 6.2). The concentrations were decreased on passing to nonmonsoon. The nitrate-N concentrations in sediment matter were comparatively higher as related to nitrite-N. The maximum monsoon nitrate concentration was observed to be 0.94 µmolg^{-1} and the minimum was 0.37 µmolg^{-1}. During nonmonsoon period, the maximum was 0.55 µmolg^{-1}and the minimum was 0.06 µmolg^{-1}.

Sediments of stations 1, 4 and 6 have produced large deviations in mean concentrations pointing to the fluctuating nature of physicochemical parameters that influence the nitrate concentrations of these sedimentary environments.

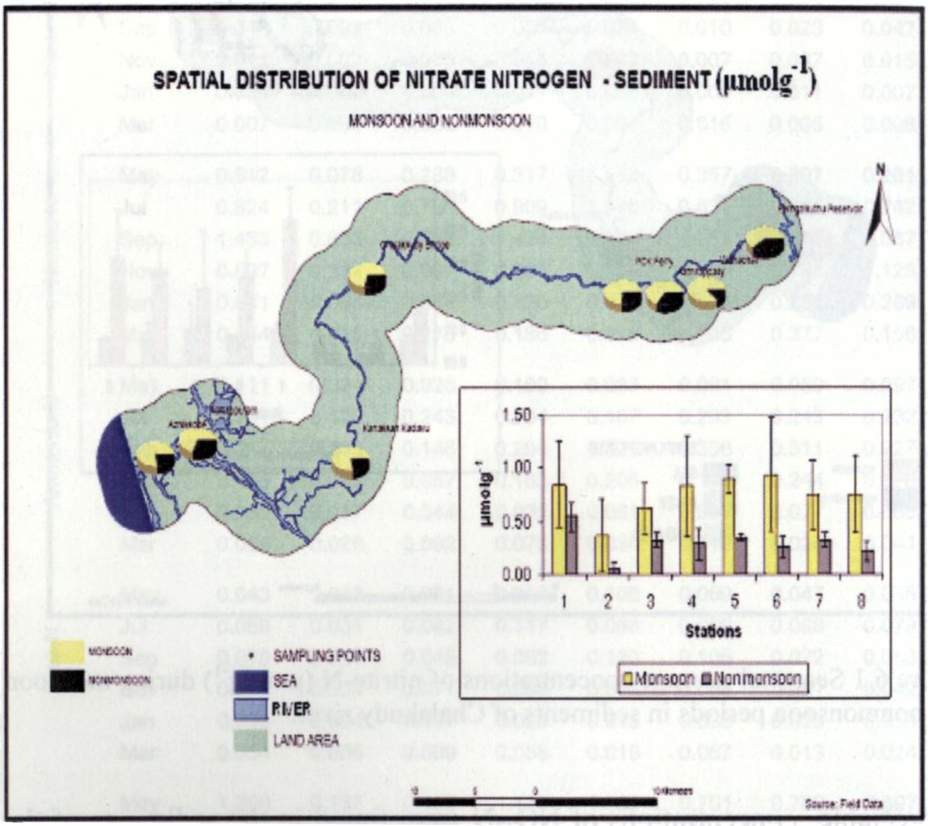

Figure 6.2 Seasonal average concentrations of nitrate-N (µmolg^{-1}) during monsoon and nonmonsoon periods in sediments of Chalakudy river.

Generally, monsoon concentrations of ammonia-N in river sediments were found to be higher in all locations (Figure 6.3). The monsoon and the nonmonsoon mean values were ranged from 0.08 to 0.21 µmolg^{-1} and 0.02 to 0.10 µmolg^{-1} respectively. It could be seen that during both seasons, the waterfall region of station 2 was having the least ammonia-N. It is important to note that these distributions represent patterns which actually occur with nutrient regimes and they need not be identical.

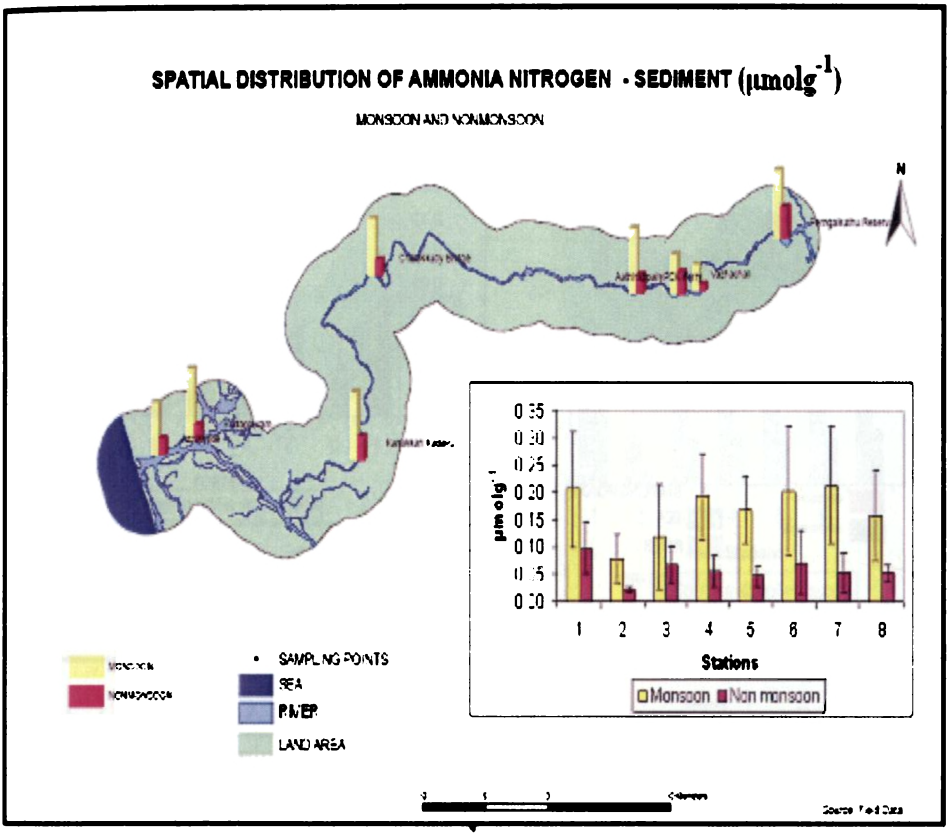

Figure 6.3 Seasonal average concentrations of ammonia-N (μmolg^{-1}) during monsoon and non monsoon periods in sediments of Chalakudy river.

The results of the seasonal and spatial estimations conducted on urea revealed lower values during both seasons (Figure 6.4). The monsoon values (0.031 to 0.097 μmolg^{-1}) were slightly higher than nonmonsoon values (0.004 to 0.047 μmolg^{-1}). The waterfalls station 2 had the least urea and reservoir station 1 presented high urea during both seasons.

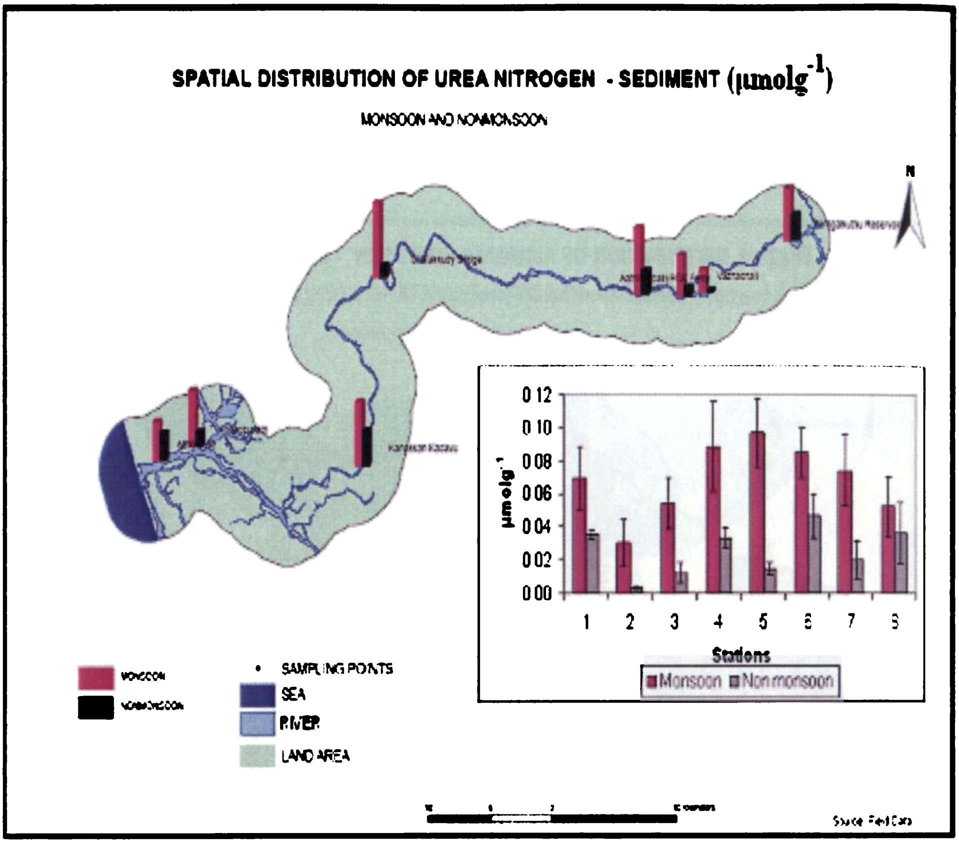

Figure 6.4 Seasonal average concentrations of urea-N (µmolg^{-1}) during monsoon and nonmonsoon periods in sediments of Chalakudy river.

The mean values of total N in sediments during the investigation period (Figure 6.5) exhibited a maximum of 1.64 and 0.95 µmolg^{-1} and a minimum of 0.51 and 0.09 µmolg^{-1} during monsoon and nonmonsoon periods respectively. A consistent and highly significant increasing trend was observed for total N values after the onset of monsoon. Lower values were observed during nonmonsoon. Both seasons recorded lower values at station 2. During nonmonsoon period, a constancy in concentration was noted from station 3 onwards towards estuary.

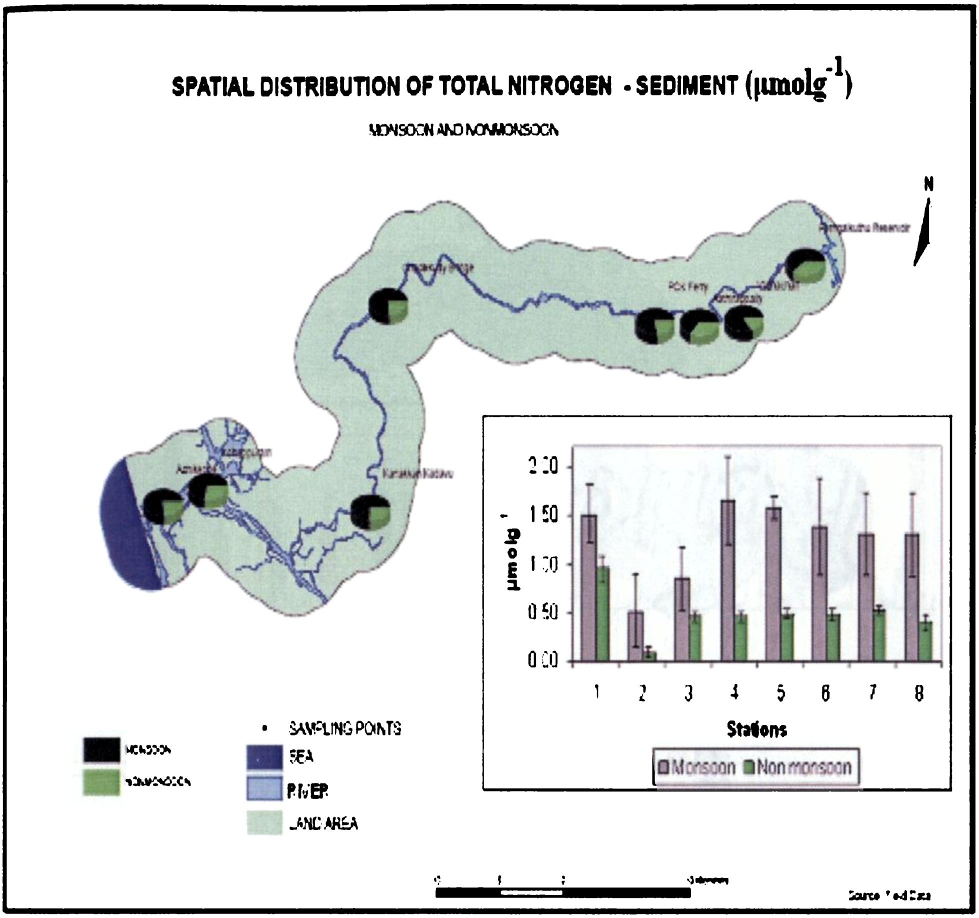

Figure 6.5 Seasonal average concentrations of total N (μmolg^{-1}) during monsoon and nonmonsoon periods in sediments of Chalakudy river.

The residual nitrogen is determined as the difference of total N and the sum of the other species analysed in this section (Figure 2.4), and mainly consists of organic forms (other than urea) such as proteins, lipids etc.

i.e,

Residual N = Total N - [nitrite-N + nitrate-N + ammonia-N + urea-N]

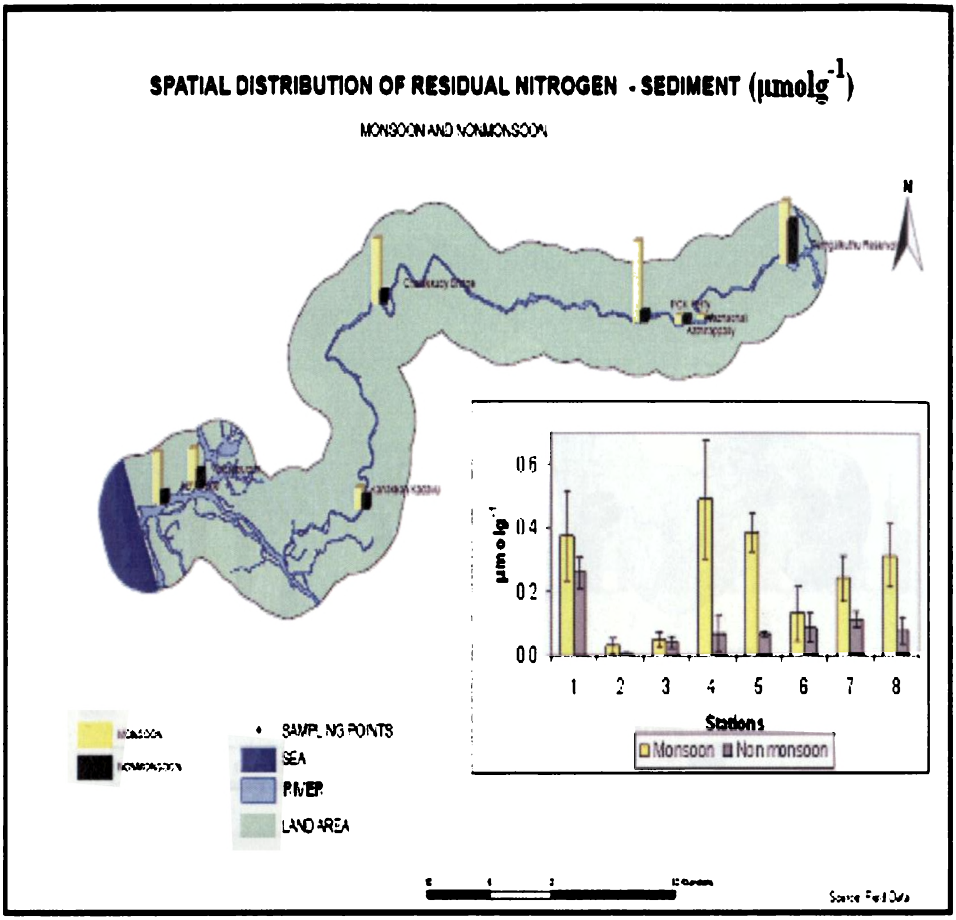

Figure 6.6 Seasonal average concentrations of residual N during monsoon and nonmonsoon periods in sediments of Chalakudy river.

The minimum and maximum mean values were 0.01 to 0.03 μmolg^{-1} and 0.26 to 0.49 μmolg^{-1} for monsoon and nonmonsoon periods respectively (Figure 6.6). Thus, during monsoon, the residual-N with appreciable values in upstream sediment showed a sharp decrease in the sediments of waterfall region, and then station 4 experienced a maximum. Again, the concentrations decreased towards riverine end and then gradually increased towards estuary. During nonmonsoon, only station 1, the reservoir, was having noticeably high residual-N which sharply decreased to an insignificant value at the second station, and all other stations had lower values around 0.1 µmolg^{-1}.

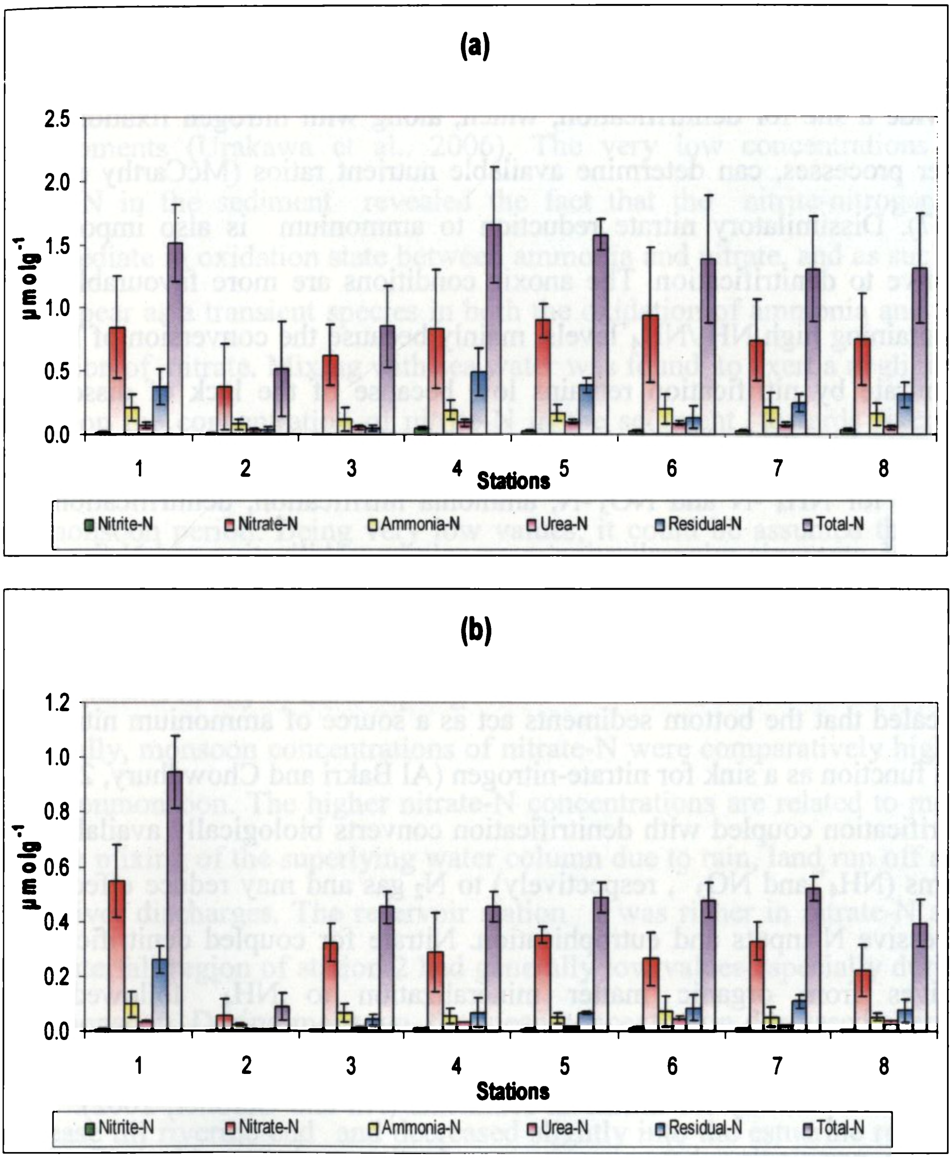

Figure 6.7 Nitrogen fractions in monsoon (a) and nonmonsoon (b) seasons.

Nitrogen is present in river sediments as fixed inorganic salts, such as nitrate, nitrite and ammonia and a range of organic nitrogen compounds, like amino acids, urea. and humic substances. Nitrate is preferably present under oxic conditions. The nitrate in the sediments of Chalakudy river is found to be higher (Figure 6.7). Ammonia is much lower Sediments provide a site for denitrification, which, along with nitrogen fixation and other processes, can determine available nutrient ratios (McCarthy et al., 2007). Dissimilatory nitrate reduction to ammonium is also important, relative to denitrification. The anoxic conditions are more favourable for maintaining high NH_3/NH_4^+levels, mainly because the conversion of NH_4^+ to nitrate by nitrification remains low because of the lack of dissolved oxygen under these conditions. The key processes in the soil zone are plant uptake for NH_4^+-N and NO_3^--N, ammonia nitrification, denitrification of NO_3^--N, ammonia mineralisation, ammonia immobilization and N fixation and all of these processes vary by land use type (Whitehead et al., 2006). Nutrient dynamics on sediments in the Suma Park Reservoir, Australia revealed that the bottom sediments act as a source of ammonium nitrogen and function as a sink for nitrate-nitrogen (Al Bakri and Chowdhury, 2006). Nitrification coupled with denitrification converts biologically available N forms (NH_4^+ and NO_3^-, respectively) to N_2 gas and may reduce effects of excessive N inputs and eutrophication. Nitrate for coupled denitrification derives from organic matter mineralization to NH_4^+ followed by nitrification. Dissimilatory nitrate reduction to ammonium (DNRA) is an alternative pathway for nitrate in sediments (An and Gardner, 2002). The relative partitioning between nitrate reduction pathways (denitrification versus DNRA) is important since denitrification removes fixed N from the system while DNRA returns it as bioavailable ammonium. The high concentrations of sedimentary nitrate-N in the present study pointed to higher rate of nitrification and less denitrification owing to the oxic condition present.

Nitrification, the conversion of ammonia (NH_3) to nitrate (NO_3^-) via nitrite (NO_2^-), is essential to the function of the nitrogen cycle in aquatic environments (Urakawa et al., 2006). The very low concentrations of nitrite-N in the sediment revealed the fact that the nitrite-nitrogen is intermediate in oxidation state between ammonia and nitrate, and as such it can appear as a transient species in both the oxidation of ammonia and the reduction of nitrate. Mixing with sea water was found to exert a negligible effect on the concentration of nitrite-N in the sediment towards riverine end. In majority of stations, the values seemed to be slightly lower during nonmonsoon period. Being very low values, it could be assumed that the nitrite-N is more or less uniformly distributed in the sediments of Chalakudy river and thus it ruled out any conditions for the existence of anoxic basins in any of the sampling sites.

Generally, monsoon concentrations of nitrate-N were comparatively higher than nonmonsoon. The higher nitrate-N concentrations are related to more intense mixing of the superlying water column due to rain, land run off and high river discharges. The reservoir station 1 was richer in nitrate-N and the waterfall region of station 2 had generally low values especially during non monsoon. During monsoon, the mean concentration decreased sharply from the reservoir towards waterfall region and then made a gradual increase till riverine end and decreased slightly into the estuarine regions. The high values were particularly important where there was influence on sediment from agriculture, industries and waste water and also physical degradation of the land area. The low values in the sediments at the waterfalls were to a greater extent due to the sandy nature of the sediments. Texture characteristics, support of aquatic organisms, and integrity of aquatic and riparian habitats essentially characterize the nutrients, especially the predominant nitrate species.

There occured a sharp decrease in ammonia-N from the reservoir towards waterfalls and then increased and exhibited fluctuating trend towards estuarine end. Release of ammonium from sediments were reported during periods of hypoxia and anoxia (Berman et al., 1999). The fluxes of ammonia from benthic recycling and from the river discharge could be of the same order of magnitude in monsoon as well as nonmonsoon seasons in this riverine system

The high values of urea-N in monsoon period pointed to the influence of river discharges in bringing urea from land during rain and getting engulfed in sediments. The levels of urea-N were not varying much within each season. The waterfall region of station 2 recorded the lowest concentrations of urea-N as in concomitance to the other forms (nitrite/ nitrate/ ammonia etc.) during both seasons. Station 5, wherein the river is flowing through Chalakudy town recorded much lower urea-N during nonmonsoon compared to the very high monsoon values which can be attributed to the locally discharged pollutants which enter the river sediment during monsoon. Nitrogenous compounds such as urea are released from sediments during periods of hypoxia and anoxia through similar mechanisms as for ammonium (Berman et al., 1999) and whatever their cause, extended periods of urea-N levels in sediments will increase the potential for sediment-associated contaminant fluxes and have a direct effect on the distribution of organisms and is particularly affecting the water quality. But urea-N being very low in the present study points to a less polluted ecosystem.

