Chemodynamics and Ecohydrology of a Tropical Estuary

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To my beloved family….

For their loving support

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CERTIFICATE

This is to certify that the thesis titled "Chemodynamics and Ecohydrology of a Tropical Estuary" is an authentic record of the research work carried out by Renjith K.R., under my supervision and guidance in the Department of Chemical Oceanography, School of Marine Sciences, Cochin University of Science and Technology, in partial fulfilment of the requirements for Ph.D degree of Cochin University of Science and Technology and no part of this has been presented before for any degree in any university.

Kochi - 16
December, 2006

Dr. N. Chandramohanakumar
(Supervising Guide)

DECLARATION

I hereby declare that this thesis entitled "Chemodynamics and Ecohydrology of a Tropical Estuary" is an authentic record of the research work carried out by me under the guidance and supervision of Dr. N. Chandramohanakumar, Professor and Head, Department of Chemical Oceanography, School of Marine Sciences, Cochin University of Science and Technology, and no part of this has previously formed the basis of the award of any degree, diploma, associateship, fellowship or any other similar title or recognition.

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…………This is an urgent matter of human development, and human dignity. Together, we can provide safe, clean water to all the world's people. The world's water resources are our lifelines for survival, and for sustainable development in the 21st century. Together, we must manage them better.

Kofi A. Annan, *United Nations Secretary-General*
(At the launching of 'Water for Life' Decade on 22nd March 2005)

WATER FOR LIFE
2005 - 2015

Preface

Human persistence and biodiversity on earth depend on our ability to maintain the integrity of ecological processes. The current geological epoch has been dubbed the "Anthropocene," because of amplified human role in shaping natural processes that transpire on a global scale. Hence the understanding of the interactions between abiotic and biotic processes is becoming crucial for curbing this human impact, which pertains particularly to water, the most dynamic abiotic factor. The UN bodies UNESCO and UNEP have recognized that water quality is a crucial factor for meeting mankind's needs and for achieving sustainable development, and that it depends on the condition of the ecosystem. Estuaries are the integral part of hydrological cycle and provide us with numerous resources upon which money value cannot easily be placed. The conscious harnessing, based on interdisciplinary knowledge of the properties of ecosystem as tools for increasing the environmental carrying capacity, is a necessity to rectify the serious threats to estuaries and coastal areas.

Vembanad-Kol wetlands (09°50' N, 76°45' E), the largest brackish water, humid tropical ecosystem in the Southwest coast of India, had been identified as a Ramsar Site. This lies parallel to the coastline, extending between Thannermukkam at south and Azheekode at north. There are six rivers debouching into the estuary on either side of the mouth. With the construction of Thannermukkam bund in 1976, an area of about 68 Km^2 of brackish water system lying south of the bund has been ecologically cut off from the salt intrusion during the months of it's closure. This aquatic system is also facing tremendous environmental stress, mainly due to the rapid expansion of the Cochin City, encroachment of low-lying areas and the industrial developments. Immediate steps are essential to prevent further damage and to reinstate the normal health of this important ecosystem.

The main objectives of the present study were to characterize the chemical dynamicity in relation to the bio, geo and physical conditions in the Cochin estuary and to propose a management scheme for its sustainable development. Detailed studies on the hydrodynamics, geochemistry and the nutrient dynamics were carried out to unravel the estuarine dynamics. Ecohydrological concept, developed during UNESCO's International Hydrological Programme is used as a new paradigm for the sustainable management of this aquatic system.

The thesis is divided into six chapters. Chapter I is *Introduction.* It gives general description on the estuarine ecosystem and on the complexity of estuarine dynamics. The general features of Vembanad-Kol and aim and scope of the work are also discussed in this chapter.

Chapter II is *Materials and Methods.* This chapter deals with the characteristics of the study area including the physical settings. It also contains the details of the sampling protocols and the various analytical techniques used in the investigation

Chapter III is *Hydrodynamics.* This chapter includes the seasonal and spatial variations of the physical, chemical and biological characteristics of the water column and the tidal variations of these factors during different seasons.

Chapter IV is *Geochemistry.* This chapter covers the geochemical aspects of the surficial sediments. This includes the sediment characteristics like the texture, benthic density and the compositions of elements carbon, nitrogen, sulphur and phosphorus. The mineralogical aspects of the sediment as well as the heavy metal composition also form part of the chapter.

Chapter V is *Nutrient Dynamics*. It contains the details about the biogeochemical cycle of phosphorus and the chemistry of phosphate speciation in sediments.

Chapter VI *Ecohydrology*. It deals with the description of the estuarine dynamics and the use of its chemical characteristics to propose a sustainable management strategy, through ecohydrological approach.

The salient features of the present investigation are summarized at the end of the thesis. The references are given at the end of each chapter.

CONTENTS

Chapter 1

INTRODUCTION

Human race and civilization are always associated with the coastal systems and rivers. The basic requirement of water was not the sole reason for this, but the enormous life promoting and protecting resources man receives from these aquatic bodies is the coercion. The terrestrial resources are becoming extinct and are not capable to serve human needs. It was predicted in the beginning of this century that aquatic resources are the only solace for the survival of mankind.

Coastal zone has different biotopes as estuaries, mangroves, coral reefs and lagoons endowed with splendid beauty and high productivity. Although these biotopes represent only 10% of the open ocean, 90% of the human needs are obtained from this zone. Among the different biotopes, estuaries play a vital role as they serve as areas of interaction between fresh and salt water (Balasubramanian, 2002).

1.1 Estuaries

The word "estuary" is of sixteenth century origin, derived from the Latin word ***aestuarium*** meaning marsh or channel, which is itself derived from *aestus*, meaning tide or billowing movement, related to the word *aestas* meaning summer. A widely used definition of an estuary has been given by Pritchard (1967): "an estuary is a semi-enclosed coastal body of water, which has a free connection with the open sea and within which sea water is measurably diluted with fresh water derived from land drainage". Since this is a transition zone between fresh water and saline water, it gains the properties of both freshwater and marine environment.

Estuaries rank along with tropical rainforests and coral reefs as the world's most productive ecosystems, more productive than both the rivers and the ocean that influence them from either side. Though they occupy only 0.5% of global marine areas, estuaries are responsible for 2.6% of marine primary production and potentially contribute 5.9% to the world fisheries harvest. They act as gigantic mixing vessels for waters of various biological, thermal, hydrochemical, and suspended matter characteristics that undergo daily, seasonal and long-term changes, defying generalization.

Estuaries play a crucial role in socio-economic development of mankind in many aspects. Most of the great cities of the world have developed around the estuaries. Of the ten largest metropolitan areas in the world, seven such as New York, Tokyo, London, Shanghai, Buenos Aires, Osaka and Los Angels border the estuarine areas. In India, the coastal population density has been quite high since many centuries and the metropolitan cities like Mumbai, Kolkata and Chennai are developed around the estuaries. Even at the time of the Harappan civilization, exploitation of estuarine and riverine resources was intensive.

Estuaries have been the focal point of the maritime studies and activities. As they are semi-enclosed, they provide natural harbour for trade and commerce. They are effective nutrient traps and also sites for effluent disposal and recycling and provide a vital source of natural resources to man and are used for commercial, industrial and recreational purposes. Biodiversity in this ecosystem is very impressive. Plants and animals have adapted specially for the different habitats of this unique ecosystem. Thousands of birds, mammals, fish and other wildlife use estuaries as places to live, feed and reproduce. Estuaries provide a nursery for the larval forms of some marine fish species, and provide shelter and food for many young and adult fish and shellfish. These in turn provide food for other levels of the food chain including shore birds, waterfowl, larger fish and marine mammals. Many seafood species such as lobster, herring, crab, oyster and clam rely on the rich food supply of estuaries during some part of their life cycle. It is estimated that 60-80% of the commercial marine fisheries resources depend on estuaries for part or all of their life cycle.

Thus estuaries provide us with numerous resources upon which a money value cannot easily be placed and estuarine processes are therefore of great interest both from a geochemical, recreational, economic and ecological point of view (Zwolsman, 1994). They are irreplaceable natural resources that must be managed carefully for the mutual benefit of all who enjoy and depend on them.

1.2 Estuarine Dynamics

Estuaries and coastal waterways are highly dynamic environments in which geomorphic change is driven by the deposition and erosion of sediment, which may occur over a range of timescales, from almost instantaneous (e.g. river floods), to progressive change over thousands of years (Cooper, 2001). Unlike many geological processes, sedimentation in coastal waterways occurs on timescales relevant to human society. Over time, continued sedimentation leads to the progressive conversion of estuarine waterbodies into intertidal and terrestrial environments, with obvious management implications (Roy *et al.*, 2001). The main components of estuarine dynamics are hydrodynamics and sediment dynamics.

1.2.1 Hydrodynamics

Water circulation in estuaries can be assessed from estimations of current speed, flow rate and residence time. Salinity, temperature, suspended particles, turbidity, dissolved oxygen, nutrients and chlorophyll are usually the key parameters responsible for maintenance of adequate conditions for reproduction, growth and survival of species in the estuarine environment.

Salinity is a parameter that affects the physiological functioning of all estuarine organisms (Kinne, 1971). While mixing, salinity behaves conservatively and accordingly has a low involvement in biological and chemical processes. Hence, it is often used as a mixing index. Salinity variations within estuaries have provided the physico-chemical basis for the long-established classification of estuaries into 'salt wedge', 'partially-mixed' and 'well-mixed types' (Pritchard, 1967; Dyer, 1986). Salinity distributions at different river flows underpin estuarine ecological investigations and enable quantification of ecological components. Changes in salinity and water temperature determine water density and influence circulation patterns, allowing the tracking of water circulation in estuaries. Phytoplankton dynamics, zooplankton biomass, concentrations of dissolved inorganic nutrients and suspended particulates and residual currents are all influenced by salinity stratification (Cloern, 1984).

Estuarine suspended particles are derived from continental and coastal erosion, *in situ* chemical and biological processes, the atmosphere, and industrial activities (Turner & Millward, 2002). Suspended sediments are the major contributor in the global transport of materials from land to sea by rivers; more significantly phosphorus, heavy metals and organic compounds (Walling, 1998). They often have severe impacts on the aquatic environment ranging from acute toxic impact on organisms to change in benthic community, reduction in diversity, and reduced plant photosynthesis (Hellawell, 1986). Suspended sediments play a key role in the availability, transport, recycling and fate of chemicals in the aquatic environment due to the episodic resuspension, deposition, generation and high reactivities (Baskaran & Santschi, 1993; Leppard *et al.*, 1998; Uher *et al.*, 2001), which are highly significant in estuaries because of the regular (tidal) and sporadic (wind or river flow-induced) variations in particle concentration and character (Lindsay *et al.*, 1996; Ford *et al.*, 1997; Ridderinkhof *et al.*, 2000; Fain *et al.*, 2001), and the modification of chemical and particle reactivities by abrupt changes in salinity, pH, redox conditions, and concentration of dissolved organic matter (Beckett & Le, 1990; Herman & Heip, 1999; Mannino & Harvey, 1999; Turner & Rawling, 2001). Properties of suspended particles determine not only their settling characteristics and residence times, but also their impact on chemical and biological cycles (Alber, 2000) and the fractionation of chemical constituents between suspended particles and the aqueous phase is an essential component of chemical transport models (Johansson *et al.*, 2001). Knowledge of the vertical distribution of current and suspended sediments in tidal seas is required for a wide range of engineering and environmental problems such as the management of navigable waterways, dispersion rate of pollutants, ecosystem behaviour etc. (Chapalain *et al.*, 1999).

Turbidity, which can make water appear cloudy or muddy, is caused by the presence of suspended and dissolved matter, such as clay, silt, finely divided organic matter, plankton and other microscopic organisms, organic acids, and dyes (ASTM International, 2003). Gravitational circulation or tidal asymmetry of velocity and suspended particles can cause convergent fluxes of suspended particles and form Estuarine Turbidity Maxima (Hamblin, 1989; Jay & Musiak, 1994; Wolanski *et al.*, 1995), which play a vital role in secondary production in many estuarine ecosystems (Simenstad *et al.*, 1995). Turbidity controls the phytoplankton biomass that can potentially develop (Cloern, 1987; Monbet, 1992) and therefore the extent to which dissolved nutrients can build up in the water column. High turbidity levels can lead to a reduction in the production and diversity of species (Cloern, 1996).

Nutrients are functionally involved in the living process of organisms (Parsons, 1975). The nutrient budget in an estuary depends on the amount of input from the land, how much is taken up by plants or re-cycled in the sediments within the estuary and how much is exported or imported to and from the ocean in the tidal water. Excessive nutrient inputs can lead to eutrophication, defined as excess inputs of organic matter particularly from increased primary production (Fisher *et al.*, 1988; Nixon, 1995). Eutrophication is arguably the biggest pollution problem facing estuaries globally, with extensive consequences including anoxic and hypoxic waters, reduced fishery harvests, toxic algal blooms, and loss of biotic diversity (NRC, 2000). According to Liebig's Law of the Minimum, biological growth is limited by the substance that is present in the minimum quantity with respect to the needs of the organism and by definition, the addition of a limiting nutrient increases phytoplankton carbon biomass and primary productivity (Howarth, 1988). Nitrogen and phosphorus are generally the limiting nutrients and silicon may also be a limiting nutrient for diatoms. Using the atomic Si:N:P ratio of 16:16:1 (Redfield, 1958) as a criterion for balanced nutrient composition, nutrient ratios used to demonstrate the potential nutrient. It is also important to confirm if this ratio is constant or variable, as it is a very dynamic environment, and if there exists a specific class of primary producers that could be benefited.

To restore the water quality of eutrophic ecosystems to an acceptable level, it is necessary to identify the growth-limiting nutrients to develop nutrient input constraints. Since the distribution and availability of the nutrients in estuaries determine the trophic state of the estuary, it is essential to have knowledge on the transport and transformation process within estuaries for efficient management of estuarine system.

Dissolved oxygen (DO) is one of the most essential of all life-supporting environmental constituents. Low dissolved oxygen concentrations can increase mortality, reduce growth rates and alter the distribution and behavior of aquatic organisms, all of which can produce significant changes in the overall estuarine food web (Breitburg, 2002). The amount of oxygen dissolved in the water changes as a function of temperature, salinity, atmospheric pressure and biological and chemical processes. The toxicity of many toxicants like lead, cyanide, hydrogen sulfide and pentachlorophenol can double when DO is reduced from 10 to 5 mg/l (ANZECC/ARMCANZ, 2000). In addition, if dissolved oxygen becomes depleted in bottom waters or sediment, nitrification may be terminated, and bioavailable orthophosphate and ammonium may be released from the sediment to the water column. These recycled nutrients can give rise to or reinforce eutrophication. Ammonia and hydrogen sulfide gas, also the result of anaerobic respiration, can be toxic to benthic organisms and fish assemblages in high concentrations (Connell & Miller, 1984). Accurate data on DO in water are essential for documenting changes to the environment caused by natural phenomena and human activities. The full diurnal range of dissolved oxygen can also be used as an indicator of primary production.

Estuaries are among the most productive of marine ecosystems supporting an abundant and diverse fauna and flora (Odum, 1971; Boynton *et al.*, 1982; Nixon *et al.*, 1986; Houde & Rutherford, 1993). Phytoplankton primary productivity in aquatic environment plays an essential role in element cycling, water quality, and food supply to heterotrophs (Cloern, 1996). Study of the spatial and temporal variability of primary production and its controlling mechanisms are essential for understanding biogeochemical cycle of carbon (Cullen *et al.*, 1992; Knauer, 1991; Longhurst & Harrison, 1989), for assessing the fertility of aquatic systems and for predicting the potential of living resources. A common method for measuring the biomass of phytoplankton is determination of the chlorophyll-a concentration, which constitutes about 1 to 2 percent of the dry weight of planktonic algae.

Zooplanktons are very sensitive to changes in the quality of water and to a wide variety of pollutants, thus providing important information about the environmental conditions in estuaries. Zooplankton can have a significant impact on phytoplankton species composition and productivity through selective grazing and nutrient recycling. These are very important because they form the connecting link between primary producers and secondary consumers (fishes). There are evidences that the efficiency of fish production relative to primary production are higher in estuaries than in shelf, upwelling or oceanic systems. Rates of secondary production are relatively efficient in aquatic ecosystems compared to terrestrial biomes because of relatively high nutritional value of the dominant primary producers in aquatic (algae) as opposed to terrestrial systems. Though limnologists have identified the apparently significant dependence of fish harvest on primary production in estuaries, the trophic linkages and mechanisms that promote efficient secondary production and trophic transfers are poorly known.

1.2.2 Sediment Dynamics

Estuarine sediment dynamics during a tidal cycle embrace particle resuspension, differential settling, transport of grains and particle–water interactions like precipitation, flocculation, desorption and adsorption (Turner *et al.*, 1994). Processes that also contribute to sediment resuspension and redistribution in estuarine systems are driven by river flow, shear stresses imposed by wind–wave action, bioturbation and dredging (Calmano *et al.*, 1994; Lindsay *et al.*, 1996). Altogether, they give rise to a complexity of internal transport routes for heterogeneously reactive chemical constituents and, consequently, to the development of internal cycling and temporary retention mechanisms (Bale *et al.*, 1985). In the absence of any physical or biological sediment disturbances, exchange occurs through diffusional processes in sediment pore waters, controlled by factors such as porosity. Estuaries are highly eco-sensitive and highest concentrations of contaminants occur in estuarine and shallow coastal marine systems, especially those in close proximity to heavily industrialized metropolitan centers (Kennish, 1997).

Sediment-water inorganic exchanges are a primary mechanism of linking sediment and water column processes in estuaries and can be more seasonally variable than either primary or secondary production (Asmus, 1986). In coastal environments where sedimentary inputs are large, microbially mediated benthic remineralisation of debris is a major recycling pathway and this stepwise breakdown of complex organic substrates into soluble inorganic species of carbon, nitrogen and phosphorus, which may be released by the benthic system into the overlying water (Klump, 1981). These Benthic releases are significant to support benthic and water-column primary production (Billen, 1984; Boynton & Kemp, 1985; Hopkinson *et al.*, 1999).

Sediment and nutrient delivery are inseparable because much of the nutrient delivered to streams is attached to sediment particles, particularly clay particles. Sediments form an important dynamic pool in estuarine nutrient budgets, acting as both sources and sinks for water column nutrients throughout the year. While external inputs may be important in terms of total nutrient loading to estuaries, nutrient cycling processes are often vital for determining the quantity and quality of the nutrient substrate available for pelagic primary production. The proportion of nutrient export from the benthic ecosystem to the water column because of macrofaunal activity supplies a significant proportion of the phytoplankton requirements (Asmus & Asmus, 1991; Smaal & Prinz, 1993), estimate ranged from 0-100%, with a mean of 28-30% (Doering, 1989). During a bloom, nutrient fluxes from the sediment represented 20% Si, 16 % P and 9% N of the primary production demand (Grenz *et al.*, 2000). The annual contribution of nitrogen from sediments to primary production in shallow marine systems was from 28 to 35 % in North Carolina (Fisher *et al.*, 1982), from 15 to 27 % during the summer in upper Chesapeake Bay (Boynton & Kemp, 1985), 65 % in the Patuxent River estuary (Boynton *et al.*, 1980), 35% in the Potomac River estuary (Callender & Hammond, 1982) and 25 % in Narragansett Bay (Nixon, 1981).

Conversely, benthic productivity may cause an uptake and depletion of dissolved nutrients (e.g. N, P and Si) from overlying waters. Nutrient cycling can also change the water column C:N:P on a seasonal basis, which impacts on the scale and composition of primary productivity. The capacity of sediments to control and buffer nutrient concentration and speciation in the water column is an important component in determining the trophic status of an estuary. Hence understanding the role of sediments in the nutrient dynamics and productivity is vital in determining the health and resilience of estuarine systems.

The importance of carbon flux in sediment is strongly determined by the origin as well as by the potential degradability of the organic matter (Grall & Chauvaud, 2002). Low specific gravity particles generally have a higher organic content than high specific gravity particles and the process of organic matter mineralisation are also a function of the temperature, geochemistry and their extend is related to the intensity of bioturbation in the benthic ecosystem (Grall & Chauvaud, 2002). The decomposition of sediment organic matter is orchestrated by a sequence of metabolic pathways that use different electron acceptors as chemistry changes with increasing depth (Canfield, 1993). Sulphate reduction and oxic respiration are the most important carbon oxidation pathways (Alongi, 1998). The biogeochemical cycling of carbon within these sediments represents an important step in the global carbon cycle (Hedges & Keil, 1995). In aquatic systems, energy (carbon) is considered to be more mobile than in terrestrial systems because water acts as a vector for particulate and dissolved organic matter (Carr *et al.,* 2003). In marine systems, high offshore secondary production adjacent to inshore waters, rich in primary productivity, led to a theory of large-scale movement of carbon from inshore to offshore habitats (Odum *et al.,* 1979).

Sediments in shallow coastal waters are known to be important sites for the accumulation of organic matter and the subsequent remineralization and recycling of nutrients (Bonanni *et al.,* 1992). High primary production associated with shallow depths and the delayed (often) responses of heterotrophs result in much of the pelagic organic matter being exported to the benthos as sinking particles (Graf, 1992). Most of the deposited organic matter is degraded at the sediment–water interface or in the upper sediment column (Jorgensen, 1983). Sediments, therefore, are important sites for recycling nutrients back to the water column. Total organic C is also indicative of biological processes (eutrophication) in the system. Elemental and isotopic compositions of sedimentary organic matter have been commonly used to distinguish organic matter from different sources (Schelske & Hodell, 1995).

The biochemical composition of sediment organic matter is the result of the dynamic equilibrium between external inputs, autochthonous production and heterotrophic utilisation. The bulk of allochthonous organic matter consists of structurally complex polysaccharides, lignocelluloses and other complex organic compounds (Benner *et al.,* 1986). Autochthonous production is also an important source of organic matter in estuaries and is generally less refractory than allochthonous carbon (Wetzel, 1983). Quality and quantity of organic matter in surface sediments have been considered of primary importance in determining the amount of organic material potentially available to consumers, thus affecting community structure and benthic metabolism (Graf *et al.,* 1983; Grant & Hargrave, 1987; Thompson & Nichols, 1988; Graf, 1992).

Sulphur cycling in aquatic sediments involves both reductive and oxidative processes (Jorgensen, 1990). Sulphur cycle has also significant interactions among other biogeochemical cycles such as carbon and phosphorus (Kleeberg, 1997). One important factor controlling the rate of sulphate reduction in lakes is the concentration of sulphate (Capone & Kiene, 1988) and an enhanced input may stimulate reduction, substantially altering the cycling of elements such as carbon, nitrogen, phosphorus and iron (Cook & Kelly, 1992). The formation and precipitation of insoluble iron sulphide compounds reduces the binding of phosphate iron oxides (Nurnberg, 1996; Kleeberg, 1997) and a release of phosphate from the sediments may enhance the eutrophic status (Caraco *et al.*, 1993; Sondergaard *et al.*, 1996; Kleeberg, 1997). The formation of sulphides primarily occurs in the surface layers in the active zone of sulphate reduction with no major changes in pool sizes below these layers. If iron limitation occurs, phosphate is released both from the redox-sensitive pools (iron bound) and during mineralization of organic matter (Nurnberg, 1996).

Processes involved in weathering and erosion of geological formations result in transfer of a wide range of metals to coastal lowlands and aquatic environments. A substantial number of metals can also be introduced into coastal environments as a result of human activities. During transport and/or deposition, metals are subject to a variety of processes associated with floods, tides and wave action; they can be adsorbed by clays and can form organic complexes (van den Berg *et al.*, 1987) or co-precipitate as inorganic mineral phases (Thornton, 1983). These partitioning of metals between the dissolved and particulate phase, due to adsorption, desorption, precipitation and flocculation, takes place frequently within the estuarine zone (Sholkovitz, 1976; Li *et al.*, 1984; L'Her Roux *et al.*, 1998), and that the rate and extent to which this occurs depend on many factors including metal reactivity and the estuarine hydrodynamics (Morris, 1990; Millward & Turner, 1995). Chemical removal of trace metals from water to sediments occurs frequently when fresh and saline waters are mixed (Paulson *et al.*, 1993; Millward & Glegg, 1997; L'Her Roux *et al.*, 1998). A number of features such as depositional conditions (pH, Eh and salinity), sediment grain size and mineralogy, effect of 'scavenger' species such as iron and manganese oxyhydroxides, and organic material content significantly influence the amount and spatial distribution of metals within estuarine and near-shore environments (Forstner *et al.*, 1976; 1984; 1989). The degradation of organic matter affects both hydrodynamic processes and geochemical redox cycles, providing driving forces for metal mobilization (Förstner, 2004). Aquatic humic substances are large organic molecules formed by micro-biotic degradation of biopolymers and polymerization of smaller organic molecules in the environment (MacCarthy & Suffet, 1989). The presence of carboxylic, phenolic and carbonyl groups gives them a high capability for the complexation of metal ions. This chemical behavior significantly influences the transport, distribution and accumulation of metals in aquatic environments (Hirade, 1992; Weber, 1998).

The accumulation of metals in an aquatic environment has direct consequences to man and to the ecosystem because of their toxicity, bioaccumulation capacity and persistence. Sediments are capable of acting as a trace metal source to the overlying water-column and to benthic biota (Chapman *et al.*, 1998). Assessment of the environmental risk posed by contaminated sediments requires knowledge of trace metal partitioning between sediment pore-water and various solid-phases (Di Toro *et al.*, 1991; Ankley *et al.*, 1996; Burton *et al.*, 2005). Interest in metals like Zn and Cu which are required for metabolic activity in organisms, lies in the narrow "window" between their essentiality and toxicity (Skidmore, 1964; Spear, 1981). Others like Cd and Pb do not play a biological role and exhibit extreme toxicity even at trace levels (Merian, 1991).

Cadmium is one of the most toxic elements with reported mutagenic, carcinogenic and teratogenic effects (Friberg *et al.*, 1986; Fischer, 1987; Kazantzis, 1987; Heinrich, 1988; Goering *et al.*, 1994). Lead is defined as potentially hazardous to most forms of life by the United States Environmental Protection Agency and is considered toxic and relatively accessible to aquatic organisms (USEPA, 1986). Although Zn has been found to have low toxicity to man, prolonged consumption of large doses can result in some health complications such as fatigue, dizziness, and neutropenia (Hess & Schmid, 2002). Elevated levels of certain metals such as Cu and Co, which are classified as essential have been found to be toxic (Spear, 1981). Toxicological effects of large amounts of Co include vasodilation, flushing and cardiomyopathy in humans and animals (Teo & Chen, 2001). Toxicity of Ni to rainbow trout has been reported (Pane *et al.*, 2003). Its toxic effects in man are related to dermal, lung and nasal sinus cancers. When copper reaches toxic concentrations, it interferes with the activity of enzymes situated on cell membranes of algae. This interference prevents cell division and causes photosynthesis to stop (Levine, 1975).

Benthic suspension feeders have a stabilizing influence on the benthic ecosystems, since they are the stable component of the ecosystem and their biomass have a slow turn over rate (Herman & Scholten, 1990). Benthic organisms transport particles and fluid during feeding, burrowing, tube construction and irrigation activity and thus influence benthic flux rates significantly. Burrowing organisms have a significant impact on sediment chemistry and physics. Bioturbation, or burrowing activities, affects the sediment profile, by physically translocating contaminated sediments, mixing and redistributing the contamination. It is important to note also that the irrigation of burrows means that organisms are exposed to overlying water more than interstitial water (Boese *et al.*, 1990). Suspension feeders are not only important in terms of direct control, but also affect nutrient recycling and sedimentation or recycling of organic particulate matter (Smaal & Prinz, 1993), contributing to secondary production in the benthos (Graf, 1992). In the coastal zone, for instance, benthic nitrogen regeneration has been estimated to supply 26–101% of the phytoplankton demand (Kristensen, 1988).