Like the other forms of N discussed, seasonality had also played a role in putting nonmonsoon period for a lower total N concentrations in the sediments of Chalakudy river. In nonmonsoon, the highest mean concentration was in the sediments of the reservoir at Peringalkuthu region (station 1) where the muddy sediments accumulating from various rivers may be able to retain total N contents to a maximum. Also, in both seasons the lowest mean concentration was at the waterfall region of Athirappalli (station 2) where the sandy nature of the sediments are very poor in retaining the total N contents or any other forms of N discussed earlier. The concentrations in the next six stations of the river were found to be increasing during monsoon, the highest quantity being felt at the ferry region of station 4. This could be because of the nature of local pollutants introduced from land getting trapped into the sediments, and also due to the fact that suspended solids are rapidly removed from the water column into the sediments in the mid-riverine and estuarine regions due to the effect of ionic concentrations (i.e, salinity). One of the remarkable features observed in the distribution of Total N was that the stations 3 to 8 exhibited almost uniform non monsoon concentrations. This could probably be due to the absence of discharges from land. Compared to the reference values the total N in the sediments of present study was not too high. With the increase of industrialization and human activities, inflow water can carry high concentrations of nutrients that mainly come from waste disposal to rivers. The relatively moderate Total-N in the sediments of Chalakudy river points to the reduced rate of human intrusion.

Residual N, which is mainly nitrogen present in organic form, is a significant component of the sedimentary N pool. Residual N dynamics can strongly impact the N pool because small changes in concentration can impart measurable changes in the biochemical environment of sediments. Similar to other forms of nitrogen experimented, a monsoonal hike in the concept of organic residual-N was also established. The lowest concentrations during both seasons were recorded by sediments of waterfall regions of station 2 and station 3. These being waterfall regions, the sediments in these stations were granulometrically categorised as sandy in nature which appreciably reduced the retention capacity for residual-N as it was primely comprised of organically bound forms. The results of CHN analysis described in Chapter III also showed low carbon and nitrogen in these stations which supports the present observation.

The relative importance of sediments as nitrogen source is greatly understood by this speciation. Various factors decide the distribution of nitrogen species in a particular sedimentary environment, since the physical and chemical characteristics of aquatic sediments are quite different. Also, a wide array of human activities is accelerating the natural fluxes of sedimentary nitrogen through rivers. Some global values related to studies on sedimentary nitrogen species are presented in Table 6.2.

Table 6.2 Some global reference values of N species in aquatic sediments

Sedimentary system	Form of nitrogen	Concentration	Reference
Lake sediments of China	Total-N	0.067 to 0.9 g/100g	Shuncai and Chen, 2000
Agriculturally loaded lakes located in southwestern Finland	Total-N	4.2 to 7.7 mg g^{-1}	Krogerus and Ekholm, 2003
Lakshadweep islands of Arabian sea	Nitrite-N	0.001 to 0.03 μmol g^{-1}	Anu et al.,2004
	Nitrate-N	0.129 to 3.25 μmol g^{-1}	
	Total-N	5.99 to 168.87 μmol g^{-1}	
Jiaozhou Bay in Qingdao City in China	Inorganic-N	0.05 to 0.25 mg g^{-1}	Xuegang et al., 2007
	Organic-N	0.02 to 0.38 mg g^{-1}	
	Total-N	0.13 to 0.41 mg g^{-1}	

Nitrogen species: Stationwise profusion (in percentage)

The stationwise percentage distribution of N species [nitrite-N, nitrate- N, ammonia-N, urea-N and residual-N] in the sediments of Chalakudy river during monsoon and nonmonsoon periods are given in Figures 6.8a and 6.8b respectively.

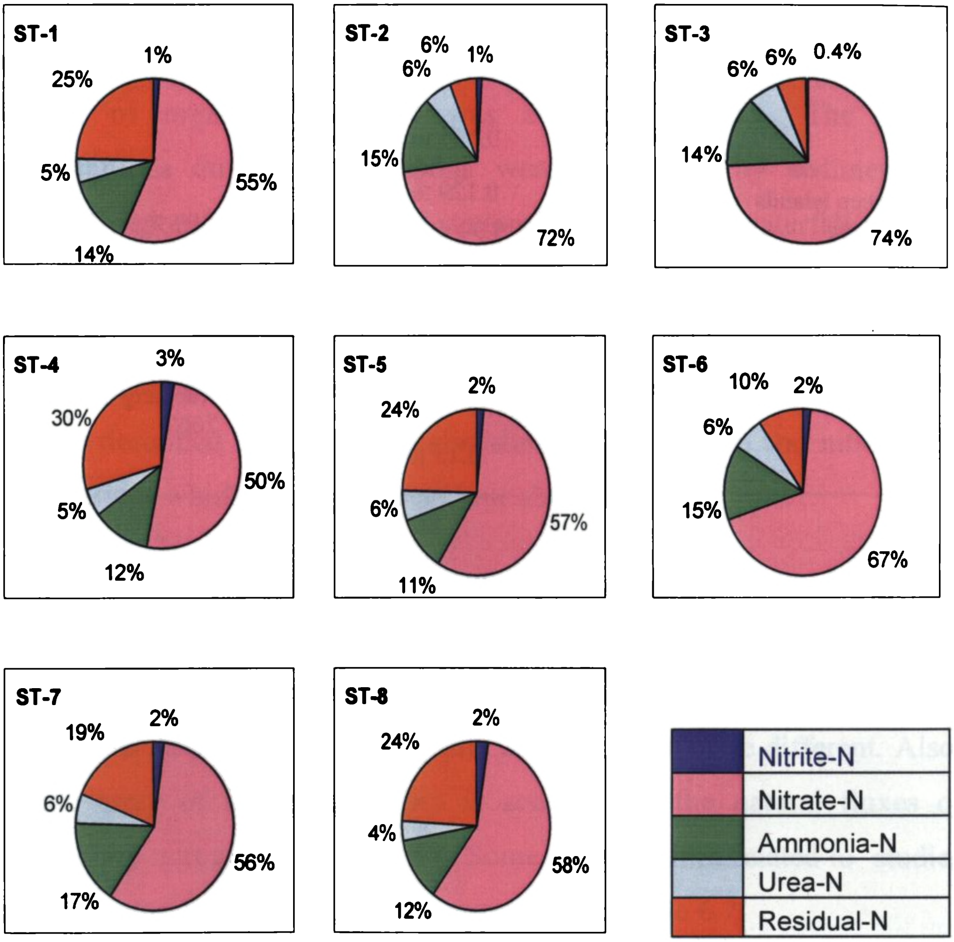

Figure 6.8a Percentage-wise distribution of nitrogen species (nitrite-N, nitrate-N, ammonia-N, urea-N and residual-N) in the sediments at different sampling stations of Chalakudy river during monsoon season.

During monsoon period, nitrite-N was found to be very low ranging fom 1 to 3% at all stations except station 3 where it is 0.4% (Figure 6.8a). Nitrate-N was the predominant form ranging from 50 to 74%. The highest percentage of nitrate–N was observed at waterfalls regions (stations 2 and 3) and Kanakkankadavu (Station 6). The ammonia-N ranged from 11 to 17%. Urea-N in sediments was low and fell in the range 4 to 6%. Residual N, mainly organic form of nitrogen, was only 6% for stations 2 and 3, the waterfalls regions, but was ranging from 19 to 30% in other stations except station 6, where the percentage was 10%. Stations 1 (dam), 4 (ferry), 5 (river through town) and 8 (the estuary) had comparatively higher percentage of residual N in their sediments. The highest percentage of residual N at the ferry region (30%) could be attributed to the discharge from land and the sedimentation which predominates in bringing organic or other residual components into the sediments during rainy season. The percentages of urea + residual-N were identical to the studies of Xuegang et al., (2007) who recorded organic N as 24%–80% of total-N in Jiaozhou Bay, a typical semi-enclosed bay in Qingdao City in China.

Nonmonsoon period nitrite-N was found to be very low ranging fom 1 to 2% (Figure 6.8b). Nitrate-N was the dominant form ranging from 55 to 72%. The ammonia-N ranged from 10 to 24%. Urea N in sediments varied from 3 to 9%. The features of these N species were quite similar to that during monsoon period and seasonality did not play an important role in all stations. But residual-N showed some variations. Residual N remains as 6% for station 2, but increased to 9% at station 3 (the waterfalls regions), compared to the monsoon values. It was ranging from 14 to 27% in other stations with noticeable fluctuations. Also, at the ferry region of station 4, the percentage of residual N decreased from 30% in monsoon to 15% in nonmonsoon. This specifically leads to the conclusion that station 4 lies comparatively in a polluted background due to agricultural activities, presence of factories and industrial establishments.

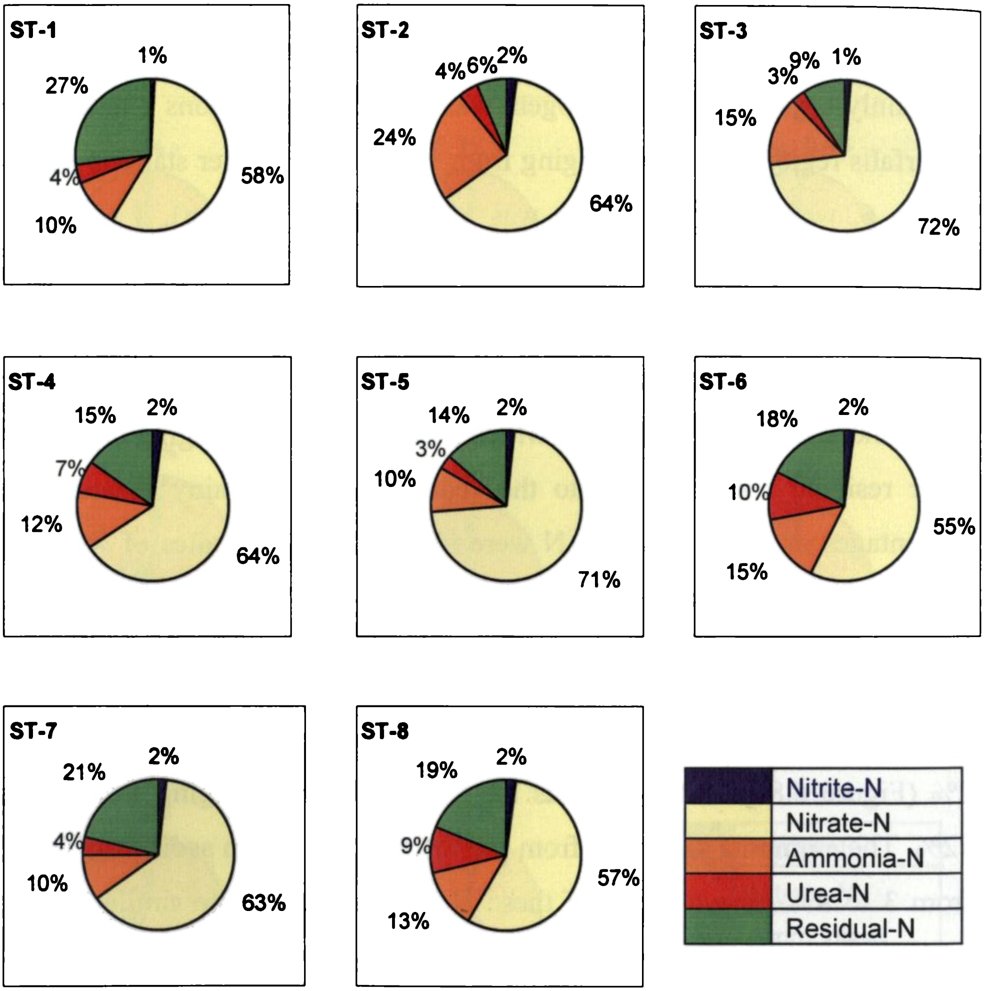

Figure 6.8b Percentage-wise distribution of nitrogen species (nitrite-N, nitrate-N, ammonia-N, urea-N and residual N) of the different sampling stations of Chalakudy river during nonmonsoon season.

Phosphorus forms: Distribution profiles

The main inorganic forms of phosphorus in sediments are labile phosphorus (exchangeable forms weakly bound to the sediment matrix), phosphorus associated to Al and Fe oxides and hydroxides, phosphorus associated to Ca minerals, polyphosphates and residual inorganic (refractory) phosphorus (included in very resistant minerals and in the crystal lattices of some silicates). The capacity of sediments to adsorb phosphate will be largely determined by the chemistry of the sediment itself and by the concentration of the sedimenting phosphate (Nair et al., 1993). Different species of phosphorus (in $\mu molg^{-1}$) in the sediments of Chalakudy river were estimated and the results are presented in this section. The whole set of values are presented in Table 6.3. Seasonal trends are also pictured based on geostatistics.

The term loosely bound phosphorus represents phosphorus in exchangeable form. The concentrations of these exchangeable P in sediments displayed very low values. The mean values ranged from 0.011 to 0.030 $\mu molg^{-1}$ during monsoon and from 0.009 to 0.030 $\mu molg^{-1}$ during nonmonsoon periods (Figure 6.9). All stations at both seasons displayed a fluctuating trend of low concentrations. Almost a steady value was noticeable during monsoon till station 5 where a slight increase was observed and then again the concentration decreased and kept more or less a uniform value along the downstream stations. But the nonmonsoon period also showed fluctuating values with a hike only at the estuarine region.

Table 6.3 Distribution of loosely bound P, iron/aluminium bound P, polyphosphates, calcium bound P, refractory P, total inorganic P and total P (in $\mu molg^{-1}$) in the sediments of Chalakudy river.

Parameters	Months	S1	S2	S3	S4	S5	S6	S7	S8
Loosely bound P	May	0.035	0.014	0.027	0.014	0.058	0.036	0.027	0.025
	Jul	0.014	0.012	0.014	0.019	0.016	0.015	0.014	0.016
	Sep	0.004	0.007	0.007	0.007	0.031	0.002	0.019	0.029
	Nov	0.011	0.012	0.016	0.013	0.014	0.010	0.014	0.009
	Jan	0.013	0.011	0.005	0.017	0.013	0.008	0.033	0.028
	Mar	0.016	0.010	0.017	0.019	0.012	0.010	0.028	0.025
Fe/Al bound P	May	0.629	0.305	0.353	0.554	0.522	0.488	0.481	0.488
	Jul	0.645	0.360	0.448	0.584	0.507	0.453	0.485	0.487
	Sep	0.653	0.331	0.323	0.582	0.550	0.530	0.348	0.358
	Nov	0.684	0.313	0.338	0.513	0.499	0.563	0.468	0.380
	Jan	0.545	0.343	0.334	0.591	0.648	0.310	0.375	0.364
	Mar	0.493	0.285	0.285	0.563	0.693	0.275	0.360	0.338
Poly phosphates	May	0.448	0.211	0.288	0.602	0.353	0.507	0.669	0.555
	Jul	0.303	0.178	0.333	0.804	0.730	0.643	0.420	0.495
	Sep	0.821	0.213	0.353	0.975	0.805	0.708	0.828	0.690
	Nov	0.770	0.213	0.202	0.903	0.517	0.733	0.538	0.935
	Jan	0.847	0.390	0.305	0.708	0.658	0.405	0.353	0.868
	Mar	0.685	0.230	0.295	0.958	0.385	0.503	0.403	0.555
Ca bound P	May	0.044	0.145	0.073	0.177	0.242	0.193	0.363	0.347
	Jul	0.010	0.051	0.043	0.240	0.258	0.270	0.275	0.293
	Sep	0.031	0.090	0.100	0.315	0.263	0.255	0.368	0.515
	Nov	0.133	0.193	0.103	0.308	0.333	0.243	0.279	0.513
	Jan	0.053	0.028	0.178	0.119	0.220	0.155	0.095	0.153
	Mar	0.041	0.073	0.180	0.223	0.230	0.115	0.140	0.033
Refractory P	May	0.198	0.023	0.023	0.165	0.145	0.050	0.060	0.033
	Jul	0.118	0.013	0.098	0.143	0.195	0.020	0.088	0.050
	Sep	0.158	0.038	0.042	0.050	0.108	0.048	0.028	0.138
	Nov	0.100	0.058	0.023	0.040	0.085	0.173	0.018	0.195
	Jan	0.025	0.090	0.023	0.178	0.040	0.083	0.210	0.150
	Mar	0.060	0.033	0.015	0.235	0.098	0.048	0.043	0.053
Total inorganic P	May	1.353	0.698	0.762	1.512	1.320	1.273	1.600	1.447
	Jul	1.089	0.613	0.934	1.790	1.706	1.400	1.282	1.341
	Sep	1.666	0.678	0.824	1.929	1.756	1.542	1.589	1.729
	Nov	1.698	0.787	0.681	1.775	1.448	1.720	1.316	2.032
	Jan	1.482	0.861	0.845	1.612	1.578	0.960	1.065	1.562
	Mar	1.295	0.630	0.792	1.997	1.417	0.950	0.973	1.003
Total P	May	2.093	0.858	1.196	2.381	2.036	1.931	2.445	2.235
	Jul	1.729	0.945	1.028	3.843	2.569	2.160	1.969	2.078
	Sep	2.554	1.006	1.165	4.081	2.659	2.378	2.415	2.711
	Nov	2.636	0.913	1.084	2.816	2.224	2.640	2.006	3.169
	Jan	2.254	0.879	1.154	2.449	2.430	1.496	1.699	2.355
	Mar	2.003	0.954	1.123	3.041	2.209	1.451	1.541	2.123
Residual P	May	0.740	0.161	0.434	0.869	0.717	0.658	0.846	0.788
	Jul	0.640	0.332	0.094	2.054	0.863	0.760	0.687	0.737
	Sep	0.888	0.328	0.341	2.152	0.903	0.836	0.826	0.982
	Nov	0.939	0.126	0.403	1.041	0.776	0.920	0.691	1.137
	Jan	0.772	0.018	0.310	0.837	0.852	0.536	0.634	0.793
	Mar	0.708	0.324	0.331	1.045	0.792	0.501	0.569	1.121

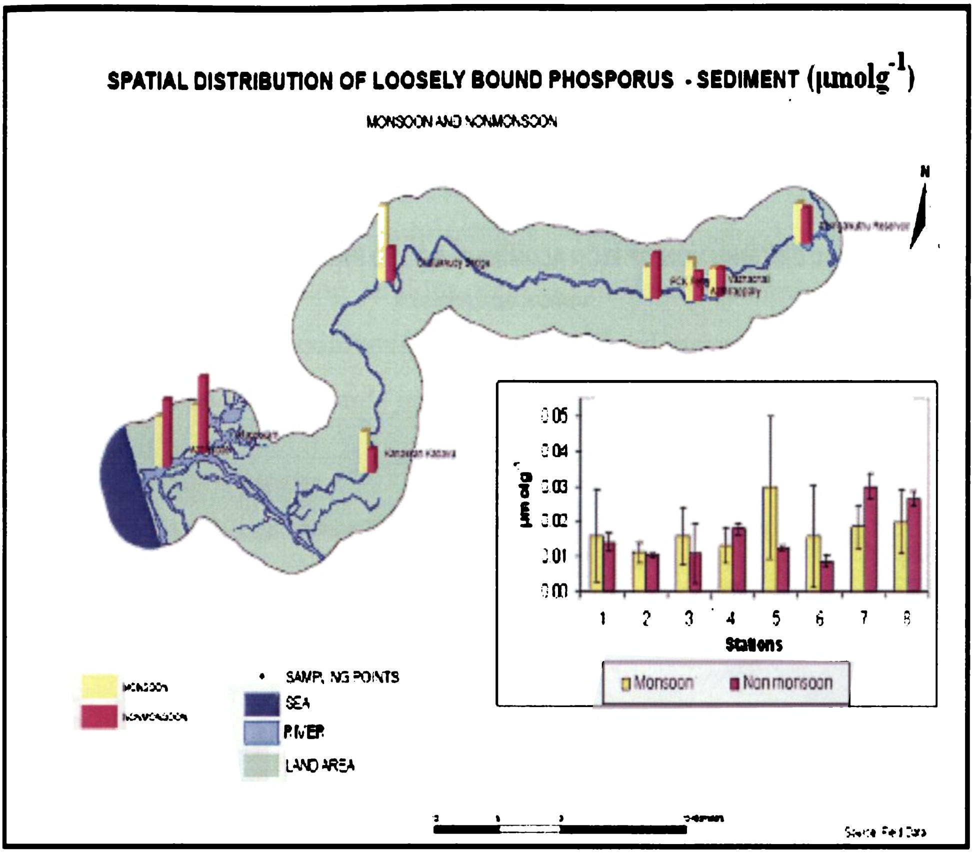

Figure 6.9 Seasonal average concentrations of loosely bound P (µmolg^{-1}) during monsoon and nonmonsoon periods in sediments of Chalakudy river.

High concentrations of Fe/Al bound P in the range of 0.33 to 0.65 µmolg^{-1} and 0.29 to 0.67 µmolg^{-1} were recorded in the monsoon and nonmonsoon seasons respectively (Figure 6.10). The monsoon visualized a high Fe/Al bound P in the reservoir (station1) which lowered at waterfall stations 2 and 3, then increased slightly at the ferry (station 4) and finally gradually descended in the sediments of each station towards estuary. However, the nonmonsoon season showed a noticeable decrease at the reservoir, whereas in other stations it decreased slightly except the sediments of station 5 which projected an increase in Fe/Al bound P and station 4, which slightly enhanced the concentration. Thus, stations 1 and 5 had the highest concentrations during monsoon and nonmonsoon seasons respectively.

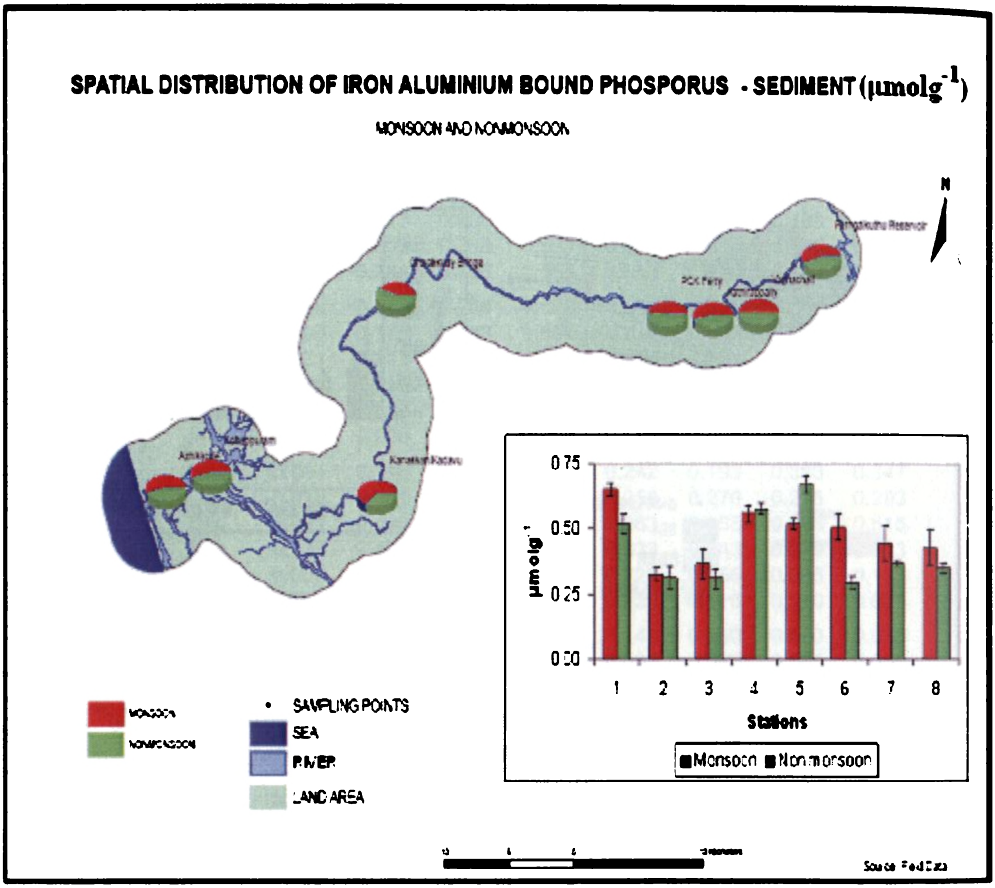

Figure 6.10 Seasonal average concentrations of Fe/Al bound P (μmolg^{-1}) during monsoon and nonmonsoon periods in sediments of Chalakudy river.

The mean monsoon values for polyphosphates in sediments ranged from 0.20 to 1.75 μmolg^{-1}, and the nonmonsoon values from 0.30 to 0.83 μmolg^{-1} (Figure 6.11). It could be seen that upstream sediments of station 1 had high mean value for polyphosphates, and it was projected higher during nonmonsoon period. As such, the ability of sediments in reservoirs to retain P is key to determining downstream water quality. The neighbouring waterfall regions had almost identical concentrations which were low during both seasons. The sediments of the next station 4, the ferry, experienced a hike in polyphosphates which remained seasonally unchanged. The remaining stations kept a constancy towards estuary in monsoon. Finally the sediments at the estuarine downstream had slightly higher polyphosphates towards nonmonsoon.

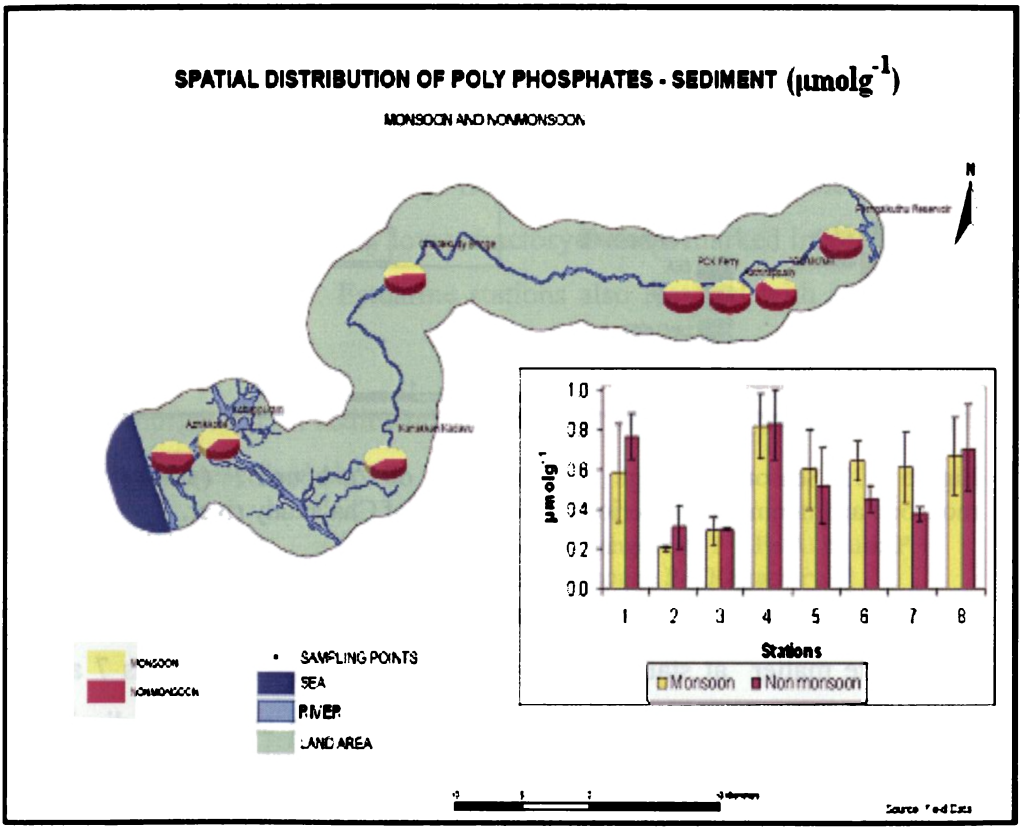

Figure 6.11 Seasonal average concentrations of polyphosphates (µmolg^{-1}) during monsoon and nonmonsoon periods in sediments of Chalakudy river.

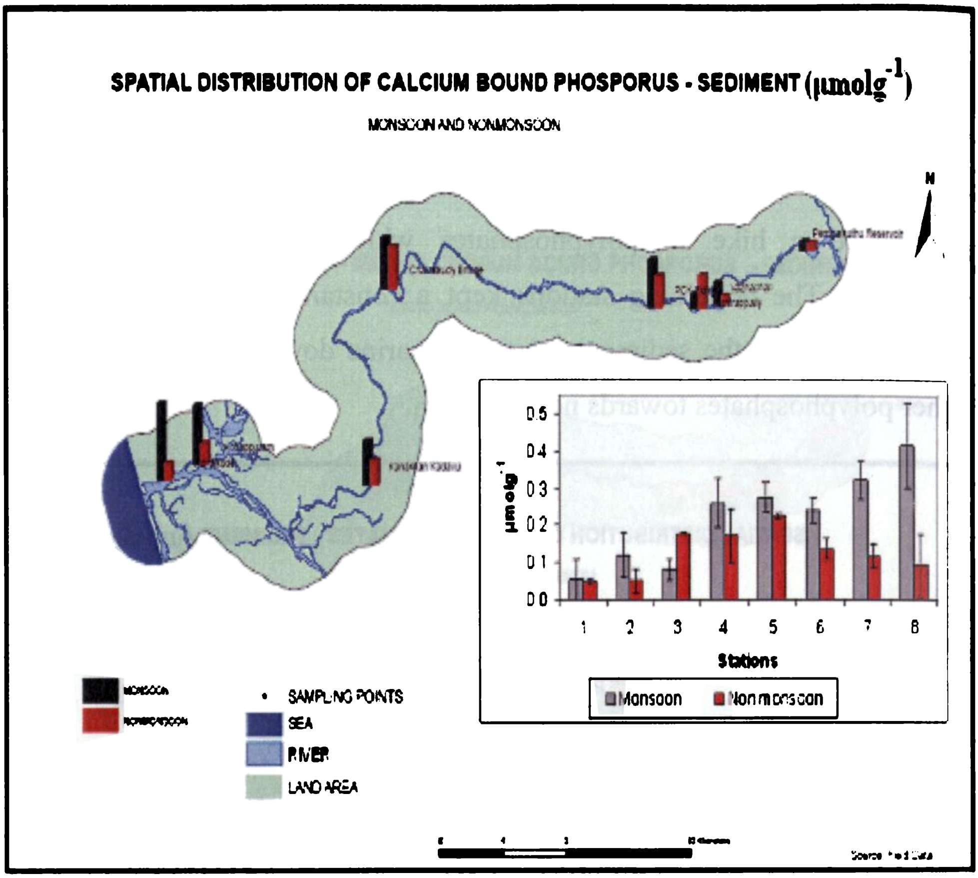

Figure 6.12 Seasonal average concentrations of Ca bound P (μmolg^{-1}) during monsoon and nonmonsoon periods in sediments of Chalakudy river.

Quite contrasting to the low concentrations of calcium bound phosphorus in particulate matter at stations 1 to 6, and a sharp rise at stations 7 and 8 (Figure 5.3), the calcium bound phosphorus in the sediments displayed entirely different behaviour at all stations from 1 to 8 (Figure 6.12) . The lowest mean concentration of 0.05 μmolg^{-1} was recorded by the dam sediments, during both seasons. The highest mean value reported was 0.42 (by station 5) and 0.23 μmolg^{-1} (by station 8) for monsoon and nonmonsoon periods respectively. The sediments of water fall regions 2 and 3 showed comparatively low calcium bound P. Generally, all other stations showed the monsoon values to be higher.

Low amounts of refractory P were detected in the sediments, and the levels exhibited a spatial variability. The mean refractory P ranged from 0.03 to 0.14 μmolg^{-1} during monsoon and from 0.02 to 0.21 μmolg^{-1} during non monsoon (Figure 6.13). The mean concentrations did not exhibit a clear seasonal variability. These lead to the presence of certain minute fraction of refractory P into all locations of the river. The monsoon depicted the highest refractory P at the upstream, then sharply decreased at the waterfall regions, then increased towards the middle, again decreased downstream ending with a hike at the estuary. But, during nonmonsoon, the upstream regions were distinguished by low refractory P and a marked increase in the ferry region of station 4. Estuarine stations also featured with appreciable presence of refractory P.

The total inorganic P in sediments is taken as the sum of the five fractions of phosphorus described above.

Total inorganic phosphorus = {Loosely bound (exchangeable) P + Fe/Al bound P + Polyphosphates + Ca bound P + Refractory P}

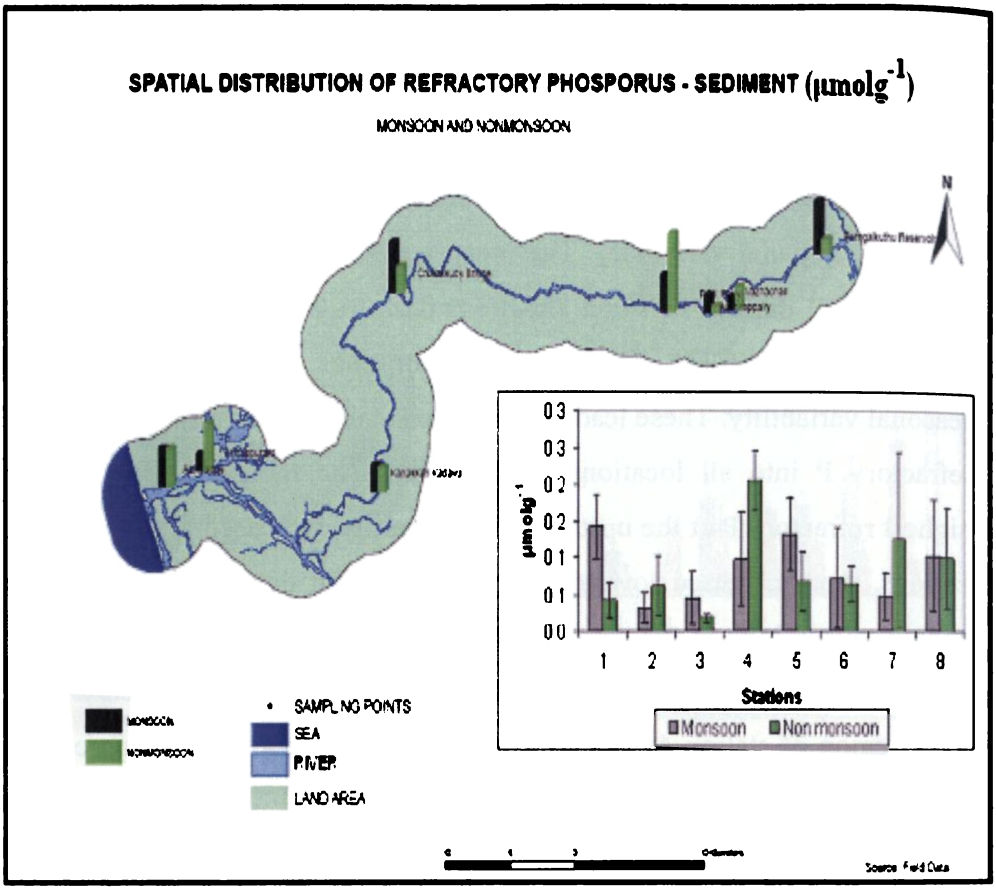

Figure 6.13 Seasonal average concentrations of refractory P (µmolg^{-1}) during monsoon and nonmonsoon periods in the sediments of Chalakudy river

The values for total inorganic P are found to be appreciably high (Table 6.3). The mean monsoon values ranged from 0.69 (station 2) to 1.75 (station 4) µmolg^{-1} and the nonmonsoon values from 0.75 (station 2) to 1.80 (station 4) µmolg^{-1} (Figure 6.14). It can be noted that the lowest inorganic P was detected in the sediments of station 2, exclusively, the waterfalls region, probably because of the sandy nature of the sediments.

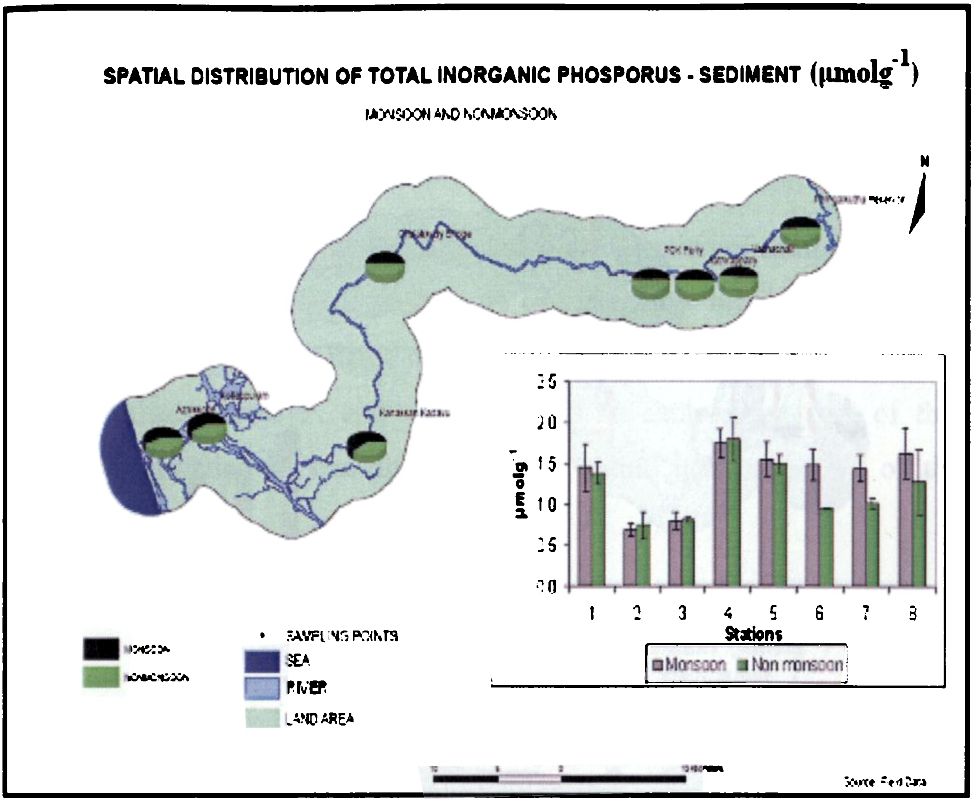

Figure 6.14 Seasonal average concentrations of total inorganic P (µmolg^{-1}) during monsoon and non monsoon periods in sediments of Chalakudy river.

During monsoon, the total inorganic P in sediments was high for reservoir, then decreased sharply towards waterfalls (stations 2 and 3), again increased appreciably at the ferry region (Station 4) and then steady decrease occurred downstream which finally pictured a marginal increase at the estuary. The sediments of upstream stations had very closer values of total inorganic P for monsoon and nonmonsoon seasons whereas, the riverine and estuarine regions had values in monsoon sharply decreasing in nonmonsoon.

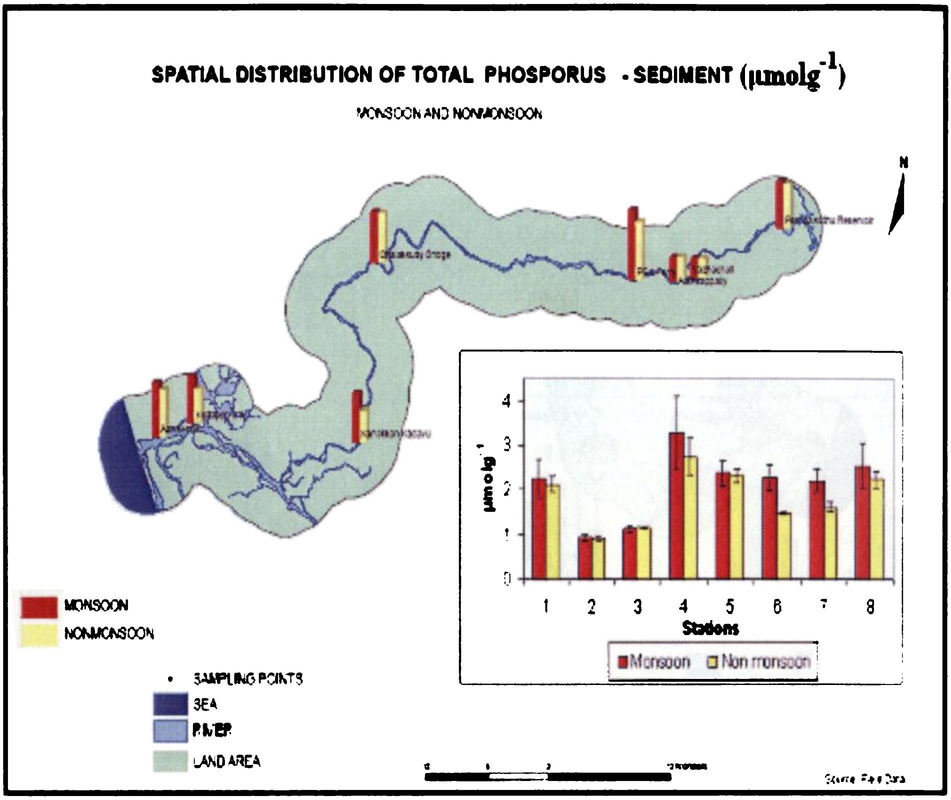

Figure 6.15 Seasonal average concentrations of total P ($\mu molg^{-1}$) during monsoon and nonmonsoon periods in sediments of Chalakudy river.

The total P estimated after digestion of the sediment sample includes all inorganic and organic forms of P and had the mean monsoon values ranged from 0.93 to 3.28 $\mu molg^{-1}$, and the nonmonsoon values ranged from 0.92 to 2.75 $\mu molg^{-1}$ (Figure 6.15). The highest concentration during both seasons was exhibited by the sediments of the ferry region (station 4), and lowest by the waterfalls station (station 2). These observations are quite similar to the concentrations of total inorganic P in sediments. The station 4 also had large deviation in its bimonthly values. Upstream monsoon and nonmonsoon values were almost closer. But towards the middle of the river and also towards estuary, monsoon values of total P were higher as compared to nonmonsoon values. It can be seen that the sediments of Chalakudy river is loaded with remarkable amount of total P.

The difference between total P (estimated after digestion of sample) and the total inorganic P (calculated as the sum of extractable inorganic fractions) is reproduced here by the name residual P which may comprised mainly of organically associated P, and the focus is to explore the role of this phosphorus fraction in contributing to the nature and properties of the sediments.

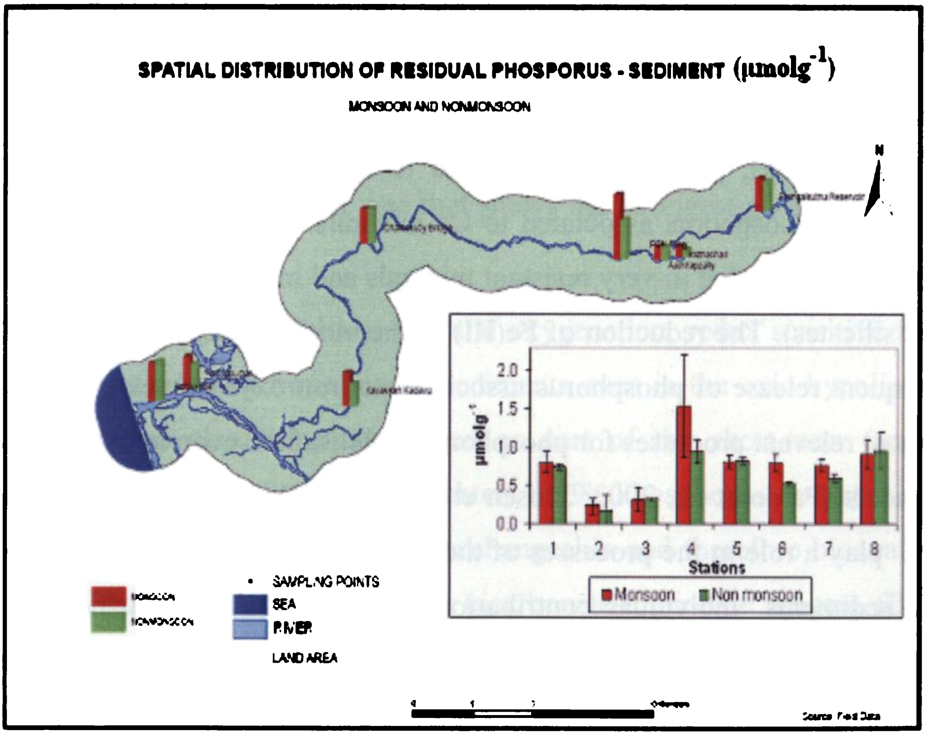

Figure 6.16 Seasonal average concentration of residual P (µmolg^{-1}) during monsoon and nonmonsoon periods in sediments of Chalakudy river.

The mean monsoon residual P values ranged from 0.24 to 1.53 μmolg^{-1}, and the nonmonsoon values from 0.17 to 0.95 μmolg^{-1} (Figure 6.16). The sediments of waterfall regions have low residual N, whereas, all other stations possessed appreciably high concentrations with the ferry station 4 recording the highest, and it should be noted that this station also featured with high deviations in bimonthly values during monsoon.

River sediments contain P in a variety of forms. The bottom sediments act as a source of filterable reactive phosphorus (Al Bakri and Chowdhury, 2006). Phosphorus is found in sediments in both organic and inorganic forms. Thus, the release of PO_4^{3-} from sediments into overlying water during anoxia is a result of the complex interaction between biotic and abiotic processes in the water column and sediments. The main inorganic forms are labile phosphorus (exchangeable forms weakly bound to the sediment matrix), phosphorus associated to Al, Fe and Mn oxides and hydroxides, phosphorus associated to Ca minerals, and residual inorganic phosphorus (included in very resistant minerals and in the crystal lattices of some silicates). The reduction of Fe(III) to the more soluble Fe(II) and the subsequent release of phosphorus associated to iron oxyhydrates is one of the most relevant processes for phosphorus mobilisation even in calcareous sediments (Pardo et al., 2003; Jensen et al., 2006). Oxides and hydroxides of Al play a role in the processes of the release and uptake of phosphorus from sediments. Individual contributions of Fe and Al are difficult to distinguish. Phosphorus sorption by Al is pH-sensitive, whereas under reducing conditions Al maintains its adsorptive capacity. This fact, and the higher affinity for P sorption which Al shows over Fe has led to the proposal of transforming Fe-P to Al-P by means of alum treatment as a method for P immobilization (Pardo et al., 2003). As for iron, sorption of P onto oxides and hydroxides of Mn is controlled by redox processes. However, Mn is usually found in sediments in minor amounts, its role in the phosphorus cycle being less relevant than that of Al and Fe. Ca-bound P can be orthophosphate adsorbed onto $CaCO_3$ (labile forms of P), or different forms of apatite (calcium phosphate). These forms of apatite are considered to be unavailable, although they are pH sensitive. So, calcium can be relevant for the removal of phosphorus from the water column and can contribute to the permanent burial of P in sediments. The organic pool of phosphorus in sediments includes humic and fulvic complexes, phosphate esters, sugar phosphates, phytate and other compounds. Organic matter can act on phosphate sorption in two ways, either by sorbing phosphate or by blocking sorption sites. The four elements mentioned above (Al, Ca, Fe and Mn) can form complexes with the organic matter of the sediment, Mn being the one that shows the strongest affinity (Pardo et al., 2003).

Notwithstanding artificial aeration and oxygenation, redox sensitive forms of P do get released from bottom sediments even in the oxic hypolimnion and therefore should be considered as part of the short-term (annual) bioavailable P pool (Pacini and Gachter, 1999). Phosphorus extracted using NaCl (NaCl-P) represents a fully exchangeable and therefore bioavailable phase. Phosphorus extracted using bicarbonate-dithionate reagent (BD-P) and that extracted using 0.1M NaOH (NaOH-P) in the sediments are released from Fe and Al bounded P and polyphosphates respectively. While Ca bound P extracted using HCl (HCl-P) and refractory P extracted using 1M NaOH accumulated entirely, majority of NaCl-P, BD-P and 0.1M

NaOH-P are released and can be considered as representative of the maximum potentially bioavailable P.

In the presence of oxygen, high concentrations of phosphates in the water will combine with suspended particles. These particles eventually settle to the river bottom and are temporarily removed from the cycling process. Phosphates often become long-term constituents of the bottom sediments. Mechanisms influencing the benthic phosphorus release are redox reactions, adsorption/desorption processes, various environmental variables like temperature, dissolved oxygen concentration, pH etc and mineralization of organic matter (Nowlin et al., 2005).

Some global reference values of different species of P in sediments are presented in Table 6.4. Fractionation of sediment phosphate reflects the role of chemical speciation of phosphates as nutrients in the riverine systems and is indicative of the processes controlling the pathways of phosphorus. Quantitatively, the fractions in isolation or in combination differ due to physicochemical as well as biochemical changes and seasonal fluctuations. Land use practices in uplands, along with processes occurring in the river banks and sediments, effect of rain water as well as sea water mixing and sedimentation of particulate matter rich in nutrients could all explain this special pattern in concentration of different phosphorus species.

Table 6.4 Some global reference values of different species of P in sediments.