Quantity and quality of organic matter in surface sediments are recognised as major factors affecting benthic fauna dynamics and metabolism (Graf *et al.*, 1983; Grant & Hargrave, 1987), influencing the community metabolism, composition and structure (Grall & Chauvaud, 2002), as mentioned earlier. Hydrodynamic processes responsible for sediment movements and physical disturbances caused by human activities can deeply modify benthic communities (Hall, 1994). The interrelationships among rates of material cycling through both benthic and water column communities play an important role in the ultimate fate of inorganic nutrients and organic matter within coastal ecosystems (Nixon, 1981;Glibert, 1982; Kemp & Boynton, 1984). Benthic activity probably inhibits sulphate reduction in surface layers, but may stimulate it deeper in the sediment by enhancing the supply of sulphate and organic matter (Banta *et al.*, 1999).

Benthic community structure and composition can provide a sensitive integration and biological reflection of contaminant affects both temporally and spatially (Gray *et al.*, 1990). Benthic communities have frequently been employed in environmental monitoring and assessment of heavy metal and organic contamination in estuaries, with demonstrated changes in macrobenthic community structure and composition in reponse to pollutant impacts (Rygg, 1985; Gray *et al.*, 1990; Warwick & Clarke, 1991; Reynoldson & Metcalfe-Smith, 1992; Warwick, 1993). For monitoring the health of coastal ecosystems, it is crucial to identify and measure the effects of eutrophic stress on coastal and estuarine benthic communities (Gray *et al.*, 1990).

1.3 Vembanad-Kol ecosystem

India has a coastline of 7500 km with an exclusive economic zone of 2.015×10^6 km^2, which is 61% of the land area. The country has 14 major, 44 medium and 162 minor rivers with a total catchment area of 3.12×10^6 km^2, discharging 1645 km^2 of freshwater every year to the seas around the country. Coastal wetlands occupy an estimated 6,750 km^2, and are largely dominated by mangrove vegetation. Kerala's coast runs some 580 km in length, while the state itself varies 35–120 km in width. The backwaters are a chain of brackish lagoons and lakes lying parallel to the Arabian Sea of Kerala. The network includes five large lakes (including Vembanad Lake and Ashtamudi Lake) linked by 1500 km of canals, fed by 38 rivers, and extending virtually the entire length of Kerala state (8% of India's waterways).

The Vembanad-Kol wetlands (09°50' N, 76°45 'E) had been identified as the Ramsar Site-1214 at the Convention on Wetlands organised by the UNESCO in the Iranian city of Ramsar in 1981. It is the largest brackishwater, humid tropical ecosystem in the Southwest coast of India. The southern arm from Cochin to Alappuzha has a length of 60 km and the northward extension is up to Azeekode. The construction of the Thannermukkam barrier in the southern arm near Vaikom, in 1976 has resulted this lake into two entirely different ecosystems, retaining estuarine conditions in the northern sector or the downstream region (Cochin to

Thannermukkam, popularly known as Cochin backwaters) and transforming the southern sector or the upstream region (Thannermukkam to Alappuzha) into a freshwater habitat during the months of barrier closure (Gopalan *et al.,* 1983). Periyar and Muvattupuzha are the major rivers, which open to this lake. Thannermukkam bund prevents the incursion of seawater into the agricultural fields in Kuttanad. This also controls the flow of four rivers Pamba, Achankovil, Manimala and Meenachil into the lake (Fig. 1.1). The estuary is generally shallow with depths ranging from 0.75 to 5 m (Kurup *et al.*, 1989), except at the navigation channel in Cochin port, where it varies from 8 to 12 m. This approach channel branches into two, the Ernakulam channel and Mattancherry channel that are on either side of the Willingdon Island, leading to the respective ship warfs.

Among the 30 estuaries in the state, the Vembanad Lake is the largest one. The Vembanad-Kol wetland system and its ten associated drainage basins cover a total area of about 16,200 km^2. There are three completed and five partially completed major-medium irrigation projects in these river basins, which have a total storage capacity of 1,345 Mm^3 to cater to the irrigation requirements of 1,00,000 ha. The nine-hydel projects in the river basins contribute to 1400 MW of the installed capacity.

It is believed that the Vembanad Lake attained its configuration in the fourth century (Anon., 1973). It was primarily a marine environment, bounded by an alluvial bar parallel to the coastline and connected to Arabian Sea at intervals. Due to intense flood in 1341 AD, parts of the present coastal districts of Ernakulam and Alappuzha were formed, thus separating a distinct body of water from sea with connecting channels at Thottapally, Andakaranazhi and Kochi. A number of islands were also formed in this water body (Menon, 1913).

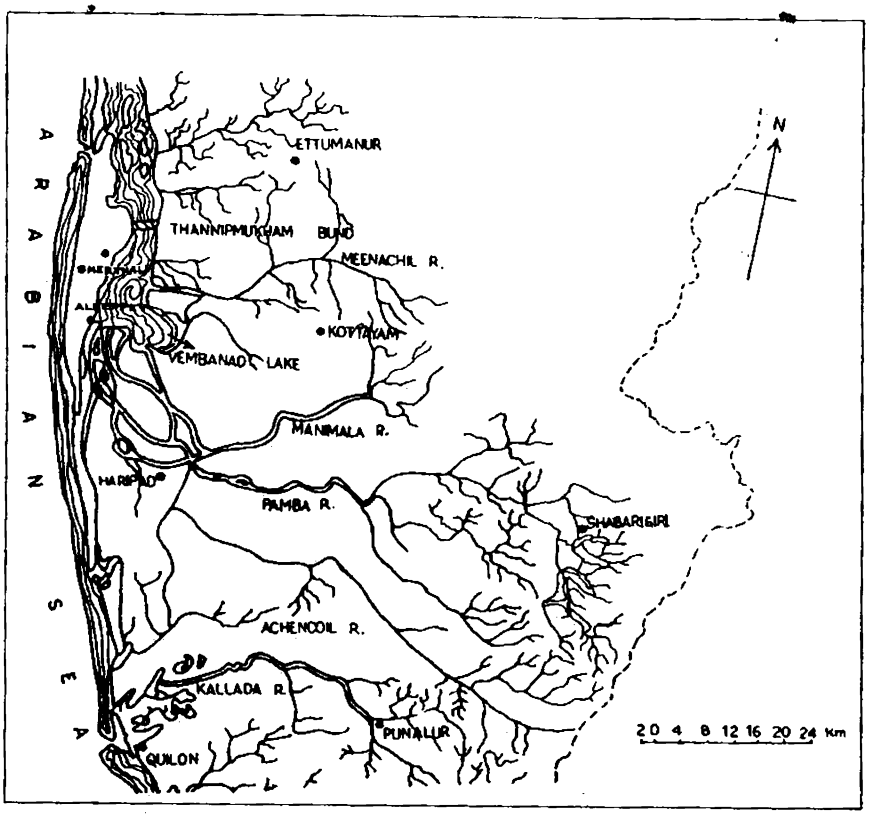

Figure 1.1 Main Rivers joining Vembanad Lake on the southern side

The Vembanad-Kol wetland system has several functions and values. This water body contains the floodwaters and saves about 3500 sq km thickly populated coastal area of 3 districts of Kerala from flood damages. Rice cultivation is practiced in the polders covering a total area of 100 sq km in the Kuttanad belt (the rice bowl of Kerala) of the Vembanad-Kol. The yield of rice from the wetland is 4-6 times more than the uplands. Prawn culture is also popular in several areas of the wetland. The wetland along with the lower reaches of the rivers draining into it serves the purpose of inland navigation. The Vembanad supports the third largest population of waterfowl in India during the winter months. Many fishes depend on the wetland for food, spawning and nursery. Vembanad is renowned for its live clam resources and sub-fossil deposits. The local production of fish from the Vembanad accounts for 5000 tonnes; almost same quantity of prawns is also available from this wetland. Vembanad lake and other backwaters of Kerala with an area of 50,000 ha. produce 14,000-17,000 MT of fish. This wetland system also serves as a sink and transformer for the agricultural and municipal wastes discharged into it. The wetland has great value from the point of view of water sports; the famous boat race of Kerala takes place in the Vembanad backwaters. Ninety-one species of resident/locally migratory and 50 species of migratory birds are found in the Kol area. The lake supports over 20,000 water birds, including the IUCN red-listed birds. Mangrove swamps were originally occupied the whole area.

1.3.1 Review of earlier works

Vembanad Lake including the Cochin estuarine system is one of the intensively studied aquatic systems of India. Several studies on the physico-chemical, biological and geological aspects of this estuary were reported.

The hydrographical conditions of the Cochin estuary and the seasonal variations were reported by Ramamirtham & Jayaraman (1963), Qasim & Gopinathan (1969), Devassy & Gopinathan (1970), Balakrishnan & Shynamma (1976), Ramaraju *et al.*, (1979), Udayavarma *et al.*, (1981), Lakshmanan *et al.*, (1982), Sankaranarayanan *et al.*,(1986), Ramamirtham & Muthuswamy (1986), Anirudhan *et al.*, (1987), Jacob *et al.*, (1987), Batcha & Damodaran (1987), Joseph & Kurup (1989; 1990), Batcha (2000) and Varma *et al.*, (2002). Josanto ($1971_{a,b}$) examined the bottom salinity and the sediment characteristics between Kochi and Alappuzha covering even smaller arms.

George & Kartha (1963) studied the tidal influence on surface salinity in the Ernakulam channel. Pillai *et al.,* (1973) analyzed the tidal currents around Cochin bar mouth and their influence of the hydrographic parameters. Ramaraju *et al.*, (1979) and Sundaresan (1990) also studied the tidal variation in Cochin harbour area. Revichandran *et al.,* (1993) examined the suspended sediment transport and residual salt flux in the lower reaches of the estuary and west of Kumbalam Island.

Seasonal variations in nutrients of Vembanad Lake were studied by Sankaranarayanan & Qasim (1969), while Joseph (1974) reported the nutrient distribution in the Cochin harbour. Sreedharan Manikoth & Salih (1974), Kunjukrishna Pillai *et al.,* (1975), Balakrishnan & Shynamma (1976), Sankaranarayanan *et al.,* (1986), Anirudhan *et al.,* (1987), Lakshmanan *et al.,* (1987), Anirudhan & Nambisan (1990), Saraladevi *et al.,* (1991) and Sheeba *et al.,* (1996) discussed the variations of different nutrient species in different parts of this estuary.

Qasim *et al.*, (1969) pioneered the studies on primary production in this estuary. Qasim & Gopinathan, (1969), Kunjukrishna Pillai *et al.*, (1975), Nair *et al.,* (1975), Joseph & Pillai, (1975), Sreekumar & Joseph (1997), Sivadasan & Joseph (1998), Rasheed *et al.*, (2000) and Selvaraj *et al.*, (2003) also made significant contributions to the productivity studies of this ecosystem. There are several reports on the seasonal and spatial changes of zooplankton of the Vembanad Lake and connected backwaters (George, 1958; Nair & Tranter, 1971; Menon *et al.*, 1971; Haridas *et al.*, 1973; Wellershaus, 1974; Madhupratap *et al.*, 1977). Several investigations have been carried out on the distribution and abundance of benthic fauna in relation to hydrographic parameters and sediment characteristics in the Cochin backwaters. Kurian (1967; 1971), Desai & Krishnankutty (1968), Jayasree (1971), Ansari (1974), Kurian *et al.,* (1975), Pillai (1977), Saraladevi & Venugopal (1989), Sunilkumar (1995), Sivadasan & Joseph (1997; 1998) are the main works amongst them.

Nair *et al.,* (1993), Seralathan *et al.,* (1993), Seralathan & Padmalal (1994) and Balachandran *et al.,* (2002) studied the geochemical aspects of this estuary. The mineralogy off Cochin was reported by Rao & Rao (1995). The distributional characteristics of heavy metals in and around this estuarine system is well documented [Venugopal *et al.,* (1982) Paul & Pillai (1983$_{a,b}$), Malik & Suchindan (1984), Ouseph (1987), Babukutty (1991), Rajammani Amma (1994), Balachandran *et al.,* (2002) Shajan (2001), Joseph (2002), Balachandran *et al.,* (2003)]. Balchand & Nair (1994) estimated the seasonal fluctuations of the different forms of phosphorus using eight different schemes of phosphorus fractionation in entire Cochin estuary. Lizen (2000) examined different fractions of nutients in the Kuttanad region of Vembanad Lake.

Vasudevan Nair, (1995) carried out studies on the distribution of petroleum hydrocarbons (PHC). Sujatha *et al.,* (1999) reported spatial and seasonal distribution of Endosulfan and Malathion in Cochin estuary. Other features of the Cochin backwaters in terms of hydroxylated aromatic compounds (Nair *et al.,* 1989), protein content (Balchand *et al.,* 1990), distribution and abundance of urea (Nair *et al.,* 1994) reveal seasonal chemical cycling and the influence of phenomenal regional diversity, signifying the role of anthropogenic inputs.

1.4 Aim and scope of the study

An increasing world population reaching 6 billion people, 60 % of them are living in coastal areas means a continuous pressure on the coastal seas. In recent times, many estuaries are subjected to over exploitation and also destruction due to industrialization and urbanization. The gigantic influence of human activity on river ecosystems is accounted for construction of enormous number of dams and reservoirs, changing of hydrological regime of water bodies; pollution of rivers and lakes from point and diffusion sources, as well as in the result of transboundary transfers of pollutants with air currents; direct withdrawal of water from water bodies for irrigation, water supply of industry and population and so on. Ecosystem restoration in highly complex, human-dominated estuaries rests on a strong conceptual foundation of sustainability, ecosystems, and adaptive management of human-induced environmental impacts. Sustainability is a powerful watchword in that captures the essential objective of environmental policy making (Baird, 2005).

Vembanad Lake is also under threat from agricultural and developmental works, sedimentation, pollution, etc. (Nair & Thrivikramaji, 1996). Changes in topography due to dredging for various purposes produces modifications like variations in salinity intrusion, tidal forcing, sedimentation etc. Reclamation and consequent shrinkage and the discharge of pollutants have made adverse impact on the estuarine ecosystem, which supported rich fish and shellfish production and biodiversity. The average area of Vembanad Lake shrunk from 315 km^2 in 1912 to 180 km^2 (43%) in 1983 (Gopalan *et al.,* 1983) and now it was reported that the area is only 120km^2 in 2003 (Kalakoumudhi weekly, 2003). Reclamation for agricultural purposes particularly paddy cum shrimp culture is taking place and Ashraf (1998) observed nearly 14% of reclamation. Further, reclamation is also rampant in the low-lying water logged areas with connection to the Lake. Kurup (1971) reported siltation rate of 180cm/year in the estuary, which affects the estuarine depth. Rate of inflow of industrial effluents has increased from negligible amount to 260 million litres/day (Anon, 1982). Similarly, the domestic effluents also increased to a level of 80 million litres/day at Kochi region (Gopalan *et al.*, 1983). The effluent discharge would have increased considerably in recent times.

With the strengthening of tourism industry in 1990's and its recent thrust, the environment of this region is facing further stress. According to recent press reports (Kalakoumudhi weekly, 2003) out of about 156 species of fishes of 56 different families reported from the Vembanad Lake, only very few are present now. Prawns, which were about 60% of the total catch, have come down to 20-25%. The number of migratory birds showed about 25% decline in less than 10 years. According to Kerala State Council for Science Technology and Environment (KSCSTE), frequent incidents of mass mortality of fishes and presence of radioactive waste materials have been reported in the Vembanad Lake.

Many new projects that are planned to come up in the lower reaches of this estuary and off shore like Vallarpadam container terminal, Mareena Park and LNG terminal, moored buoy terminal etc. are likely to affect the dynamics and ecology of this estuary. The study region is also under high stress due to the lateral expansion of the city of Kochi, which is the commercial capital of Kerala. The study region at present is undergoing a great deal of environmental changes due to various developmental activities. The construction of a new railway line and the commissioning of Kochi by pass road accelerated the developments in this region.

Reclamation of the low-lying water logged areas with free connection to estuary is going on in a big way. Many new constructions including a five star hotel and a multi speciality hospital have come up recently. Present widening of the road for four-lane traffic would also increase such activities.

It is very important to have a detailed knowledge of the environmental conditions and the dynamics to assess the natural and anthropogenic changes in estuaries and to develop and implement an effective management plan. Therefore it is imperative to monitor the conditions on a continuous basis. Estuarine dynamics is very complex in nature and undergo daily, seasonal and long-term change, defying generalization. Consequently, every coastal waterway has intrinsic characteristics that make it different from all others, and determine its needs for, and responses to, management strategies (Perillo, 1995). Our National Water Policy (Ministry of Water Resources, 2002) also reminds that water is a scarce and precious national resource to be planned, developed, conserved and managed as such, and on an integrated and environmentally sound basis, keeping in view the socio-economic aspects and needs of the States. It is one of the most crucial elements in developmental planning.

It can be seen from the earlier section that the studies on Cochin estuary are mainly limited to the main arm or near the bar mouth. The inner arms of the estuary were not seriously attended in the earlier studies. Hence, it is imperative that detailed studies on the hydrography of the Cochin estuary covering the inner areas only can derive a long-term sustainable management scheme for this important ecosystem.

The main objectives of the present study were to assess the chemical dynamicity in relation to the bio, geo and physical conditions in the Cochin estuary and to propose a management scheme for its sustainable development. In this context, the following processes are studied in detail,

- Hydrodynamics- Seasonal variations of physical, chemical and biological parameters were measured along with their tidal variations
- Geochemistry- Biogeochemical processes and their spatial and temporal variations
- Nutrient dynamics - Transport pathways, biological interactions, and chemical speciation key of phosphorus, an important nutrient in each system.

Primary and secondary productivity of the estuary and their variations with the environmental parameters were examined to evaluate the fertility, trophical level and the potential of living resources. An attempt was also made to classify the estuary based on observed mixing pattern. A detailed study of the geochemistry and dynamics were carried out to envisage the estuarine dynamics. These informations are used as inputs for developing numerical models with an ultimate aim to determine an effective management strategy. A new environmental problem-solving concept 'Ecohydrology', developed during UNESCO's International Hydrological Programme (Zalewski *et al.*, 1997) is applied, which is based upon the assumption that sustainable development of water resources is dependent on the ability to maintain evolutionarily established processes of water and nutrient circulation and energy flows at the basin scale. The ecohydrological concept is redefined in a chemical perspective and used as a new paradigm for the sustainable management of this important aquatic system.

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Chapter 2

MATERIALS & METHODS

2.1 Description of the study Area

The study area is the Panangad region of the Cochin estuary and is situated about 10 km from the bar mouth. The study area is mainly the inner arm of the Lake and surrounds Nettoor and Panangad islands, which includes portion of Nettoor Canal, Kaithapuzha Kayal and adjacent regions. Nettoor canal is very narrow and the average width of the canal is only around 100 m, while Kaithapuzha Kayal is comparatively wider. Average depth in the study region is about 2.5 m and the maximum depth is about 5m. The presence of small arms and islands make circulation pattern very complex. Total aquatic area of the study region is about 6.25 Km^2. In this area, 12 sampling stations were fixed, based on a reconnaissance survey (Fig.2.1).

The stations selected were near college of Fisheries jetty, Kundanoor-Thevara Bridge, East of Nettoor Island, near prawn culture fields in Nettoor, Le Meridian Hotel, After Kundannoor-Panangad bridge, Lakeshore Hospital, Cheppanam, Chathammel, South end of Chathammel, South end of Kumbalam and near Kumbalam-Panangad bridge. Only the stations 2, 3 10 and 11 are in the main arm of Cochin estuary and all the other stations represent the narrow inner parts of the estuary, where the generation of eddies like circular movements are common, showing significant variation from general circulation pattern. Estuarine dynamics in these inner parts were not studied earlier.

This is a typical monsoon influenced estuary and its physical and hydrobiological characteristics vary seasonally. Annual rainfall in Kerala is about 3000 mm, while the southwest monsoon (June to September) accounts for 71%, 16% is during northeast monsoon. The remaining is due to summer rains (Jayaprakash, 2002). As a result, Kerala averages some 120–140 rainy days per year. The rainfall data of 2003 (India Meteorological Department) showed that during the study period there was a significant contribution of summer rains in the estuarine region (Fig. 2.2), influencing the seasonal behaviour.

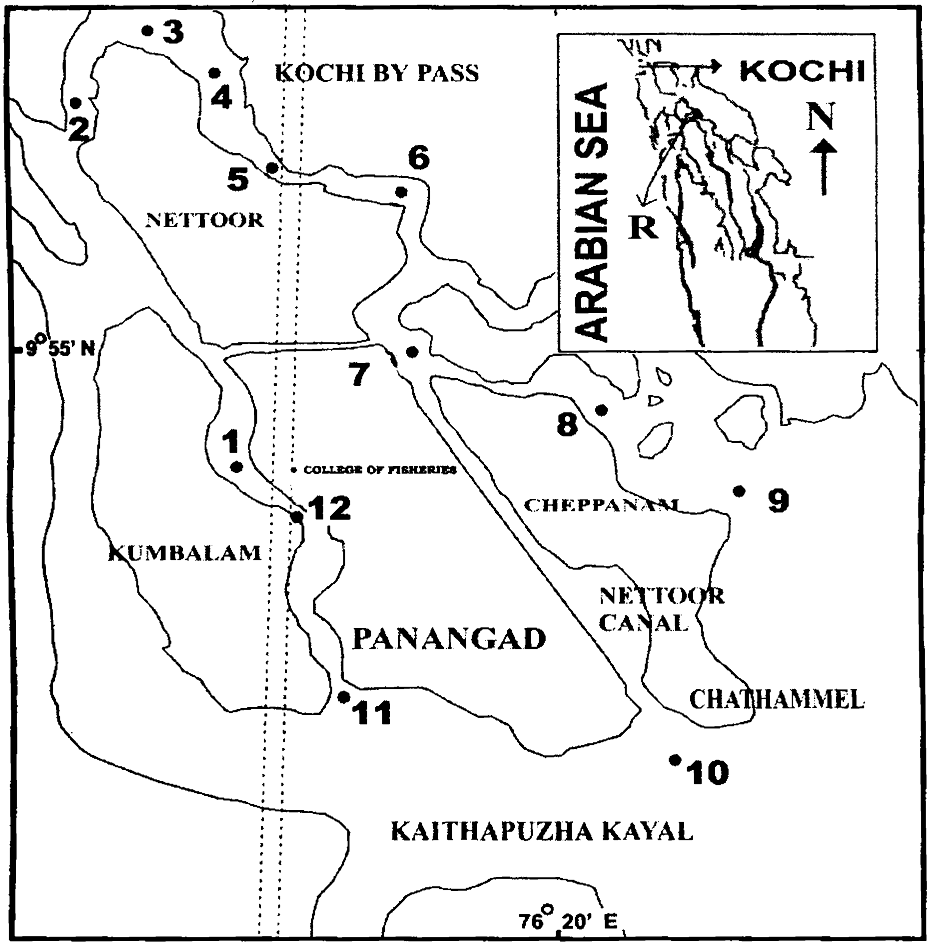

Figure 2.1 Study region

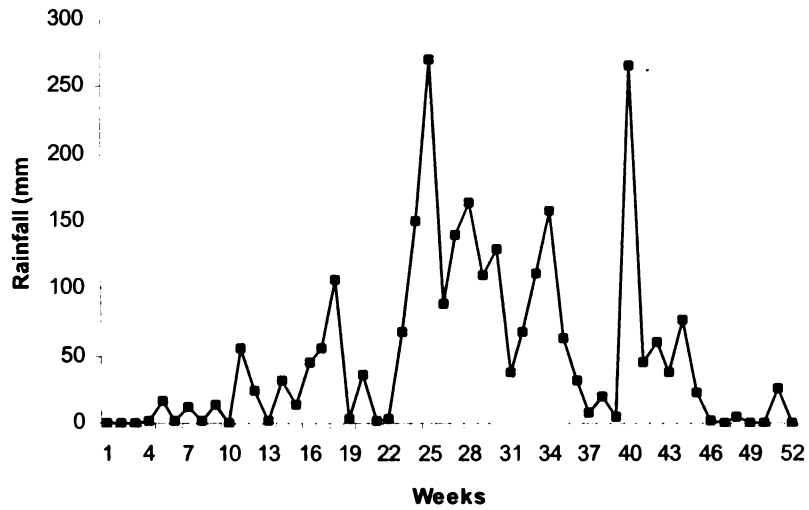

Figure 2.2 Weekly rainfall data in 2003

The monthly runoff data from all five rivers from the upper reaches, which affect the study region for recent years including the study period, are presented in Fig. 2.3. Maximum discharge is in July-August followed by a secondary maximum around October-November. Runoff in 2002 was less than that in 2001, for all rivers. Slight increase was seen in 2003. A constant run off was seen in Muvattupuzha during lean season also, which is due to the diversion of water from Idukki hydroelectric project in Periyar. Generally the southwest monsoon accounts for 70-90 % of total sediment load in the rivers and the water chemistry revealed a healthy character of the river water, without any significant contamination, in the upper reaches (Central Water commission).

Tides at Kochi are of a mixed semi-diurnal type, with the spring tide range of about 1meter (Srinivas, 1999). The tidal range progressively diminishes southward and northward of the Cochin barmouth. The tidal propagation studies in the southern arm of Cochin estuary by automatic tide gauges showed that the tides, which had a prominent semi diurnal component in the beginning of post-monsoon, became more of a diurnal type towards the end of season. The damping of tide inside the estuary because of the effect of flushing of freshwater was seen with the monsoon onset. A slight amplification at Thannermukkam because of the reflection at bund was also observed (Varma & srinivas, *Per.comm.*)

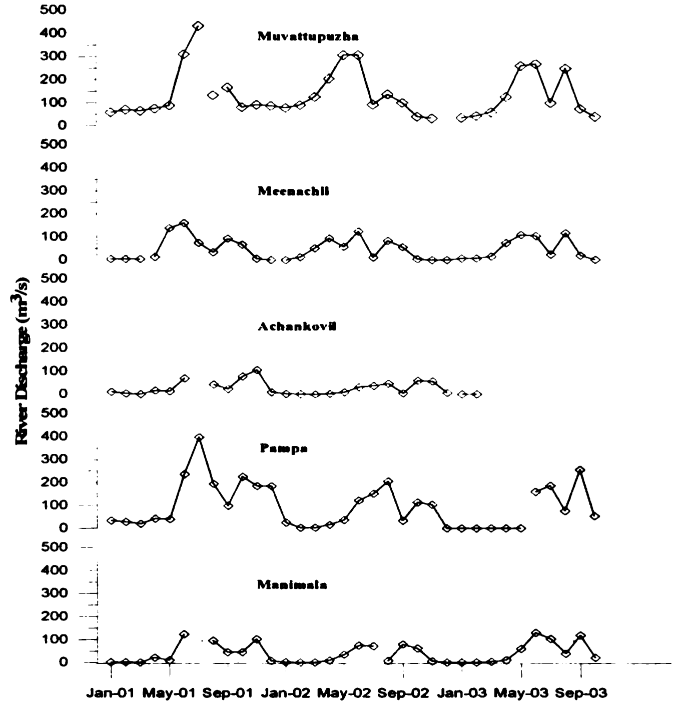

Figure 2.3 Run off data for five rivers on the south of Thannermukkam

2.2 Sampling and Analysis

A detailed study was carried out on a monthly basis in and around the study region from January to December 2003. Data collections were organized on days of higher tidal range (near spring tide). As far as possible, the observations were made immediately after low water slack period. Surface water samples were collected using a clean bucket and near bottom samples using Van Dorn water sampler. Surficial sediments were collected using a van Veen grab (0.042 m^2). For collecting zooplankton, 60 liters of water was filtered through plankton net (No.25). Samples were immediately frozen and transported to the laboratory for analysis. The monthly sampling details from different stations for hydrodynamical analysis are presented in Table 2.1.

To study the tidal variations of the physico-chemical parameters in the study area, hourly observations covering one complete tidal cycle (13 hours) were made from two representative stations. Stations 1 and 5 were selected for the tidal analysis and the observations were made for two different seasons viz. pre-monsoon and post-monsoon.