Sedimentary system	Form of phosphorus	Concentration	Reference
Southwest coast of India (using different extraction techniques)	Exchangeable P	11.8–59.4 μg g^{-1}	Nair et al., 1993
	Fe/Al bound P	12.4–34.6 μg g^{-1}	
	Ca bound P	2.0–44.3 μg g^{-1}	
Reservoir of Bort-Les-Orgues, France	NAIP	0.26 – 1.43 mg g^{-1}	Ruban and Demare, 1998
	OP	0.13 –0.90 mg g^{-1}	
	AP	0.1 – 0.44 mg g^{-1}	
	TP	0.43 – 2.56 mg g^{-1}	
Agriculturally loaded lakes in southwestern Finland	Total P	0.9–1.2 mg g^{-1}	Krogerus and Ekholm, 2003
Besos River basin, Barcelona,Spain	Total P	1355±16 mg kg^{-1}	Pardo et al., 2003
	Organic P	205± 7 mg kg^{-1}	
	Inorganic P	1107±20 mg kg^{-1}	
	Apatite P	505±17 mg kg^{-1}	
Fertilizer loaded pine plantations sediments 10-cm depth, Piedmont of Georgia (Athens and Eatonton)	Extractable P	0.8–14 μg g^{-1}	Sartori et al., 2007
	Total-P	339–691 μg g^{-1}	
Mapire river,Venezuela	Labile P	0.1–3.5 mg kg^{-1}	Chaco´n et al., 2008
	Fe/ Al bound P	1.6–50.9 mg kg^{-1}	
	Resistant inorganic P	9.8–33.0 mg kg^{-1}	
	Residual-P	46.7–143 mg kg^{-1}	
	Total-P	179.2–373.9 mg kg^{-1}	
Jiaozhou Bay in Qingdao City in China	Inorganic P	0.08–0.21 mg g^{-1}	Xuegang et al., 2007
	Organic P	0.01– 0.16 mg g^{-1}	
	Total-P	0.12–0.34 mg g^{-1}	

The chloride extraction step is designed to identify the adsorbed, exchangeable- P which is released as a result of an increase in salinity

(Psenner et al. 1988). Actually, the mean concentration of exchangeable P was very low and showed only mild variations in all stations. This lead to the conclusion that exchangeable P was not a prime factor as far as the sedimentary environment of Chalakudy river was concerned.

Both seasons were characterized with high Fe/Al bound P in the sediments (Figure 6.17). The high amount of this bicarbonate-dithionate extracted P, observed at low discharges is probably due to the coating of sediment particles with iron oxides and hydroxides bound P (Pacini and Gachter, 1999). Desorption of inorganic P fractions is in turn dependent for example on chemical conditions such as the concentration of phosphates and the prevailing temperature and pH of the water. Fe bound-P (Fe-P) often occupies a larger proportion of total P in sediments under oxidizing conditions, and this proportion should decrease under reducing conditions as P is released from anaerobic conditions (Moore and Reddy, 1994). Fe-P concentration also decreases with depth, because of its mobilization in deeper reduced sediments (Moore et al., 1991). Chaco′n et al. (2008) found that in Mapire river, Venezuela, the most labile P and Fe/Al bound P forms were highly dependent on seasons.

The sandy nature of sediments explain the low polyphosphates at the waterfalls stations and also the reduction in discharge of local pollutants at this station in comparison to the other stations. The mid-station 5 and downstream stations 6 and 7 behave differently in that the monsoon values were higher showing, particularly, the influence of rain in bringing the local pollutants generated by human activities. Assimilation of polyphosphates by organisms may also reduce the concentrations of polyphosphates in the sediments of these stations in nonmonsoon season. Certain bacteria can accumulate phosphate as polyphosphate granules in the cells, and they can cleave intracellular polyphosphate to generate energy necessary for substrate uptake, which causes release of phosphorus (Zou et al., 2006).

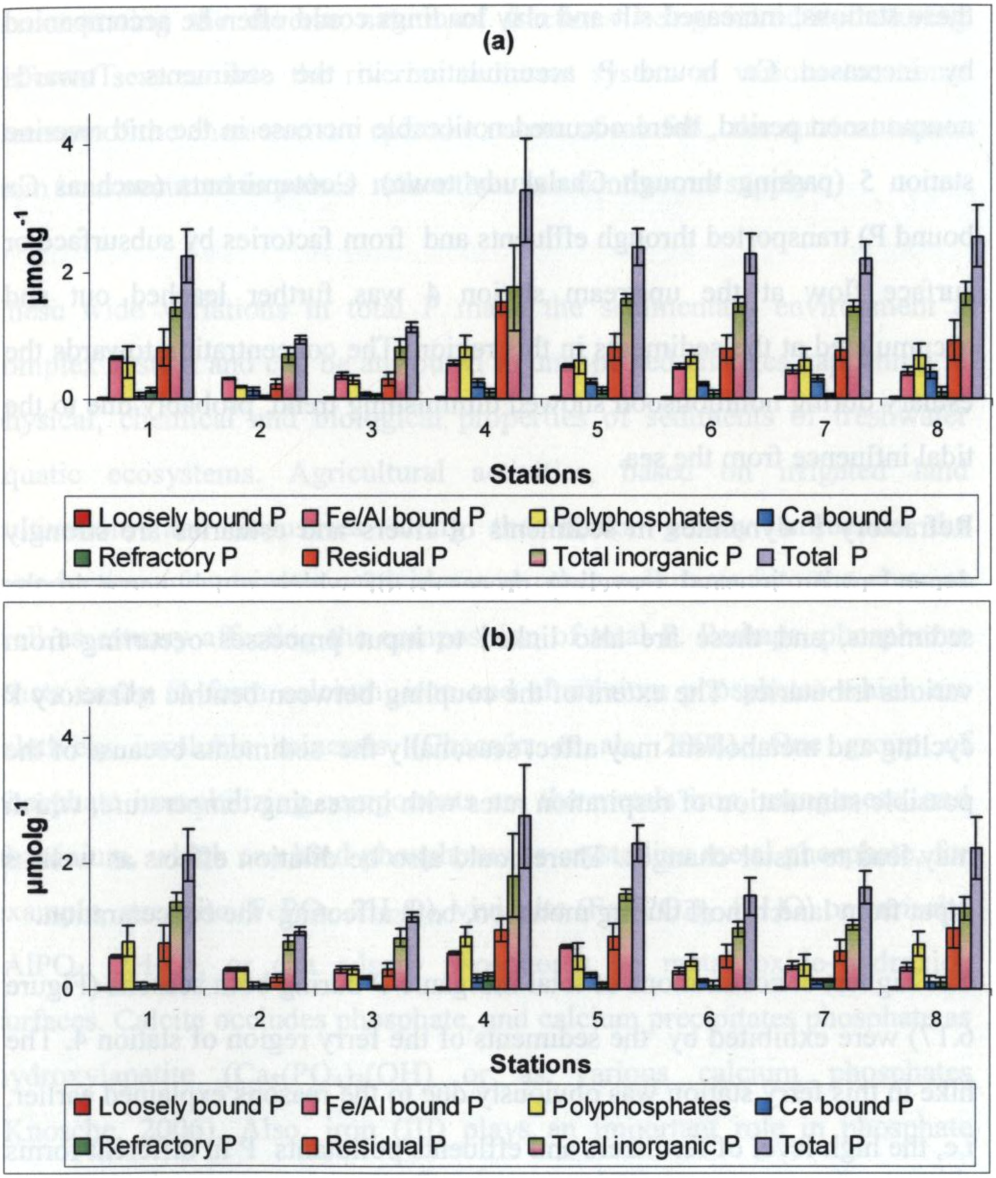

Figure 6.17 Phosphorus forms in monsoon (a) and nonmonsoon (b) periods at various stations.

This situations is consistent with the general tendency for phosphorus in sediments to be high in runoff from land. During monsoon, the estuarine regions recorded comparatively higher and appreciable Ca bound P. In these stations, increased silt and clay loadings could often be accompanied by increased Ca bound P accumulation in the sediments. Towards nonmonsoon period, there occurred noticeable increase in the mid riverine station 5 (passing through Chalakudy town). Contaminants (such as Ca bound P) transported through effluents and from factories by subsurface or surface flow at the upstream station 4 was further leached out and accumulated at the sediments in this region. The concentration towards the estuary during nonmonsoon showed diminishing trend, probably due to the tidal influence from the sea.

Refractory P dynamics in sediments of rivers and estuaries are strongly dependent on internal recycling processes of which much occur in the sediments, and these are also linked to input processes occurring from various tributaries. The extent of the coupling between benthic refractory P cycling and metabolism may affect seasonally the sediments because of the possible stimulation of respiration rates with increasing temperature, which may lead to faster changes. There could also be dilution effects as well as input from land runoff during monsoon, both affecting the concentration.

The highest concentrations of total inorganic P during both seasons (Figure 6.17) were exhibited by the sediments of the ferry region of station 4. The hike in this ferry station was obviously due to the reasons explained earlier, i.e, the high level of fertilizers and effluents/pollutants P in different forms were being accumulated in the sediments of this region. While P extracted using NaCl represents a fully exchangeable P and therefore easily available phase, the bioavailability of other fractions will depend on geochemical transformation and on the time allowed for diagenesis. Significant variations in the total inorganic P were observed among all stations, demonstrating the diverse nature of fractions being introduced during different seasons into the riverine sediment system at various locations. Because of the characteristic episodic nature of rainfall, the nutrient inputs from land occurred in pulses rather than as a continuous supply.

These wide variations in total P make the sedimentary environment a complex system and can be attributed to unexpected changes happening in physical, chemical and biological properties of sediments of freshwater aquatic ecosystems. Agricultural activities, based on irrigated land cultivation, and industries along the banks greatly influence the introduction of nutrients, pesticides and other pollutants into the river as well as estuary affecting the composition of total P. Perhaps, phosphorus reacts easily to form calcium, iron and aluminium phosphates which are relatively insoluble minerals (Chaco´n et al., 2008). One group of phosphate immobilizing components are the metals iron, manganese, and aluminium, which can bind phosphorus as crystalline metal phosphate, for example, strengite ($FePO_4 .2H_2O$), vivianite ($Fe_3(PO_4)_2 .8H_2O$) or variscite ($AlPO_4 .2H_2O$), or can adsorb phosphorus on metal oxide–hydroxide surfaces. Calcite occludes phosphate, and calcium precipitates phosphate as hydroxylapatite ($Ca_5(PO_4)_3(OH)$) or as various calcium phosphates (Knosche, 2006). Also, iron (III) plays an important role in phosphate sorption to humic compounds, forming iron (III)–humus complexes with phosphate. Most of the phosphorus are transported in particulate form and get sedimented during transportation (Gayer et al., 2006). Vertical mixing regulates the distribution of ions and suspended particles which get sedimented, and water column mixing processes are undoubtedly one of the dominant factors that control on total P in sediments. Changes in climate of heavy rains to drier conditions alter the hydrologic properties of individual rivers as well as estuaries and can disrupt properties like phosphorus recycling. Besides chemical factors and external physical factors (light, temperature, mixing regime etc.), biotic components are also of major importance for conditioning the total P. The estuarine station, permanently under the tidal influence of sea, presented high monsoon and nonmonsoon values. Phosphorus is considered as a more direct and reliable indicator of trophic condition because phosphorus is the key nutrient in stimulating algal and plant growth in rivers (Garcia and de Iorio 2003; Zou et al., 2006). Total P fluxes for complex aquatic systems, are extremely variable and this has an important influence on the budget of the element P and sediment burial is responsible for the retention of only up to 4% of the total P input (Brion et al., 2004).

The distribution of total phosphorus in the sediments of certain stations of Chalakudy river was quite different to that of total inorganic P, but ultimately showed higher values. This can be attributed to a very fast recovery of certain fractions of phosphorus determined during the investigation, which might be caught in the lattices of silica and was not extractable using the procedure followed during the present investigation for speciation of P. These appeared on digestion, thereby enhancing the values of total P. In freshwaters, dissolved organic carbon forms complexes with metals such as iron (Fe) and aluminum (Al), and these complexes may sequester dissolved reactive phosphorus thereby decreasing bioavailable P (Jones et al., 1993) in rivers after getting sedimented.

In the studied samples, phosphorus was mainly associated to inorganic compounds as can be concluded from the data, though residual fraction also played a role. This probably addressed to the complex nature of the residual organic matter itself (humic and fulvic substances, etc) and to the intricate relationships among the different sediment components (coating formation, particle cementation, competition for adsorption sites, etc.). Organic P forms are generally associated with living organisms and consist of easily decomposable P compounds (nucleic acids, phospholipids, and sugar phosphates) and slowly decomposable organic P compounds (inositol phosphates—phytin) (Reddy et. al., 1999). The high deviations in bimonthly values of residual P during monsoon indicated primarily the differences in contribution of various processes like sources of runoff, sedimentation, transformation reactions etc. Thus, as a key nutrient, phosphorus plays a relevant role in the trophic state of aquatic systems. Phosphorus mobility is related to its interaction with the different sediment matrix components, and so the knowledge of the different forms in which phosphorus is present in sediments is necessitated.

Phosphorus forms: Stationwise profusion (in percentage)

The stationwise percentage graphs of loosely bound P, Fe/Al bound P, polyphosphates, Ca bound P and refractory P in the sediments of Chalakudy river during monsoon and nonmonsoon periods are given in Figures 6.18a and 6.18b respectively. Residual-P, which was mainly organic fractions was the predominant form in all stations except the waterfalls and accounted for more than 30% of total-P.

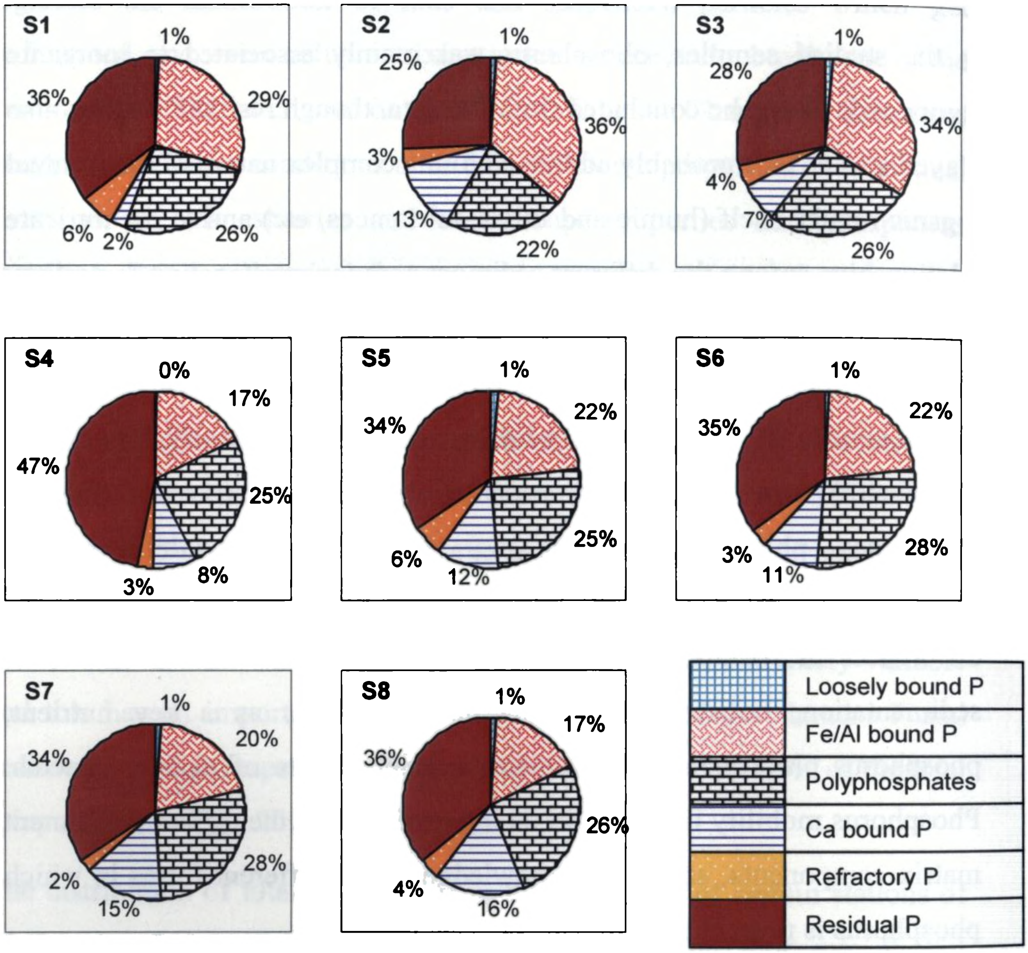

Fig 6.18a Percentage-wise distributions of phosphorus species (loosely bound P, Fe/Al bound P, polyphosphates, Ca bound P and refractory P) in sediments at different sampling stations of Chalakudy river during monsoon season.

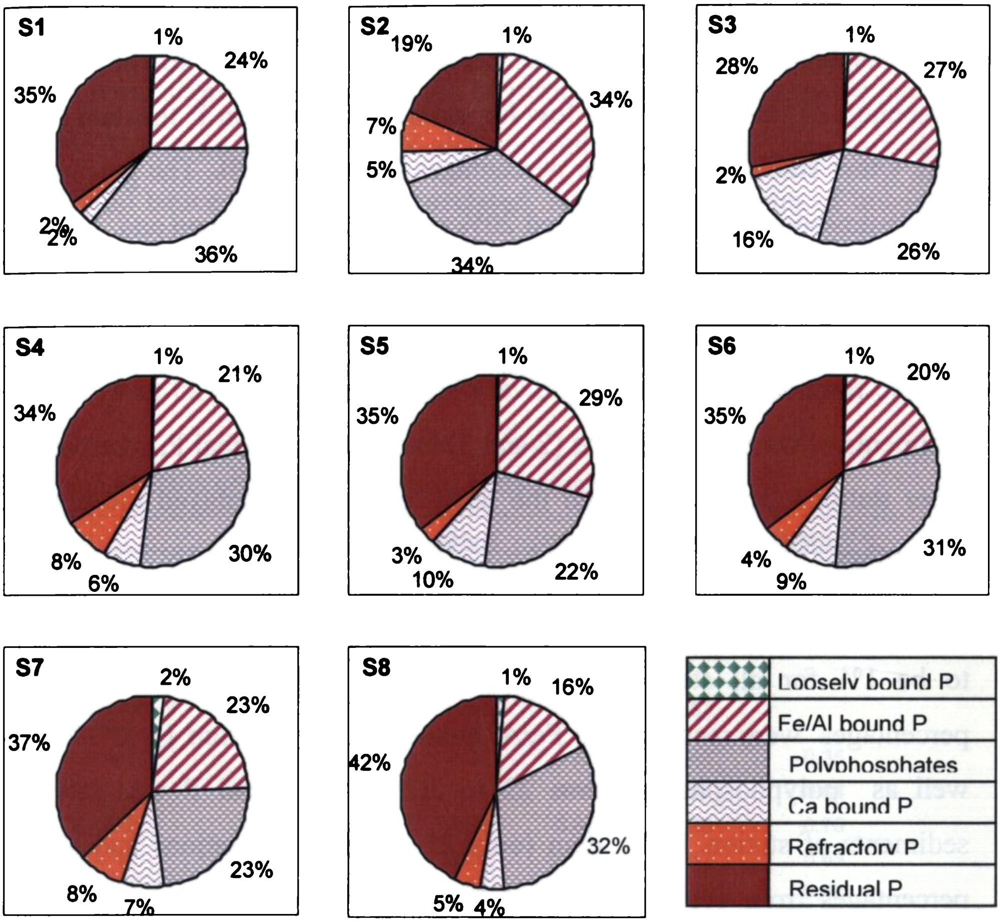

Fig 6.18b Percentage-wise distributions of phosphorus species (loosely bound P, Fe/Al bound P, polyphosphates, Ca bound P and refractory P) in sediments at different sampling stations of Chalakudy river during nonmonsoon season.

The percentage of loosely bound P was found to be very low (≤1%). Fe/Al bound P showed comparatively higher values ranging from 17 to 36%. Polyphosphates also had higher percentages from 22 to 28%. The percentage of Ca bound P was low for sediments of station 1, the dam (only 2%). Other stations had higher percentages from 7 to 16%. The percentage of calcium-bound P did not exceed 20% as recorded by Ruban and Demare (1998) in reservoir of Bort-les-Orgues (France). Refractory P was low in the range, 2 to 6%. The percentage of residual P, which contained mainly organic fraction, was found to be very high ranging from 25 to 47%. The sediments of waterfalls regions (2 and 3) had lesser residual P, whereas the other stations increased it, and the ferry region (4) displayed the highest percentage.

During nonmonsoon season, the percentage of loosely bound P was found to be 1% for all stations except station 7 where it was 2%. Higher percentages were recorded for Fe/Al bound P (ranging from 16 to 34%) as well as polyphosphates (from 22 to 36%). Ca bound P was low for sediments of station 1, the dam (only 2%) and other stations had higher percentages from 4 to 10% except station 3 where it increased to 16%. Refractory P was low in the range, 2 to 8%. The percentage of residual P, was found to be very high ranging from 19 to 42%. Waterfalls regions 2 and 3 had lesser percentages of residual P whereas other stations had increasing trend and the estuarine region 8 was the major contributor. All these observations point to the relevance of organically bound P web in the sediment. Xuegang et al. (2007) had recorded a similar high composition of organic P (<40%–50% of total-P) in the sediments of Jiaozhou Bay, a typical semi-enclosed bay in Qingdao City in China.

Correlation

Data from the correlation study (Table 6.5) indicated that nitrate-N and total-N were significantly correlated as nitrate comprised the major part of total-N. Ammonia-N and urea-N also showed a significant contribution to total-N and hence significantly correlated. All nitrogen species of nutrients were inter related. Components of nitrogen species were less correlated to moisture content of sediments. The residual–N is positively related to the percentages of C, H and N showing its organic nature.

Table 6.5 Pearson correlation matrix of N fractions

	NO_2^--N	NO_3^--N	NH_3-N	Urea-N	Total-N	Residual-N
NO_3^--N	0.30					
NH_3-N	0.46	0.69				
Urea-N	0.53	0.70	0.71			
Total-N	0.54	0.93	0.78	0.81		
Residual-N	0.68	0.33	0.36	0.52	0.63	
Moisture content	0.26	0.37	0.26	0.23	0.42	0.35
SOC	0.17	0.43	0.34	0.27	0.47	0.34
% of C	0.36	0.41	0.38	0.47	0.60	0.75
% of H	0.32	0.31	0.28	0.33	0.47	0.63
% of N	0.32	0.26	0.26	0.27	0.45	0.67
% of sand	-0.56	-0.42	-0.32	-0.54	-0.56	-0.61
% of silt	0.45	0.38	0.28	0.49	0.49	0.49
% of clay	0.37	0.39	0.26	0.40	0.50	0.54

Table 6.6 Pearson correlation matrix of P fractions

	Loosely bound P	Fe/Al bound P	Polyphosphates	Ca bound P	Refractory P	Total Inorganic P	Total P	Residual P
Fe/Al bound P	0.04							
Polyphosphates	-0.04	0.49						
Ca bound P	0.10	0.07	0.46					
Refractory P	0.25	0.41	0.38	0.09				
Total Inorganic P	0.08	0.67	0.92	0.60	0.53			
Total P	0.08	0.64	0.89	0.56	0.45	0.95		
Residual P	0.07	0.54	0.76	0.45	0.32	0.78	0.94	
Total-N	-0.06	0.48	0.54	0.46	0.24	0.64	0.64	0.58
Moisture content	0.05	0.39	0.65	0.29	0.23	0.62	0.66	0.63
% of sand	-0.21	-0.57	-0.70	-0.45	-0.43	-0.78	-0.77	-0.68
% of silt	0.24	0.53	0.65	0.43	0.43	0.74	0.69	0.56
% of clay	0.32	0.42	0.42	0.28	0.37	0.52	0.49	0.40

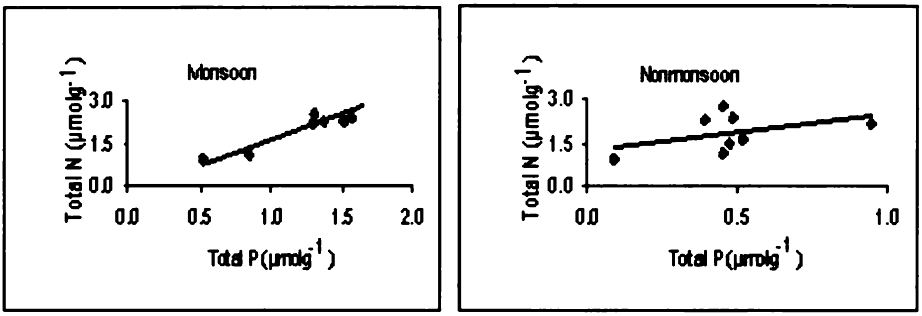

Figure 6.19a Relation of total N with total P during monsoon and nonmonsoon seasons

An important point to be noted was the significant positive relation between total N and total P (Figure 6.19a) in the sediments of Chalakudy riverine system and there was a tendency for them to be proportional. The processes operating, that supply or make available both nutrients, were important determinants and they contributed almost equally within the sediment. Total inorganic P as well as residual-P were strongly positively related towards total-P (Table 6.6). Residual-P and polyphosphates were important in their contribution towards total P. Moisture content was seen to be related to different forms of phosphorus.