In order to envisage the estuarine dynamics and to compare the results from the study area with the features in the main arm of the estuary, observations were carried out between the barmouth and the Thannermukkam bund during pre-monsoon period. Observations were made at seven different transects of the estuary for complete tidal cycle (13 hours). The locations were Cochin Port-Ernakulam, Thevara-Edakochi North, Kumbalam South-Edakochi North, Perumbalam North-Arookutty, Perumbalam South-Panavally, Kattachira and North of Thannermukkam bund (Fig. 2.4). Each transect consists of three stations. On each day of observations, two transects were covered by continuously moving between stations so that data at an interval of two hours are obtained from each station. In the case of transect near bar mouth, hourly data were collected from all three stations.

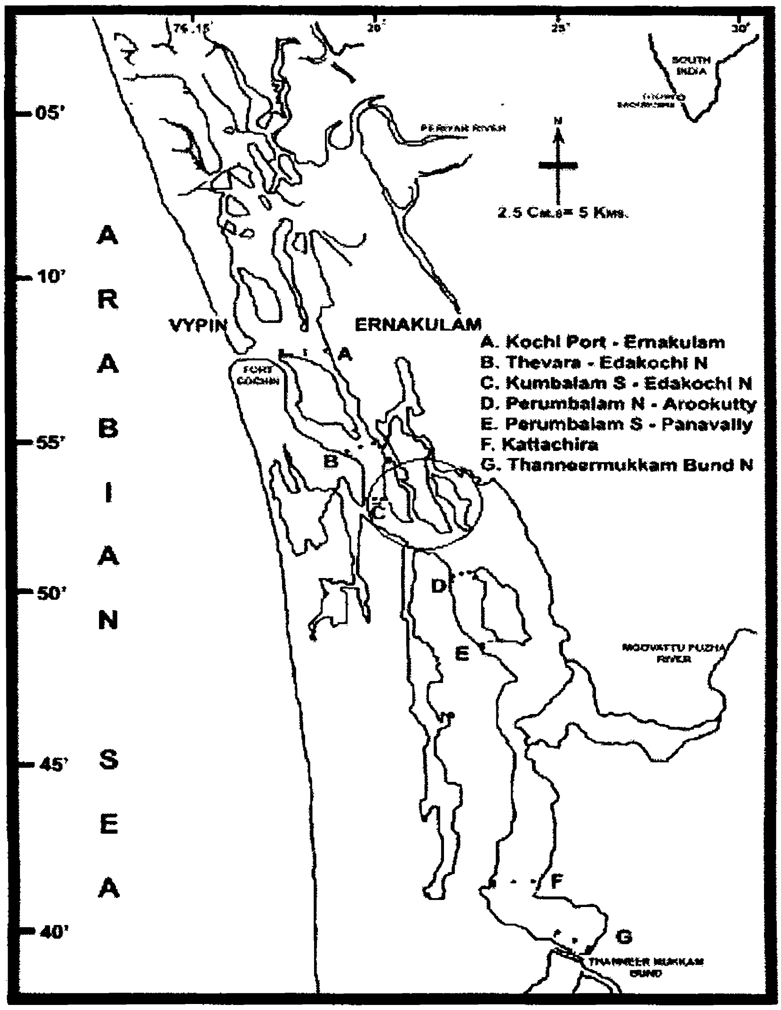

Figure 2.4 Locations of transects in Cochin estuary (Study compartment is marked in the circle)

2.2.1 Hydrodynamics

Salinity and temperature were noted at a depth interval of 0.5m using STD meter [Salinity-Temperature-Conductivity Depth Meter (EMCON) with the specifications; Salinity range: 0-38 ppt ± 0.1 ppt, Temp.range: 0-50 °C ± 0.1 °C, Depth: 0-50 m ± 0.1 m]. Water current was measured at these depths using a direct reading current meter (EMCON, specifications; Current: 0-400 cm/s ± 1 %, Direction: 0-360 ° ± 5°). Secchi disc transparency was also noted. Suspended sediment load was estimated by filtering samples through a pre-weighed 0.45μ filter paper. Turbidity was measured in NTU units using a Nephlo-turbidity meter. Standard methods were used for the analysis of nutrients (Grasshoff *et al.*, 1983). Dissolved oxygen was estimated by Winkler's method (Strickland & Parsons, 1972). Primary production was estimated using Gaarder and Graan's dark and light bottle method (Strickland & Parsons, 1972). Incubation for 3 hours was done on the boat itself. Chlorophyll-a was determined from these stations by filtering the samples through GF/C filter paper and extracting with 90% acetone (Strickland & Parsons, 1972). Zooplankton samples were preserved in 5% formalin. Each sample was made up to a known volume and 1 ml sub samples of these were counted under a stereoscopic binocular microscope. About 5 sub samples were analysed and average is taken as the population density.

Table 2.1 Monthly sampling details for hydrodynamical analysis

Stn. No.	Physical				Chemical		Biological	
	Salinity	Temp.	Current	T.S.S & Turbidity	DO	Nutrients	Chlorophyll	Production
1	√	√	√	√	√	√		
2	√	√	√	√	√	√		
3	√	√	√	√	√	√		
4	√	√	√					
5	√	√	√	√	√	√	√	√
6	√	√	√					
7	√	√	√	√	√	√	√	√
8	√	√	√	√	√	√	√	√
9	√	√	√					
10	√	√	√	√	√	√	√	√
11	√	√	√	√	√	√		
12	√	√	√					

2.2.2 Geochemistry

Textural analysis of the sediment was done based on Stoke's law using the method of Krumbein & Pettijohn (1938). Organic matter was removed by treatment of wet sediment with H_2O_2. Sediment was dispersed in sodium hexametaphoshate overnight and then wet sieved through a 63 µm sieve to collect the sand fraction. The mud fraction was divided into silt and clay fractions by timed gravimetric extraction of dispersed sediments (Folk, 1974). Powder X-ray diffraction (XRD) analyses of the finely powered samples without any chemical treatments were used for identifying the minerals in surficial sediments of the study region (Moore & Reynolds, 1997).

Total carbon, nitrogen and sulphur of the surficial sediments were analysed using CHN analyzer (VarioEL lll CHNS). Organic carbon was also determined using CHN analyzer by removing the inorganic carbon with dil. HCl, as suggested by Tung & Tanner (2003). For trace metal analysis, about 0.5 g of the finely powdered air dried sediment samples were weighed into beakers. Each sample was carefully digested with 10 ml of an acid solution ($HClO_4$, HNO_3 and HCl in the ratio 1:1:3) at 90°C until complete digestion and the mixture was evaporated to dryness. The residue was washed with Milli-Q water and the resultant solution centrifuged at 4000 rpm and made up to 25 ml. Analytical blanks were also prepared. The metal concentrations in the solution were determined by atomic absorption spectrophotometry (Perkin-Elmer 3110 AAS). Estimation of the accuracy and precision of the analysis was performed using standard reference material for marine and estuarine sediments (BCSS-1) obtained from National Research Council of Canada and the details are given in chapter 4.

ICP-AES (IRIS INTREPID II XSP, Thermo Electron Corporation) was used to estimate Aluminium and Calcium in the study region. For benthic analysis, all organisms retained on a 0.5mm mesh sieve were collected and preserved in 10% neutral formalin. Specimens were identified and counted.

2.2.3 Phosphorus speciation

Sequential extractions (Fig. 2.5) were carried out to understand the association of phosphorus with various sedimentary components and to estimate its mobility, biological availability and the diagenesis. An extraction scheme using chelating agents developed by Golterman (1996) modified by Diaz-Espejo *et al.,* (1999) was used in this study and its advantage over different schemes available is detailed in chapter 5. The Ca-NTA was replaced by Ca-EDTA to extract iron-bound phosphate (Fe(OOH)_P). The pH of Na-EDTA solution was fixed at 4.5 in order to minimize duration of $CaCO_3$_P extractions.

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

$$CaCO_3\text{\_P} + \text{Na- EDTA} \longrightarrow \text{Ca-EDTA} + \text{o-P} + Na^{+}$$

About 0.8 g of the finely powdered sediments was used for the fractionation of total P in the whole sediment. In the study, the sediments were dry sieved to separate fine and coarse fractions to fine the variations of different phosphorus forms in theses fractions. Fe(OOH)-P was extracted with buffered Ca-EDTA/dithionite and $CaCO_3$-P subsequently with Na-EDTA. In the next step, acid hydrolysable Organic-P (Acid-OP) was extracted with H_2SO_4 and then the remaining Organic-P (Alkali-OP) with 2M NaOH at 90°C for 30 minutes. Residual-P was measured after 1 hour $K_2S_2O_8$ mineralisation in an acid medium. Soluble orthophosphate is determined by spectrophotometric method (Grasshoff *et al.,* 1983). Iron and calcium fractions of phosphorus were further analysed for inorganic and organic forms by acid persulphate digestion, which will give the total fraction.

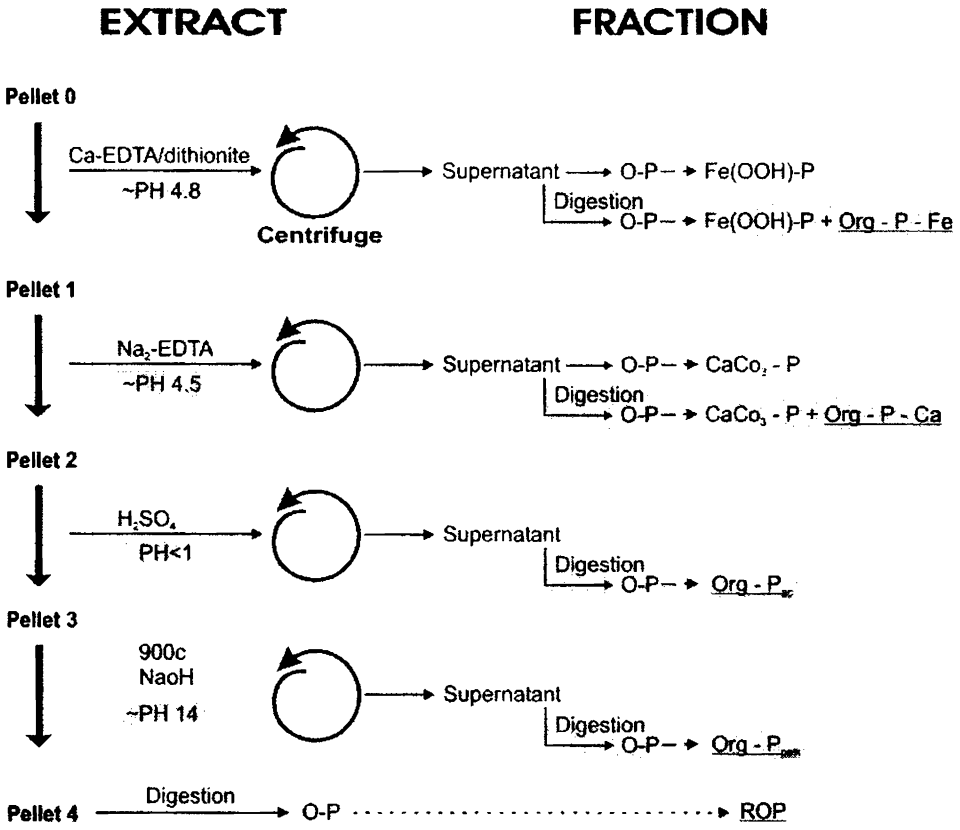

Figure 2.5 Sequential extraction scheme for Phosphorus fractionation

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Chapter 3

HYDRODYNAMICS

3.1 Introduction

Estuaries are an integral part of the hydrological cycle and they regulate the particle delivery from rivers to the coastal environments and to the ocean. They are highly dynamic, characterized by temporal changes occurring over a large spectrum, ranging from short-term (hourly) variations driven primarily by tidal currents to long-term (seasonal or inter-annual) variations caused by changes in meteorological forcing and river discharge. Estuaries are spatially heterogeneous and often have large gradients in water properties that result from morphology, circulation and mixing, sources or sinks of dissolved and suspended constituents, anthropogenic pressures, etc. Water circulation is an integral aspect to be investigated in the study of an estuary. A hydrodynamic analysis of a complex estuarine system requires a reasonable knowledge of all the factors influencing estuarine circulation.

Circulation in estuaries is multifarious and mainly dependent on the relative magnitudes of tidal variations in water levels and currents, freshwater inflow, gravitational forces caused by density differences between the ocean and fresh water, and to a lesser extent, the coriolis acceleration. Wind and waves are also important and determine the circulation pattern and contribute to the vertical mixing of the water column. The mixing regime and resultant salinity distribution depend on the relative magnitudes of all these forces. The amplitude of a tidal wave progressing up an estuary is also geometry dependant. Hence generalization is very extremely difficult in the case of estuaries.

The basic feature is the instability of an estuary due to the ebb and flood of the tide, which is the main force driving estuarine dynamics and hence the hydrography of the estuary depends mainly on the tides. The major currents in estuaries result from the movement of water caused by tides. The relative importance of fresh water input compared to tides introduces changes in hydrographical conditions. While the fresh water input inhibits turbulence, the tides generate turbulence, increasing mixing. However, for a given fresh water flow, the variations will be controlled by tides. Tidal prism and the estuarine volume are required to calculate the flushing time with this method and can be easily obtained from tidal gauge records. The flushing time represents the shortest possible time during which the entire freshwater fraction of an estuary can be removed.

Non-tidal currents are caused by the fresh water discharge flow into an estuary and by the resulting density differences. In comparison with tidal currents, non-tidal currents move slowly. The structure and functioning of the river-estuary interface region is governed primarily by the quality, quantity and supply pattern of fresh water received. Furthermore, the interface region has strong influences on the physico-chemical as well as the biological structure and functioning of the entire system. The influence of Man-made alterations on estuarine structure and hydrodynamics, brought about by bridges and dams, and the likely impact of the transfer of impounded water between catchments.

Estuaries are generally recognized as perhaps the most vulnerable and misused of all ecosystems worldwide (Spellerberg, 1991) and the mechanisms by which spatially and temporally variable physical and chemical parameters influence estuarine ecology are poorly understood. Basic research is essential not only for inventory and data-base establishment but is also critical to our understanding of naturally induced spatial and temporal changes in such ecosystems, along with providing information by which the impacts of anthropogenic variations can be assessed (Dickinson & Mark, 1999) It becomes increasingly recognized that hydrodynamics play an important role in shallow water ecosystems and high-resolution hydrodynamic models are a common tool to simulate water dynamics in estuaries (Christiansen *et al.*, 1997).

This chapter attempts to find how ecological processes, including secondary production, are controlled by estuarine hydrodynamics. The vertical (depth-wise) and longitudinal (spatial) variations of physico-chemical and biological parameters in the study region and also their long term (seasonal) and short-term (tidal) are described. The implication of water chemistry to the physical and biological parameters and their dynamics are detailed in this chapter. Observations covering tidal cycle provide information on the variations of these parameters in relation to tides, which is the dominant player in estuarine dynamics, while such observations in different seasons will bring out the relative importance of tides. These field data will demonstrate the behavior of estuary under the specific set of conditions that existed during the time of sampling. Estimates of the separate effects of tides, river discharge and other variables can be obtained and can reveal the seasonal, inter-annual and the anthropogenic variations by comparing with the historical data. These data can help to identify problem areas, define the magnitude of problems, and can also be used in an attempt to identify changes caused by a modification to the estuary. These data are also being useful as an indispensable element in verification of numerical and physical models, the modeler to adjust the model and to check the reliability of model results.

3.2 Results

The physical, chemical and biological characteristics of the water column in the study region and their spatial and temporal variations are described in this section. Their tidal variations in different seasons are also explained in detail. The monthly data of physical, chemical and biological parameters are given in Appendix A, B and C respectively.

3.2.1 Physical characteristics

3.2.1.1 Salinity

Salinity showed large fluctuations in the study region with a bimodal pattern (Fig. 3.1). Fresh water condition was seen during June-August when the river run off is very high and after that salinity started to increase. Subsequently, a fall was noticed during October, which is due to the affect of run off associated with the northeast monsoon. Increase was again noticed during pre-monsoon period and maximum salinity ranged from 25 to 30 ‰ during March-April.

Vertical distribution of salinity varied with changes in fresh water flow and location. During pre-monsoon season, the study region showed vertically homogenous situation, indicating a well-mixed condition. During monsoon, because of the complete flushing out from this region of the estuary due to the high run off, it virtually became the tidal extension of the adjoining rivers and vertical stratification was completely absent. During post-monsoon, with the decrease in fresh water input, the vertical salinity gradient appeared, which indicates a partially mixed condition at stations along the main arms of the estuary. During this time, the present stations along the narrow inner arm did not show vertical stratification.

Though spatial variation was not prominent, station 2 recorded higher salinity in all seasons, because this station, in the main arm, is nearer to the mouth of the estuary. The minimum values were observed at stations 7 and 8 in the inner arm, which were away from the mouth of the estuary. A clear pattern of vertical stratification was noticed in these areas during post-monsoon. Station 5, located in the narrow arm of the estuary showed homogenous condition throughout the year.

3.2.1.2 Temperature

Temperature did not show wide fluctuations like salinity. It ranged between 28.4 and 33.5°C, with a bimodal annual variation (Fig. 3.2). The highest temperature was observed during the pre-monsoon months (March-April) and decreased during monsoon (June-august) because of heavy rains and low insolation due to the cloudiness. A secondary minimum was noted during northeast monsoon.

Like salinity, vertical stratification was seen during post-monsoon and well-mixed conditions existed during pre-monsoon and monsoon seasons. The stations in the inner arm showed vertically homogeneous conditions throughout the year. It could be seen that the stations in the inner arm of the study region are generally warmer than that in the open parts of the estuary, though the difference was not pronounced.

3.2.1.3 Current

Monthly spot observations of water current were not highly significant and the full tidal range is required for proper data interpretation, which can be used as an indicator of tidal mixing. Hence the data for only two stations in the inner arm, on either side of the Panangad Island are presented in Fig. 3.3.

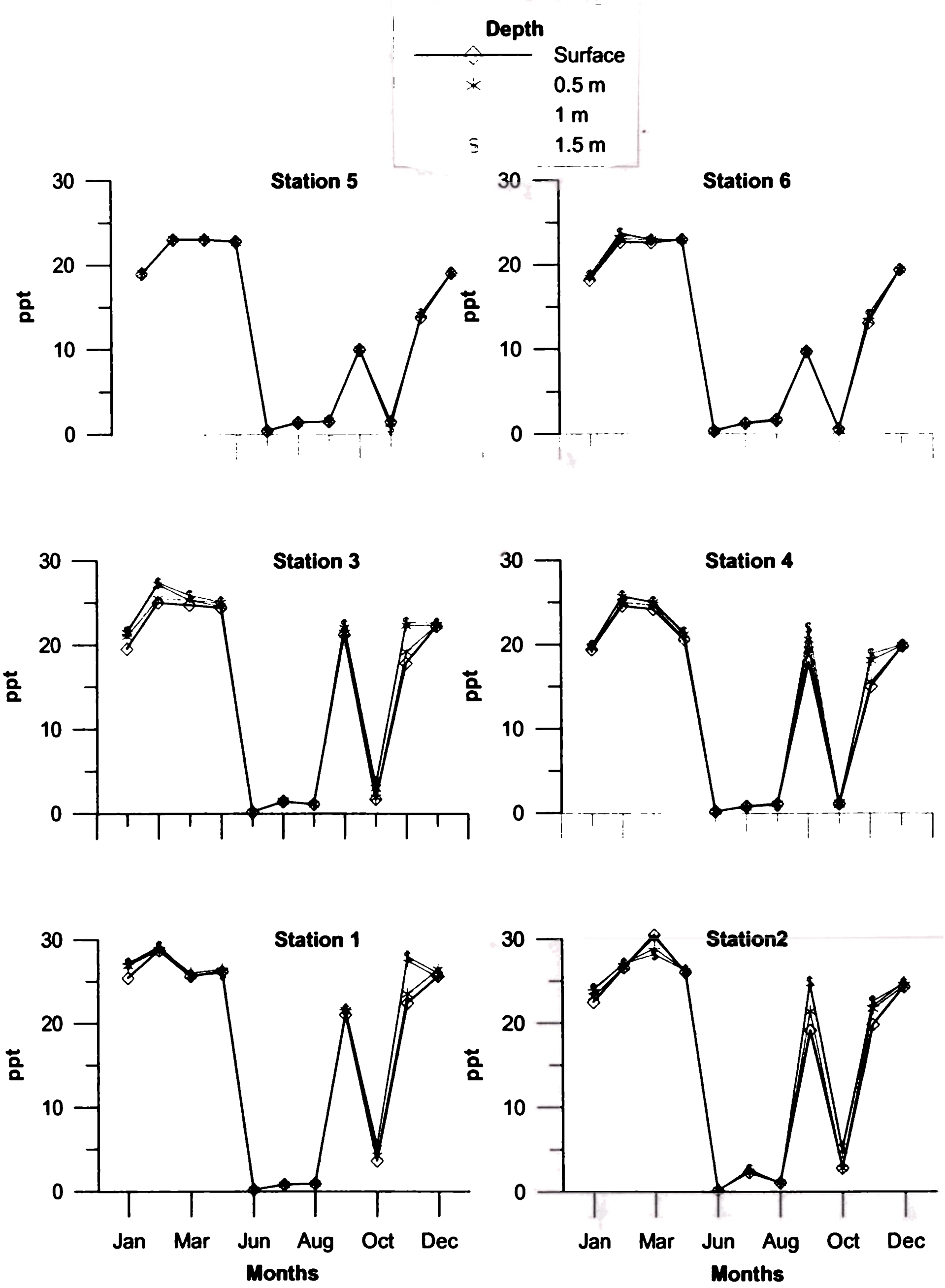


Figure 3.1 Annual variation of salinity in the study region

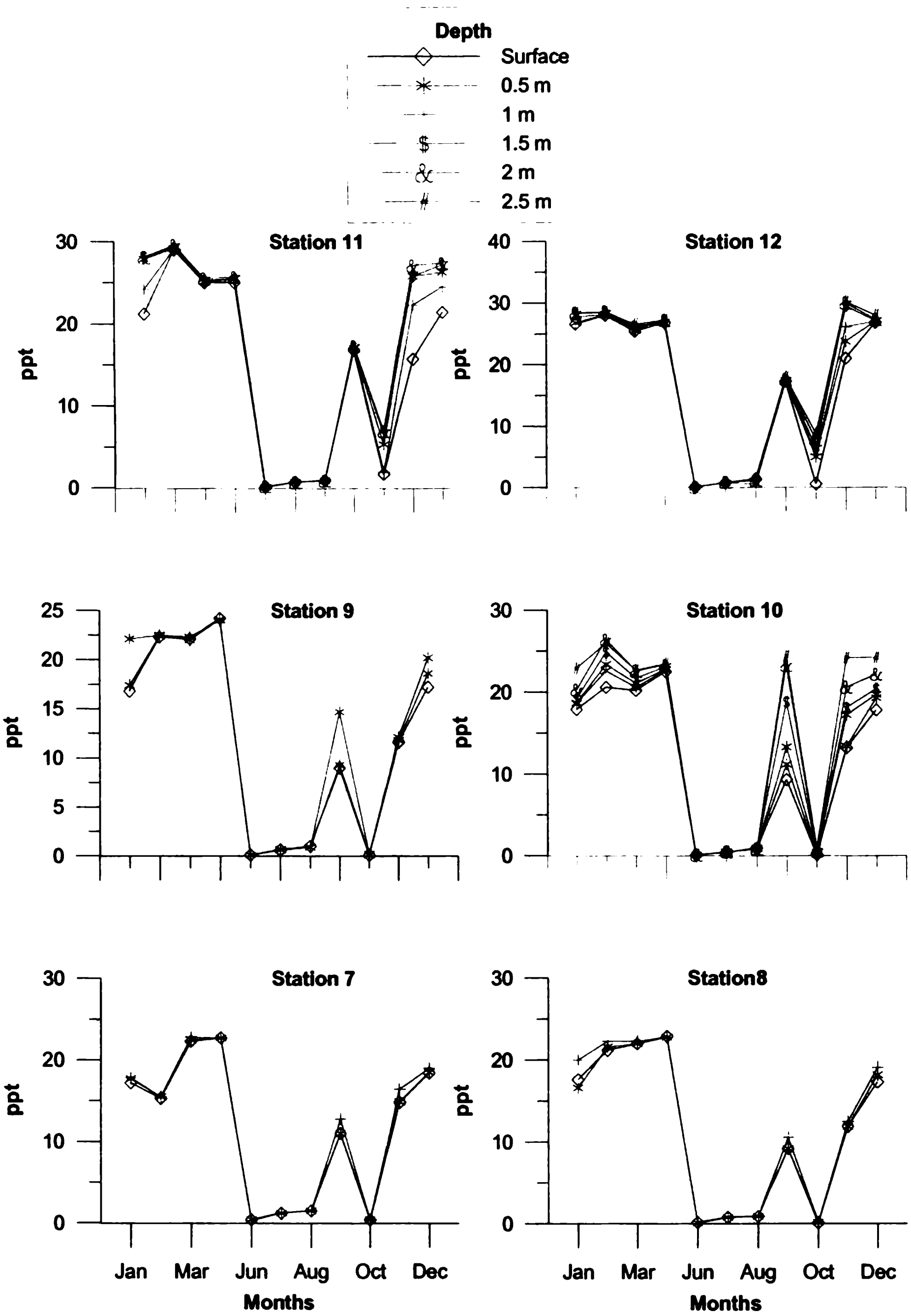


Figure 3.1 (Contd.)