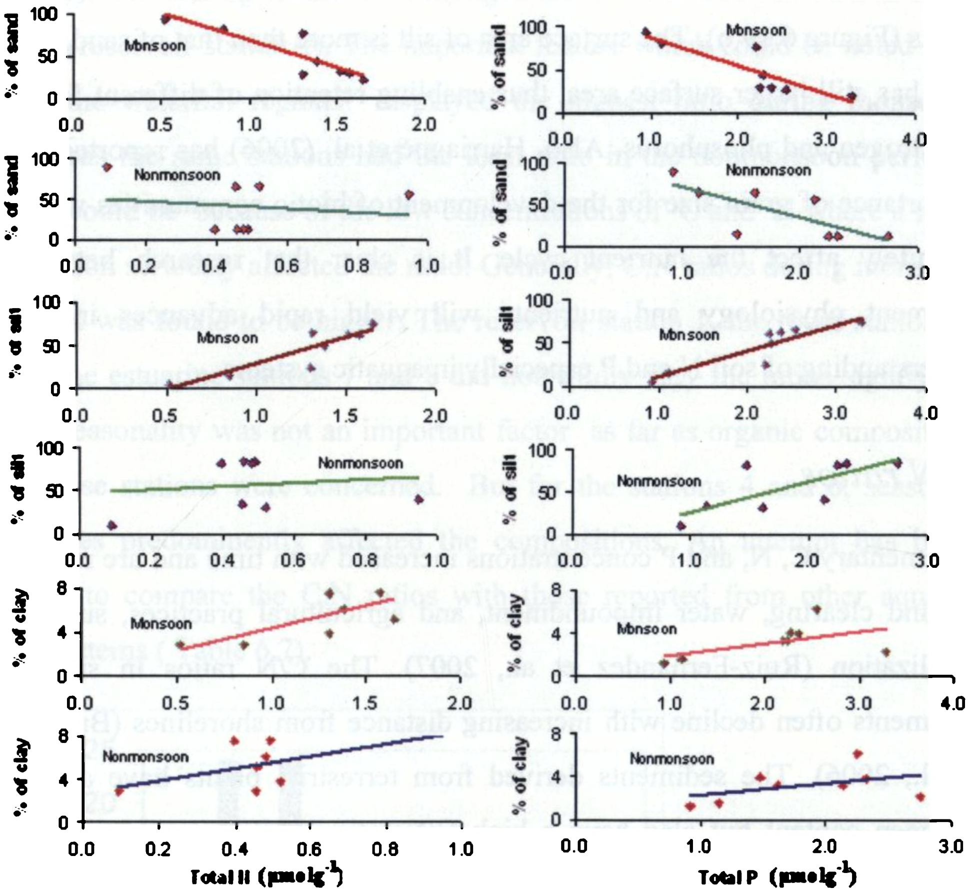

Figure 6.19 b Relation of total N and total P with texture during monsoon and nonmonsoon seasons

In river-estuarine sediments, grain size plays a key role in inorganic nutrient recycling, in early primary prodiction and in the transfer of energy and material to higher trophic levels. Data presented in this context suggest that sand had always been negative to all nitrogen fractions with significance toward nitrite-N, total-N and residual-N, whereas, silt and clay were positively correlated (Figure 6.19 b). Similarly all the P fractions, as in the case of N species, were negatively related to sand, whereas silt and clay were found to be positive with regard to the presence of different forms (Figure 6.19 b). The surface area of silt is more than that of sand, and clay has still larger surface area, thus enabling retention of different forms of nitrogen and phosphorus. Also, Harriague et al. (2006) has reported the importance of grain size for the development of biotic communities which definitely affect the nutrient cycle. It is clear that research between sediment physiology and nutrients will yield rapid advances in our understanding of soil N and P especially in aquatic systems.

C:N ratios

Sedimentary C, N, and P concentrations increased with time and are related to land clearing, water impoundment, and agricultural practices, such as fertilization (Ruiz-Fernandez et al., 2007). The C/N ratios in surface sediments often decline with increasing distance from shorelines (Brenner et al., 2006). The sediments derived from terrestrial plants have a high nitrogen content but also have a high C/N ratio, while nitrogen sources from autochthonous plankton have a high nitrogen content but have a low C/N ratio, as some aquatic systems located near cities are eutrophied or hypertrophied (Shuncai and Chen, 2000). One of the main factors controlling profiles of nitrogen nutrients in sediments is its quality in terms of C:N ratio. The bacterial mineralization of organic matter depends on the C:N ratio of the available substrate.

Atomic C:N ratios [obtained from the CHN analysis -detailed in Chapter III] are also presented as bar diagrams in the Figure 6.20. The C:N during monsoon varied from 8.6 (estuarine station 8) to 24 (water fall stations 2 and 3). C:N during nonmonsoon ranged from 1.3 (water fall station 2) to 11.7 (reservoir station 1). The important feature which could be noted was that the waterfall regions displayed the highest ratio during monsoon, whereas the same stations had the least ratio in the nonmonsoon periods. This could be because of the low concentrations of C and N where a mild variation seriously affected the ratio. Generally, C:N ratios during monsoon period was found to be higher. The reservoir station 1, the town station 5, and the estuarine stations 7 and 8 did not wildly vary the ratios signifying that seasonality was not an important factor as far as organic composition of these stations were concerned. But for the stations 4 and 6, seasonal changes predominently affected the compositions. An attempt has been made to compare the C:N ratios with those reported from other aquatic ecosystems (Table 6.7).

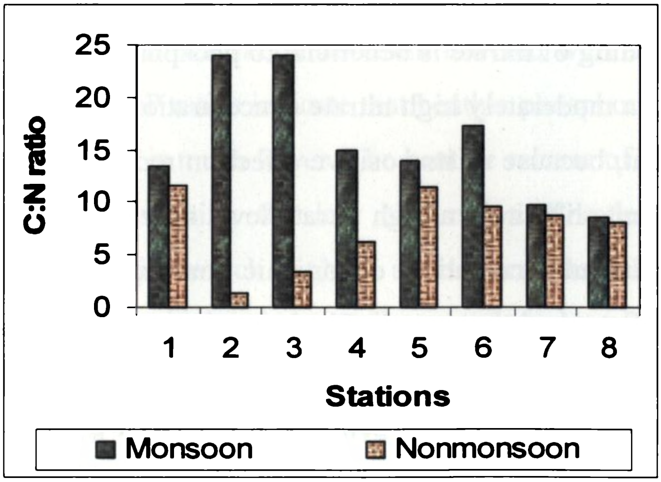

Figure 6.20 C:N ratios of sediments of Chalakudy river

Table 6.7 Some global references for C:N ratios in sediments

Sedimentary environment	C:N ratio	Reference
Po delta lagoon (Italy)	8 to 15	Barbanti et al., 1992
Lake sediment of China	7.6 to 22.7	Shuncai and Chen, 2000
Intertidal sediments of the Yangtze estuary	9.6 to 10.2	Hou et al., 2006
Sediments of Lake Panasoffkee, Florida (USA)	15 to 35	Brenner et al., 2006
Fertilizer loaded pine plantations sediments 10-cm depth, Piedmont of Georgia (Athens and Eatonton)	16 to 30	Sartori et al., 2007
Saguaro Lake, Arizona	8.1 to 68.6	Leenheer et al., 2007

N:P ratios

The role of nitrogen in sediments is less certain, particularly because nitrogen may be fixed in the benthic and at the sediment surface. The continuous and steady feeding of nitrate is beneficial to phosphate removal (Zou et al., 2006). While a moderately high nitrate concentration may help to retain P in the sediment, because of its positive effect on redox and the binding capacity of elements like iron, a high nitrate level may promote P release by stimulating the mineralisation of organic matter, and thus enhance periphyton and phytoplankton growth. Since the nitrogen produced is mainly from autochtonous source, variation on N:P ratio depends on phosphorus which is mostly obtained from external source. The Redfield atomic N:P ratio of 16:1 (Redfield, 1958) is fairly constant over much of the oceans, but varies in rivers and estuaries due to dramatically diverging changes in these natural ecosystems.

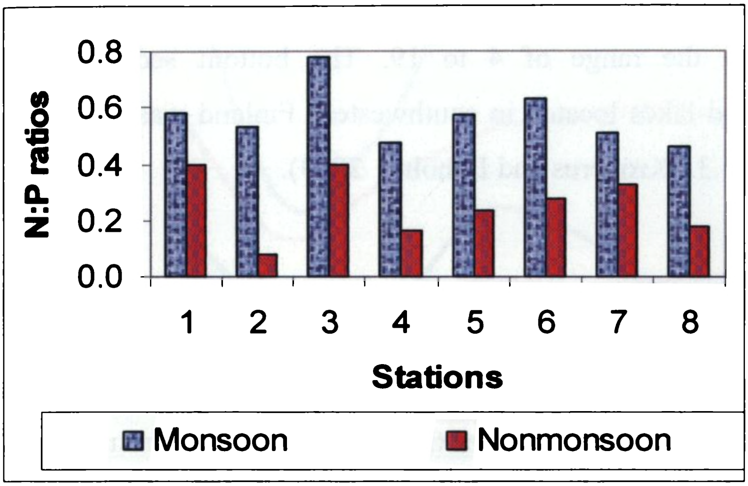

Figure 6.21 N:P ratios of sediments of Chalakudy river

The annual N:P ratios in sediments of Chalakudy river vary from 0.37 to 0.65. The monsoon ratios ranged from 0.46 to 0.78 (Figure 6.21) and the nonmonsoon N:P ratios were still lowered with a range from 0.08 to 0.40. The low N:P ratios indicate that benthic phosphorous recycling is in excess of P and N is much lower. The benthic release of phosphorus might play a role in sustaining the low N:P ratios. The low N:P ratio pointed to denitrification which might be accelerated after the algal blooms and also to low nitrate which may be attributed to low rate of decomposition of organic matter.

The present N:P values are low compared to the following reports. Alongi (1990) reported that N:P ratio of sediments of Hinchinbrook channel (Australia) ranged from 5.0 to 16.5. The benthic flux measured (Friedrich et al., 2002) in the coastal zone of the north-western Black Sea produced the N/P ratio in the range of 4 to 19. The bottom sediments of agriculturally loaded lakes located in southwestern Finland was found to have the N/P ratio 4.3. (Krogerus and Ekholm, 2003).

Overall summary

This study has been directed to the regional examination of nitrogen and phosphorus speciations and ratios in the sedimentary environment of Chalakudy riverine systems. The overall trends of N species in monsoon and non monsoon periods are displayed in Figures 6.21a and 6.21b respectively. The concentration of nitrite-N was insignificantly low in sediments of over all locations during both seasons. Nitrate-N is very predominant during both seasons, projecting a lowering during nonmonsoon. Ammonia- N is comparatively low with higher values during monsoon. Urea-N is very low with fluctuating value and monsoon season projected only slight variations. Total-N was appreciable during both seasons with a dominance in monsoon.

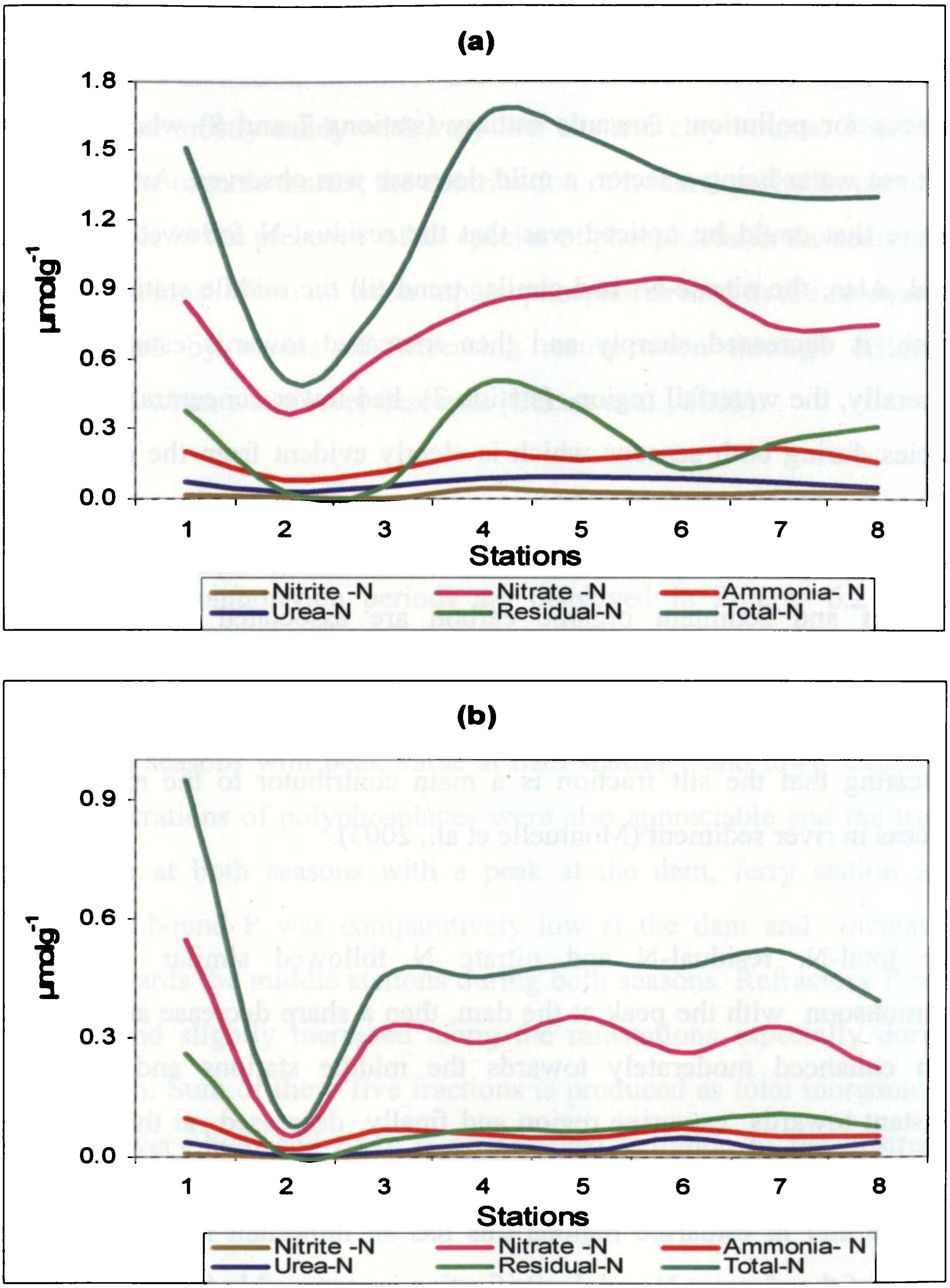

Figure 6.21(a,b) Trends of various nitrogen species in monsoon (a) and nonmonsoon (b) periods.

During monsoon, total-N was high in the highland region at the reservoir, ferry region (station 4) and town region (station 5) where there were chances for pollution. Towards estuary (stations 7 and 8) where mixing with sea water being a factor, a mild decrease was observed. An important feature that could be noticed was that the residual-N followed the same trend. Also, the nitrate-N had similar trend till the middle station 5, after which, it decreased sharply and then increased towards estuarine end. Generally, the waterfall region (station 2) had lower concentrations of all species during both seasons which is clearly evident from the depression curves in the Figure 6.21a. This is mainly due to the sandy nature of sediments of that region which has low retaining capacity. Sediment nutrients and sediment organic carbon are associated with the finer fractions (silt and clay) of sediments (Nayar et al., 2007). Silt-clay fraction exhibited the highest functional nitrifying community per mass unit indicating that the silt fraction is a main contributor to the nitrification process in river sediment (Montuelle et al., 2003).

The total-N, residual-N and nitrate N followed similar trend in nonmonsoon with the peak at the dam, then a sharp decrease at station 2, then enhanced moderately towards the middle stations and remained constant towards estuarine region and finally decreased at the estuarine mouth (Figure 6.21b). Total N fluxes for complex system, are extremely variable and in estuarine regions this has an important influence on the budget of the element N and denitrification is responsible for the loss of 16 to 30% of the total N inputs (Brion et al., 2004).

Usually, the contribution of phosphorus in sediments occurs from the organic matter as well as from mineral matter. In the waterfall regions, the sediments are mostly sandy with very low silt and clay counts. Therfore, apart from the organic matter, the contribution of mineral probably plays an important role in the presence of all species of phosphorus in the sediments of these locations. When no water inputs, phosphorus load in the ecosystem is maintained by means of increasing resuspension through different mechanisms when water level descends (Eckert et al., 2003).

The P fractions varied wildly in each and every location. Trends of P in monsoon and nonmonsoon periods are displayed in Figures 6.21c and 6.21d respectively. Exchangeable P (loosely bound P) was insignificantly low. Fe/Al bound phosphorus in sediments pictured a moderate share during both seasons with peak value at dam station 1 and town station 5. The concentrations of polyphosphates were also appreciable and the trend was similar at both seasons with a peak at the dam, ferry station and estuary. Ca bound P was comparatively low at the dam and increased slightly towards the middle stations during both seasons. Refractory P was very low and slightly increased along the midstations especially during nonmonsoon. Sum of these five fractions is produced as total inorganic P. Total P is very high and there is no seasonal variation in the upstream whereas, there is deviation from the high monsoon value towards downstream.

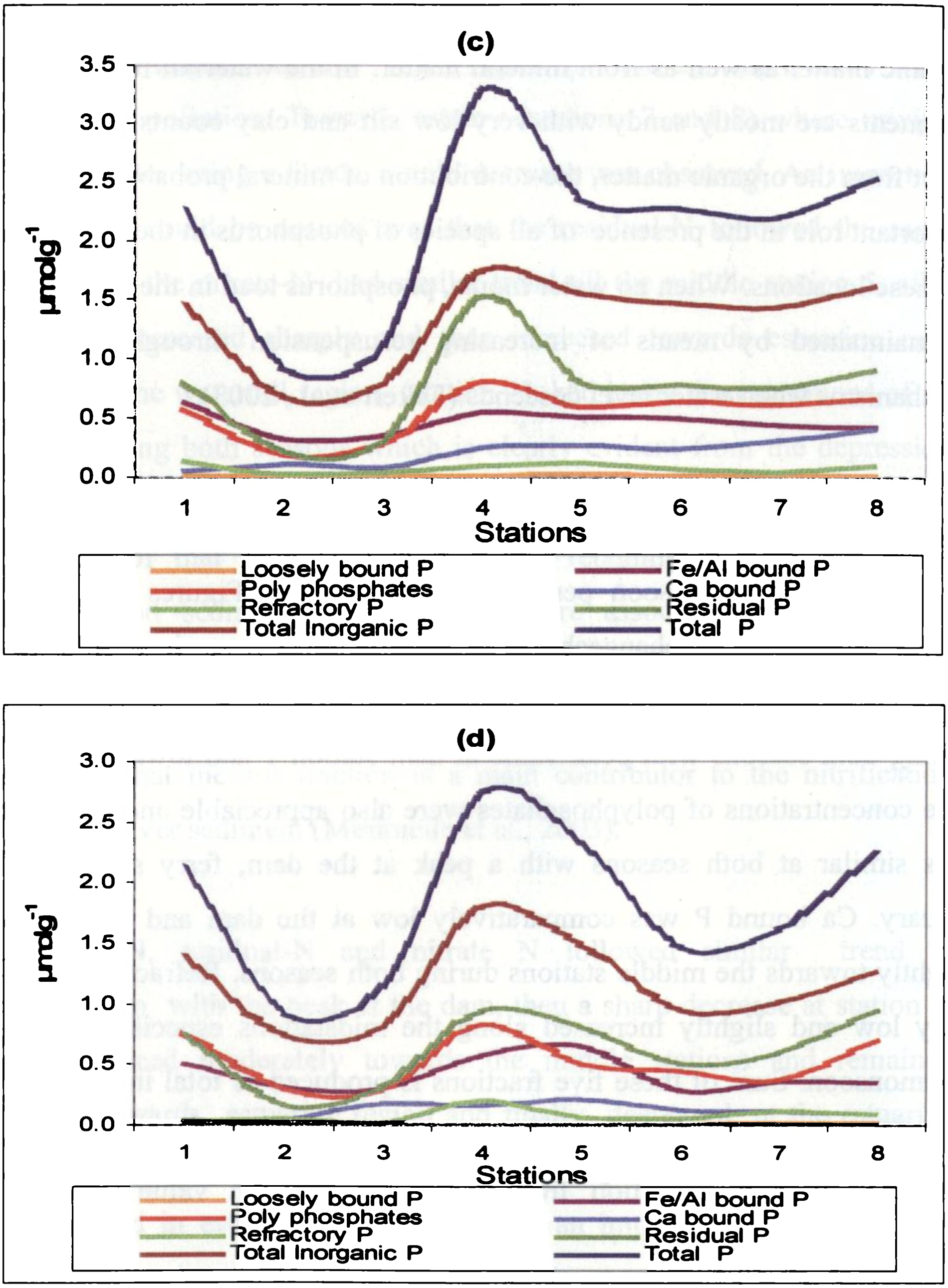

Figure 6.21(c,d) Trends of various phosphorus species in monsoon (c) and nonmonsoon (d) periods

Total P, total inorganic P and residual P had the same pattern of variation with hike at dam, incline at waterfalls, then peak at middle station 4 and then decreased more or less steadily. The same trend is followed during nonmonsoon also, with more regional peaks at middle stations.

Presence of P and its release from sediments are not strictly a result of abiotic chemical processes mediated by physical conditions of the river. For example, under low oxic conditions, high concentrations of nitrate (NO_3^-) in waters overlying sediments can raise the redox potential by providing denitrifying bacteria with an alternate electron acceptor, thereby enhancing Fe oxidation and sediment sorption of PO_4^{3-} (Nowlin et al., 2005). In contrast, the growth of Fe-reducing bacteria may be stimulated by high NO_3^- levels, leading to higher decomposition rates of organic matter and enhancement of PO_4^{3-} release from sediments.

The results showed that the N and P were appreciable in the sediments of the river, and the sedimentary environment of Chalakudy river be an extremely complex system subjected to large inter-annual variability of freshwater land run-off, discharge of various N and P components, and marine water circulation occurring at the estuarine site. Quantitatively, the fractions containing N and P in isolation or in combination vary in content due to chemo estuarine / riverine variability and seasonal fluctuations.

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CHAPTER VII

INTEGRATED GIS WATER QUALITY MODEL

CONTENTS

INTRODUCTION

In the present study, the ecosystem based water quality model is applied to the Chalakudy river estuary. An integrated ArcGIS model system including the hydrodynamics, sediment and water quality models has been developed to simulate nutrient cycles in the Chalakudy river estuary. The model domain covers almost the whole region of the Chalakudy river estuary, and the model owns higher horizontal and vertical resolution of chlorophyll, total nitrogen and total phosphorus. The model system has successfully reproduced the distribution trends of nutrients both in the horizontal and vertical planes during the rainy as well as dry season, and it shows that the model has considered the key part of the dynamical, chemical and biological processes existing in the Chalakudy river estuary.

Decision Support Systems (DSS) are defined as computer based information systems designed to support decision makers interactively in thinking and making decisions about relatively unstructured problems. Traditionally, DSSs have three major components, a database, a model base and a user interface as depicted in Figure 7.1a. An extension of the DSS concept, Spatial Decision Support Systems (SDSS), which are the integration of DSS and GIS (Figure 7.1b) was initiated by Densham and Goodchild (1988).

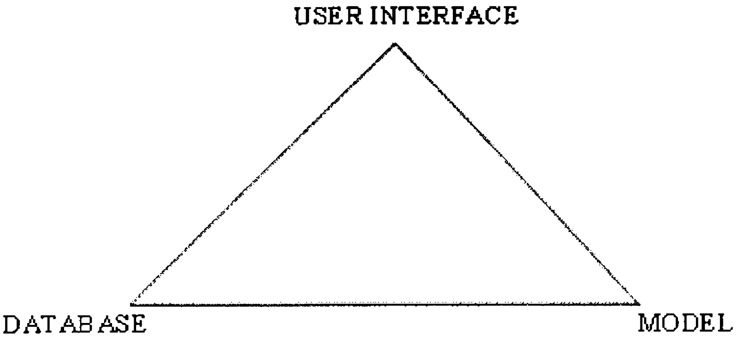


Fig. 7.1 a Components of DSS

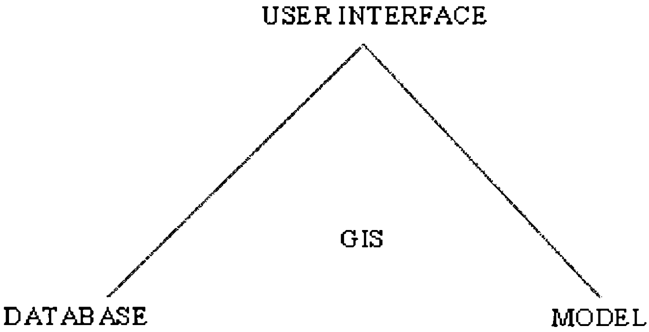


Fig. 7.1 b Components of SDSS

GIS is a general purpose technology for handling geographic data in digital form, with the ability to preprocess data into a form suitable for analysis, to support analysis and modelling directly, and to post-process results (Goodchild, 1993). A significant capability of the SDSS is the ability to use spatial analysis and display tools with the sectoral models and that would form the model base of SDSSs. The modeling capability allows the user of the SDSS to simulate changes in objects and attributes. The database component of the SDSS can supply input data for the models. After the models are run, the resulting output can be written to the database for later display via the user interface, in tabular, chart or map form. For planning purposes, this ability to dynamically change information, forecast and perform sensitivity analysis is essential. Both GIS and DSS have been widely used in natural resources management. In summary, SDSS provide unique advantages for land and water resources management in the following aspects:

1. spatial representation, that is representing the spatial relations of the real world in a visual and analytical form;
2. comprehensive database, which is the basis for the integration of socioeconomic, environmental and physical components of the real world; and
3. modeling capability, which can integrate simulation/optimization techniques to solve complex natural resources management problems.

These advantages make SDSS a proactive tool for sustainable natural resources management. In the present study, while selecting an appropriate model for developing Spatial Decision Support System, the following considerations were made:

- the ability to model at scales ranging from watershed to basin (regional) scales

- the ability to model water quantity and quality, silt production and riparian growth
- the ease of use of the model and ready availability of inputs data
- the ability to link to Geographical Information System (GIS)
- the documentation and degree of support available.

BASINS (Better Assessment Science Integrating Point and Nonpoint Sources) version 3.0, is the updated software system developed by the U.S. Environmental Protection Agency Office of Water in order to meet the requirements of developing Total Maximum Daily Load (TMDL) programs. BASINS provides an enhanced set of nation-wide databases, several new and interchangeable tools and models integrated in a new modular architecture, operating within ArcView Geographical Information System (GIS) for desktop PCs. This chapter describes the integration of three key components: (1) a tool that optimizes the automatic definition and segmentation of the watershed and stream network based on topography (Digital Elevation Models), NHD (National Hydrography Dataset) or other ancillary stream data; (2) a tool to define the Hydrologic Response Units (HRUs) over the watershed and subwatersheds; and (3) SWAT (Soil and Water Assessment Tool) model and a respective integrated user-friendly interface. The first two components, improve the simplistic methods for the hydrologic definition, segmentation and basic geomorphic assessment of the watershed and open to the usage of external datasets besides those distributed with the whole BASINS package. In addition, these components share generating datasets, hereby promoting the usage by other tools and models as well as other models that in the future could be introduced in BASINS. The third component introduces the SWAT model into BASINS.

Instead of using regression equations, it utilizes theory-based hydrologic and climate equations (Lemonds and McCray, 2002). Data from the watershed is used as input to these equations. Other important attributes of SWAT include its computational efficiency that allows for complex watersheds to be modeled in a straightforward manner, its incorporation of easily accessible data and its ability to simulate long-term impacts of pollutant buildup and downstream impact. The model takes into account such data as climate, soil and water properties and produces outputs with the use of hydrological and other equations. Apart from the ability to incorporate land use and soil data, SWAT differs from other physical models in its ability to separate the watershed into sub-basins and Hydrological Response Units (HRUs). The main basin is divided into smaller ones, by selecting points on the stream network that act as outlets. In this way, the model can provide output data, such as concentrations, at specific points of the river network. For the accurate implementation of hydrological equations, detailed input data are needed. Of significant value to the simulation are the digital elevation model (DEM) of the watershed, the soil and land use data and the climatic data of the area. SWAT tracks the movement and transformation of several forms of nitrogen and phosphorus in the watershed. These are governed by the nitrogen and phosphorus cycles (Mineralization, Decomposition, Immobilization, denitrification, volatilization etc). Nutrient estimations require knowledge of pollution point sources and agricultural management practices. The nutrient calibration, of total N and P can be achieved through the application of SWAT model in annual and monthly simulation step (Bekiaris et al., 2005).

The hydrological response of the SWAT model to calculated soil properties is significant and therefore preference should be given to the calculation of the derived hydrologic soil properties prior to averaging of the profile data (Romanowicz et al., 2005). The resolution and fragmentation of the original map objects are significantly affected by the internal aggregation procedures of the SWAT model. The catchment size threshold value (CSTV) is thereby a key parameter controlling the internal aggregation procedure in the model.

Based on the above considerations, the Soil and Water Assessment Tool (SWAT) model was selected. The SWAT model is a combination of the SWRRB, GLEAMS and ROTO models and hence it is able to model both the hydrology and water quality of a watershed. The model is reported to be able to operate on both a raster and sub-watershed (hydrologic response unit) basis.In addition, the model is linked to GIS packages like GRASS (Geographic Resources Analysis Support System) via the SWAT-GRASS interface and ARC-View through the SWAT-ARC View interface (Di Luzio *et al*, 1997), thus easing the task of data input and output display. SWAT is a hydrologic distributed model with proven success in watershed assessment of both agricultural and urban scenario management effects on water quality (Di Luzio et al., 2008).

Distributed hydrologic models are particularly adversely affected by the lack of daily data or the existence of very inaccurate data as they impart large uncertainties to the model prediction. A daily weather generator algorithm (dGen) uses the currently available weather statistics with the model "Soil and Water Assessment Tool" (SWAT) river parameters were then compared with the measured ones (Schuol and Abbaspour, 2007). It was seen that using the dGen-simulated daily weather data resulted in a much better match with the measured data in combination with the SWAT internal weather generator WXGEN. WXGEN is used in SWAT to fill missing data using monthly statistics, which could be calculated from the existing daily data. For annual and monthly hydrological simulations, dGen-generated daily rainfall and temperature data appears to have a high degree of reliability (Schuol and Abbaspour, 2007).

Generation of prediction and probability surfaces

Kriging and varicography methods within the Geostatistical Analysis in ArcGIS were used, along with the measured concentrations, to predict concentrations at unmeasured locations. Kriging weights the surrounding measured values to derive a prediction for an unmeasured location. The general formula for the predicted value is formed as a weighted sum of the data:

$$F(xy) = \sum_{i=1}^{n} w_i f_i$$

where F(x,y) is the predicted value at location x,y; n is the number of data points in the set; f_i are the values of the scattered measured points; and w_i are weights assigned to each point (Oertel and Giles available online). This equation is essentially the same as the equation used for inverse distance weighted interpolation except that rather than using weights based on an arbitrary function of distance, the weights used in kriging are based on a model variogram. With the kriging method, the weights are based not only on the distance between the measured points and the prediction location but also on the overall spatial arrangement of the measured points. To use this spatial arrangement in the weights, the spatial autocorrelation must be quantified. This was accomplished using the standard variogram technique. The variogram defines the weights that determine the contribution of each data point to the prediction of new values at unmeasured locations.

In ordinary kriging, the weight depends on a fitted model to the measured points, the distance to the prediction location, and the spatial relationships among the measured values around the prediction location. Ordinary kriging is the most general and widely used of the kriging methods and is the default in geostatistical analyst. It assumes the constant mean is unknown. Universal Kriging assumes that there is an overriding trend in the data and that it can be modeled by a deterministic function, such as a polynomial. This trend is subtracted from the original measured points, and the autocorrelation is modeled from the remaining random errors. Once the model is fit to the random errors and before making a prediction, the trend is added back to the predictions to give meaningful results.

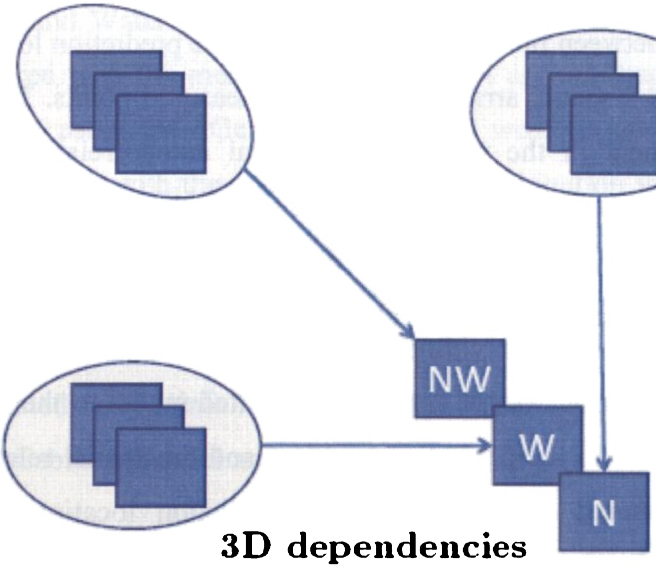


Figure 7.2 The three-dimensional (3D) dependency among the elements affecting a river estuarine system

The weighted matrices imply a three- dimensional (3D) dependency among the elements of the matrix as shown in Figure 7.2 (Aji et al., 2008). Future use of additional data, can lead to better convergence between simulated and observed values. As for the qualitative simulation, a quite good convergence was achieved for the unmeasured subbasins, by adjusting model parameters concerning the concentrations of soluble and sedimented N and P in the river.

DATA ANALYSES: RESULTS AND DISCUSSIONS

ArcGIS is an integrated collection of GIS software products for building a complete GIS. It consists of number of frameworks for deploying GIS:

ArcGIS Desktop, ArcGIS Engine, Server GIS and Mobile GIS. ArcGIS is an information system for geographic data developed by the Environmental Systems Research Institute, Redlands, California. To show hydrogeochemical variations, sample points are taken at reference locations in a landscape and creates a continuous surface as pictured in Figures 7.3.

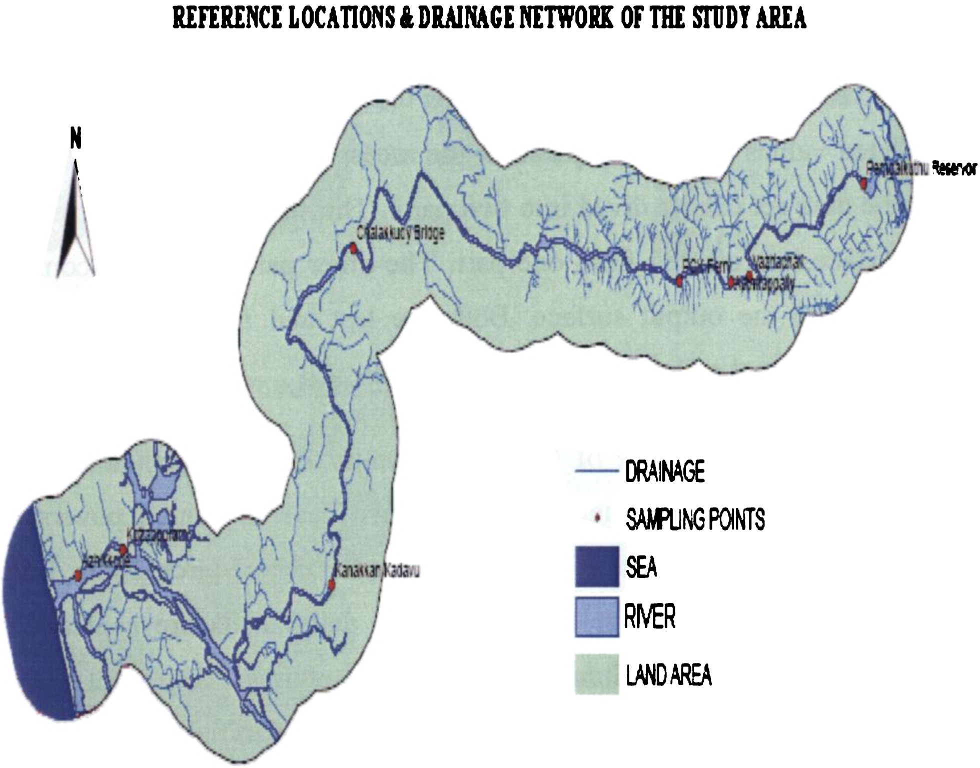
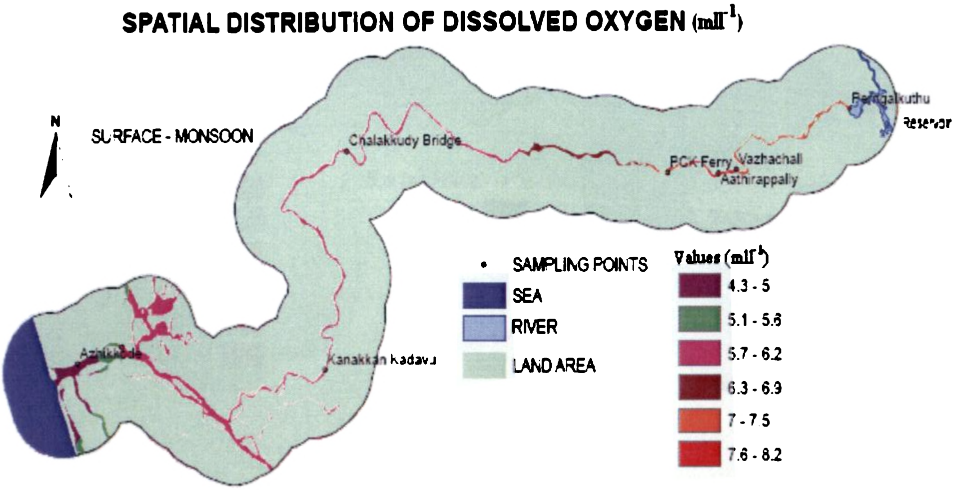


Figure 7.3 Reference locations and drainage network of the study area

A surface is derived using the values from the measured locations to predict values for each location in the landscape. There are two interpolation techniques available: deterministic and probabilistic. Exploratory Spatial

Data Analysis (ESDA) tools are used to explore data. The tools available in ESDA are as follows: Histogram, Voroni map, Normal plot and General QQ plot, Trend analysis, Semi-variogram/Covariance cloud and Cross-covariance cloud. Geostatistical Wizard can be used to generate surface using the various interpolation techniques available in it. Inverse Distance Weighted, Radial Basis Function, Global Polynomial Interpolation, Local Polynomial Interpolation, Kriging and Co-kriging are the various methods used. Create Subset can be used to assess the quality of the surface and the predicted values can be compared to the measured values in the field. For this the data set can be dived into two parts. The structure is modeled and the surface is produced from one part. The other part is used to compare and validate the output surface. Both the test and training sets can be generated using the Create subset dialogue box.

The length of simulation of the water quality model together with the hydrodynamics and sediment models is two seasons which covers the period of the field investigations from May, 2005 to March 2006. Initial constituents of concern for total maximum daily loads are centered on suspended particulate, sediment and dissolved phases. The river quality model runs under specified initial conditions. The initial conditions are replaced by the results at Day 60 and the model runs again. Repeating these processes for several times may obviously eliminate the influences of initial conditions. The model results are mapped in figures 7.4 to 7.18.



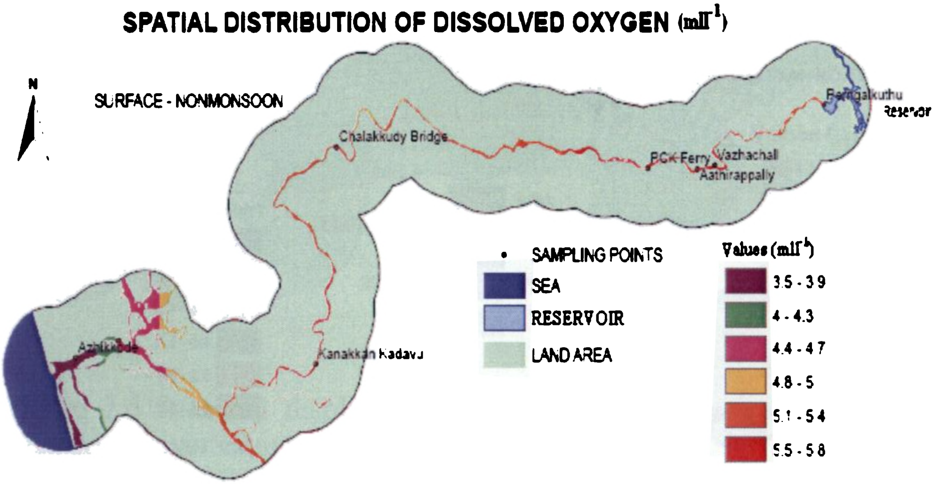
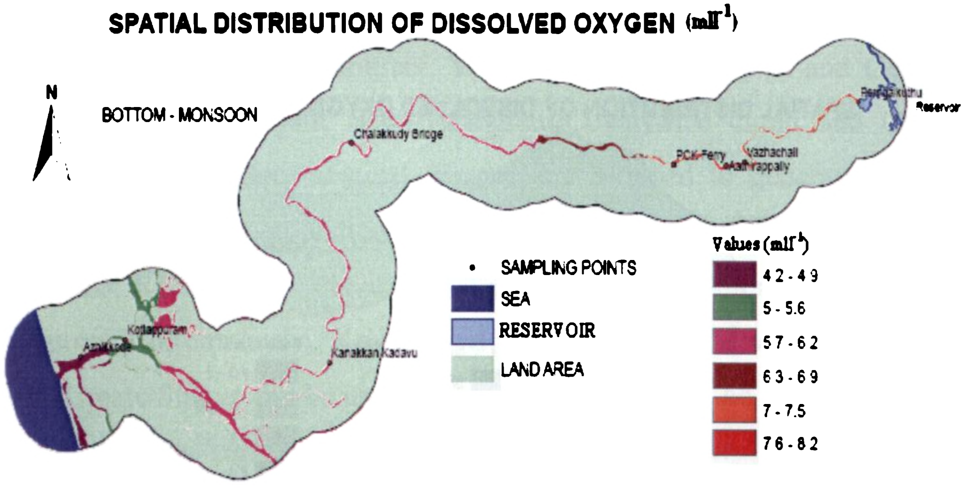


Figure 7.4 Seasonal display of dissolved oxygen along the surface waters of Chalakudy river estuary



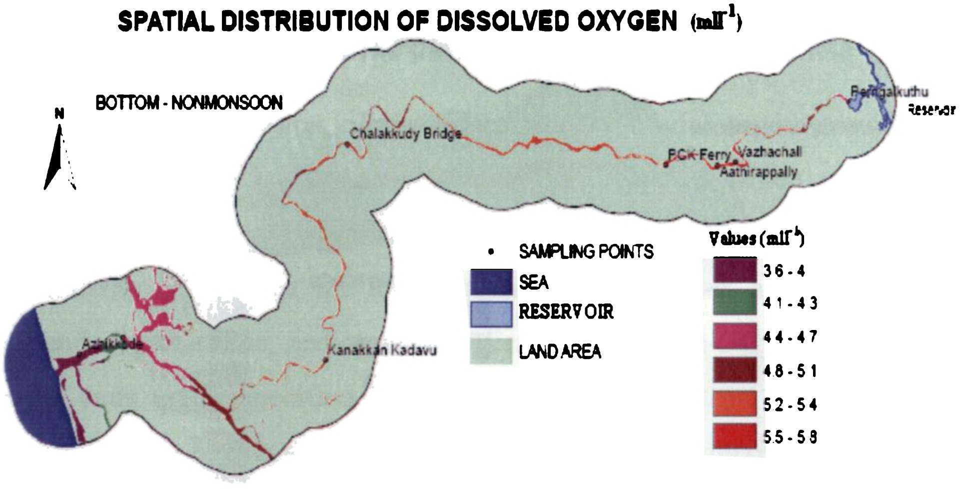
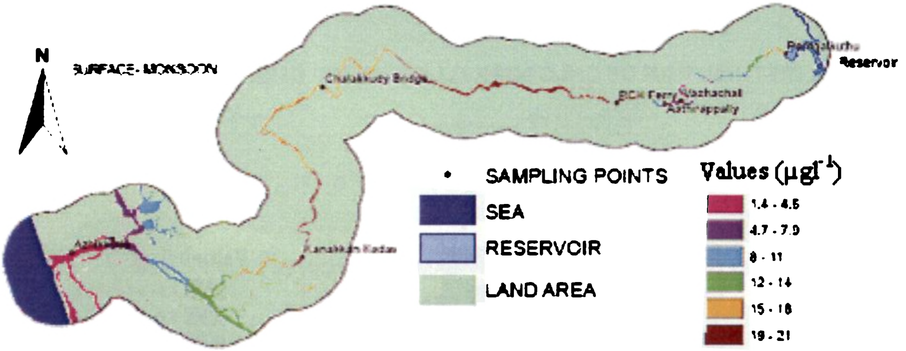


Figure 7.5 Seasonal display of dissolved oxygen along the bottom waters of Chalakudy river estuary

SPATIAL DISTRIBUTION OF CHLOROPHYLL IN WATER ($\mu g l^{-1}$)



SPATIAL DISTRIBUTION OF CHLOROPHYLL IN WATER ($\mu g l^{-1}$)

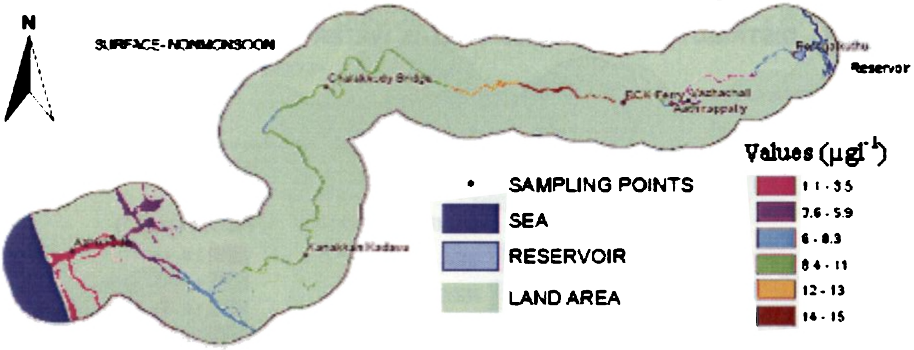


Figure 7.6 Seasonal display of chlorophyll along the surface waters of Chalakudy river estuary

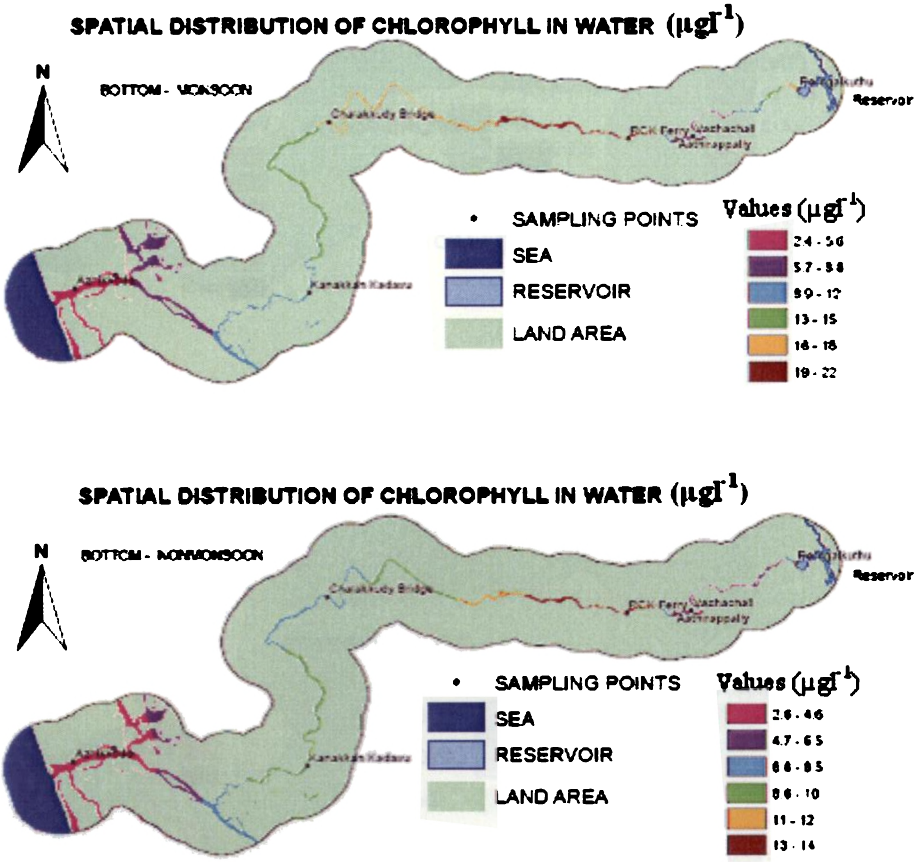
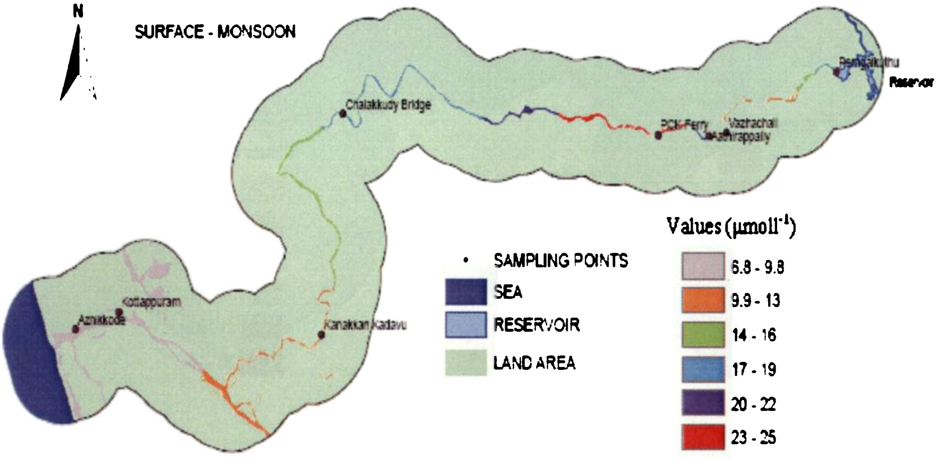