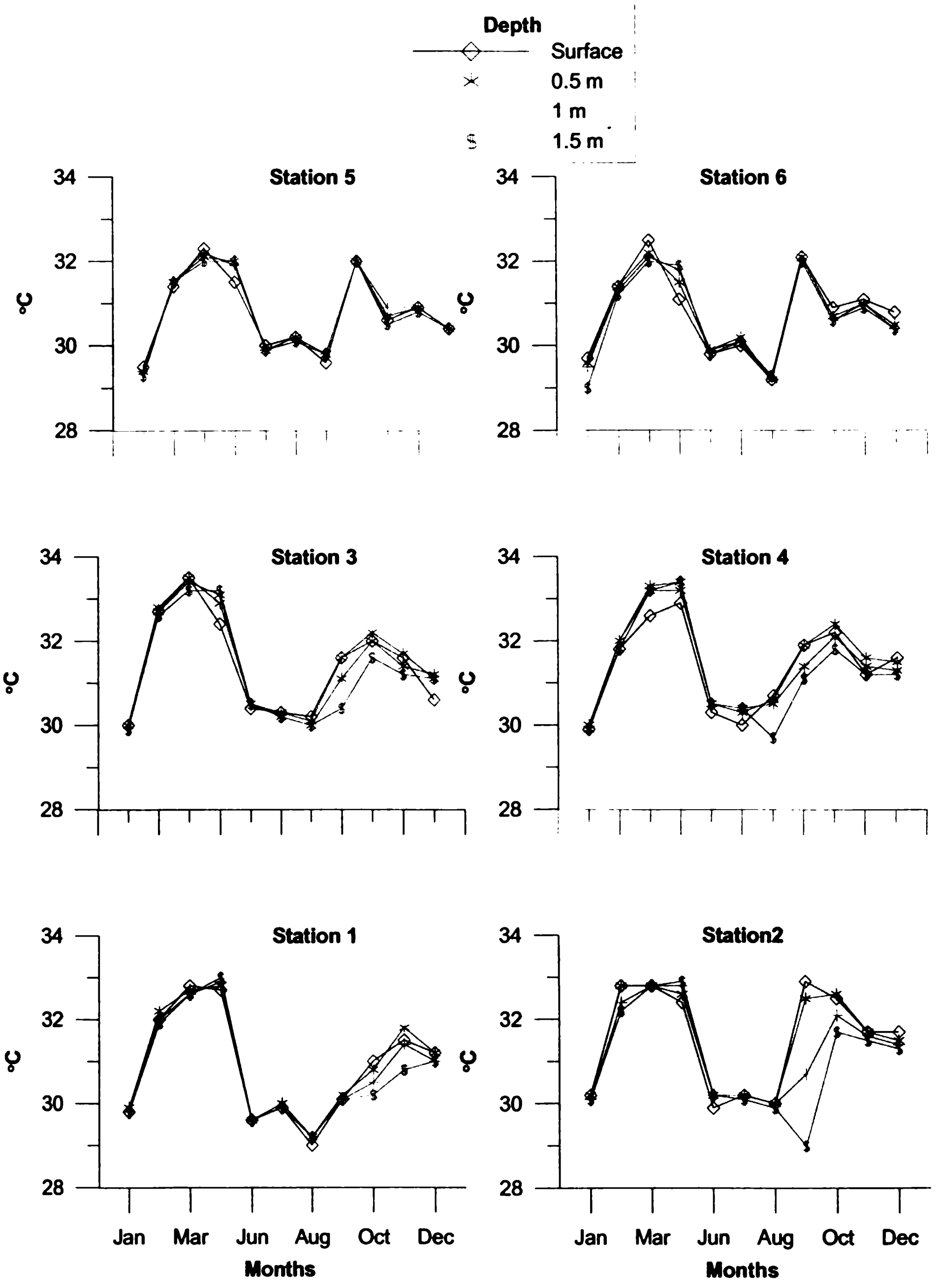


Figure 3.2 Annual variation of temperature in the study region

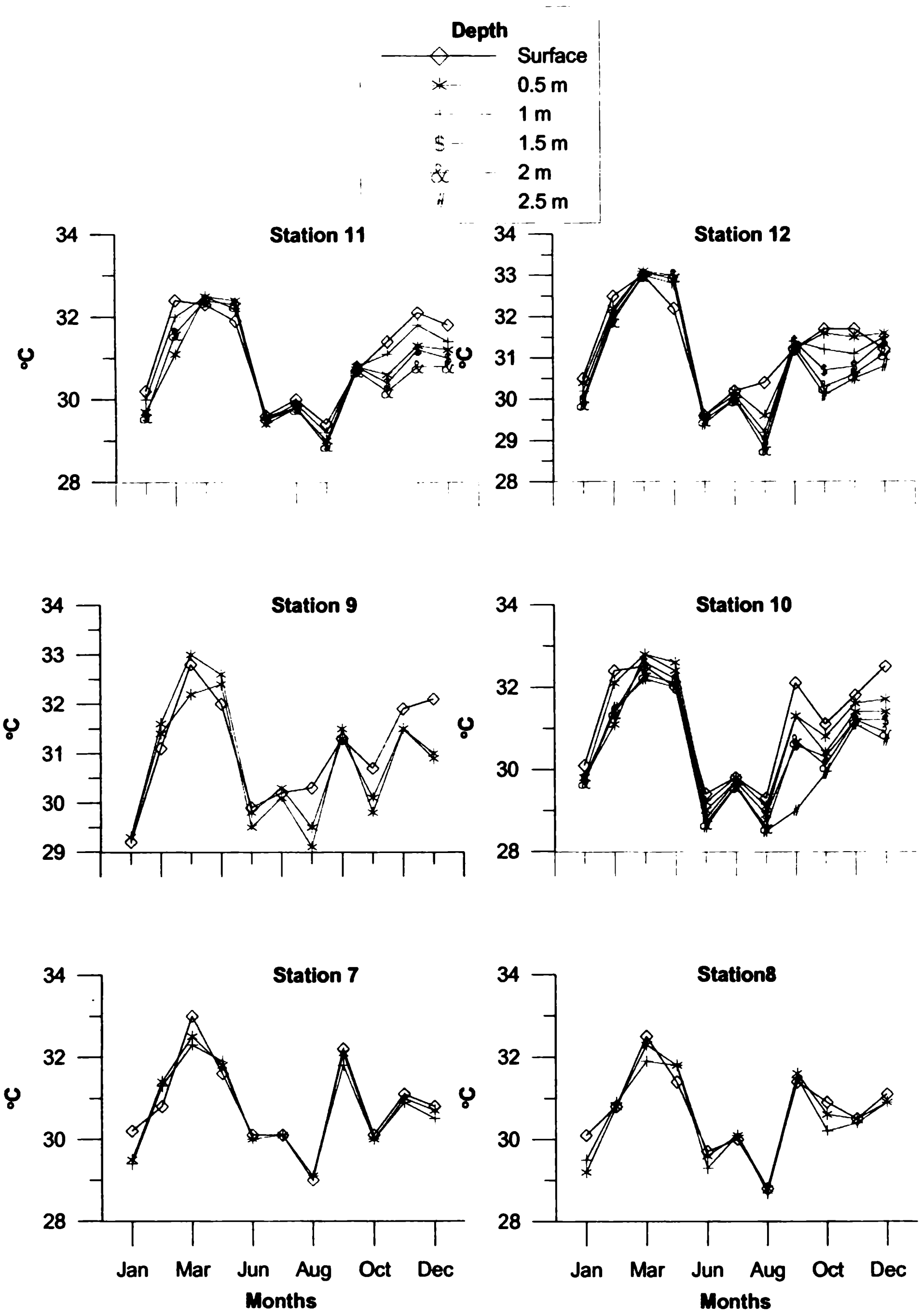


Figure 3.2 (Contd.)

Higher current speed was observed during the monsoon period and the picture was more complicated in the station 5. It is interesting to note that although current speed increased towards both ends of the canal, a region of sharp increase in current is seen between stations 10 and 11. Though there was marked vertical fluctuation, it also lacked a clear pattern. Still roughly it can be stated that the surface layers recorded slightly higher values than the bottom layers.

3.2.1.4 Transparency

Transparency in the study region varied between 0.5 and 2 meters. It was generally low in the monsoon period, and an increase was noticed soon after the end of monsoon period.

3.2.1.5 Suspended Sediments

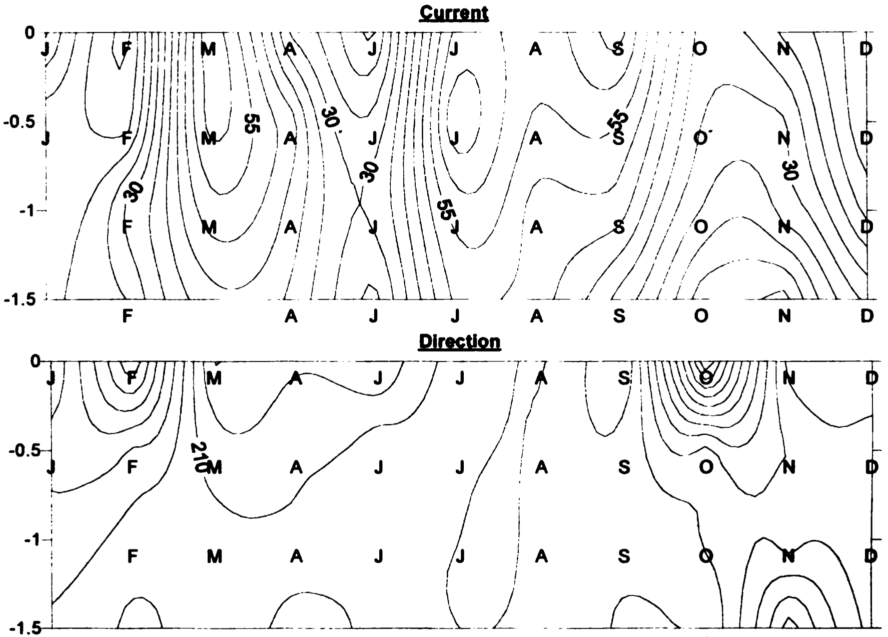
Suspended sediments ranged between 2 and 50 mg/l and showed seasonal variations (Fig.3.4). During pre-monsoon TSS ranged between 4 and 46.9 mg/l with an average of 17.7 mg/l at surface and from 2 to 41 mg/l with an average of 24 mg/l at bottom. An increase was noticed during southwest monsoon, ranging between 6.5 and 50 mg/l (average 22.7 mg/l) at surface and from 8.4 to 48.3 mg/l (average 24.1 mg/l) at bottom. During post-monsoon the surface values ranged between 4 and 29.1 mg/l (average 16.1 mg/l) and at bottom the range was from 2 to 43 mg/l (average 19 mg/l).

Suspended sediment was higher at bottom than at surface during most of the observations. Stations in main channels generally showed lower suspended sediment load. The general increase noted during monsoon was more conspicuous at the stations in the main arm of the estuary. At the stations in the inner arms of the study region, there are many fluctuations superimposed on this monsoon high. Analysis of variance (ANOVA) also established significant spatial ($p<0.01$) and highly significant temporal ($p< 0.001$) variations in TSS (Table 3.2). Significantly high TSS was noticed in July and low in April, while station 5 recorded high values and station 10 low.

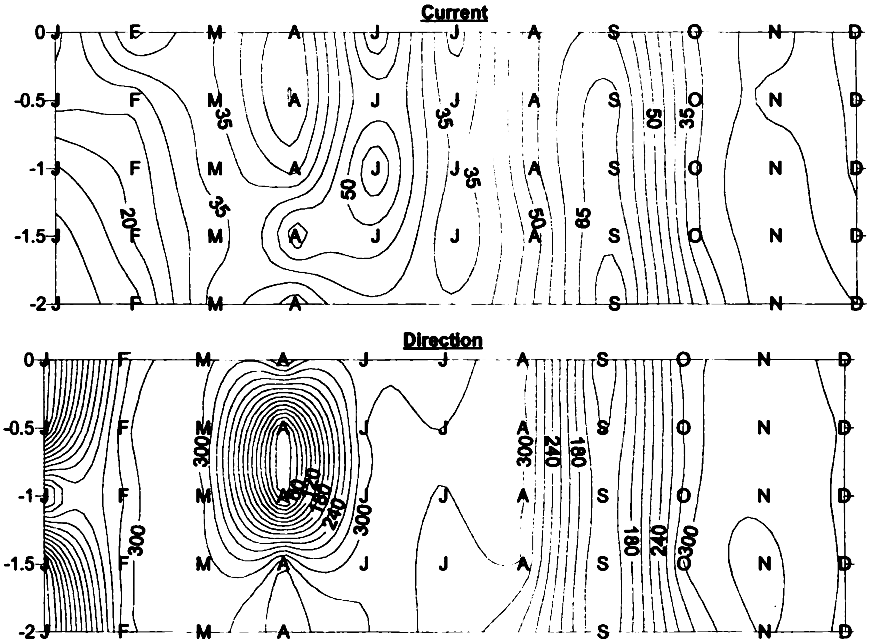
3.2.1.6 Turbidity

Turbidity, similar to TSS, showed clear seasonal variation, but the variations were much regular compared to the latter (Fig. 3.5). A sharp increase was seen during southwest monsoon, while it decreased after the rainy season ended. A secondary increase coinciding with northeast monsoon was also noted. During pre-monsoon, turbidity ranged between 0.9 and 15.5 NTU at surface with an average of 5.8 NTU and at bottom, the range was from 1.4 to 12.7 NTU with an average of 7.3 NTU. During southwest monsoon it increased and ranged between 0.49 and 28.7 NTU (average 12.2 NTU) at surface and ranged from 0.56 to 36.9 NTU (average 16 NTU) at bottom. During post monsoon the surface and bottom values ranged between 0.1 and 13.3 NTU (average 3.4 NTU) and from 0.23 to 26.5 NTU (average 6.1 NTU) respectively.

Turbidity was also slightly higher at the bottom compared to surface. Like TSS, turbidity was also found to be higher in the inner arms of the study region. ANOVA established highly significant temporal variation ($p< 0.001$) with highest values during August and lowest during November. But spatial variations were not statistically significant (Table 3.2).



Station 1



Station 5

Figure 3.3 Variations in water current and directions in two typical stations

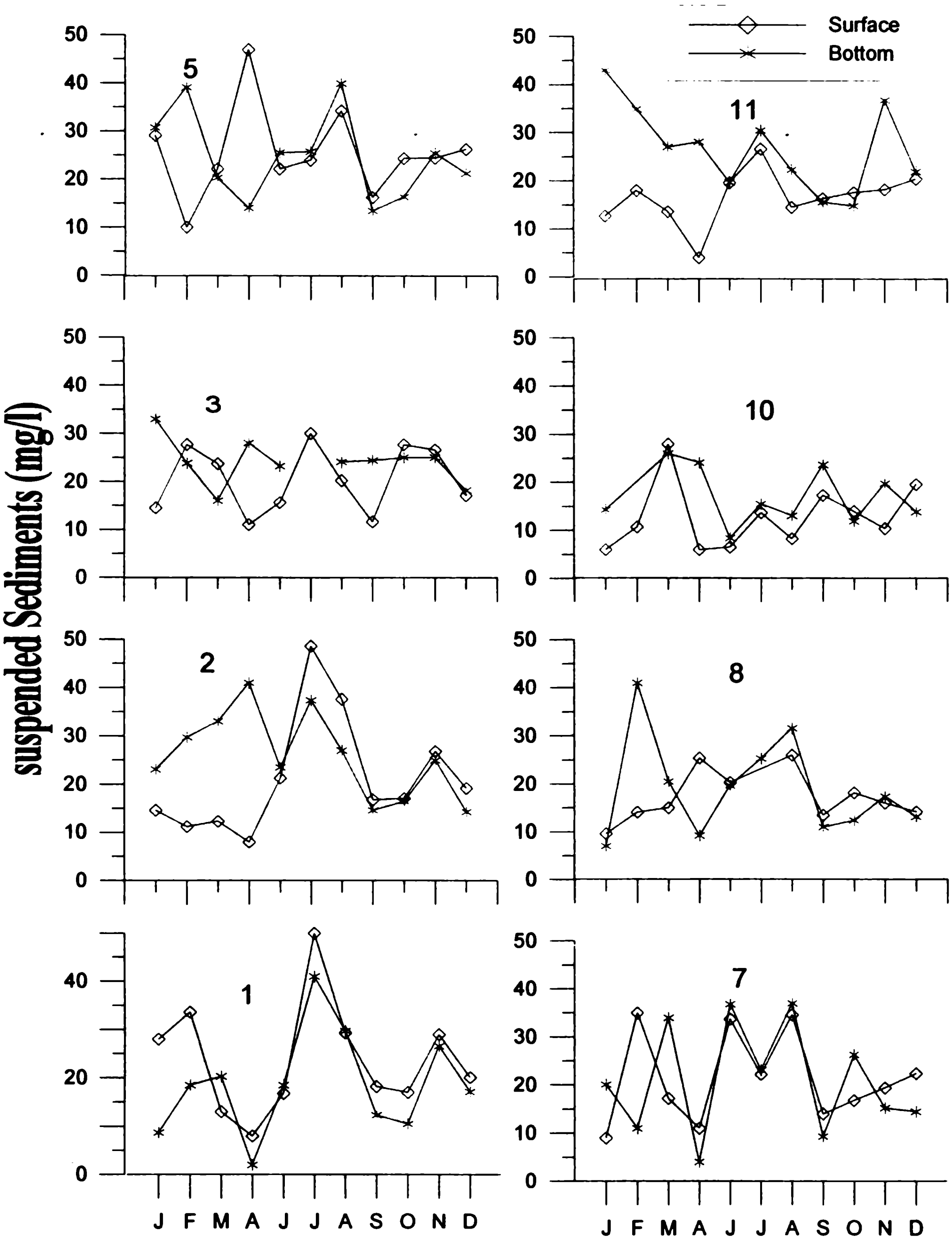


Figure 3.4 Annual variation of TSS (mg/l) in the study region

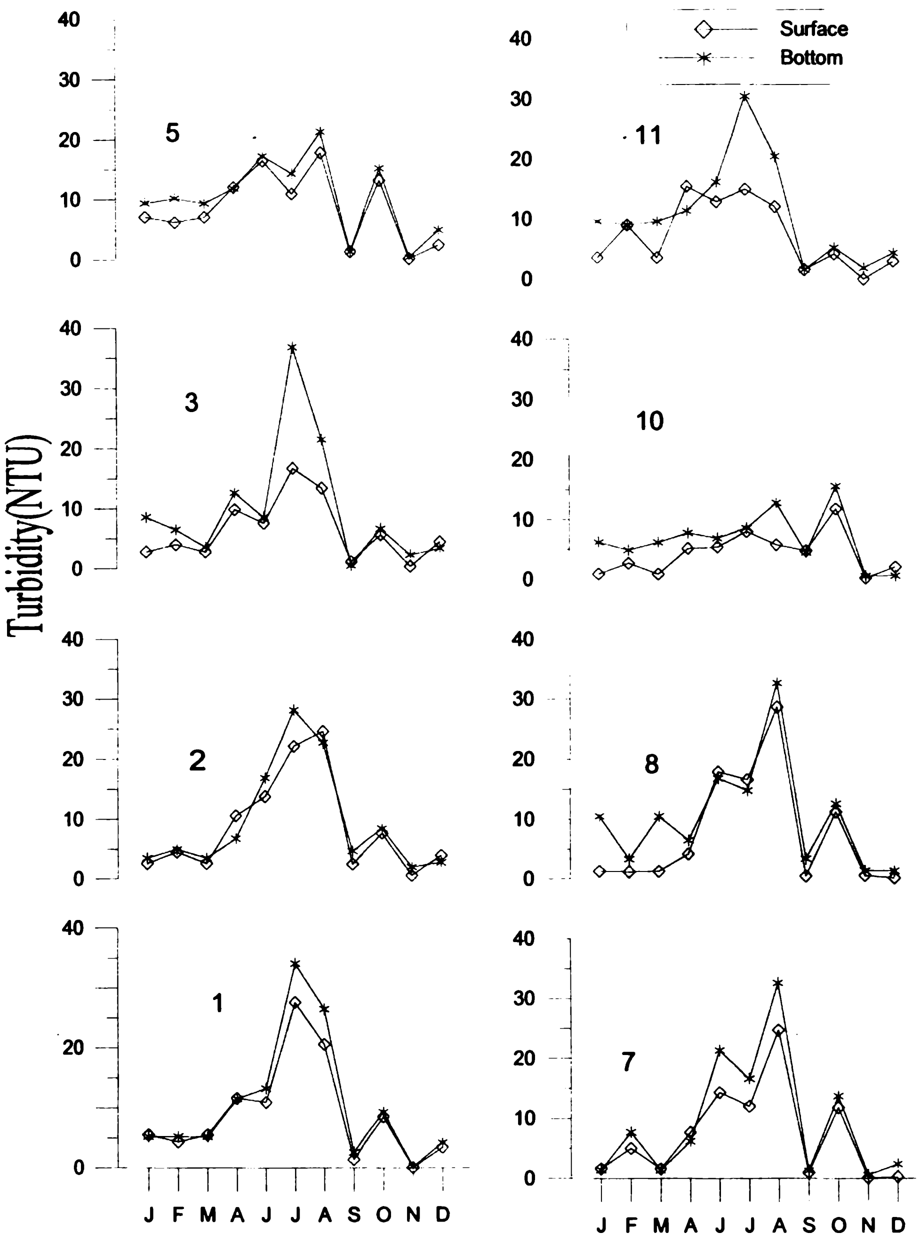


Figure 3.5 Annual variation of Turbidity (NTU) in the study region

3.2.2 Chemical Characteristics

3.2.2.1 Nutrients

Phosphate-P

In the present study, phosphate showed seasonal variations. High values were observed during the monsoon months while very low values were observed during the pre-monsoon months (Fig. 3.6). In the pre-monsoon, the surface range was between below detectable level and 4.85 µmol/l with average of 1.41 µmol/l and for the bottom, the range was between not detected and 4.46 µmol/l with average of 1.44 µmol/l. During southwest monsoon an increase was noticed and for surface, the average was 3.57 µmol/l with a range from not detected to 17.30 µmol/l and for bottom the range was between not detected and17.80 µmol/l with an average of 3.30 µmol/l. The surface values ranged from not detected to 8.30 µmol/l in post-monsoon with an average of 1.21µmol/l and for bottom the range was between not detected and 7.73 µmol/l with an average of 1.23 µmol/l.

Nitrate-N

Seasonal variation of nitrate was very prominent than that of phosphate. High values were observed during the southwest and northeast monsoon periods when freshwater condition prevailed and low values during the highly saline pre-monsoon months (Fig.3.7). During pre-monsoon the range was between 0.07 and 3.06 µmol/l with an average of 1.41 µmol/l and in the case of bottom, it was between 0.12 and 5.08 µmol/l with an average of 1.63 µmol/l. During southwest monsoon, surface recorded a higher average (7.90 µmol/l) and ranged between 0.60-18.29

µmol/l and near bottom waters also showed the same trend with a range of 0.35 - 22.17 µmol/l and the average was 8.73 µmol/l. For post-monsoon, the surface range was 0.40 to 20.40 µmol/l with an average of 4.13 µmol/l and for bottom; the range was from 0.80 to 10.45 µmol/l with an average of 3.94 µmol/l.

Nitrite-N

Unlike the other nutrients, the variation of nitrite was not pronounced (Fig.3.8). Although an increase was noted during monsoon period, there was an increase also during pre-monsoon period for some stations. During pre-monsoon the range was between not detected and 4.18 µmol/l with an average of 0.73 µmol/l in the surface and in the case of bottom, it was between not detected and 4.30 µmol/l with an average of 0.78 µmol/l. During southwest monsoon, the surface range was from not detected to 3.24 µmol/l with an average of 1.01 µmol/l and for bottom it was not detected to 2.69 µmol/l and average was 0.98 µmol/l. For post monsoon, the surface range was from not detected to 1.80 µmol/l with an average of 0.66 µmol/l and for bottom; the range from was not detected to 1.79 µmol/l with an average of 0.65 µmol/l.

Silicate-Si

Silicate showed large fluctuations during the study period and the many fold increase during the monsoon and the subsequent drastic reduction shows that the silicon cycle was entirely dependent upon the freshwater discharge (Fig.3.9). Thus a progressive decrease was noted from monsoon to pre-monsoon with some fluctuations, possibly due to local precipitation and run offs. In the pre-monsoon, the surface range was between 20.94 and 82.24 µmol/l with average value of 40.67 µmol/l and for the bottom, the range was between 19.78 and 142.97 µmol/l with average of 43.57 µmol/l. During southwest monsoon, for surface the range was between 8.17 and 197.08 µmol/l with an average of 100.62 µmol/l and for bottom, the range was between 13.63 and 197.08 µmol/l with an average of 103.38 µmol/l. The surface values ranged from 3.02 to 130.15 µmol/l in post-monsoon with an average of 54.87 µmol/l and for bottom the range was between 2.44 to 129.28 µmol/l with an average of 53.08 µmol/l.

Nutrients, in general, showed marked seasonal fluctuations in the study region and the main source was the land run off. Maximum values were obtained during July-August and declined in September when southwest monsoon ended. Subsequently with the onset of northeast monsoon, a secondary increase was also noted. Some fluctuations are also seen because of local effects. In general the entire water column behaved identically without any pronounced depth wise variation. The stations, which are located in the inner arms of the study region, had high nutrient concentration compared to the main arm. Phosphate showed significant (ANOVA, $p<0.001$) spatial and temporal variations in the study region with significantly higher and lower values at stations 3 and 10 respectively. All other nutrients showed significant temporal variations ($p<0.001$) with higher concentration during monsoon months and lower during pre-monsoon months, while nitrate and nitrite showed lower ($p<0.05$) spatial variability (Table 3.2).

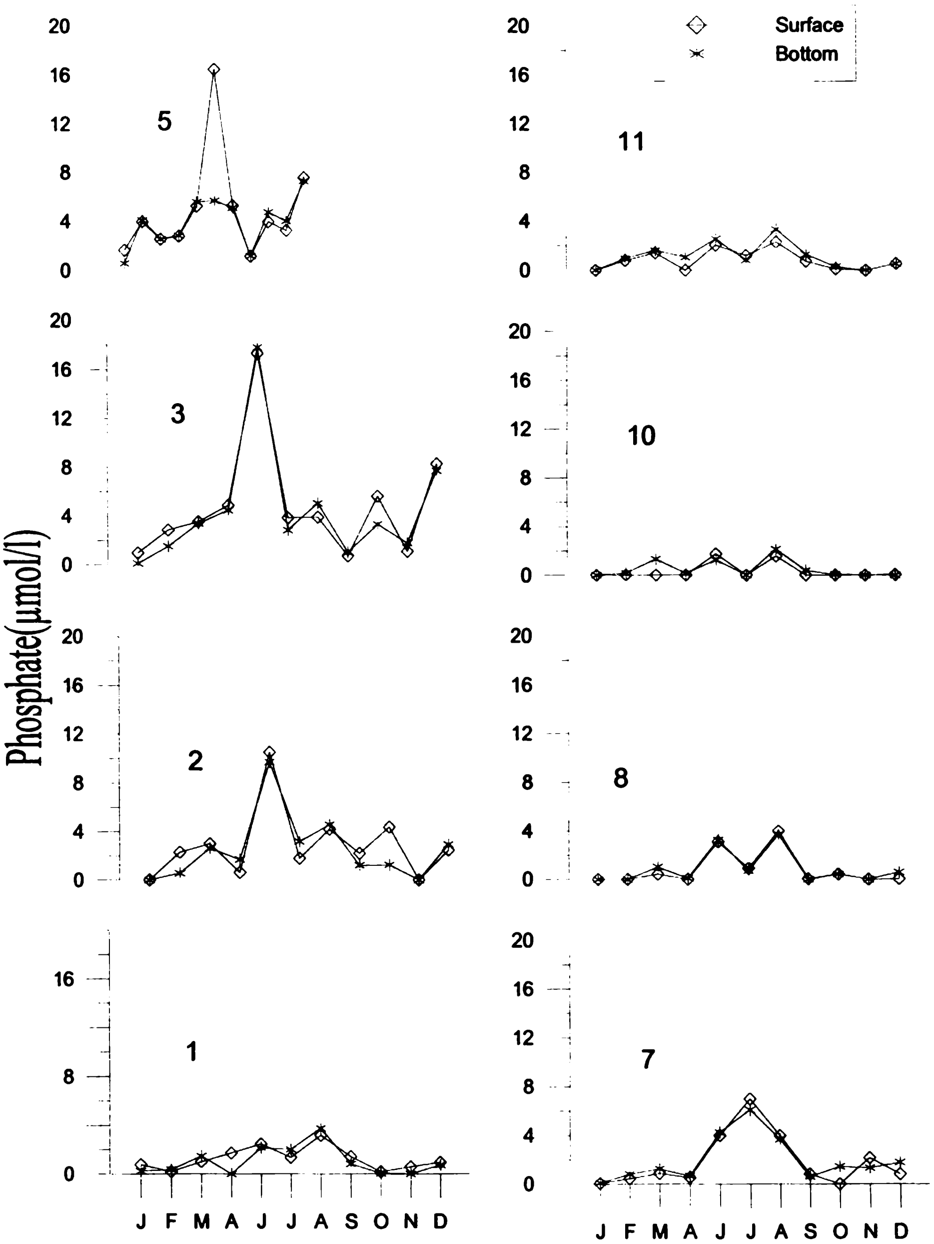


Figure 3.6 Annual variation of phosphate in the study region

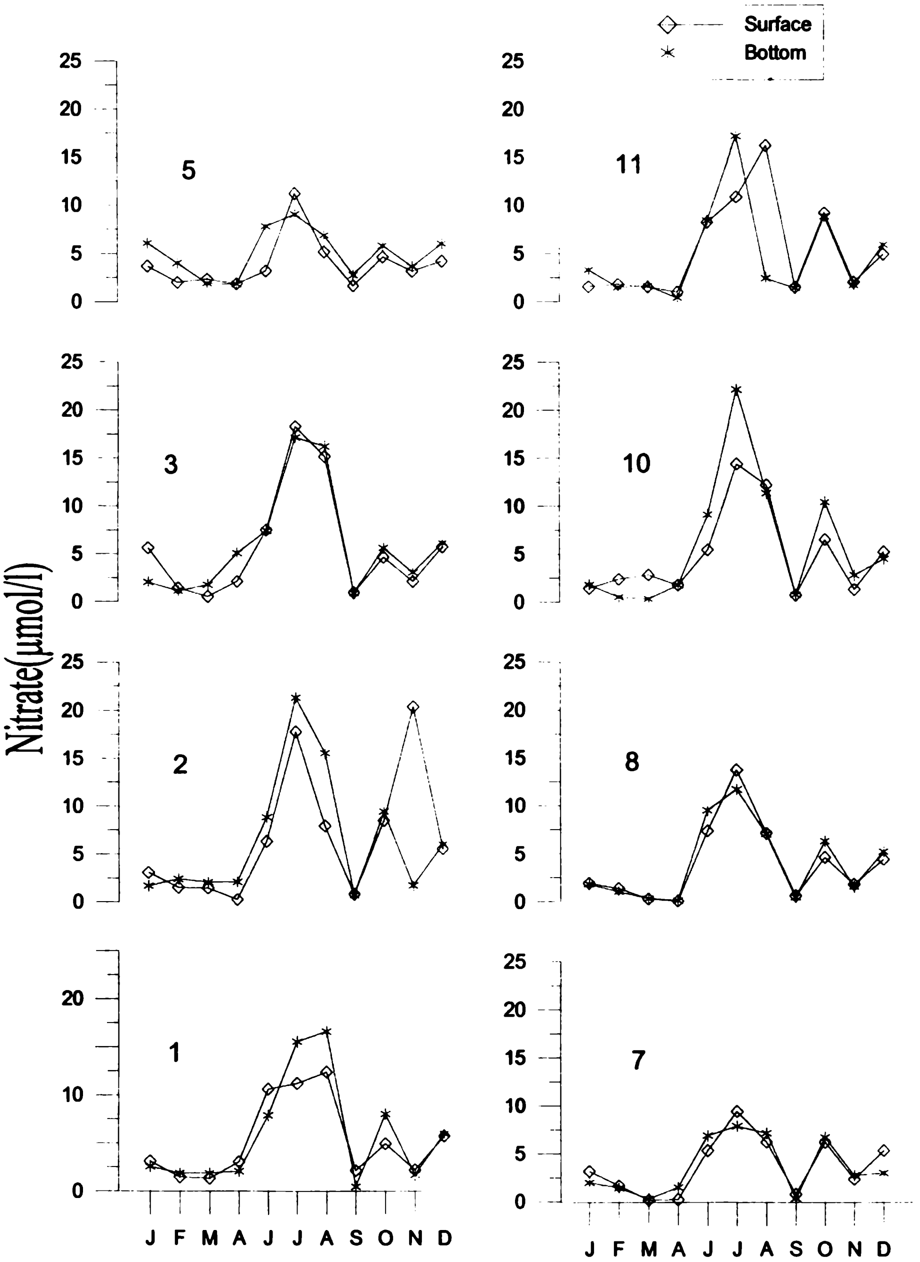


Figure 3.7 Annual variation of nitrate in the study region

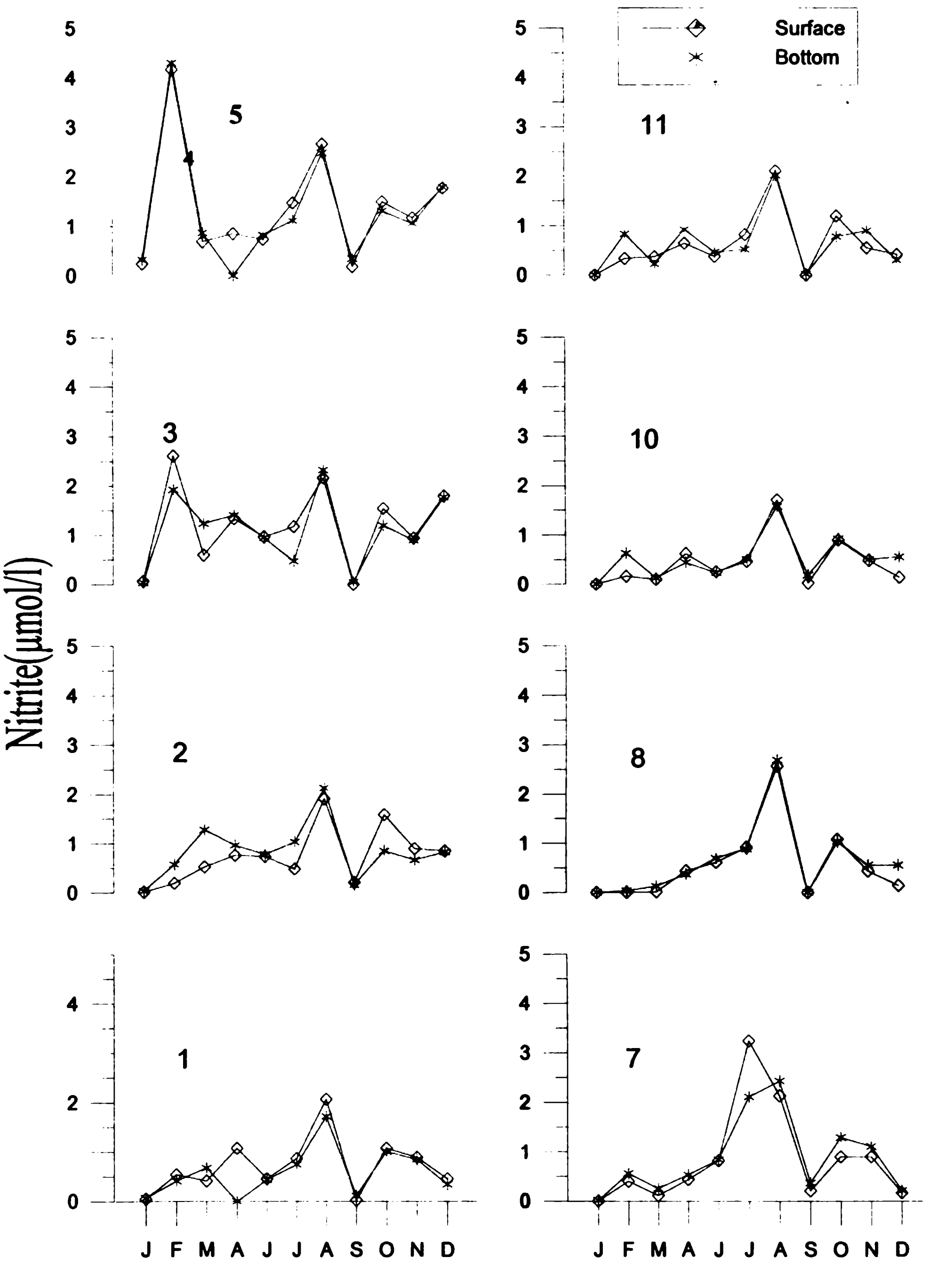


Figure 3.8 Annual variation of nitrite in the study region

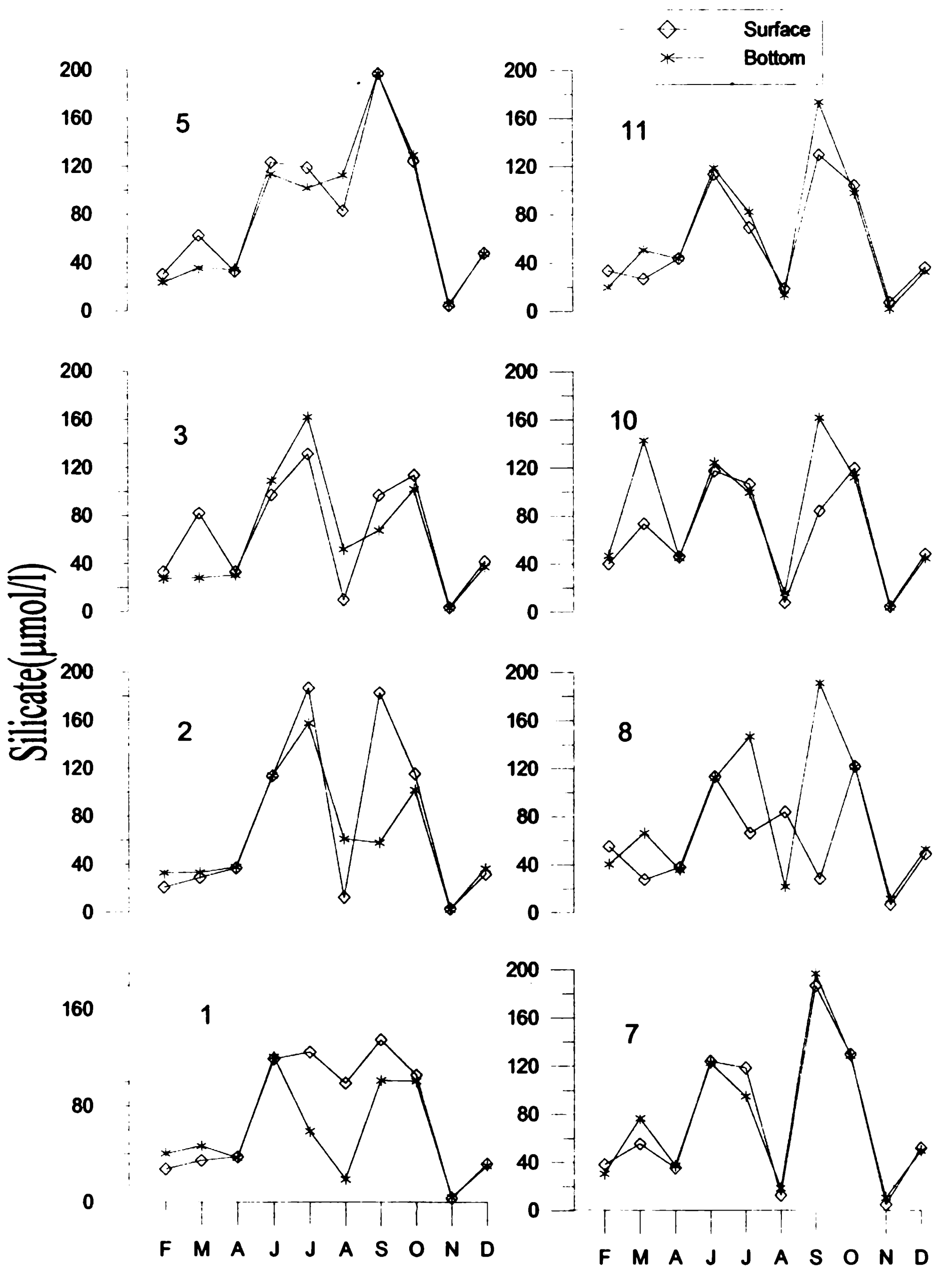


Figure 3.9 Annual variation of silicate in the study region

3.2.2.2 Dissolved Oxygen

Dissolved oxygen showed clear seasonal variations (Fig. 3.10). In the pre-monsoon, when the area is under the predominant influence of marine conditions, the levels of oxygen were comparatively low. At surface it ranged between 3.63 and 8.46 mg/l with an average of 5.63 mg/l and in bottom waters the range was from 2.31 to 7.28 mg/l with an average of 4.81 mg/l. It increased during monsoon and the surface range was 3.97-10.15 mg/l with an average of 6.69 mg/l, while at bottom range was from 3.31 to 9.27 mg/l with an average of 5.30 mg/l. In the post-monsoon, surface range was 3.71-8.93 mg/l with an average of 6.79 mg/l and for bottom the range was 2.94-8.70 mg/l with an average of 5.80 mg/l.

From the present study, DO in this region was found to be near saturated levels and only a marginal drop was seen even during pre-monsoon. There was not much vertical difference. The inner arms appeared to be more oxygenated than the main arm of the estuary. ANOVA also established significant temporal ($p<0.001$) variation with higher values during November and lower during April. Significantly high ($p<0.001$) and low DO was obtained for stations 7 and 3 respectively (Table 3.2).

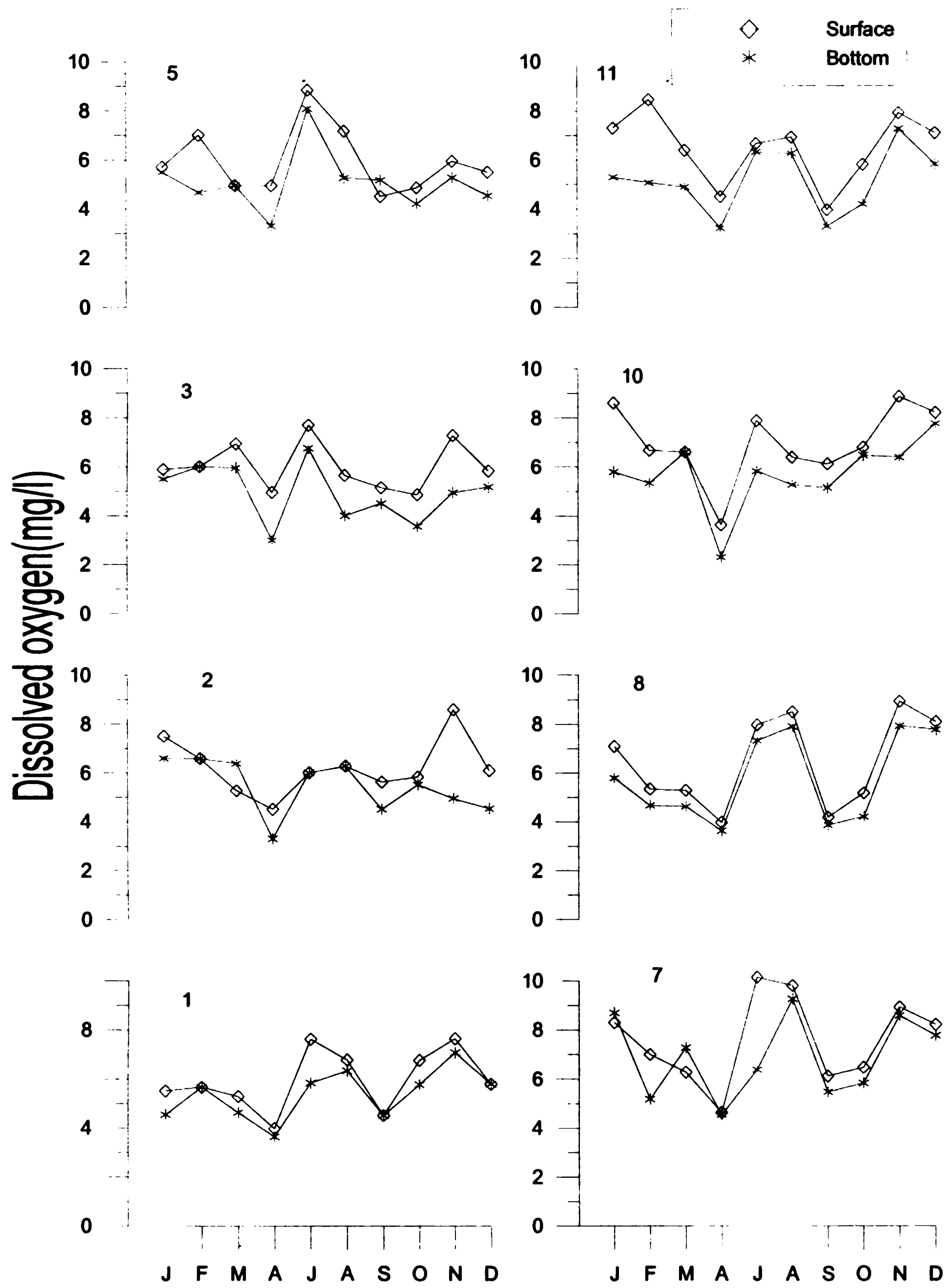


Figure 3.10 Annual variation of dissolved oxygen in the study region

3.2.3 Biological Characteristics

3.2.3.1 Primary Production

The monthly variation of primary production (Fig.3.11), in general, showed a tri-modal distribution pattern with maximum values during November, July and April. Maximum gross production (183.33 mg $C/m^3/hr$) was observed during November at station 7, while minimum (52.08 mg $C/m^3/hr$) was seen at the Station 10 during June. The corresponding maxima and minima of net productions were 111.46 mg $C/m^3/hr$ and 26.04 mg $C/m^3/hr$, respectively. Primary production, averaged for all stations (Table 3.1) was slightly higher during post monsoon. The annual averages of gross and net production in the study region were 99.36 and 65.12 mg $C/m^3/hr$ respectively. The net primary production comes to about 70% of the gross primary production, which means that about 30% is utilized for respiration. Stations 5 and 7 (in the inner arm) are generally more productive. Station 10, which is in the main arm recorded lowest production throughout the study period.

The annual column production works out to be 475.67 g C/m^2 by considering that primary production occurs for 10 hours a day and the euphotic depth as 2 m. The assumption for taking 2m as euphotic depth because the annual average of Secchi depth transparency was 1m in the study region and euphotic depth is generally considered to be its double (Aarup, 2002). Moreover, the average depth of the study area is only 2.5 m. Although depths might be different at different parts, present assumption is justified because parts close to the banks are also considered as a part of the study area. The total annual production in the study region (area ~6.25 km^2) was about 2971 tonnes of carbon.

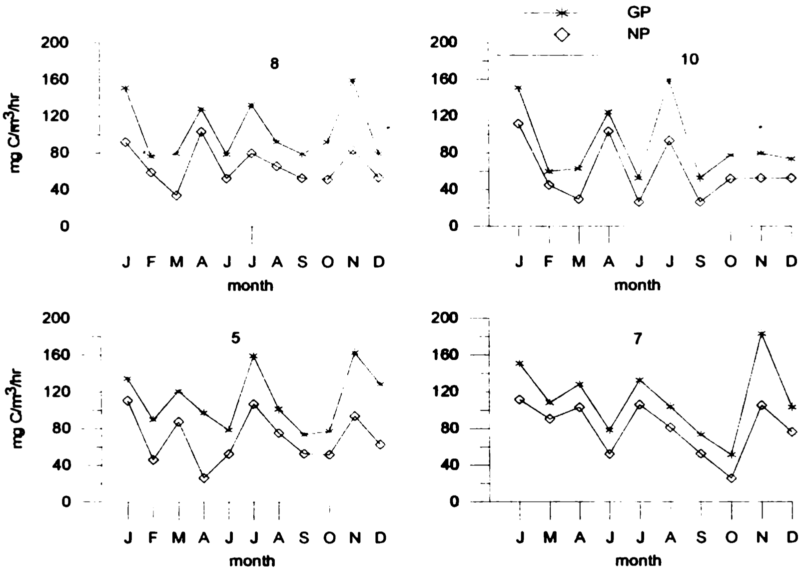


Figure 3.11 Monthly variation of primary production in the study region

Table 3.1 Seasonal average of gross primary production (Net primary production is shown in parenthesis)

Season	Station 5	Station 7	Station 8	Station 10
Pre-monsoon	102.43 (53.13)	118.18 (67.11)	94.44 (65.21)	81.94 (59.03)
Monsoon	102.94 (71.54)	96.93 (72.97)	95.32 (62.42)	87.88 (48.44)
Post-monsoon	125.55 (79.53)	122.24 (96.88)	120.31 (69.79)	95.08 (66.67)

3.2.3.2 Chlorophyll-a

Chlorophyll-a ranged between 1 and 34.61 μg/l, the average being 9.83 μg/l. Chlorophyll distribution followed the same trend of primary production, showing a primary peak at November and others during July and April. Stations 5 and 7, in the inner arms of the study region recorded maximum chlorophyll and the station 10, which is in the main arm recorded lowest values throughout the study period, same as seen for primary production.

3.2.3.3 Zooplankton

Planktonic groups obtained from the study region were copepods, nauplius, zoea, cladocerans, chaetognaths, appendicularians, fish eggs and fish larvae. Copepods were the dominant group. The total zooplankton ranged between 1000/m^3 and 15800/m^3. The maximum zooplankton was at Station 5 during February and the minimum was at Station 10 during November. Copepods ranged between 1000/m^3 and 12500/m^3, the maximum was during February and minimum was during July and August. Zooplankton distributions showed seasonal variation with maximum during pre-monsoon period and minimum during monsoon (Fig. 3.12). ANOVA (Table 3.2) also established significant temporal (p<0.001) variation, which was absent for stations.

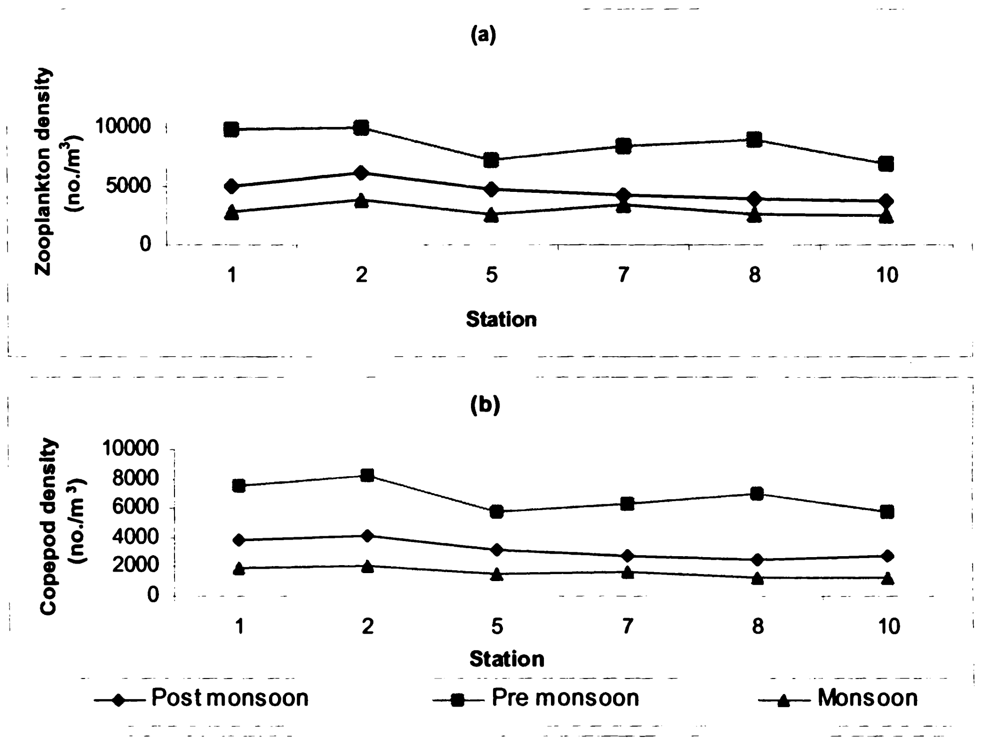


Figure 3.12 Distribution of seasonal average of a) Total zooplankton (b) Copepods

Table 3.2 ANOVA (two way without replication) of hydrographical parameters

TSS	**SS**	**df**	**MS**	**F**	**P-value**	**F crit**
Months	1643.625	10	164.3625	4.388278	8.73E-05	1.968875
Stations	714.6618	7	102.0945	2.7258	0.014673	2.14348
Error	2621.842	70	37.45489			
Total	4980.129	87				
Turbidity	**SS**	**df**	**MS**	**F**	**P-value**	**F crit**
Months	3852.133	10	385.2133	25.54864	1.4E-19	2.585224
Stations	138.7375	7	19.81964	1.314505	0.256454	2.906035
Error	1055.435	70	15.07765			
Total	5046.306	87				
Phosphate	**SS**	**df**	**MS**	**F**	**P-value**	**F crit**
Months	211.197	10	21.1197	5.676368	3.58E-06	1.968875
Stations	206.8435	7	29.54907	7.941939	4.56E-07	2.14348
Error	260.4445	70	3.720636			
Total	678.485	87				
Nitrate	**SS**	**df**	**MS**	**F**	**P-value**	**F crit**
Months	1477.279	10	147.7279	40.94981	2.51E-25	1.968875
Stations	75.81616	7	10.83088	3.002292	0.008147	2.14348
Error	252.5276	70	3.607537			
Total	1805.623	87				
Nitrite	**SS**	**df**	**MS**	**F**	**P-value**	**F crit**
Months	26.50566	10	2.650566	10.64027	1.05E-10	1.968875
Stations	6.981755	7	0.997394	4.003875	0.000976	2.14348
Error	17.4375	70	0.249107			
Total	50.92491	87				
Silicate	**SS**	**df**	**MS**	**F**	**P-value**	**F crit**
Months	152000.3	9	16888.93	39.70366	1.2E-22	2.032245
Stations	3387.946	7	483.9923	1.137803	0.351366	2.158828
Error	26798.59	63	425.3745			
Total	182186.9	79				
DO	**SS**	**df**	**MS**	**F**	**P-value**	**F crit**
Months	84.45301	10	9.383668	13.99081	4.64E-12	1.968875
Stations	23.37563	7	3.339376	4.978924	0.000158	2.14348
Error	42.25424	70	0.670702			
Total	150.0829	87				
Zooplankton	**SS**	**df**	**MS**	**F**	**P-value**	**F crit**
Month	510.4	10	42.5	11.5	1E-11	2.487099
Station	38.7	7	7.7	2.1	0.0776	2.880711
Error	221.1	70	3.7			
Total	770.2	87				

3.2.4 Tidal variations

The tidal variations of different hydrographical parameters for pre and post-monsoon seasons at two selected stations in the study region were described in this section. The hourly observations for 13-hours are tidally averaged and presented in Table 3.3.

3.2.4.1 Station 1

Pre-monsoon (02-05-03)

The variations of different parameters are shown in Fig. 3.13. Tidal range was 45cm. Salinity varied between 26.4 and 30.8 ‰. Maximum salinity lagged high tide by about 2 hours. Salinity did not vary vertically indicating well-mixed condition during pre-monsoon, due to the predominance of tides over freshwater flow. Temperature ranged between 31.4 and 32.8 °C. The variation appeared to be mainly due to diurnal heating cycle. The maximum was recorded during midday and subsequently decreased slightly, coinciding with flood slack. Rapid cooling during evening hours was noticed. The fall in temperature during flood slack indicated the possibility of tidal effects. As in the case of salinity, the vertical temperature gradient was not seen. Maximum flood current (70 cm/sec) occurred around high water. Depth wise difference of currents was negligible. Reversal from flood to ebb occurred after the slack period, as expected. Suspended sediment data was not available during higher current speeds and during the remaining period, it varied between 39.6 and 67.5 mg/l. Turbidity varied between 5.8 and 30.5 NTU and bottom waters were more turbid. Higher values coincided with higher current speed.

Dissolved oxygen ranged from 4.93 to 6.58 mg/l and was generally more at surface than at bottom. The variation, in general, did not follow the tidal rhythm. Oxygen concentrations usually exhibit a characteristic diurnal pattern with concentrations increasing from morning into mid afternoon as photosynthesis outstrips respiration. Declining oxygen concentrations occur during the late afternoon or evening as photosynthetic rate declines and throughout the night when photosynthesis does not occur. In the case of nutrients comparatively low concentrations were noticed during the entire observation period. Phosphate was at detectable levels only on a few occasions and the maximum was about 1.42 µmol/l, which occurred around noon, coinciding with the flood. Nitrite was below detection level and nitrate ranged between 0.60 and 2.19 µmol/l. Higher concentrations were recorded around noon, end of flood and the minimum during start of flood tide. Silicate varied between not detected and 12 µmol/l. Vertical stratification and clear tidal rhythm was not seen for all nutrients. Average gross primary production was 86.81 mg $C/m^3/hr$ and the net production was 40.28 mg $C/m^3/hr$.

Post-monsoon (19-09-02)

Variations of different parameters are presented in Fig. 3.14. A higher tidal range (60 cm) was observed than during the day of observation in pre-monsoon. Salinity showed wide fluctuation and varied between 6.6 and 22.5 ‰. Salinity followed the tidal rhythm than seen during pre-monsoon. Maximum salinity coincided with slack water. It is interesting to note that though the estuary was vertically homogeneous during rising tide, it became stratified at the end of flood. Temperature ranged between 29.6 and 31.8°C. The pattern of temperature fluctuations was similar to that of salinity. Surface temperature more or less followed the diurnal heating pattern while bottom temperature followed the tidal rhythm. This resulted in large vertical gradient around high tide.