Figure 7.7 Seasonal display of chlorophyll along the bottom waters of Chalakudy river estuary

SPATIAL DISTRIBUTION OF DISSOLVED INORGANIC NITROGEN - WATER (μmoll^{-1})



SPATIAL DISTRIBUTION OF DISSOLVED INORGANIC NITROGEN - WATER (μmoll^{-1})

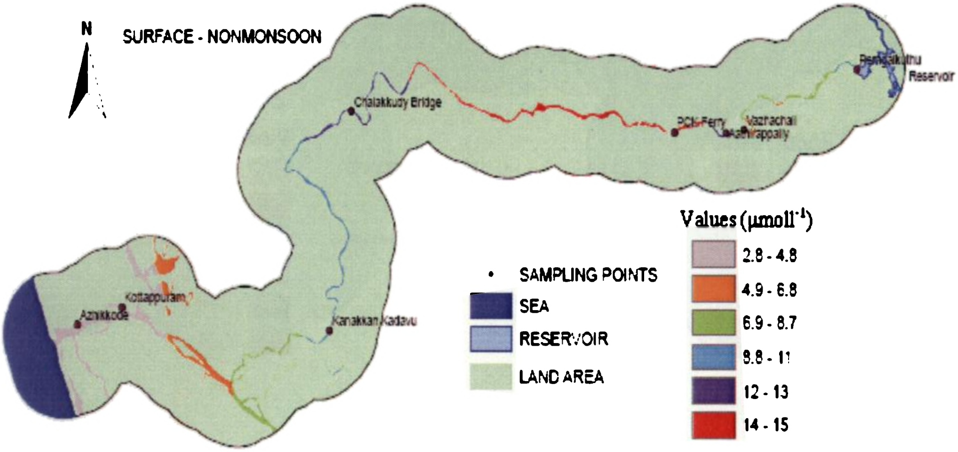


Figure 7.8 Seasonal display of dissolved inorganic nitrogen along the surface waters of Chalakudy river estuary

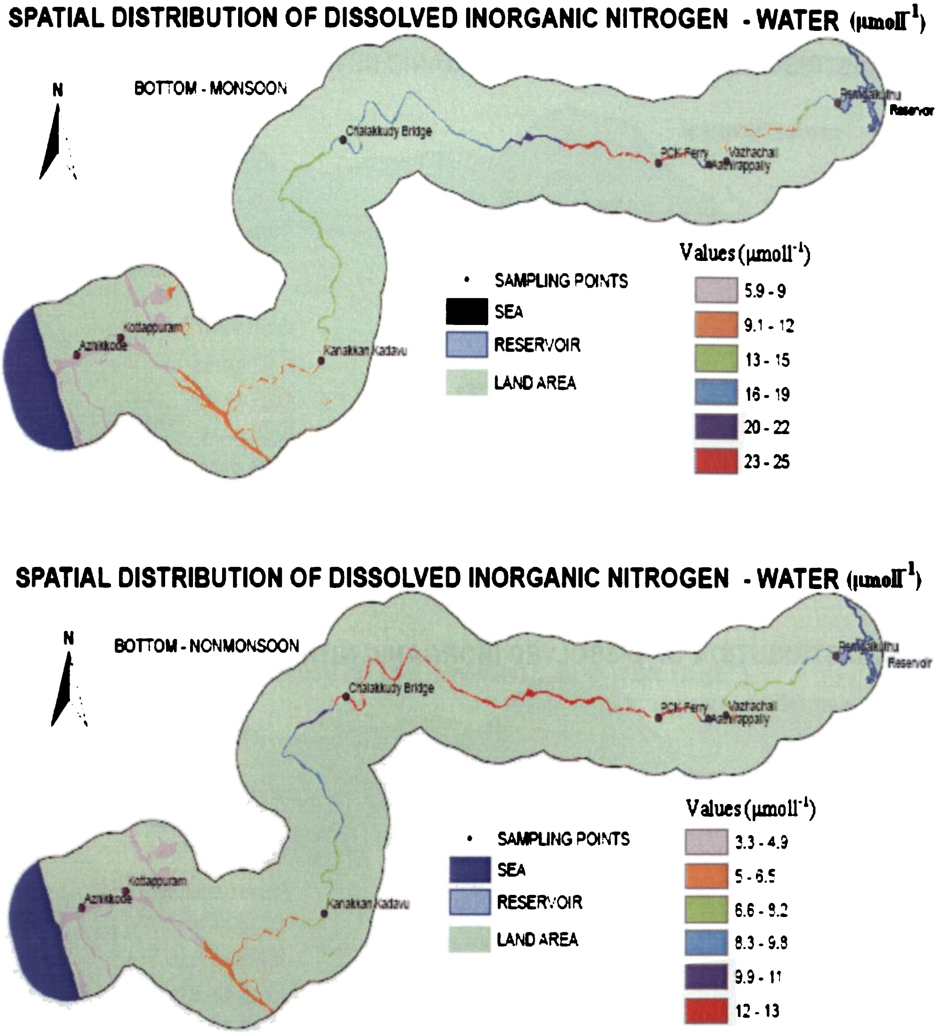
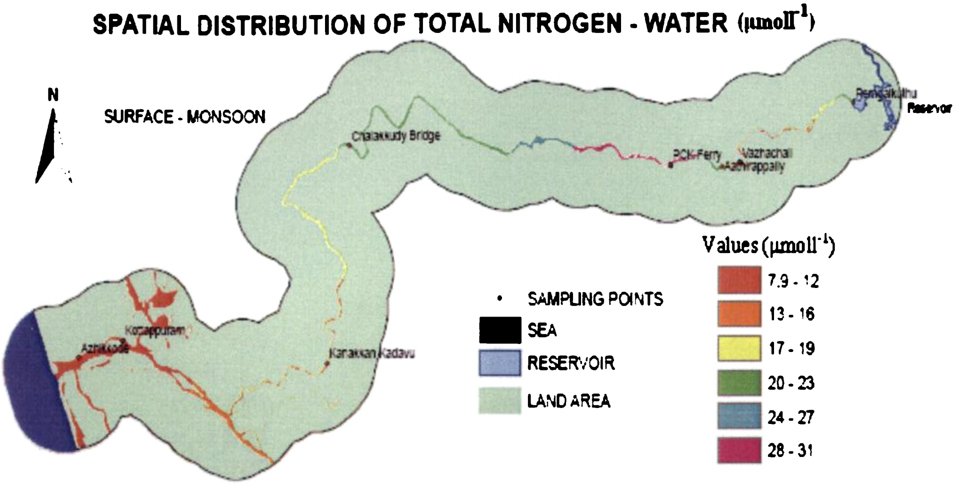


Figure 7.9 Seasonal display of dissolved inorganic nitrogen along the bottom waters of Chalakudy river estuary



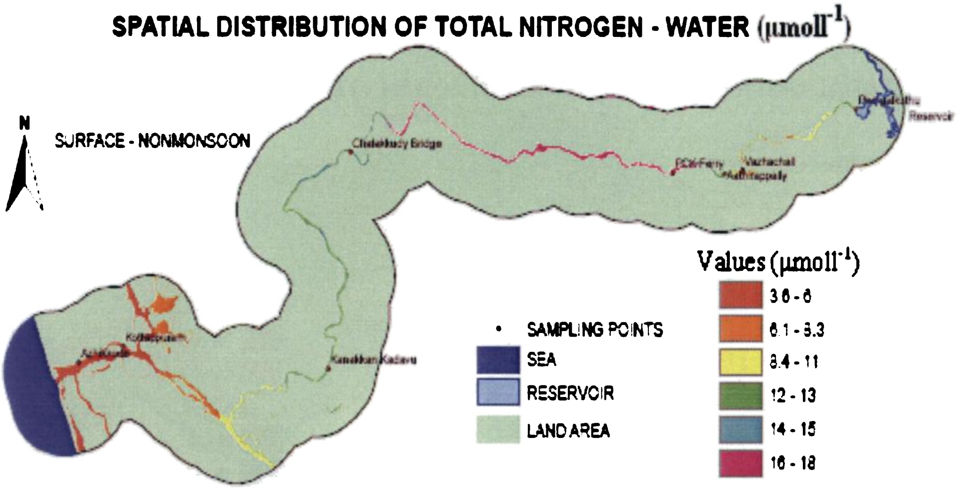
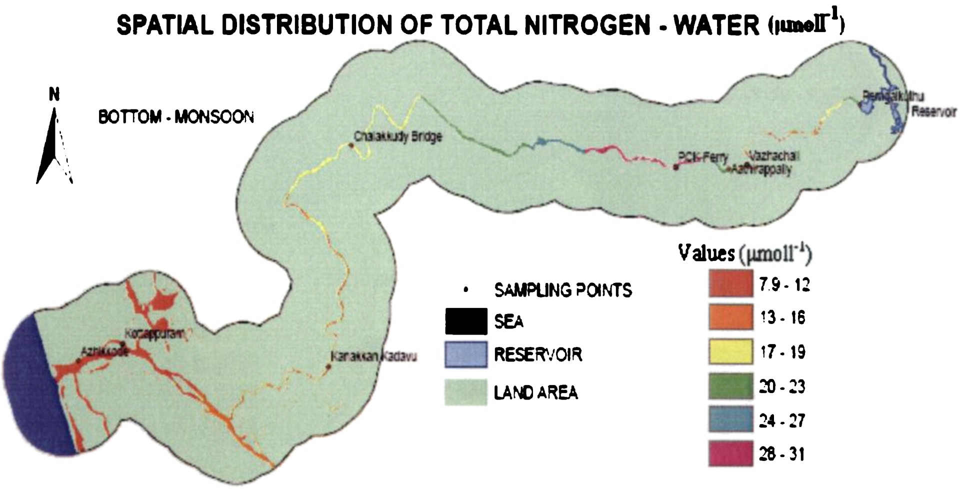


Figure 7.10 Seasonal display of total nitrogen along the surface waters of Chalakudy river estuary


SPATIAL DISTRIBUTION OF TOTAL NITROGEN - WATER (µmoll^{-1})

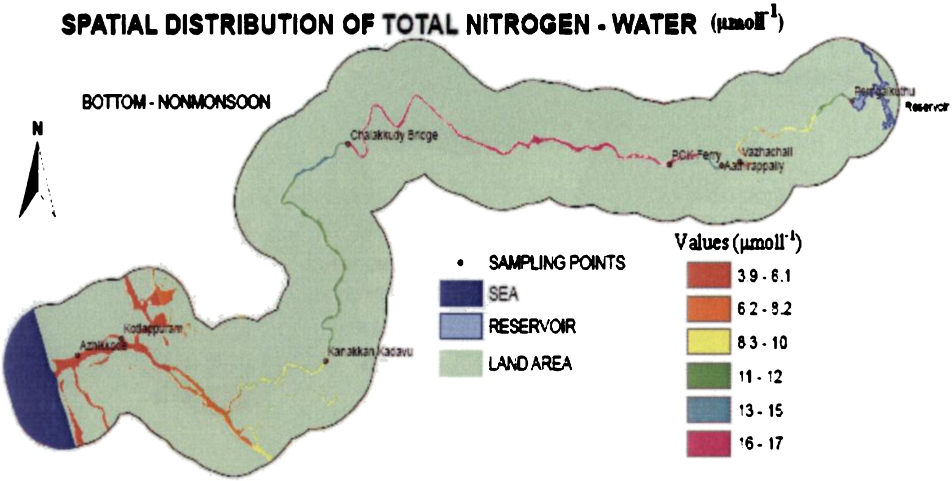
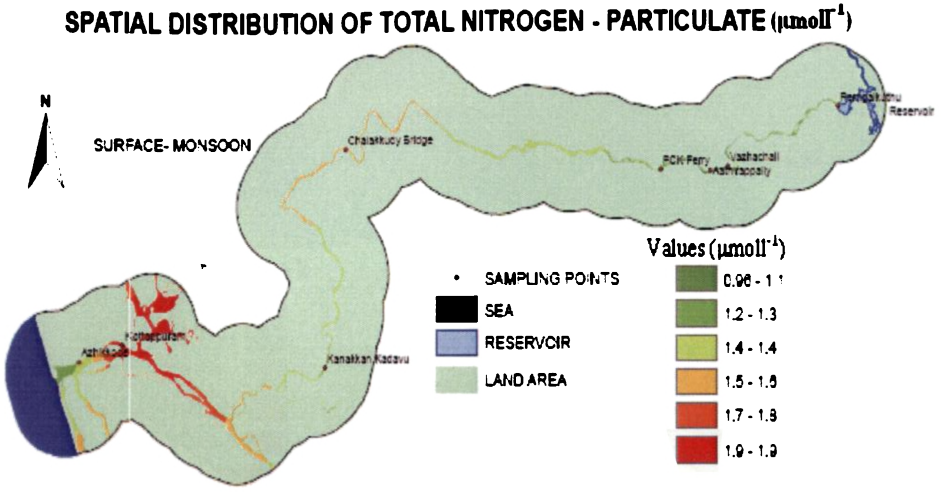

SPATIAL DISTRIBUTION OF TOTAL NITROGEN - WATER (µmoll^{-1})

Figure 7.11 Seasonal display of total nitrogen along the bottom waters of Chalakudy river estuary



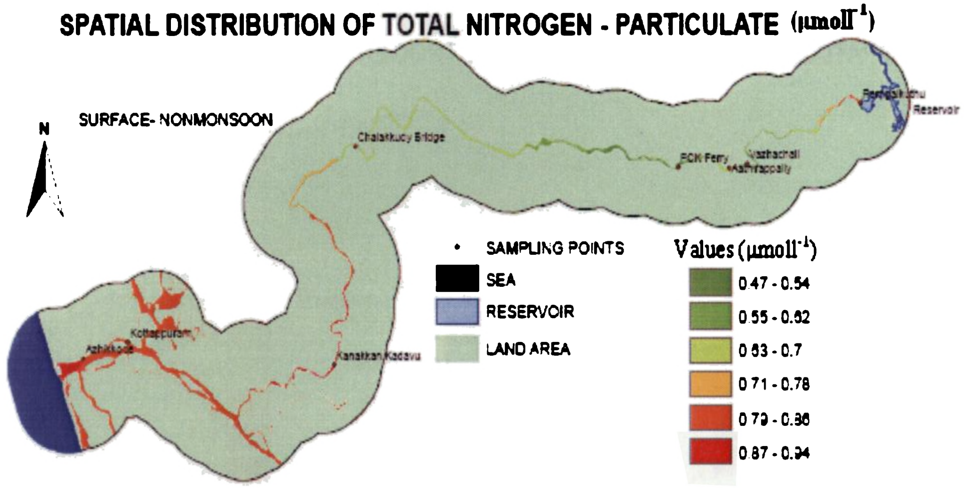
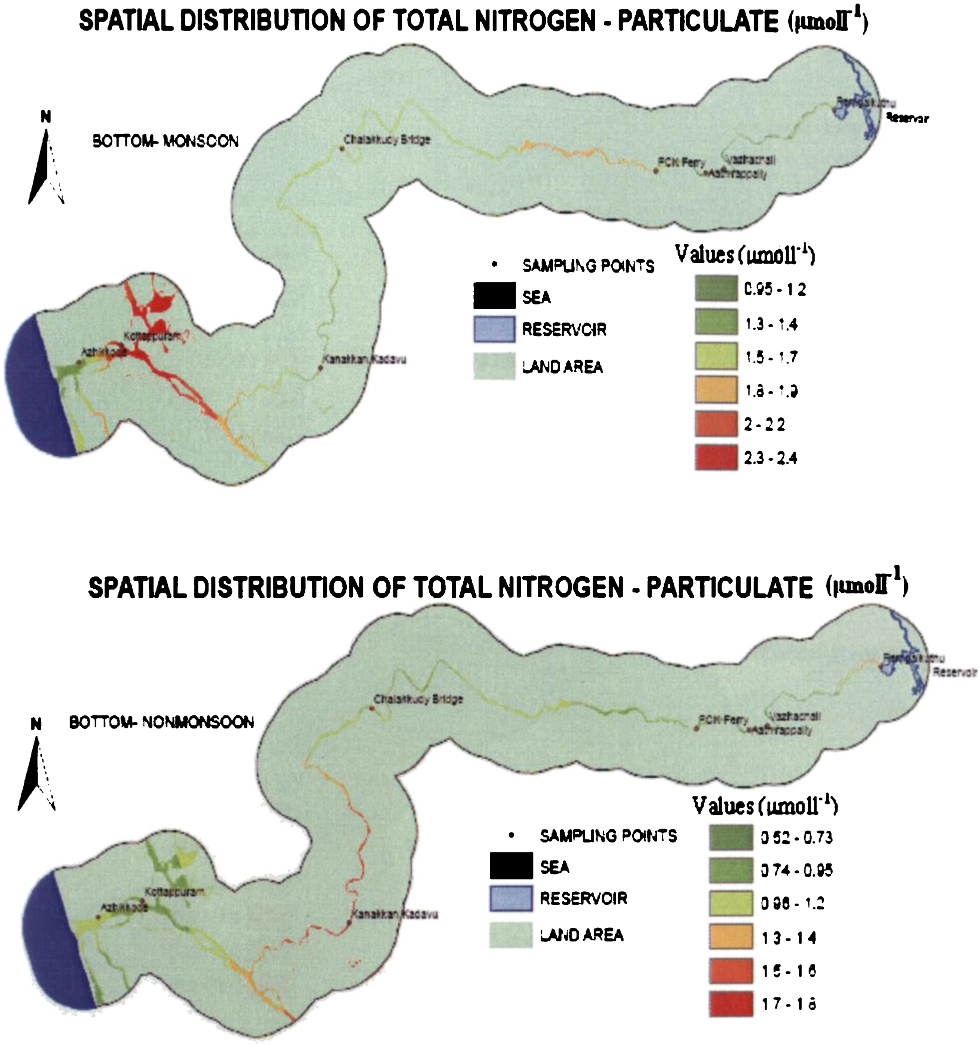
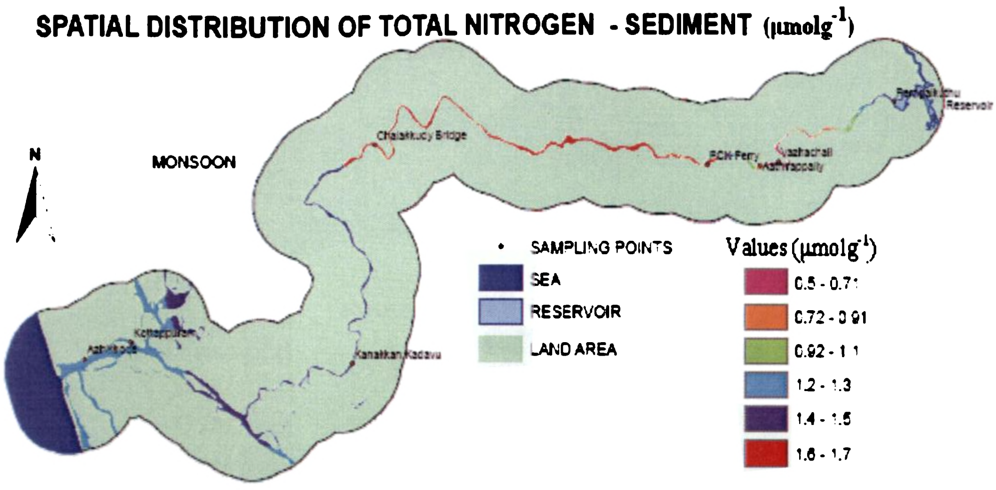


Figure 7.12 Seasonal display of total nitrogen along the surface particulates of Chalakudy river estuary


SPATIAL DISTRIBUTION OF TOTAL NITROGEN - PARTICULATE ($\mu molI^{-1}$)

SPATIAL DISTRIBUTION OF TOTAL NITROGEN - PARTICULATE ($\mu molI^{-1}$)

Figure 7.13 Seasonal display of total nitrogen along the bottom particulates of Chalakudy river estuary



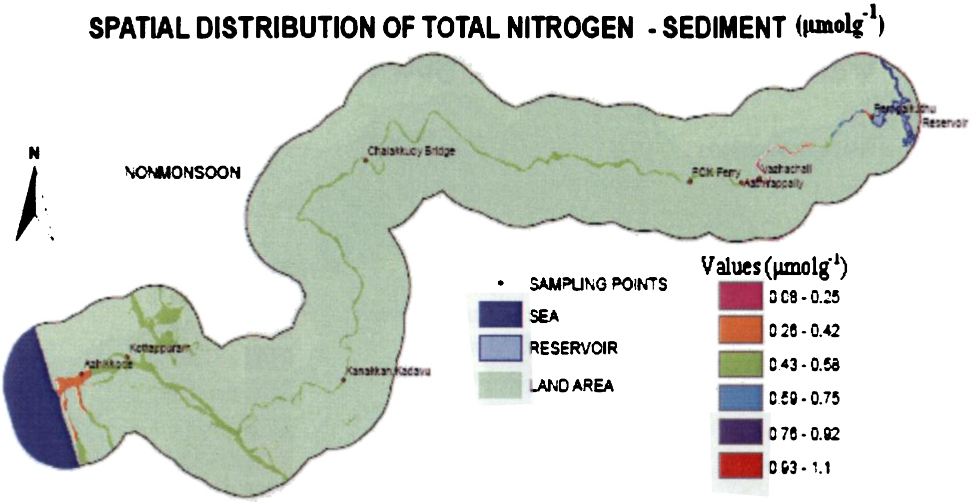
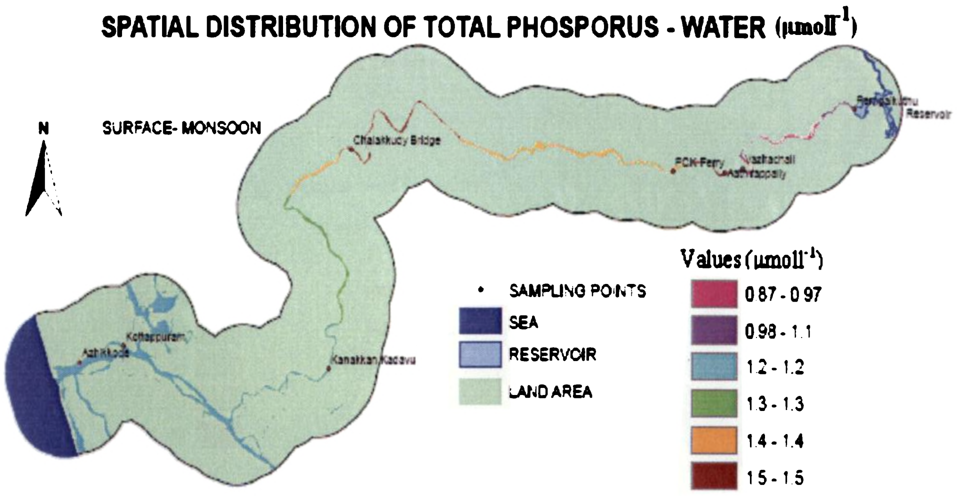


Figure 7.13 Seasonal display of total nitrogen along the sedimentary environment of Chalakudy river estuary



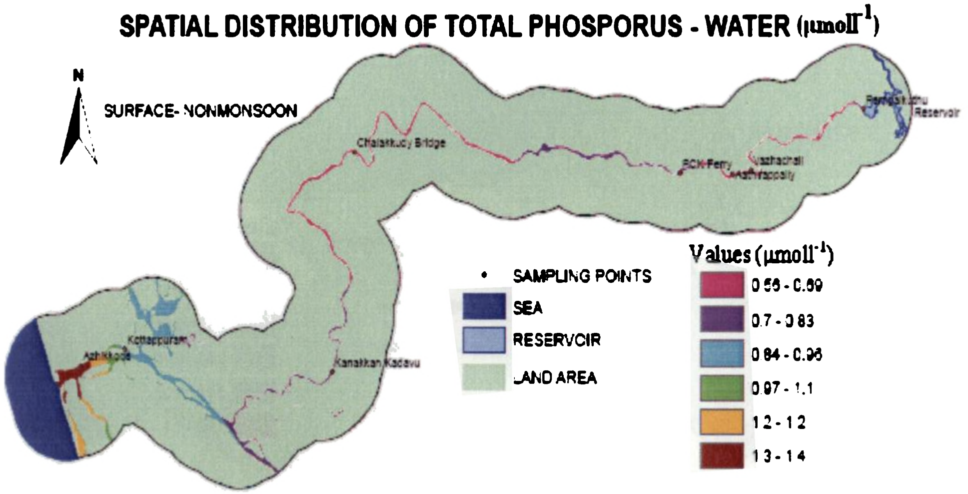


Figure 7.14 Seasonal display of total phosphorus along the surface waters of Chalakudy river estuary