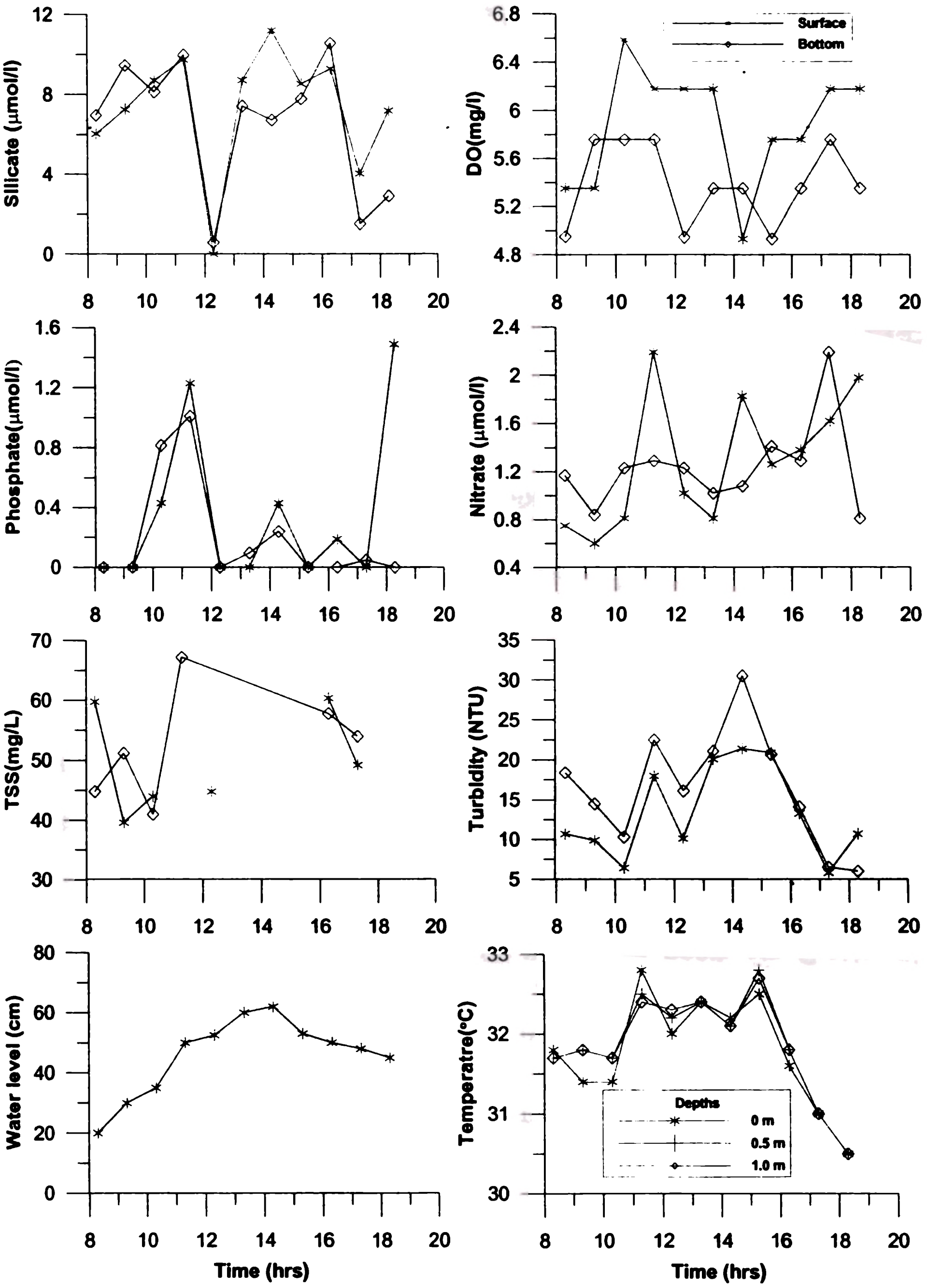


Figure 3.13 Tidal variations at Station 1 during pre-monsoon

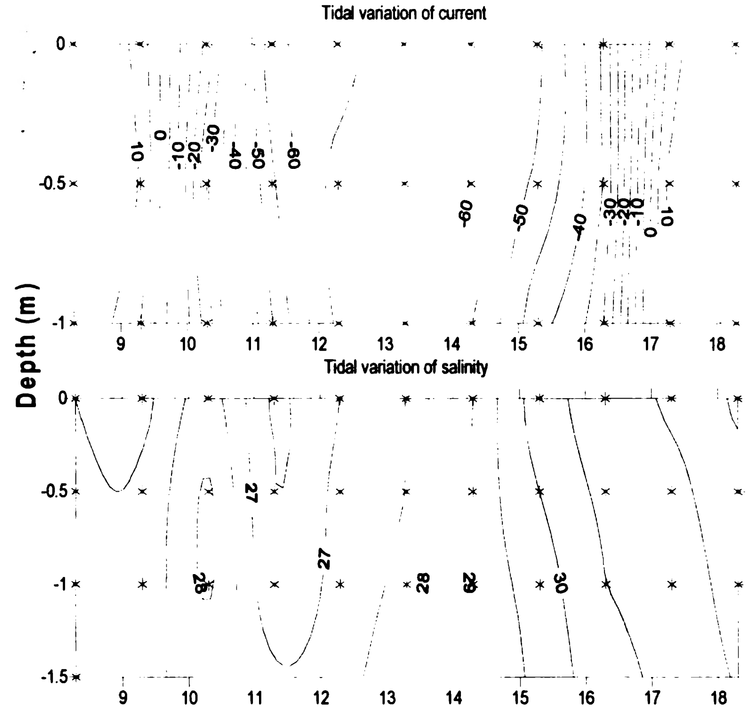


Figure 3.13 (Contd.)

The maximum flood speed (44 cm/sec) is less than that observed during pre-monsoon. The reversal from flood to ebb almost coincided with slack water. Suspended sediments ranged between 2 to 65 mg/l and were lower during the flood slack and found to very high at the bottom. Turbidity ranged between 4 to 10.6 NTU and showed an increase during the ebb tide.

Dissolved oxygen values ranged between 3.79 and 8.20 mg/l. The maximum was recorded around noon and the minimum during morning. Higher values were in general, at surface because of the lack of mixing due to vertical stratification and it continued to be higher in the afternoon also. Phosphate ranged between 0.48 and 1.2 µmol/l, nitrite between not detected and 0.66 µmol/l and nitrate between 0 .17 and 2.92 µmol/l. Although a direct tidal influence was lacking, the maximum nutrients were around slack period and stratification was absent. Average gross primary production was 142.36 mg C/m^3/hr and the net production was 74.65 mg C/m^3/hr, higher than during pre-monsoon.

3.2.4.2 Station 5

Pre-monsoon (26-05-03)

Tidal variations of different parameters are presented in Fig.3.15. Tides at Cochin port are also presented. Tidal range was 15 cm, which was lower than at Cochin harbour. High water lagged at this station by about 1 hour and lag for low water was about 2 hours. Salinity was very low during the observation compared to the station earlier occupied, during this season, because of the pre-monsoon showers around the time of these observations. Salinity varied between about 14.3 to 16.8 ‰ and also mild vertical stratification was noticed, unlike the other station occupied during the season. The salinity also showed fluctuations superimposed on tidal variations. Temperature ranged between 31.4 and 33.7° C. Vertical gradient was seen around the time of maximum temperature and it was low after the slack period. Maximum flood observed was 40 cm/sec. Current speed was low during ebb, not exceeding 17 cm/sec. Current did not show any clear relation to the phase of tide and several fluctuations were seen. Suspended sediments ranged from 11.2 to 27.7 mg/l and were higher at surface than bottom. TSS increased during flood and turbidity range was from 1.9 to 8.4 NTU and found to be higher at slack period.

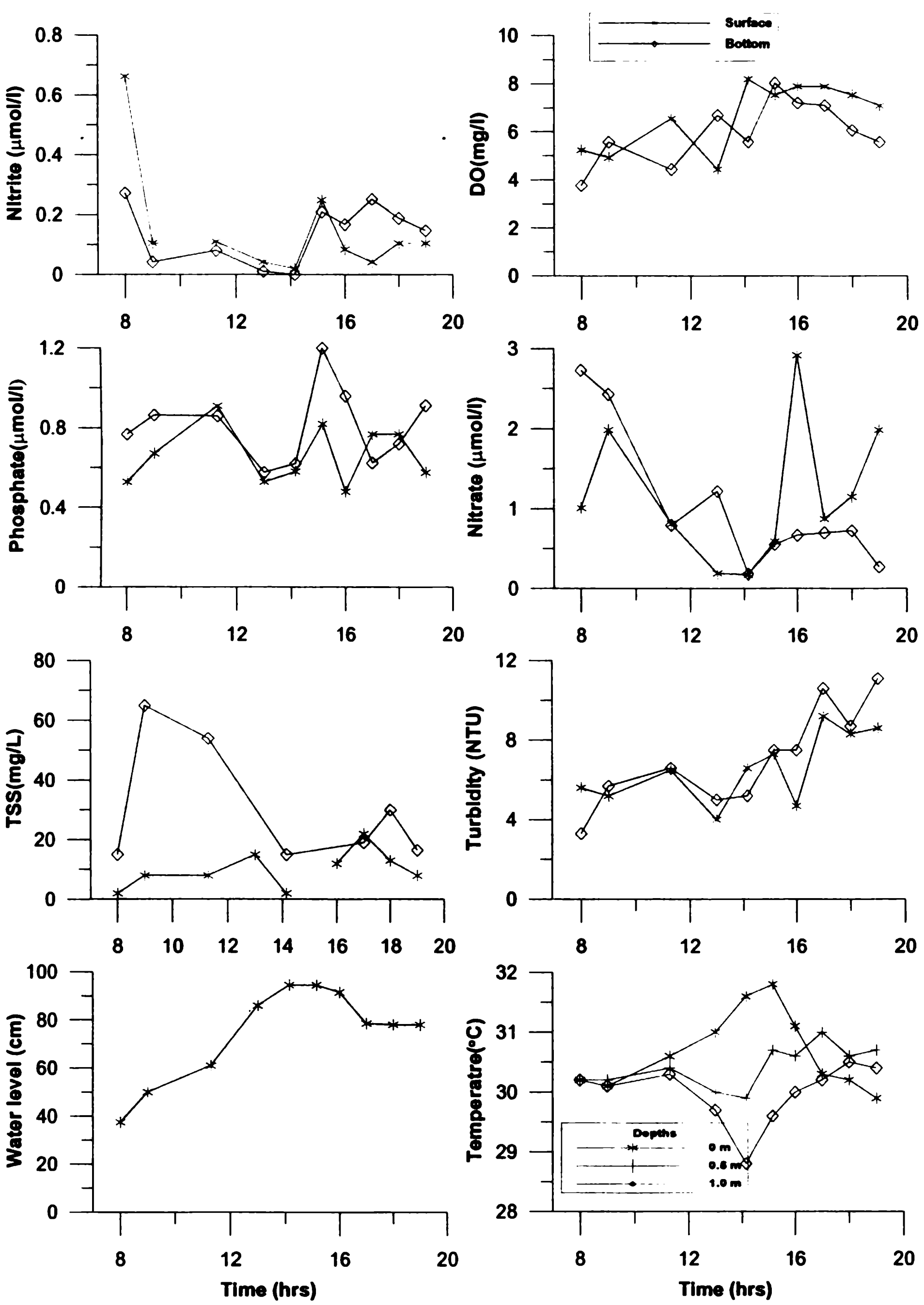


Figure 3.14 Tidal variations at Station 1 during post-monsoon

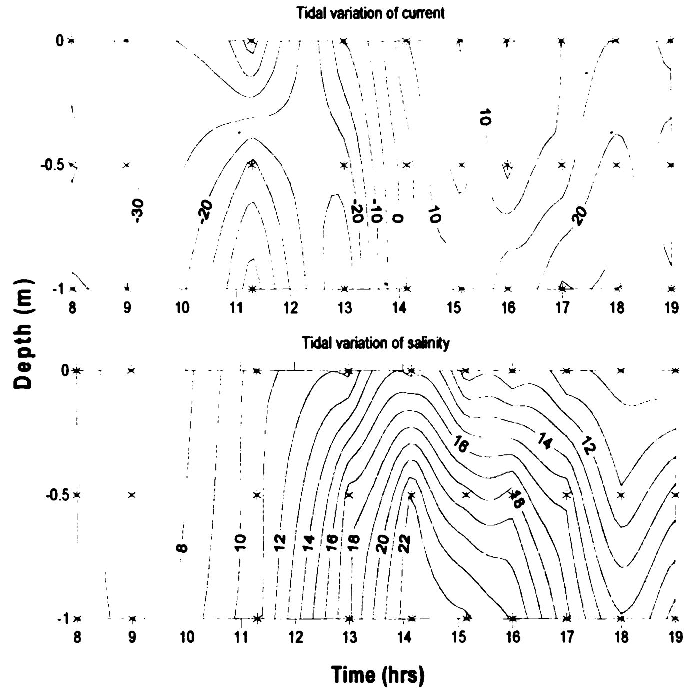


Figure 3.14 (Contd.)

Dissolved oxygen showed higher values during this observations (5.84 to 11.66 mg/l). The variation according to tide is not clear and there was an increasing trend in the early afternoon hours. Nutrients did not have any clear variation with tides. Although the variation was irregular, there was a decreasing trend towards afternoon hours. Phosphate ranged between 1.73 and 17.52 µmol/l. Vertical variation was noticed. Nitrite ranged between 0.34 and 1.77 µmol/l and were more at the bottom layers than at the surface layers. Nitrate varied from 6.38 to 14.58 µmol/l and higher values may be due to the increased land run off. A sudden increase in the nitrate concentration was noticed during the end of flood. Silicate also showed higher values and the variations did not show tidal rhythm. The primary production was higher and the average gross and net productions were 131.94 and 80.56 mg C/m^3/hr, respectively.

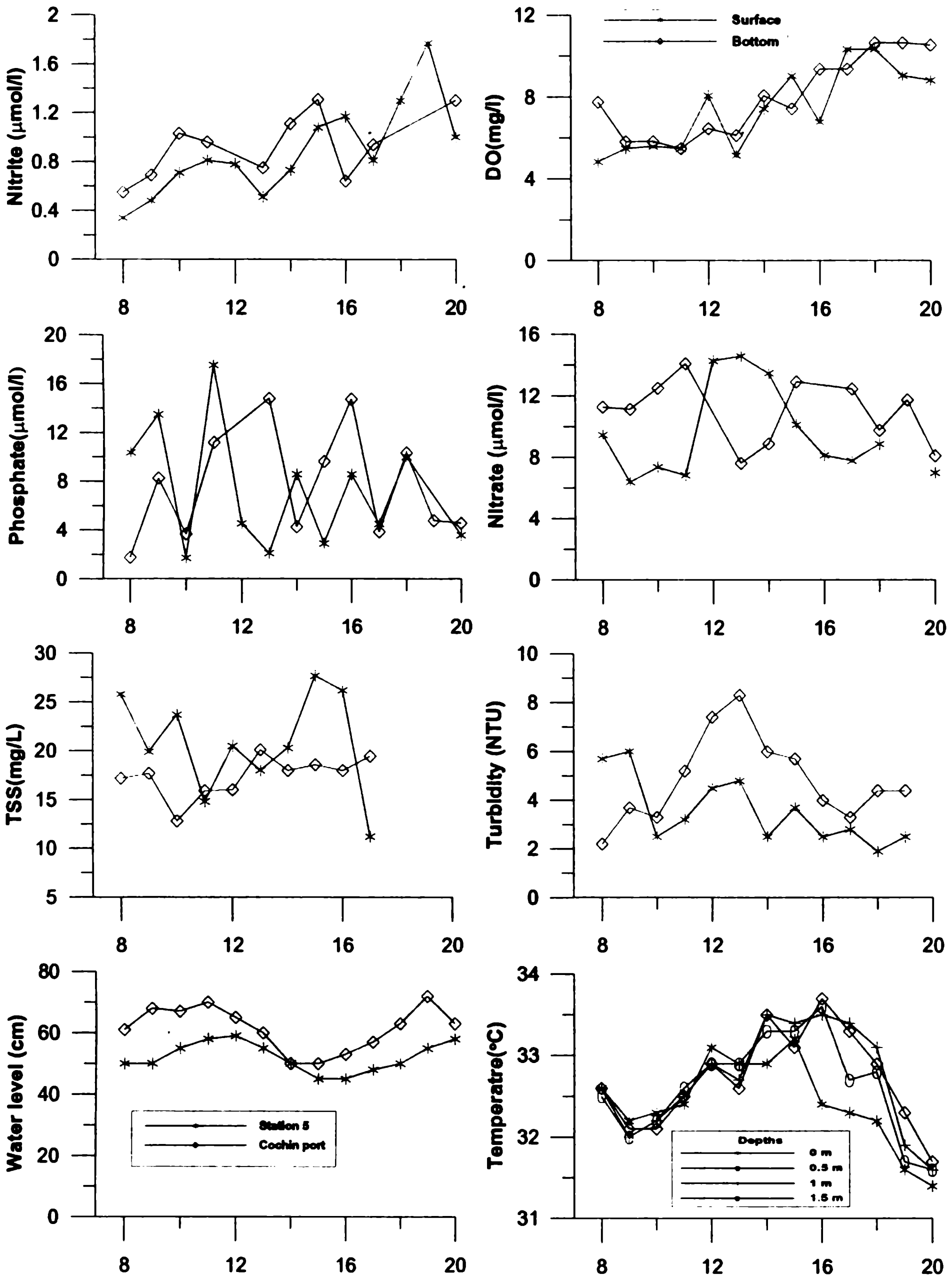


Figure 3.15 Tidal variations at Station 5 during pre-monsoon

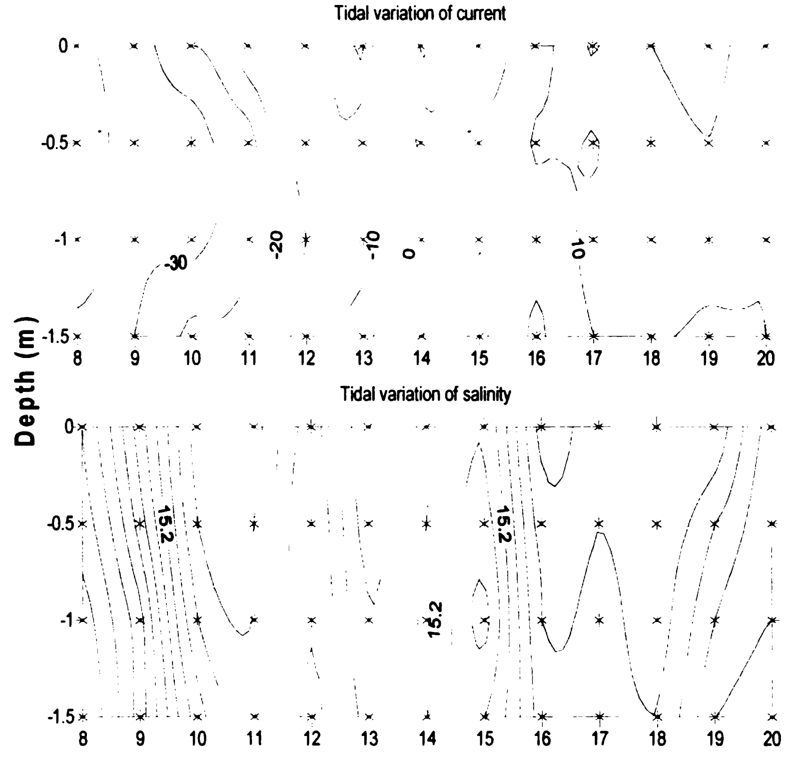


Figure 3.15 (Contd.)

Post-monsoon (21-10-02)

Tidal range was 35 cm, which was lower when compared to Cochin harbour (60 cm) on the same day (Fig. 3.16). A lag of about 1 hour was noticed for high water and about 2 hours for low tide between Cochin harbour and this station. Very low salinity or near freshwater conditions (0.6 to 1.0 ‰) prevailed during observation. This was the result of very heavy rains for a few days before these observations. Temperature ranged between 29.6 and 31.7° C. The maximum was recorded after midday at the surface and the minimum during early morning. Surface layers were, in general, warmer. However, mild inversion resulting from lower surface temperature was noticed during ebb. The hours of higher subsurface temperature coincide with complicated current pattern. Flood speed was low compared to pre-monsoon, maximum being about 30 cm/sec. Flood to ebb reversal almost coincided with high water. TSS ranged between 2 and 44 mg/l and turbidity between 4.9 and 14.3; higher at bottom than surface. Both showed an increase during the ebb tide as seen in the other station.

Dissolved oxygen ranged between 3.67 and 5.08 mg/l and the maximum was recorded during ebb. The surface values were higher than that at bottom. Phosphate ranged between 2.51 and 8.87 μmol/l, nitrite between 0.92 and 2.54 μmol/l and nitrate between 2.05 to 8.8 μmol/l. Vertical variation in nutrients was noticed. In the case of phosphate and nitrate there was increase after flood slack. Primary production was very low and the average gross production and net production was 53.13 and 31.25 mg C/m^3/hr respectively, might due to the cloudiness.

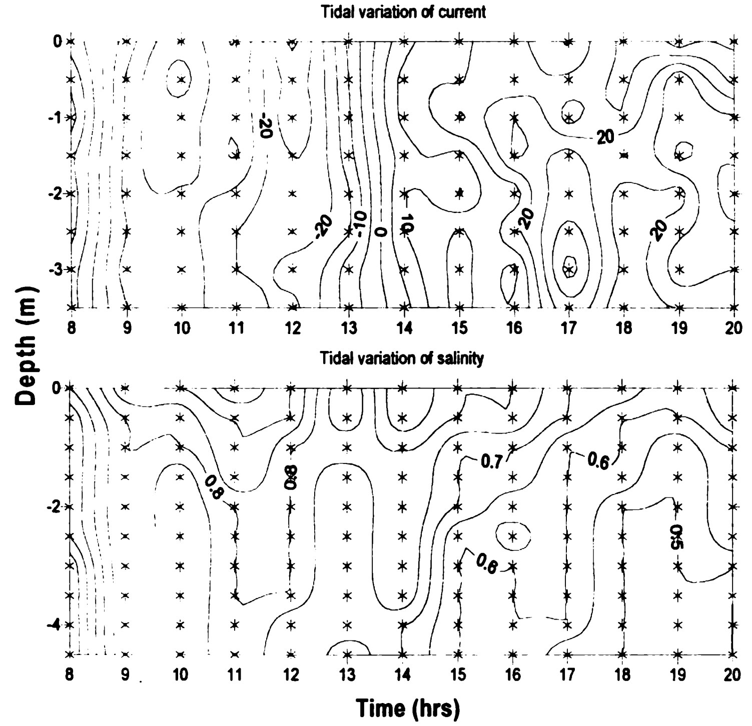


Figure 3.16 Tidal variations at Station 5 during post-monsoon

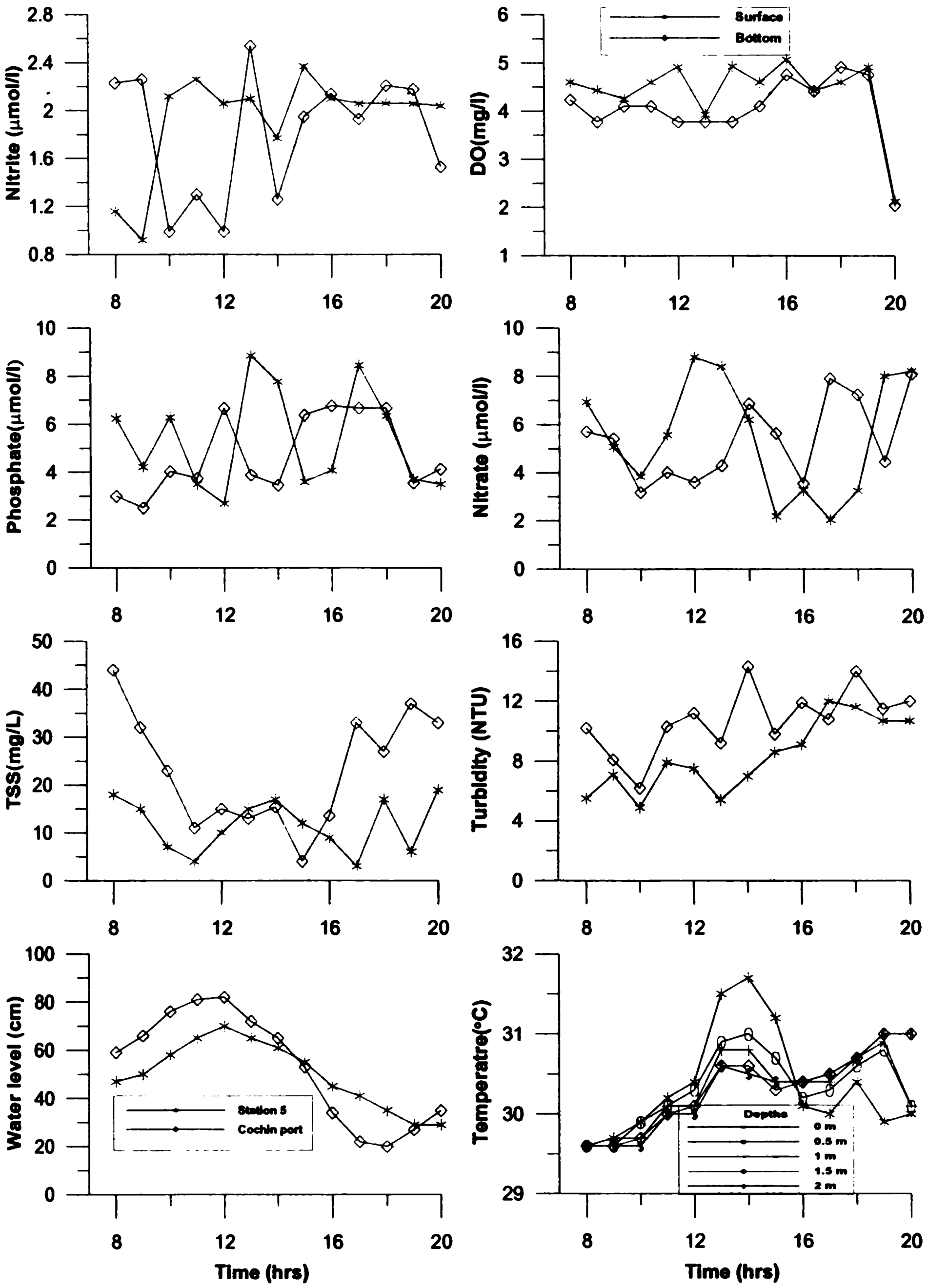


Figure 3.16 (contd.)

Table 3.3 Tidal variations of physico-chemical parameters
(Tidal average is shown in parenthesis)

Station 1: pre-monsoon

Depth (m.)	Salinity (ppt)	Temp. (° C)	Current (cm/s)	TSS (mg/l)	Turbidity (NTU)	Phosphate (μmol/l)	Nitrite (μmol/l)	Nitrate (μmol/l)	DO (mg/l)
Surface	26.4-30.8 (28.1)	31.4-32.8 (31.7)	-70 - +18 (-27.7)	39.6-60.4 (49.6)	5.8-21.4 (13.4)	ND-1.49 (0.75)	ND (-)	0.60-2.19 (1.30)	4.93-6.58 (5.88)
Bottom	26.6-30.5 (28.1)	31.7-37.7 (31.8)	-68 -+13 (-26.7)	41.4-67.5 (52.7)	6-30.5 (16.4)	ND-1.10 (0.44)	ND (-)	ND-2.19 (1.23)	4.93-5.76 (5.39)

Station 1: post- monsoon

Depth (m.)	Salinity (ppt)	Temp. (° C)	Current (cm/s)	TSS (mg/l)	Turbidity (NTU)	Phosphate (μmol/l)	Nitrite (μmol/l)	Nitrate (μmol/l)	DO (mg/l)
Surface	6.6-14.6 (10.2)	29.9-31.8 (30.7)	-44 - +23 (-3.8)	2-22 (10)	4-9.2 (6.6)	0.48-0.91 (0.66)	0.02-0.66 (0.15)	0.17-2.92 (1.17)	4.92-8.20 (6.73)
Bottom	6.6-22.5 (15.6)	29.6-30.5 (30.0)	-30 -+26 (+0.9)	15-65 (30.6)	3.3-11.1 (7.1)	0.58-1.20 (0.81)	ND-0.27 (0.14)	0.18-2.73 (1.03)	3.76-8.04 (6.01)

Station 5: pre-monsoon

Depth (m.)	Salinity (ppt)	Temp. (° C)	Current (cm/s)	TSS (mg/l)	Turbidity (NTU)	Phosphate (μmol/l)	Nitrite (μmol/l)	Nitrate (μmol/l)	DO (mg/l)
Surface	14.3-16.4 (14.9)	31.4-33.2 (32.4)	-36 – +16 (-5.5)	11.2-27.7 (20.8)	1.9-6 (3.7)	ND-17.58 (7.33)	ND-1.77 (0.88)	ND-14.58 (9.52)	4.83-10.4 (7.36)
Bottom	14.6-16.8 (15.2)	31.7-33.7 (32.7)	-33 – +11 (-5.1)	12.8-20.1 (17.4)	2.2-8.4 (4.8)	ND-14.78 (7.66)	ND-1.31 (0.93)	ND-14.09 (10.95)	5.48-10.67 (7.82)

Station 5: post-monsoon

Depth (m.)	Salinity (ppt)	Temp. (° C)	Current (cm/s)	TSS (mg/l)	Turbidity (NTU)	Phosphate (μmol/l)	Nitrite (μmol/l)	Nitrate (μmol/l)	DO (mg/l)
Surface	0.6-1.0 (0.8)	29.6-31.7 (30.4)	-32 - +26 (+2.2)	3-19 (11.7)	4.9-12.0 (8.3)	2.69-8.87 (5.33)	0.92-2.37 (1.93)	2.05-8.80 (5.53)	2.12-5.08 (4.42)
Bottom	0.6-0.8 (0.7)	29.6-31.0 (30.3)	-25 -+31 (+3.8)	4-44 (23.2)	6.2-14.3 (10.7)	2.51-6.77 (4.73)	0.99-2.54 (1.81)	3.19-8.10 (5.39)	2.05-4.92 (4.04)

3.3 Discussion

Statistical Analysis using Spearman's correlation was made to study the significant relationships between the different parameters. Because of the bulkiness of the data and the shallow nature of the study region, the values at different depths were column averaged and used for correlation (n=44). The results are shown in Table 3.4.

3.3.1 Monthly observations

3.3.1.1 Physical characteristics

Salinity values were maximum in pre-monsoon months in study region and fresh water conditions prevailed during monsoon, which is a distinctive feature of tropical estuaries. Varma *et al.*, (2002) on analyzing long-term daily variations at a station near Panangad jetty noticed salinity range between 0-32 ‰ and bimodal variation, similar to the present study. Stratification was completely absent in the study region during monsoon, although it was reported at lower reaches of the estuary because of salt-water intrusion at bottom layers (Balakrishnan & Shynamma, 1976; Ramaraju *et al.*, 1979; Udayavarma *et al.*, 1981; Sankaranarayanan *et al.*, 1986; Joseph & Kurup, 1990; Ajith, 1996). Complete flushing out from this region of the estuary due to the high run off and the shallow nature is found to be the main reason for such behaviour. During post-monsoon, river discharge gradually diminished and tidal influence gained momentum as the estuarine conditions changed to a partially mixed type, developing density stratification. This is mainly a transitional period. Stratification during post-monsoon was reported from other parts of the estuary (Sankaranarayanan *et al.*, 1986; Joseph & Kurup, 1989; Ajith, 1996). In pre-monsoon, the river discharge is minimum and seawater influence is maximum at upstream; the estuary is well mixed and homogeneity exists in the water column.

Salinity showed significant negative correlation (r= -0.914) with river runoff. Vertical distribution of salinity varied with changes in fresh water flow and location. Highest stratification (up to 12 ‰) was observed at the stations farthest from the mouth (9,10,11). The absence of stratification in the narrow inner arms of the study region could be due to the increased mixing in the shallow regions.

Present trends in temperature, gradual increase from February to April, followed by a fall during July-August are in agreement with earlier studies in different parts of Vembanad Lake (Menon *et al.,* 1971; Kunjukrishna Pillai *et al.,* 1975; Balakrishnan & Shynamma, 1976; Antony, 1980). Studying the daily temperature data spanning more than a year from a station near Panangad Jetty, Varma *et al.,* (2002) also observed the bimodal pattern with the annual range of 27 to 35 °C. Temperature showed significant negative correlation with runoff and positive relation salinity. Like salinity, stratification was seen during post-monsoon periods and homogeneity in water column was observed during other seasons. Highest depth variations (up to 2°C) were obtained at stations 10 and 11. Station 5 in the inner arm showed vertical homogeneity throughout the study period, because of increased mixing.

Current speed showed significant correlation with runoff (r= 0.345), indicating higher speed during the heavy runoff monsoon period. Directional values of current indicated that monthly observations were made at all stations in the same tidal phase. This would help to nullify the tide-induced variations, which was observed during tidal cycle analysis.

3.4 correlations between different hydrographical parameters in the study region (n=44)

	Runoff	Salinity	Temperature	Current	Transparency	TSS	Turbidity	Phosphate	Nitrate	Nitrite	Silicate	DO	Production	Chl-a	Zooplankton
Runoff	1.000	-.914(**)	-.578(**)	.345(*)	-.345(*)	.326(*)	.624(**)	.437(**)	.815(**)	.336(*)	.438(**)	.402(**)	.077	.252	-.600(**)
Salinity	-.914(**)	1.000	.633(**)	-.326(*)	.410(**)	-.286	-.665(**)	-.384(*)	-.759(**)	-.314(*)	-.518(**)	-.321(*)	.062	-.201	.605(**)
Temperature	-.578(**)	.633(**)	1.000	-.151	.410(**)	-.215	-.582(**)	-.308(*)	-.626(**)	-.355(*)	.032	-.478(**)	-.207	-.206	.478(**)
Current	.345(*)	-.326(*)	-.151	1.000	.060	.397(**)	.318(*)	.522(**)	.147	.260	.413(**)	-.024	-.025	.455(*)	-.251
Transparency	-.345(*)	.410(**)	.410(**)	.060	1.000	-.344(*)	-.629(**)	-.414(**)	-.389(**)	-.488(**)	.061	-.164	-.161	-.085	.103
TSS	.326(*)	-.286	-.215	.397(**)	-.344(*)	1.000	.561(**)	.493(**)	.153	.399(**)	.082	.304(*)	-.090	.270	.012
Turbidity	.624(**)	-.665(**)	-.582(**)	.318(*)	-.629(**)	.561(**)	1.000	.529(**)	.498(**)	.589(**)	.175	.215	-.083	.137	-.350(*)
Phosphate	.437(**)	-.384(*)	-.308(*)	.522(**)	-.414(**)	.493(**)	.529(**)	1.000	.288	.687(**)	.087	.148	.205	.780(**)	-.131
Nitrate	.815(**)	-.759(**)	-.626(**)	.147	-.389(**)	.153	.498(**)	.288	1.000	.295	.230	.386(**)	.178	.139	-.495(**)
Nitrite	.336(*)	-.314(*)	-.355(*)	.260	-.488(**)	.399(**)	.589(**)	.687(**)	.295	1.000	-.141	.141	.227	.563(**)	.035
Silicate	.438(**)	-.518(**)	.032	.413(**)	.061	.082	.175	.087	.230	-.141	1.000	-.120	-.473(**)	-.006	-.421(**)
DO	.402(**)	-.321(*)	-.478(**)	-.024	-.164	.304(*)	.215	.148	.386(**)	.141	-.120	1.000	.207	.050	-.327(*)
Production	.077	.062	-.207	-.025	-.161	-.090	-.083	.205	.178	.227	-.473(**)	.207	1.000	.428(*)	.152
Chlorophyll-a	.252	-.201	-.206	.455(*)	-.085	.270	.137	.780(**)	.139	.563(**)	-.006	.050	.428(*)	1.000	-.010
Zooplankton	-.600(**)	.605(**)	.478(**)	-.251	.103	.012	-.350(*)	-.131	-.495(**)	.035	-.421(**)	-.327(*)	.152	-.010	1.000

** Correlation is significant at the 0.01 level (2-tailed). * Correlation is significant at the 0.05 level (2-tailed).

Secchi disc transparency, which is the indicator of the attenuation of the sunlight, was low during the monsoon period, apparent by the inverse correlation with runoff. But it also showed negative relationship with TSS and turbidity. Since the monsoonal increase in TSS and turbidity were not drastic, the decrease in transparency during monsoon could be mainly due to the cloudiness associated with the showers, rather than the suspended matters.

Most estuaries have suspended sediment concentrations that range between 20–100 mg/l (Table 3.5), although, in periods of high sediment runoff this may increase to as much as 1000 mg/l (Fahey & Coker, 1992). TSS in the study region is comparable to these values, although the rapid increase was absent and these are not high to induce light-limitation for primary production (Cloern, 1996) in this shallow estuary. Seasonal pattern in the TSS and turbidity suggest that their main source is the run-off from the catchment areas. The absence of a drastic increase during monsoon shows the dominance of changes in the availability of erodible deposits, rather than hydrological factors, in determining the sediment supply (Bogen, 2004). Although hydrodynamics and flow regimes are critical controls on sediment transport processes, the supply of available material, derived from either upland erosion within the drainage basin or channel margins can be of equal or greater importance (van Sickle & Beschta, 1983; Asselman, 1999; Bronsdon & Naden, 2000).

Their spatial variation could be attributed to the current pattern prevailed in the two different regions of study area, which was marked from the tidal cycle analysis. At the stations in the main arm, the directions of tidal current are along the stream and circular movements were generally not noticed. At the stations in the inner arms of the study region, although an increase was seen in monsoon, there are many fluctuations superimposed on these. The eddy like currents formed in the inner arm indicates that in shallow and curved portions, current patterns are modified and current fluctuations get superimposed on tidal currents. This could churn up more sediment, thus obliterating monsoon high. The role of water current in the distribution and re suspension of sediments is evident by their positive correlation. TSS and turbidity showed significant positive correlation (r=0.561), indicating their interdependence. The low r-value is probably related to differences in size, composition, and refractive index of particles (Earhart, 1984).

Table 3.5 suspended sediments (mg/l) in some of the estuaries

Estuary	TSS(mg/l)	Reference
Beypore, Kerala	1-88	Anilkumar *et al.,* (1999).
James river, Australia	100-270	Nichols (1993)
Scheldt , Europe	50-2500	Chen *et al.,* (2005)
Atna river basin, Norway	<1 - 2023.8	Bogen, (2004)
North San-Francisco Bay, *USA*	30-100	Cloern *et al.,* (1985)
Cochin estuary	2-50	**Present study**

3.3.1.2 Chemical characteristics

The nutrient concentration in this estuary followed marked seasonal rhythm induced by the local precipitation and land run off. Large temporal variations with the pre-monsoon period, when the system is predominantly marine, showing low nutrient concentration and high input during the monsoon due to the maximum influx of freshwater were observed. These seasonal trends were previously reported in different parts of the Vembanad Lake (Sankaranarayanan & Qasim, 1969; Reddy & Sankaranarayan, 1972; Joseph, 1974; Sreedharan Manikoth & Salih, 1974; Kunjukrishna Pillai *et al.,* 1975; Silas & Pillai, 1975; Joseph & Pillai, 1975; Balakrishnan & Shynamma, 1976; Sankaranarayanan *et al.,*1982; Anirudhan *et al.,*1987; Lakshmanan *et .al.,* 1987; Nair *et al.,*1988; Anirudhan & Nambisan, 1990). The high nutrients observed during monsoon were utilized for primary production and their concentration decreased gradually, resulting in very low values during the high saline pre-monsoon season (Sankaranarayanan & Qasim, 1969). The levels of nutrients were comparable to that of earlier studies in this estuary and also to other estuaries around the world (Table 3.6). It was suggested that the main reason for the spatial variation might be due to the variation in the regenerative property of the bottom sediments (Reddy & Sankaranarayan, 1972).

Nutrients showed significant positive correlations with river runoff and negative correlation with salinity (Fig. 3.17), indicating their terrestrial origin. Higher co-efficients for nitrate and silicate suggest that the contribution from sea is less. Nutrient concentration and turnover rates in coastal waters are influenced by hydrologic conditions such as temperature, residence time, tidal or wind-forced currents (Burkholder *et al.,* 1994) and riverine fluxes (Schramm, 1999). Anirudhan *et al.,* (1987) and Anirudhan & Nambisan (1990) also reported significant negative correlation of salinity with silicate in Cochin backwaters. Chicharo *et al.,* (2001) also found inverse relationship of nutrients with salinity in Guadiana Estuary (south Portugal). Though Vijayakumar *et al.,* (2000) reported significant interrelationship among nutrients in Malki estuary, southwest coast of India, it was absent during the present study.

A conservative behaviour was observed in the case of silicate, characterized by reduction mainly due to mixing with saline water. Sankaranarayanan & Qasim (1969) reported that silicon content of the backwater was generally high, because of considerable freshwater discharge and land drainage. Sankaranarayanan *et al.*, (1984) observed a gradual decrease in silicate from monsoon to pre-monsoon. Anirudhan *et al.*, (1987) reported the same trend and also suggested that the dilution with seawater can be the major process controlling their concentration in this estuary. Anirudhan & Nambisan (1990) also stated that silicate concentration in the estuary is largely dependent on sources such as river discharge and land drainage. They found that mixing with seawater also plays a decisive role in controlling the distribution of silicate-silicon in the estuary.

Only phosphate showed significant spatial variation in the study region. This may be because of the fact that phosphate being a high surface-active species is the only nutrient that shows exchange with soil (Jacksen, 1958). Sediments act as traps or buffers of phosphorus (Rigler, 1973). Hence the concentration of inorganic phosphate in the overlying water depends on the ability of the sediments to retain or release phosphate. Nair *et al.*,(1987) also reported that the sediment activity influences the distribution of nutrient pool in the Cochin estuary.

Table 3.6 Nutrient concentrations in different estuaries

Estuary	Nutrients (µmol/l)		Reference
Cochin estuary	Phosphate	ND- 2.5	Sankaranarayanan & Qasim (1969)
	Nitrate	up to 30	
	Nitrite	`1	
	Silicate	2-50	
	Phosphate	0.85-5.4	Sreedharan Manikoth & Salih (1974)
	Nitrate	1.5-30	
	Nitrite	ND-32	Joseph & Pillai (1975)
	Silicate	ND-6	
	Phosphate	18.97-20.22	Sheeba *et.al.,* (1996)
	Nitrate	10.09-14.53	
	Nitrite	4.04-4.75	
	Phosphate	ND-17.80	***Present study***
	Nitrate	0.07-22.17	
	Nitrite	ND-4.30	
	Silicate	2.44-197.08	
Poonthura Estuary	Phosphate	0.12-10.60	Anila Kumary & Abdul Azis (1992)
	Nitrate	0.15-30.50	
	Nitrite	0.15-11.50	
	Silicate	3.30-32.07	
Mandovi estuary	Phosphate	5.13	Krishna Kumari *et al.,* (2002)
	Nitrate	8.06	
	Nitrite	0.55	
Zuari estuary	Phosphate	2.85	Krishna Kumari *et al.,* (2002)
	Nitrate	0.93	
	Nitrite	0.36	
Gurupur estuary	Phosphate	0.28-4.6	Gowda *et al.,* (2002)
	Nitrate	1.23-8.5	
	Silicate	10.12-65.34	
Malki estuary	Phosphate	0.1-3.97	Vijayakumar *et al.,* (2002)
	Nitrate	1.9-79.3	
	Nitrite	0.18-1.47	
	Silicate	1.57-101.64	
Rushikulya Estuary	Phosphate	0.05-3.3	Gouda & Panigrahy (1992)
	Nitrate	0.2-22.27	
	Silicate	4.12-195.27	
Mahanadi Estuary	Phosphate	0.53-4.01	Sen Gupta& Upadhyay (1987).
	Nitrate	4.5-5.25	

Other estuaries			
Guadiana Estuary,	Phosphate	2.3	Chicharo *et al.*, (2001)
(south Portugal)	Nitrate+ Nitrite	11.06	
	Silicate	4.13	
Wash estuary	Phosphate	15-30	Fichez *et al.*, (1992)
	Nitrate	200-750	
Ria de Aveiro estuary	Phosphate	ND-2.14	Almeida *et al.*, (2002)
Portugal	Nitrate+ Nitrite	ND-5.53	

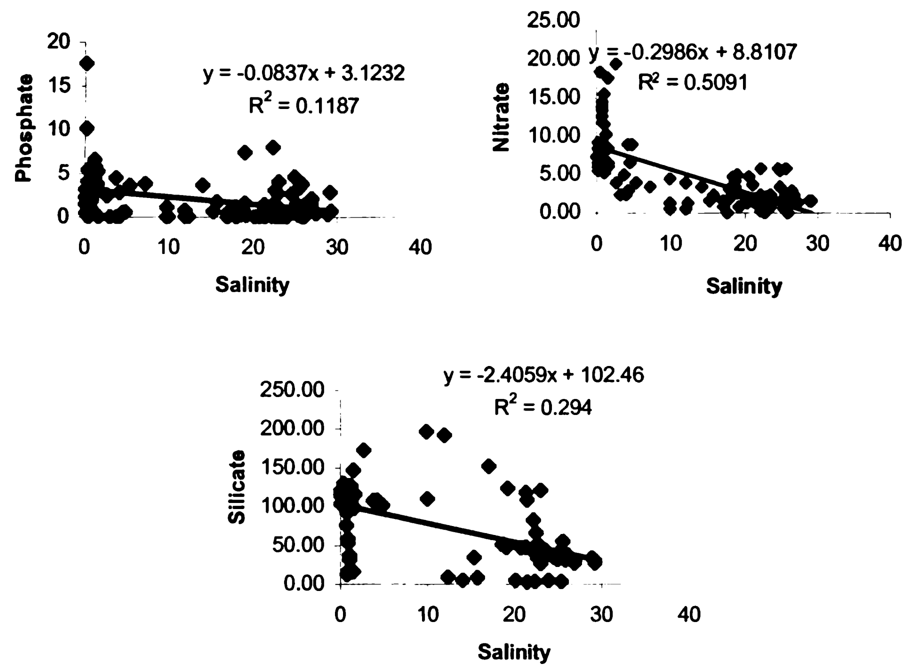


Figure 3.17 Relationship of nutrients with salinity in the study region

Phosphate showed significant positive correlations with current and TSS. It indicates that the sediments play a crucial role in the phosphorus dynamics in the estuary. It is associated and liberated by particles, through a complex series of absorption and disassociation reactions (Millero & Sohn, 1992). The transformation of dissolved phosphate into particulate form (biological uptake, chemical precipitation and adsorption) is a critical process influencing phosphorus concentrations in natural waters (Nedwell *et al.,* 1999; Benitez-Nelson, 2000; Reynolds & Davies, 2001).

To characterize ecological problems, ecological stoichiometry is being used with increasing frequency (Chaneton, *et al.,* 1996). For example, nitrogen to phosphorus (N:P) ratios have been used as diagnostic indicators of nitrogen saturation (Fenn *et al.,*1996) and limitation of vegetative growth by these nutrients (Penning de Vries *et al.,* 1980). Elemental ratios are believed to play an important role for the growth and the competition of algae (Redfield, 1958). More recently, N:P ratios have been applied to identify thresholds of nutrient limitation (Koerselman & Meuleman 1996; Verhoeven, *et al.,*1996). Limiting nutrient conditions may be suggested when the *in situ* concentration of the limiting nutrient is below the half-saturation constant for uptake by phytoplankton (Fisher *et al.*, 1988). Nitrogen was previously thought to be limiting nutrient (Ryther & Dunstan, 1971; Burkholder *et al.,* 1994; and phosphorus also (Piriou & Menesguen, 1992). But Smith (1984) argued that considering single nutrient as limiting nutrient is an unacceptable oversimplification. The N:Si:P atomic ratio in an estuarine environment establish which is the limiting nutrient for the primary production and what is the productivity that will be supported in the estuary. These define six different areas, each characterized by potentially limiting nutrients in order of priority, when Si:N, N:P and Si:P ratios are calculated and plotted on an XY logarithmic graph (Rocha *et al.,* 2002). The utility of this ratio was held to be in indicating competitive advantage when one of two nutrients became limiting (Mykelstad, 1977; Rhee & Gotham, 1980;Turpin, 1986). Estuaries that received nutrient concentrations with a high N:P coefficient, were limited by the phosphorous, and only those with a low coefficient are limited by the nitrogen (Boynton *et al.*, 1982). Parsons *et al.*, (1984) and Rhee (1978) that it would be more appropriate to place the N:P ratio in an interval of 10:1 to 20:1. In estuaries, phytoplankton nutrient limitations are often complicated by the transitions between N and P limitation, which may occur in both spatial and temporal scales.

The importance of nutrients in controlling primary production was examined in detail by inferring the potential for nutrient limitation from nutrient ratios and concentrations, though this approach provides only a crude index of nutrient limitation. The concentrations of silicate were much higher than those described by Wassmann *et al.*, (1999) for silicate to be a limiting nutrient. Historically also, many rivers had dissolved inorganic silicon (DSi) concentrations well in excess of dissolved inorganic nitrogen (DIN) or dissolved inorganic phosphorus (DIP), contributing to N or P deficiency in river plumes and adjacent coastal waters (Humborg *et al.*, 2000). Average N: P ratios during pre-monsoon, monsoon and post-monsoon were 1.65, 3.79 and 17.12 respectively. Closer to Redfield ratio during post-monsoon suggest that nutrients are not limiting factors for production during this season. This could be the reason for high primary production seen during this season. However lower values during other two seasons indicate the possibility of nitrogen limiting factor since the N: P molar ratios in N-limited phytoplankton populations were found to range from 5.4 to 17 (Menzel & Ryther, 1964). This also is in confirmation with the results of Falkowski *et al.*, (1998) who demonstrated that N, and not P, stimulates primary productivity by nutrient addition bioassays and the distribution of N : P ratios over the major oceanic basins, coastal areas and estuaries.

According to Rhee (1978) and Fuhs, (1958), the cellular N:P ratio would be specific, which would be of great ecological importance in that, in a specific environment, the growth of one species could be limited by one nutrient, while the growth of other species could be regulated by other nutrients. The potency of each limitation could determine the result of the competition, and the interval between the relations could determine the level in which the coexistence is possible. Also the nutrient concentration in the environment does hot have an important effect on photosynthetic parameters on a longer time-scale as the intracellular concentration (Heath et al., 1990). An assessment of the availability of N for phytoplankton uptake and assimilation based on DIN alone is erroneous. DIN:DIP ratios would remain dubious even if the ambient concentrations of bio-available DON were incorporated because many forms of DIN and DON are rapidly recycled and taken up by the microbial community (Glibert, 1982; Tamminen & Irmisch,1996). Considering this, the use of DIN:DIP ratios should be used with caution in ecosystem models of other dynamic, density stratified estuaries and coastal ecosystems (Twomey *et al.,* 2005).

During periods of great flux, the concentrations of all nutrients were very high, resulting in low ratio. But the higher ratio during post-monsoon (peak period for primary production) indicated the chances for rapid removal of DIP by some mechanisms like adsorption and sedimentation and also the absence of accretion of phosphorous from sediments. Dissolved oxygen at levels lower than 2 mg/l in the hypolimnion will generate hypoxia (Malone *et al.*, 1986) and stimulate denitrification (Knowles, 1979). Since the bottom water is rich in DO during this period, there is no chance of anoxic conditions. . This also suggests that mechanisms such as denitrification processes, deposits of nitrogen particulates that rapidly removing DIN in the water column are not taking place. There is chance for rapid reduction of phosphorus during flocculation of Fe, Mn;, Al, organic carbon and humic substances as salinity increases from 0 to 15-20 ppt (Sholkovitz, 1976). Phosphorus is also readily adsorbed onto the surface of sediments and lost from the water column as sediments get deposited (Jitts, 1959). Also an increase in nitrate concentrations in the overlying water signifies higher phosphate binding efficiency in sediment (Andersen, 1982).

The dissolved oxygen levels, in general, agree with earlier studies at other parts of the Vembanad Lake (Kumaran & Rao, 1975; Kunjukrishna Pillai *et al.*, 1975; Balakrishnan & Shynamma, 1976; Ramamirtham *et al.*, 1986; Saraladevi & Venugopal, 1989; Sheeba *et al.*, 1996; Selvaraj *et al.*, 2003). Similar trends were also reported from different estuaries of India (e.g. Qasim and Sen Gupta, (1981) in Mandovi and Zuari estuaries of Goa, Gowda *et al.*, (2002) in Gurupur estuary, Easwari & Ramani Bai (2002) in Adayar estuary and Cooum estuaries).

Comparatively higher oxygen at the surface could be due to the diffusion of oxygen from the atmosphere. Further, the possible organic decay would use oxygen, thus reducing oxygen level in the bottom waters. The lower difference between surface and bottom levels might be because that during the present study, density stratification was not observed even during monsoon, as the study area is under complete influence of freshwater, resulting in uniform oxygen concentration.

The comparatively low dissolved oxygen during pre-monsoon was due to the higher salinity and increased temperature, which reduces the solubility. It is evident from their significantly negative relationships. The slight decrease in primary production would also have contributed to the decrease. Higher respiration due to the increase in zooplankton communities during this season, evident by their negative correlation also adds to this. Moreover, during this season; benthos was more and the higher respiration of bottom communities might also contribute to the low dissolved oxygen. The increase of dissolved oxygen in monsoon could be due to the renewal of water because of heavy rainfall and freshwater discharge, which decreases the salinity and temperature. Run off was also positively correlated with dissolved oxygen in the study region. The higher dissolved oxygen during post-monsoon period might be because of the increase in primary production during that time.

Higher oxygen levels in the inner arms could plausibly be the impact of increased mixing in inner arms because of strong currents. The increased primary production in the inner arms of the study region might also be contributing to this.

3.3.1.3 Biological characteristics

Primary production in this study area is in agreement with the previous observations and found to be higher than that reported for many coastal areas and other estuaries in India and world over (Table 3.7). The tri-modal pattern in the present study agree with the findings of Qasim *et al.,* (1969), Qasim (1979) and Gopinathan *et al.,* (1984) in Cochin backwaters. On the other hand, Qasim *et al.,* (1974), Nair *et al.,* (1975) and Gopinathan *et al.,* (1984) reported high production during monsoon and early post-monsoon periods when salinity was low or moderate in Cochin backwaters. Higher production during pre and post-monsoon were also reported in Vellar estuary (Joseph, 1982), Edaiyar- Sanders estuarine system (Nair, 1990) and in Mandovi and Zuari estuarine systems of Goa

(Devassy & Goes, 1989). Hence it is worth mentioning that primary production occurs in small pulses and without seasonal rhythm.

Higher productivity of the inner arms might be the effect of input of nutrients from neighboring paddy/prawn filtration fields. Further it is possible that the effect of turbulence caused by tidal currents in narrow parts might be aiding in the release of nutrients from bottom sediments. From the gross and net productivity data, about 30% of the gross production could be used for respiration, which is comparable to the 20% - 45% obtained by Qasim *et al.,* (1969). Estimated annual respiration was high and ranged between 30 and 56% of annual gross production in Schelde estuary, Belgium (Muylaert *et al.,* 2005).

Nutrients, light, temperature and species composition are the main factors influencing the phytoplankton productivity (Smith, 1980; Eppley *et al.,* 1985). Grazing by zooplankton is also an important factor (Reynolds, 1997). In estuaries, nutrients and light are generally the major factors that regulate primary production (Underwood & Kromkamp, 1999). Light conditions in the water column and the residence time of water masses are also the main factors controlling primary productivity in estuaries.

Since estuaries are generally turbid and nutrient rich, light availability may be the most important factor controlling biomass-specific productivity (Colijn & Ludden, 1983; Cloern, 1996). It was showed variability of *in situ* estimates of daily primary production could largely be attributed to variation in phytoplankton biomass and light availability (Cole & Cloern, 1984; 1987).