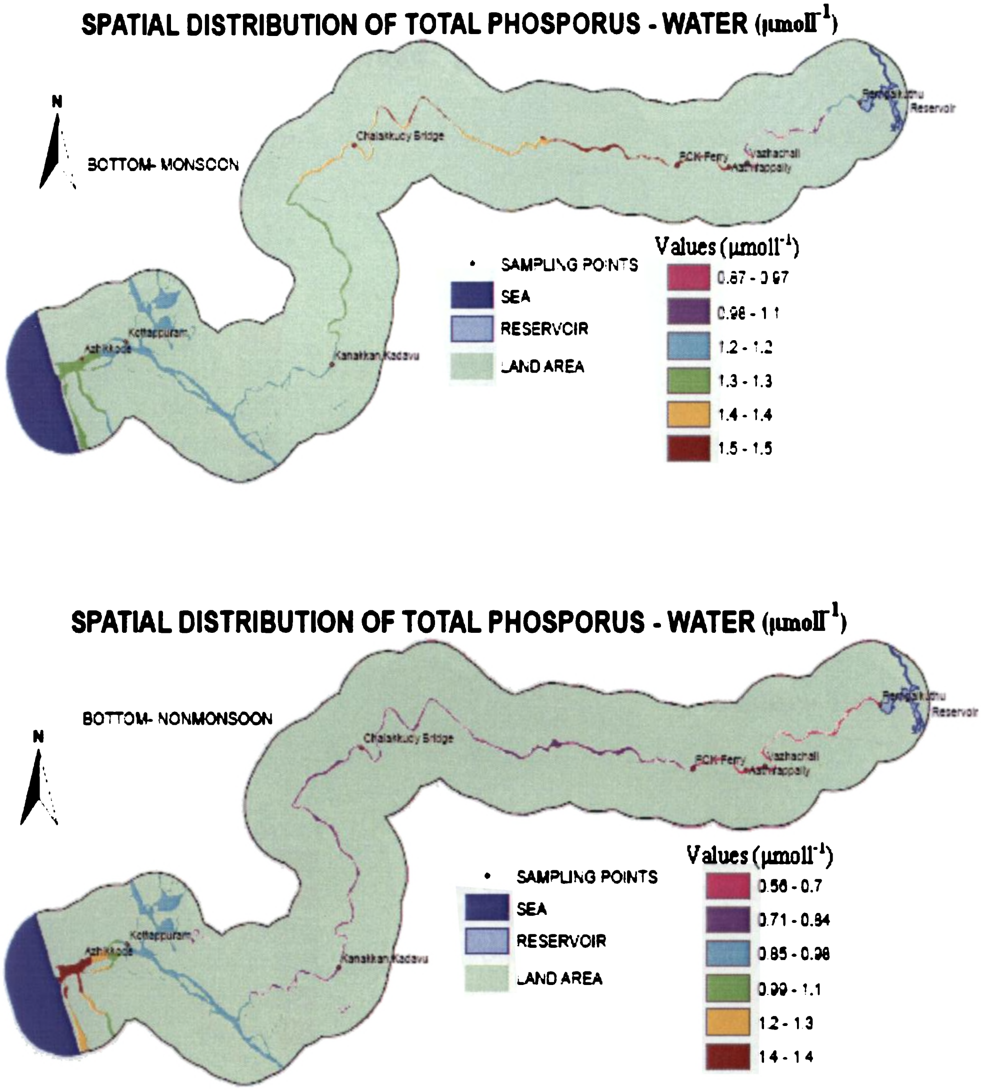


Figure 7.15 Seasonal display of total phosphorus along the bottom waters of Chalakudy river estuary

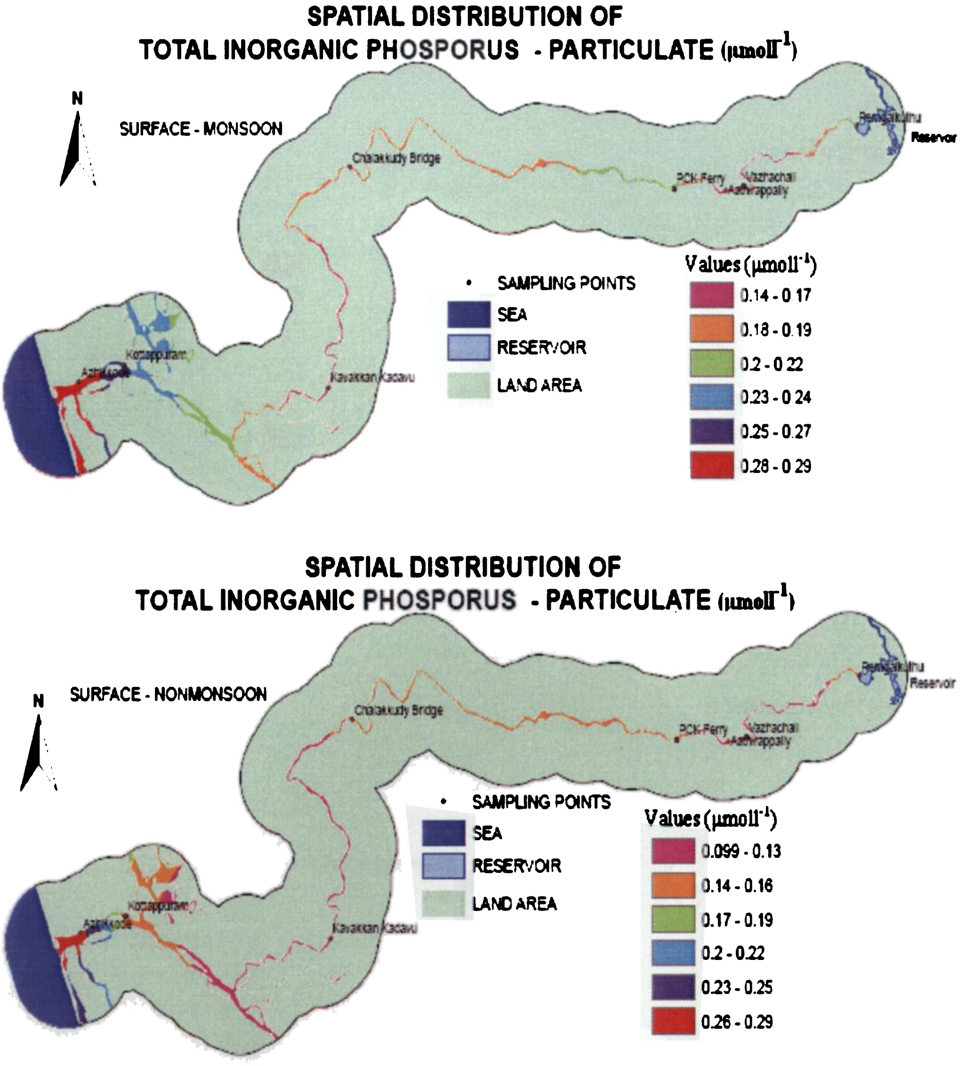


Figure 7.16 Seasonal display of total inorganic phosphorus along the surface particulates of Chalakudy river estuary

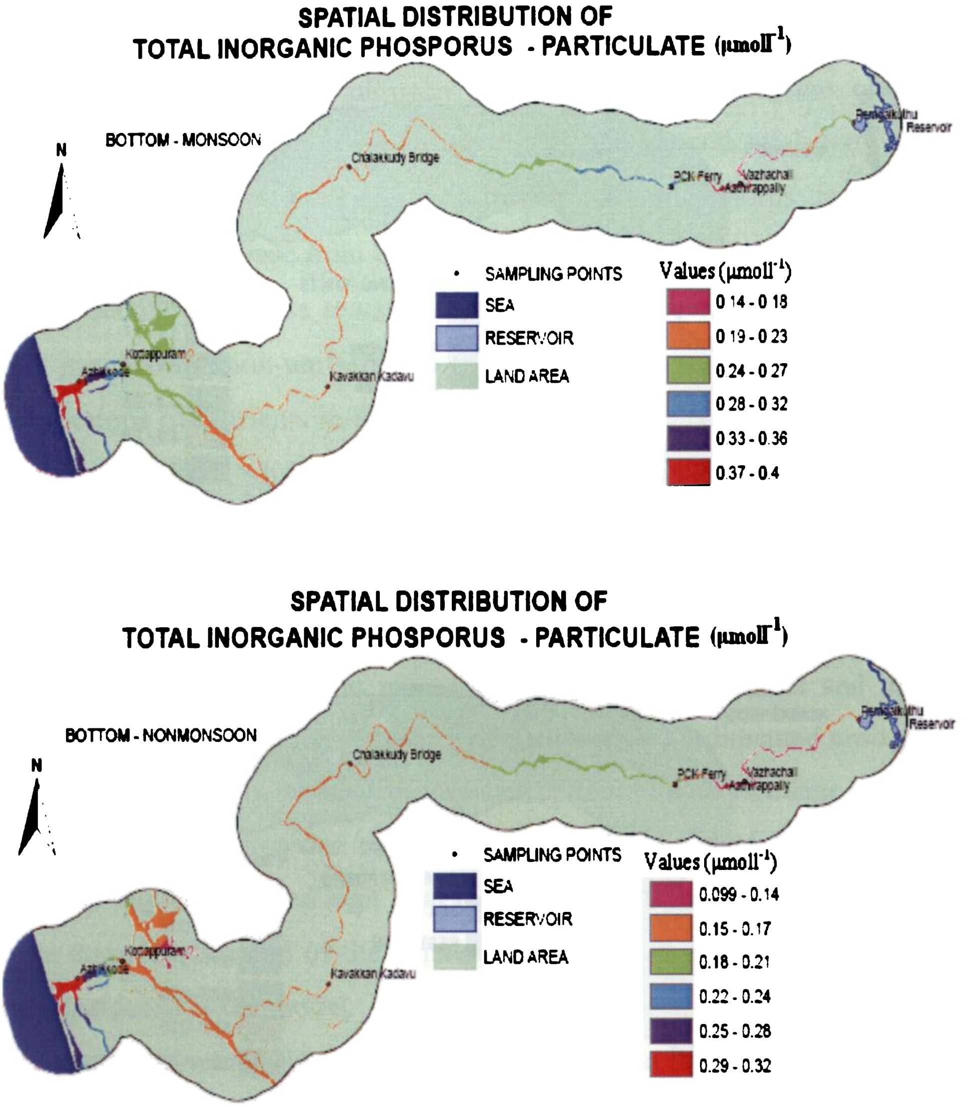
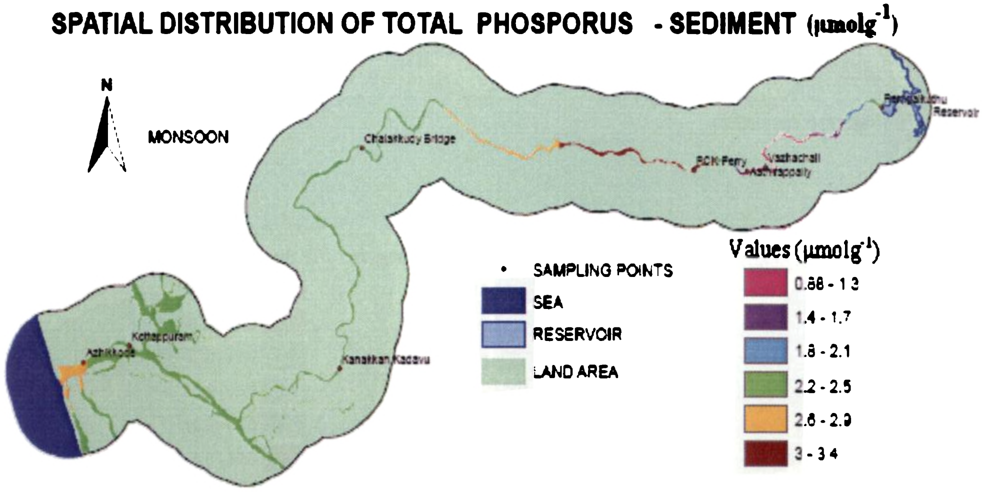


Figure 7.17 Seasonal display of total inorganic phosphorus along the bottom particulates of Chalakudy river estuary



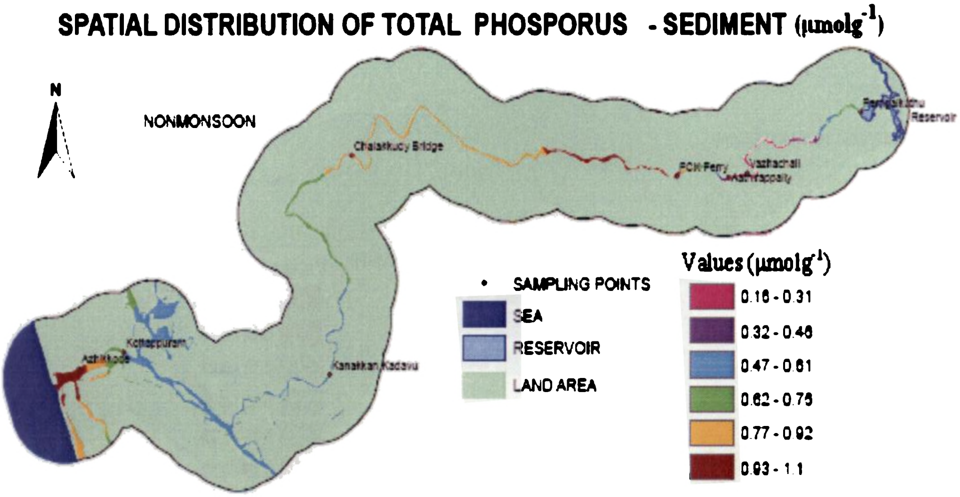


Figure 7.18 Seasonal display of total phosphorus along the sedimentary environment of Chalakudy river estuary

Overall Sumary

Dissolved and sedimented nitrogen and phosphorus species are observed throughout the Chalakudy river. In the model, the general total distribution trend of the dissolved inorganic nitrogen and phosphorus is that the concentrations decrease from dam to waterfall, then increased at midstream with a decrease/increase towards estuary. But the interactions among the river mouths and non-uniformities of the biomasses of plankton make the distributions of nutrients in the Chalakudy river estuary more complicated. In the field data, dissolved inorganic nitrogen is replaced with the summation of NO_3-N, NO_2-N and NH_4-N. The contribution of specific N compounds, especially DIN and total-N suggests a seasonal dependency with lower values during nonmonsoon as could be observed from the GIS maps and predictions could be done at unmeasured locations. The initial and middle regions reflected the higher influence of dissolved and sedimented nitrogen as well as phosphorus, however with slight exceptions of high estuarine dissolved P in nonmonsoon. Riverine end reflected higher particulate N whereas, the estuarine region projected high total inorganic P. The observed data become more complex because of the existence of pollutant sources and these are not considered in the model.

The studies illustrate that nitrogen and phosphorus are in plenty and limit the phytoplankton biomass in the Chalakudy river estuary during both monsoon and nonmonsoon seasons. The content of chlorophyll and nutrients in water is expected to be affected by many factors such as the state of surface, hydrodynamic and biochemical processes. The distribution of dissolved oxygen is much high and exceeds the saturation point somewhere. In the meantime, experiments were utilized to survey responses of the model on various changes and some conclusions are achieved. For instance, if the impact of grain size is inclued, the area of higher nutrient concentration will move towards the clay region of the river estuary, and therefore this experiment demonstrates that the clay greatly enhances nutrient retention.

The experiments illuminate that nitrogen is abundant while phosphorus limit the dissolved system in the river whereas phosphorus is getting higher at the estuary, being limited by nitrogen. Comparison between the observed and modeled data at all stations along the longitudinal transect show that the variation trends and values of biochemical elements in the model are close to those in observation, that is to say, the model successfully reproduces the observed results especially along the longitudinal transect of the Chalakudy river estuary. The use of distributed watershed models to evaluate the impact of a series of small subwatersheds on one water body has presently become important in watershed management and non-point source control.

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SUMMARY

River resource in Kerala are under a continuous threat of pollution because of the insufficient levels of sewage treatment and diffuse contamination from agriculture and industrial effluents. Rivers all over the world have suffered since more than 100 years from anthropogenic pollution, mainly untreated wastewater or effluents. The lack of good quality water hinders economic development and the potential for long term sustainability. One of the most harmful effects of human activities on surface waters is nutrient pollution, caused mainly by nitrogen (N) and phosphorus (P), with several undesirable effects, most of which are related to the increased growth of phytoplankton and other aquatic plants. This leads to a shift in the biological structure, and in severe cases even to oxygen depletion, production of toxins, and the collapse of entire aquatic ecosystems. However, in spite of its importance, not many studies have been done on the Chalakudy river on transport of nutrients and organic material to the estuary. Therefore, both scientific interest and environmental concerns dictated the need to investigate distribution, movement and deposition of nutrients mobilized and transported within the river and its estuary. Chalakudy riverine ecosystem is undergoing anthropogenic stress from large increases in population and urbanization. In many regions, changes in freshwater and material inputs to the rivers are altering the biogeochemical capacities of ecosystems. Here is considered the nature and relative importance of riverine inputs of nitrogen and phosphorus.

The qualitative and quantitative determination of nutrients (i.e. concentrations and loads) in Chalakudy river characterised and predicted

the system responses and as a consequence, accurate estimates of nutrient levels were obtained. An effort was made to identify the main factors that can potentially control the terrestrial landscape contribution towards nutrients. Riparian vegetation are undoubtedly one of the most important parameter related to varying riverine nutrients defining the aquatic ecosystem as well as acting as the boundary between aquatic and terrestrial ecosystems. The moist and often wet soils and high water tables associated with riparian areas make them one of the most important and diverse parts of a river ecosystem. These systems vary considerably in their size, vegetation, species abundance, and diversity in the Chalakudy riverine ecosystem. Nutrient loading during the study appeared to be substantially impacted by rainfall, as ambient concentrations of all measured nutrients increased following significant rain events. A period of profound environmental change occurred in the river regions during the transition from monsoon to nonmonsoon. Changes in various species had been noted in association with seasonal variations in the waterway, especially following enhanced river runoff during the monsoon. Nutrient inputs showed a strong temporal variation linked to heavy precipitation events. A detailed analysis of the variation among hydrochemical parameters revealed significant relation with various nitrogen and phosphorus species in the dissolved, particulate and sedimented stages. The specificity of the river water included intensive chemical interaction of water and sediment, significant influences of rainfall and surface run-off, highly wind-dependent turbulence and turbidity of the waterbody, high particulate nitrogen concentrations and uneven distribution of particulate nitrogen and phosphorus within the waterbody. Thus, a higher number of important variables as well as of chaotic events make it practically more difficult to follow the seasonally dependent course of N and P concentrations and the studies were a helpful completion of the standard geochemical mapping in order to characterize the river. Sediment, under certain conditions, acts as a source or becomes the sink in the exchange of nitrogen and phosphorus between overlying water and suspended particles. The analyses carried out have indicated that the annual survey give a very important information on the latent factors influencing the quality of Chalakudy river and reveal a specific information concerning the river water quality.

The growing concern about agricultural and other anthropogenic nutrients entering water bodies and causing deterioration in water quality, has however resulted in the need for nutrient transport models. An integrated GIS water quality modeling was performed and was found to be the most suitable. The model assisted the collation and interpretation of information, upon which decisions can be made for the management of water resources. Nutrient transport within a watershed depends almost entirely upon hydrology. Nutrient modelling has been much successful.

The river water is characterized by high concentrations of chlorophyll *a*. During seaward transport, the phytoplankton appeared from the river water concomitantly with the elements of N and P, indicating that an increased retention of these elements leads to increase in primary productivity. Although a linear rise of nutrient loads with increasing river flow was measured in some cases, this does not give a clear indication as to whether the inflowing freshwater is the ultimate source of particulate nutrients to the estuary since estuarine concentrations were lower. Increase in salinity actually decreased the dissolved nutrient loads. The concentrations of N species did reveal a clear trend and it could be realized that monsoon concentrations were slightly higher. The likely effects on peak ammonia and nitrate at certain locations are especially of interest because of the effects of nitrogen on the biological diversity of streams. Soluble ammonia and nitrate increased in the mid reaches of the river because of local input and because of mineralization. Pronounced differences were present with regard to the concentrations of NH_3, NO_2^- and NO_3^- and urea. The concentrations exhibited a decreasing trend after the end of the wet season. The nitrate was the major contributor of total-N in all the regions. The percentage of nitrate-N was found to be between 62% and 87% in all stations, except the estuarine region which decreased this to 55 to 57% during monsoon. The percentage composition of nitrite during both monsoon and nonmonsoon seasons amounted to only $\leq$ 3%, pointing to water column nitrate and ammonia regeneration and uptake, N sinks (i.e. denitrification), and water column versus benthic N cycling, as marked factors related to water quality. The ferry station presented very high concentrations of all N species, substantiating the introduction of more inorganic as well as organic components mainly of anthropogenic origin through fertilizer utilization and factory effluents into the vicinity of this station. Phosphate was high in midstream during monsoon, whereas the concentration increased towards estuary in nonmonsoon. High concentrations of total and soluble reactive phosphorus were measured during the period of rising water in all sites, which displayed only mild consistent differences. Compared to nitrate, phosphorus was less variable over time and less divergent between sites. The percentage composition of this dissolved inorganic phosphorus was very high and ringed around 95% of total phosphate as compared to residual phosphorus, which is mainly organic form. The seasonal N:P ratios of dissolved phase were very high for riverine stations, whereas the ratio remained low for estuarine stations owing to chemo-estuarine fluctuations.

In the Chalakudy riverine system, the suspended solid is found to be a phase affected by processes such as denitrification and mineralization of organic matter. The degradation process occurs within the uppermost and lowermost water layers, where bioturbation, advection and diffusion cause rapid exchange of solutes and particles with the overlying water. Particulate nitrogen and phosphorus nutrient profiles provide hints on the intensity of mineralization and decomposition pathways along the river. Results indicated that nitrite-N was very low in percent (2 to 4%) and nitrate-N was the predominant form which ranged in composition from 50% to 68%. The total inorganic P was appreciable owing to comparatively high percentage of Fe/Al bound P, polyphosphates and Ca bound P even though, the other P fractions were low. The N:P ratios of suspended impurities ranged from 1.8 to 6.6 during both seasons and these low ratios was attributed to the increase of particulate P relative to N. The estuarine particulate matter was found to be richer in Ca bound P.

The results primarily indicate the monsoonal build-up of the nutrient loads in the sedimentary environment of this tropical fluvial system. Nitrate-N is the predominent form of total nitrogen and accounts about 50%–74%. Residual-N which denotes mainly the organic-N (excluding urea-N) preserved as organic reserve, is considerable and occupies 6%–30% of total nitrogen and it has a massive role in the riverine productivity. The sediments show a broad variability in N content and in the distribution of its different oxidation forms, which has a direct relation with processes controlling geochemistry in a system contributed by both natural and anthropogenic inputs. Values of various species of phosphorus showed an oscillating trend with no distinct seasonal variation. But it could be seen that stations 7 and 8 having mixing with seawater are specific in their low composition of loosely bound P, and the very high percentage of Ca bound P, polyphosphates and Fe/Al bound P. Residual-P is the predominant form among the various P fractions quantified and it accounts for more than 30% of total phosphorus. Fe/Al bound P and polyphosphates also contribute appreciably towards total phosphorus. Comparatively low values of N:P ratios signifies the benthic enrichment of P nutrient in relation to N, and also the variability in the dynamicity of their recycling processes.

The relationships among N components in all the three phases showed that these originated from the same source. Nutrient concentrations were similar in reservoir and midstream sites during the rainy season when interchange between the mainstem and land was greatest, and the concentrations diverged during the period of falling water level. Nitrogen and phosphorus fractions were markedly lower in the waterfalls, during the period of high as well as low water levels. The study showed that nitrogen is mainly present as nitrate in all the three phases. Total nitrogen concentrations were very high at all sites except waterfalls. Sediment phosphorus concentrations were also lower during high/low water levels at both reservoir and midstream sites. In the mainstem as well as estuary, higher values were observed at the beginning of the rainy season. Dissolved organic nitrogen represented 10%, and particulate and sedimentary organic nitrogen upto 30%. Almost half of the phosphate is particulate phosphate, the largest part of which is calcium bound phosphate. The concentration of nutrients at all stations sank rapidly to a minimum in the waterfalls. Thus, the course of the measured N and P concentrations were mainly characterized.

Options to reduce pollution due to nutrients included reducing nitrogen and phosphorus fertilizers by reducing application rates, and recreating vegetation along the river banks to enhance natural denitrification processes and also to reduce detritus entering the riverine system. Integrating climate change and land use change is particularly challenging because of numerous process interactions and different effects of all the driving variables. It can be said that the quality of receiving waters with respect to nutrients in the river examined is a function of different sources of nutrients and the amount of riverine constituents as well as the morphology of each area and the circulation of waters. It can also be concluded that all stations of chalakudy river are polluted with various nitrogen and phosphorus components of anthropogenic origin. Generally analyses suggested that the nutrient limitation patterns of the river are spatially and seasonally variable, and demonstrate the importance of not only N, but also P, as the main agent for the biogeochemical processes. The findings of this study reinforce the concept that management of point and non-point sources should be integrated as the combination of both sources connected with land use results in deleterious effects on water quality. The enrichment of nutrients in the samples clearly suggested that these can affect significantly the trophic status of the Chalakudy river. It is emphasized that river quality monitoring is a helpful tool not only to evaluate the impacts of pollution sources but also to ensure an efficient management of riverine resources and the protection of aquatic life as well as humanity.

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