Table 3.7 Primary production in different estuaries and coastal areas

Area	Primary production		Reference
Cochin estuary	GP	300 g C/m^2/ year	Qasim *et.al.*, (1969)
	GP	150 to 650 g C/m^2/day	Nair *et al.*, (1975)
	GP	125 mg C/m^3/hr	Kunjukrishna Pillai *et al.*,(1975)
	GP	0.45-1.32 gC/m^3/day	
	NP	0.36-1.05 gC/m^3/day	Selvaraj *et.al.*, (2003)
	GP	52.08-183.33 mg C/m^3/hr	
	NP	26.04-111.46 mg C/m^3/hr	***Present study***
Vellar-Coolrum	GP	11.77-36.99 mg C/m3/hr	Venugopal (1969)
	NP	6.72-26.22 mg C/m^3/hr	
Gurupur estuary	GP	0.43-52.21 mg C/m^3/hr	Gowda *et. al*, (2002)
Mandovi estuary	GP	0.19-67.69 mg C/m^3/hr	Krishna Kumari *et al.,(*2002)
Zuari estuary	GP	0.17-63.24 mg C/m^3/hr	Krishna Kumari *et al.,(*2002)
Hooghly estuary	GP	15.62 - 41.66 mg C/m^3/hr	Lal (1990).
Vellar Estuary	GP	19.51-343.55 mg C/m^3/hr	Vijayalakshmi (1986)
	NP	275.2- 3773.6mgC/m^3/day	
Entire EEZ of India	GP	453.67 mg C/m^2/day	Sarupriya & Bhargava (1993)
off Fort Cochin	GP	430.3-524.0 mg C/m^2/day	Akram *et. al*, (2003)
Off Arabian Sea (SW)	GP	770-1782 mg C/m^2/day	Parsanna Kumar *et al.*, (2001)
Off Bay of Bengal (M)	GP	328–520 mg C/m^2/day	Madhupratap *et al.*, (2003)
Others			
Chesapeake bay, US	GP	347 to 662 g C /m^2/year	Harding *et al.*, (2002).
German Wadden Sea	GP	5 to 2200 mg C/m^2 /day	Tillmann *et al.*, 2000
	GP	124- 176 g C/m^2 /year	
	NP	100 - 138 g C/m^2 /year	
Mediterranean Sea	GP	150-450 mg C/m^2 /day	Moutin & Raimbault (2002)
Changjiang estuary, China	GP	68-1,500 mg C /m^2/day	Hama *et al.*, (1997)
Ría de Vigo, NW Spain	GP	65- 3689 mg C/ m^3/day	Tilstone *et al.*, (1999)
Off the Texas coast	GP	0.017 - 2.07 g C/m^2/ day	Chen *et al.*, (2000)
Ria de Aveiro estuary Portugal.	GP	1.5 - 512.9 mg C/ m^2/ hr	Almeida *et al.*, (2002)
Schelde estuary,Belgium	NP	108 - 294 mg C/ m^2 /year.	Muylaert *et al.*, (2005)
Hudson estuary	GP	0- 18 g C /m^2/ day	Howarth *et al.*, (2000)
Ems Dolland, Europe	GP	70-293 mg C/m^2 /year	Colijn (1983)
Westerschelde, Europe	GP	122-212 mg C/m^2 /year	van Spaendonk *et al.*, (1993)
Ooterschelde, Europe	GP	176-550 mg C/m^2 /year	Wetsteyn & Kromkamp (1994)
Amur Bay, Sea of Japan	GP	2.5–4.0 g C/m^2 day	Zvalinsky *et al.*, (2005)

Primary production was not correlated with salinity, temperature and nutrients. Though being a tropical estuary, light can also be a crucial factor in this estuary during southwest monsoon. Because of this, low production was expected during monsoon. However, in the present study, although lower production was observed during June, it was higher during July. This indicates the possibility that light could be critical only when very cloudy or overcast conditions are present. Also, the fresh water condition prevailed during monsoon also does not seem to affect primary production. This is in agreement with Qasim *et al.,* (1972), who observed that the euryhaline and stenohaline species would occupy the salinity variation and maintain the production rate more or less constant. Due to the high flushing and low residence time, the production was comparatively lower in monsoon even though the nutrients were high. During post-monsoon months the steady light intensity induces effective utilization of nutrients brought by monsoon run off, resulting in an increase in production. Low freshwater discharge increases water residence times and the observed stratification and deepening of the photic zone could also lead to the observed increase in primary production. In addition, the absence of nutrient deficiency (near Redfield ratio), as mentioned earlier also attribute to this high production during post-monsoon. Subsequently, during the higher salinity pre-monsoon period, nutrients are low because of the decrease in run off, which may be the reason for comparatively lesser production during this period. The lower N:P ratio also prove the nitrogen deficiency during this period. The ratio of gross production to respiration was also higher during pre-monsoon due to the increase in zooplankton and higher consumers, thus decreasing the net production.

Limiting nutrient conditions for primary production can occur only when there is no light limitation. This conclusion is however derived from the comparison of actual in-organic nutrient concentrations with threshold values derived from published half-saturation constants for coastal phytoplankton species (Fisher *et al.,* 1988). The impact of nutrients might be underestimated since the phytoplankton in this estuary may be adapted to high nutrient concentrations prevailing most of the year and probably need higher nutrient concentrations to sustain maximum growth rates (Tilmann *et al.,* 2000). On the other hand instantaneous nutrient recycling must be considered because of the presence of large amount of heterotrophs both in water column and sediments in this estuary. Even at times of low nutrient concentrations in the water column, no distinct depression in production was observed. Under starving nutrient conditions, cells may accumulate storage products and may regulate their cellular/Chlorophyll ratio, resulting in unchanged chlorophyll-specific production rates (Tilmann *et.al.,* 2000). Hence it can be concluded that nutrients, especially nitrogen play a major role in phytoplankton production in this estuary and light limitation is only of minor importance.

Chlorophyll-a, like primary production, is comparable to the earlier reports and relatively higher than other Indian and world estuaries and coastal regions (Table 3.8). Primary production showed significant correlation with chlorophyll-a, which is a best indicator of algal biomass. The lower value of correlation (r= 0 .428) indicates the influence of other factors like grazing, leading to loss of standing crop. Harding *et al.,* (2002) who also got low correlations in Chesapeake Bay, suggested that phytoplankton biomass alone insufficient to explain the observed variability in primary production.

Table 3.8 chlorophyll-a values in different estuaries and coastal areas

Area	Chlorophyll-a (µg/l)	Reference
Cochin estuary	2-21	Nair *et al.*, (1975)
	4.93-8.85	Selvaraj *et al.*, (2003)
	1-34.61	**Present study**
Gurupur estuary	1.69-10.59	Gowda *et al.*, (2002)
Mandovi estuary	0.01-4.43	Krishna Kumari *et al.*, (2002)
Zuari estuary	0.16-3.95	Krishna Kumari *et al.*, (2002)
Vishakapattanam	0.61-51.18	Lal (1990).
Vellar Estuary	2.15-21.3	Vijayalakshmi (1986).
Mahi estuary	2.22 - 8.22	Jiyalal Ram (1991)
Off Arabian Sea (SW)	0.26-0.6	Parsanna Kumar *et al.*, (2001)
Off Bay of Bengal(M)	0.06–0.28	Madhupratap *et al.*, (2003)
Dutch estuaries	<1 - >20	Kromkamp & Peene (1995)
South San Francisco Bay	1-70	Cloern (1996)
Ria de Aveiro estuary, Portugal	0.9-33.5	Almeida *et al.*, (2002)

Zooplankton density appeared to be controlled by the change in the salinity brought out by the variation in the river discharge. As the seawater intrusion is more during pre-monsoon period, many marine forms are also brought into the estuary along with the seawater, enriching the density (Rao *et al.*, 1975). During monsoon, due to fresh water influx, the tidal force is reduced and thus the seawater is restricted to mouth of the estuary. With this drastic change in the environmental conditions, the picture of abundance reversed totally (Madhupratap, 1978) the marine forms would disappear or would be restricted to the mouth region. Only the fresh water forms that can tolerate low salinity would prevail. During post-monsoon, when the fresh water influx decreases and salinity starts to increase, the organisms get repopulated. Favourable food supply due to increase in primary production also would have helped the repopulation (Silas & Pillai, 1975). In the study area, the contribution of copepods to the total zooplankton during post-monsoon, pre-monsoon and monsoon were 68%, 79% and 49%, respectively. Similar to this, Nair & Tranter (1971) observed that in Vembanad Lake, copepods dominated the plankton community during pre-monsoon and post-monsoon (75%-95%) and its contribution decreased during monsoon. Correlation analysis showed that zooplankton density was positively correlated with salinity, and temperature and negatively with the river runoff, as evident from the distribution pattern. Kunjukrishna Pillai *et al.,* (1975) suggested that the correlation between zooplankton and temperature could be spurious because the partial correlation coefficient of temperature on salinity is not significant and that there existed a significant correlation between salinity and temperature. Temperature fluctuations are not very significantly influence zooplankton in this estuary (Madhupratap & Haridas, 1975). It was also negatively correlated with the turbidity. Significant variation between stations was not noticed from ANOVA, possibly because the study region was confined to a small area.

Herbivory is generally more prevalent in aquatic than in terrestrial ecosystems (Cyr & Pace, 1993), the production of herbivore biomass on average three times higher in aquatic than in terrestrial ecosystems for a given value of primary production thereby turning over and transferring carbon to higher trophic levels only slightly faster than they do in terrestrial ecosystems. However the grazing effects of dominant zooplankton species never exceed the daily phytoplankton production in the estuary and a large surplus of basic food is available in the Lake (Qasim *et al.*, 1969). Changes in production and composition of aquatic plants affected the productivity of fisheries within the system and the distribution patterns of some fish species in the estuary (Bennett & Moyle, 1996; Kimmerer & Orsi, 1996; Jassby *et al.*, 2002).

Based on present observations on primary production, an attempt has been made here to estimate the fish production potential. The wet weight production in the study region comes to be about 22030 tonnes by using a conversion factor 7.41 (Vinagradov, 1953), which was used in Vembanad Lake by Madhupratap *et.al.*, (1977). A rate of about 0.2% - 0.4 % of the primary production could be taken as the fish production (Parsons *et al.*, 1977; Ware, 2000). According to Neilson & Jensen (1957), the landings of commercial fish catch in intensely exploited waters are about 0.4% of the organic matter produced by phytoplankton. Qasim *et al.*, (1978) suggested that 1% could be taken to get fish production in coastal waters. By taking a conversion rate of 0.6% and the fishery potential of the study area works out to be about 132 tonnes. However, as the study region is a part of large aquatic system, the boundaries are arbitrary and final conclusion on these lines must take the entire area into consideration.

Estuaries generally are considered to be eutrophic when their annual rate of GPP exceeds 500 g C/m^2/y (Nixon 1995; NRC, 2000), which corresponds to a daily rate of approximately 2–3 g C/m^2/day on average during the active growing season. Also the trophic status of the estuary can be classified according to chlorophyll-a and the PDS index (Carlson, 1977). From both points of view, the present study region is not eutrophic. However these comparisons do not take benthic primary production in to consideration, which accounts for about 1.4 g C/m^2/day, almost equal to the planktonic production (Sreekumar & Joseph, 1997). Moreover calculations are based exclusively on the surface layer, which may be completely different if only water column production data is considered. A proper choice must be made according to the trophic relationship addressed.

3.3.2 Tidal observations

Estuarine dynamics depend entirely on the tides. Even the mean circulation in estuaries cannot be understood without consideration this periodic phenomenon. Since the tides in this estuary are of mixed semi-diurnal type (chapter 2), hourly observations covering one tidal cycle (13-hour) were carried out. Because of the heavy monsoon showers and the associated flushing, the study region becomes a tidal extension of the adjoining rivers and the tides have no practical significance during monsoon season, observations were carried out during other two seasons only. Two stations in the inner arm, on either side of the main island, Panangad, were selected for tidal observations because of the absence of basic knowledge about circulation in these inner areas (chapter 1). These two stations have distinctly different hydrographical characteristics as evident from the results of monthly observations discussed above.

The dominant influence on the tides in estuaries is the change of water depth and it was lower in the study region because of the micro tidal nature and the distance from the bar mouth. Comparatively higher tidal range was observed during the post-monsoon than pre-monsoon, indicating the influence of the freshwater flow. Reduction in flood current speed was observed during post monsoon, compared to pre-monsoon as a result of higher run off. Tidal asymmetry of weaker longer duration of ebb and stronger shorter duration flood was occurred generally.

In general, it was seen that there is a lag between high tide and slack water, which is typical of mixed semidiurnal tide. The timing of higher magnitudes of currents, in general, agrees with the observation near the mouth of this estuary (Joseph & Kurup, 1987) where higher magnitudes of currents coincided with mid tide or even after that. The reversal from flood to ebb almost coincided with slack water. During pre-monsoon, net flow was upstream, the stronger currents being at Station 1. At Station 5, weak net ebb was seen and the weak flood reversed to ebb at the bottom at Station 1. Ebb velocities are higher than flood. . Current velocities did not show larger dependence on the tidal range, although lower velocities were sometimes associated with lower tidal ranges. Typically wide, station 1 showed less current than the narrow inner arms, with the slowest currents being along the banks, and the sharp bends produced stronger flows on the outer bank.

The lagging of salinity maxima with high tide at the station 1 during pre-monsoon is typical of mixed tide having components of both progressive and standing waves. The tidal rhythm of salinity (unlike the lag during pre-monsoon) during post-monsoon indicates the predominance of progressive type component of tide. This indicates the changing nature of the tidal components with seasons in the estuary. Salinity variation followed tidal and seasonal rhythm, in general, with high values during the high tide and the vertical stratification during post-monsoon with the rising tide.

The absence of stratification during tidal observations of pre-monsoon indicates the well-mixed condition prevailed in the estuary during the season. But during post-monsoon observations at station 1, the estuary became stratified at the end of flood, though it was vertically homogeneous during rising tide. This kind of variable stratification during different phases of tides can be possible if the saline water intrudes during flood through the bottom and this saline water is pushed back during ebb due to the effect of fresh water and then the entire water column becomes of lower in salinity. While freshwater discharge is very high during southwest monsoon, fresh water input continues during post-monsoon season also with lesser intensity. In this process, as the salt wedge that occurs nearer to the mouth breaks down, a diffuse wedge forms and moves upstream and downstream with flood and ebb, respectively. Thus at this area during flood vertical stratification and during ebb non-stratified low saline condition are seen. From this salinity pattern, it can be concluded that this area confirms with the general pattern of well-mixed condition during pre-monsoon and partially mixed condition during post-monsoon seasons. Similar tidal variation in salinity at different seasons were reported by Balakrishnan & Shynamma (1976) in Cochin harbour and Sankaranarayanan *et al.,*(1978) in estuarine waters of Goa.

There were diurnal changes in surface temperature in which peaks occurred in the late afternoon and decreasing in the evening hours, probably due to solar irradiance. This has been reported earlier also. Balakrishnan & Shynamma (1976) in Cochin harbour reported a diel variation with layers becoming warmer towards evening during the post-monsoon and during pre-monsoon, thermal stratification were weaker as in the present observations. Temperature followed the same trend as temperature at station 1 during both seasons. During pre-monsoon, stratification was absent, indicating well-mixed conditions. During post-monsoon, because of the restriction in mixing due to stratification, the surface more or less followed the diurnal heating pattern while bottom followed the tidal rhythm. This resulted in large vertical gradient around high tide as mentioned in the case of salinity.

Higher TSS and turbidity coincided with higher current speed, which was observed during monthly analysis, and lacked a clear tidal pattern. Lesht *et al.*, (1980) reported that the concentration was proportional to the wave orbital velocity when the velocity was above a threshold value (approximately 20 cm/s). Wang *et al.*, (2000) related the sediment concentration to the current speed. TSS varied between 20 and 525 mg/l (average of 85 mg/l) with high concentrations around low water and low concentrations around high water in the Ho Bugt estuary (Christiansen *et al.*, 2004), while Wang *et al.*, (2000) found a range between 10 and 35 mg/l (avg. 10 mg/l) in a moderate energetic estuary. But the suspended sediment load generally did not show dependence with the stage of tide and current speed in the study region. The reason for this could be comparatively less sand fraction at station 1. Similar observations are reported by Das *et al.*, (1972) in Combarjua canal.

At station 5, although sand fraction was more, TSS does not seem to be related to current speed. Localized circulation, mentioned earlier, could be keeping the materials suspended, rather continuously. Strong flood currents associated with high turbidity and weak ebb currents with low turbidity in Hawkesbury River, a micro-tidal estuary in Australia due to the large amount of fine-grained sediment available for suspension (Hughes *et al.*, 1998). But there were not large variations in turbidity in the study region. This may be because of the absence of strong currents (critical erosion velocity), which is needed to churn up the bottom sediments and to keep it in suspension. Although critical erosion velocity, which was calculated to be around 70 cm/sec (Wolanski *et al.*, 1995; Chen *et al.*, 2005), may vary with estuaries, the tidal currents in the study region was only once reached that level at station 1 during pre-monsoon. During that time, there were significant variations in TSS and turbidity and also these values were higher during higher current speed. The differences in suspended matter concentration between ebb and food tide result, in the first place, from the differences in the current velocity and turbulence patterns (Winterwerp *et al.*, 2001). Tidal currents introduced major variations in suspended sediment concentrations in the water column over the tidal cycle in the Fitzroy estuary, Australia (Margvelashvili *et al.*, 2003).

Clear tidal rhythm was not seen for all nutrients. One possibility of decrease of nutrients in the early afternoon could be a result of utilization for primary production. Higher primary production during post-monsoon is in confirmation with the seasonal trends observed during the monthly collections. Balakrishnan & Shynamma (1976) also reported nonexistence of direct relationship of phosphate with the time of day and the stage of tide during different seasons in Cochin harbour region. Tidal and meteorological induced variations in nutrient dynamics are important at all depth intervals in the Ho Bugt estuary with a ±20% variation in nitrate concentrations due to sedimentation/re suspension effects during the tidal cycle (Christiansen *et al.*, 2004).

Dissolved oxygen followed diurnal rhythm than the tidal variations. Oxygen concentrations usually exhibit a characteristic diurnal pattern with concentrations increasing from morning into mid afternoon as photosynthesis outstrips respiration. Declining oxygen concentrations occur during the late afternoon or evening as photosynthetic rate declines and throughout the night when photosynthesis does not occur. Balakrishnan & Shynamma (1976) reported fluctuating dissolved oxygen values with low values during daybreak and gradual increase as day advances, in Cochin harbour. In estuarine waters of Goa, Sankaranarayanan *et al.,(*1978) found low dissolved oxygen during high tide and a progressive increase as flood begins. The higher difference in surface and bottom values of dissolved oxygen during post-monsoon might be because of the limited vertical exchange due to stratification. Higher values during post-monsoon also confirm the general seasonal trends in dissolved oxygen distribution.

Qasim *et al.,* (1969) reported tidal variation in primary production in this estuary. In Ria de Aveiro estuary, Portugal, higher primary production was generally observed at low tide (Almeida *et al.,* 2002).

The distinct variations between the stations in the inner arm of the study region were because of the geomorphology of the locations, as established by the tidal cycle observations. This is due to the peculiarity of the location of the station, where depth variation is seen across the width of the estuary. On one end the depth was more than 5m, whereas on other side it was about 2m. This generates chances for the formation of local eddies. Circular water movements were observed on the outer side of the curve. The side is deeper, as a result of the tendency of the flow to scour and deepen the outer side of any curve. Moreover, the curve near the station itself can generate eddies. Hence the general trends in the tidal variations at the station 1, in the main arm are not applicable to the station in the inner arm.

Salinity at station 5 was very low during the pre-monsoon observation compared to the station 1 occupied few days before, during this season. This was because of the pre-monsoon showers around the time of these observations, which increased the run off, reducing the salinity. Run off data from the available three rivers showed about two-fold increase in discharge during 10 days prior to the observations. The average discharge from Muvattupuzha, Meenachil and Manimala rivers were 39.6, 8 and 8.8 m^3 for 10 days before observations at Station 1 for the pre-monsoon and for Station 5, these were 78.4, 15.7 and 10.9 m^3 respectively (Central Water Commission).

Salinity stratification was noticed, unlike station 1 during the pre-monsoon season. The fluctuations in salinity could be plausibly because of the trapping of high salinity water brought during flood in the deeper part and its subsequent release by the eddies mentioned earlier. Temperature also showed vertical stratification. Higher dissolved oxygen and primary production was noticed during this period. These may be indicative of the pulses in production suggested by Qasim *et al.,* (1969). Salinity was very low or near freshwater conditions prevailed at station 5 during post-monsoon observations. . This was also the result of very heavy rains for a few days before these observations. Hence partially mixed condition was not observed, as expected to occur during this season. Though the post-monsoon season is characterized by higher production as described earlier, the lower values in the present observations could be the result of rainy conditions around the day of observation and the associated cloudiness. Thus it can be concluded that the estuary is subjected to local effects. This can change the general seasonal pattern in the estuary at least for short durations, as indicated by the above tidal analysis.

Summary and Conclusion

From the monthly observations in the study region, it was seen that the hydrography of this estuary is under the profound influence of the southwest monsoon and the seasonal variations were very prominent. The hydrodynamics of this estuary is very complex and unique. The hydrographical conditions of the Cochin backwaters were greatly influenced by seawater intrusion and influx of river water as indicated by the distribution of temperature and salinity. From the observed salinity pattern, it can be concluded in general that during southwest monsoon this part is in the tidal section of the rivers. It gets transformed subsequently to a partially mixed estuary. During pre-monsoon, when river run off is least, this part become well mixed. There was a significant increase in nutrients and suspended matter in the study region with the onset of monsoon. The hydrographical parameters showed spatial variation attributed to the complex circulation patterns because of the geomorphology. Stoichiometric analysis of the major nutrients showed the possibility of nitrogen limitation during pre-monsoon and monsoon seasons. Light limitation is only of minor importance in this estuary and primary production was found to be higher than that reported for many coastal areas and other estuaries in India, with a sufficient stock of standing crop. Though post-monsoon was found to be higher in production and zooplankton also showed a clear seasonal trend. The grazing effects of zooplankton species never exceed the daily production in the estuary and a large surplus of basic food is available in the estuary for transfer to higher trophic levels. The study area also showed a higher fishery potential.

Tidal cycle observations provided information on the variation of hydrographical parameters in relation to tides; the relative importance of tides was evident from the seasonal changes. Natural factors including meteorological variations, diel effects and tidal variations affect the hydrodynamics of the estuary. There was little influence of the tidal cycle on physical parameters such as stratification and water residence time when freshwater discharge was low. But when discharge is high, the tidal cycle has a pronounced effect on physical circulation and therefore on GPP. Tidal asymmetry of weaker longer duration of ebb and stronger shorter duration flood was occurred generally. The tidal rhythm of salinity during post-monsoon indicated the predominance of progressive type component of tide and the tidal lag during pre-monsoon was typical of mixed tide having components of both progressive and standing waves. Hence the changing nature of the tidal components with seasons can be observed by the tidal observations. Dissolved oxygen followed diurnal rhythm than the tidal variations and clear tidal rhythm was not seen for all nutrients. The distinct variations between the two stations in the inner because of the geomorphology of the locations were established by the tidal cycle observations. This is due to the peculiarity of the location of the station, where depth variation is seen across the width of the estuary. Another peculiar behaviour of the study region, *i.e.* the effect of local rains and runoffs, was also established with the tidal cycle observations. This can change the general seasonal pattern in the estuary at least for short durations, as indicated by the above tidal analysis. During the present observations, the entire tidal cycle could not be covered because of the mixed nature of the tides in the study region. Hence, a detailed work covering longer duration would give a complete picture of the complex dynamics of the estuary.

Since the sediments conserve important environmental information, their analysis will give detailed information on interacting hydrodynamical, biological and geochemical processes in the estuary. Next chapter is an attempt to analyse the geochemistry of the surficial sediments, thereby to find the major biogeochemical processes operating in this estuary.

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Chapter 4

GEOCHEMISTRY

4.1 Introduction

Aquatic sediments are principally derived from weathering processes, with major transportation from terrestrial sources under high runoff. Land use, geology and topography of the catchment determines the erosion and transport processes. In addition, discharges from urban, industrial and mining activities are potential sources of particulates. Anthropogenic contaminants, including metals, organics and nutrient elements are associated with particulate and dissolved inputs to natural waters. Typically, sediments are characterised as coarse material, clay/silt and sand fractions, higher fractions may consist of shells, rocks, wood, and other detrital materials, and are usually not a source of bioavailable contaminants (Mudroch *et al.*, 1997). Sediment is transported as suspended load (silt and clay held in the water column above the bottom by turbulence), bed load (sand, gravel and coarser material moved by rolling, sliding, and bouncing along the streambed), and dissolved load (products of chemical weathering of rocks carried in solution). As earth material, sediment is obviously an important material affecting the physical, chemical and biological conditions of the environment.

Sediments act as potential sink for many hazardous chemicals, which once adsorbed or incorporated into the particulate matter become deposited on the bottom, from which the solid/liquid equilibrium generally results in an enrichment in toxic elements and compounds in interstitial waters (Salomons *et al.*, 1987; Tessier & Campbell, 1987). Since sediment quality assessment is considerably more complex than water quality assessment because of the many site-specific parameters, detailed information on interacting hydromechanical, biological and geochemical processes is essential, which are not a factor for water (Förstner, 2004). The transport properties and various chemical properties of the sediment in transport are strongly related to the sediment mineralogy and particle size; which are influenced by numerous factors including the source of the sediment and the flow rate in the sediment.

There is little export of fluvial material in estuaries, but on the other hand most of the materials delivered by rivers to the ocean are trapped in estuaries (Chen & Windom, 1997). According to Barnes (1984), estuaries are the regions where fine sediments accumulate and for this reason, most of these tend to be muddy. The biogeochemistry of estuaries is strongly influenced by temporally variable events occurring at their riverine and marine end members, as well as those impinging on the estuarine water column and sediments. Estuarine responses to temporal variability are complex and often difficult to understand. As mentioned above, estuarine bed sediments act as a net trap for sediments and associated trace metals from land-based sources over the long term (Mulholland & Olsen, 1992; Duursma, 1995). However, over the short term, ebb advection of freshwater and saltwater intrusion during flood tides dramatically influence the master variables of the water column, such as suspended particulate matter and redox potential (Harbison 1986; Montani *et al.,* 1998), and bottom sediment dynamics (Vale *et al.,* 1993). The extent of such variations depends on spring and neap tide state, or tidal amplitude (Allen *et al.,* 1980; Uncles & Stephens, 1996).

Sediments conserve important environmental information (VonGunten *et al.*, 1997), and are increasingly recognised as both a carrier and a possible source of contaminants in aquatic systems (Förstner & Salomons, 1991; Tessier *et al.*, 1994). Estuaries are particularly vulnerable such to input changes because of the limited water exchange (Bartoli *et al.*, 1996; Kamer *et al.*, 2001) and sediments are effectively trapped by estuarine circulation processes, but may be eroded, transported; and deposited many times before they accumulate below the actively reworked surface layer (Sanford, 1992; Geyer, 1993; Dellapenna *et al.*, 1998; Schaffner *et al.*, 2001). Mineralogical studies of the estuarine sediments help to model the sources, transport paths, and depositional sites of argillaceous sediments (Ramanathan *et al.*, 1993).

This chapter describes the spatial and temporal variability of the geochemical parameters in the surficial sediments of the study region along with their mineral and textural characteristics. The space–time distribution and variations of benthic density is also analysed. Since sediments are highly complex mixture of discrete minerals and organic compounds to which a number of ions are differently attached, their complete analysis is impractical. Hence the data on sediments are subdivided into 5 major groups according to chemical classification scheme by Kemp *et al.*, (1976). They are major elements, carbonate elements, nutrient elements, mobile elements and trace elements. Major elements (Si, Al, K, Na and Mg) are conservative and make up the bulk (about 70%) of the sediment matrix and are unlikely to be affected by diagenesis or eutrophication. In fact, they reflect the major mineralogical species derived from terrigenous sources (Kemp *et al.*, 1976). Carbonate elements (Ca, Mg and CO_3-C) are the second largest group in sediments, constituting about 15 % of the weight. Organic carbon, nitrogen and phosphorus are the nutrient elements essential to the biota, accounting approximately 5 % of the sediment composition. Iron, sulphur and manganese are the mobile elements and make up about 10 % of the total sediment weight. Mobile elements can easily change redox status and solubility, hence precipitating or dissolving when the physico-chemical conditions at the water-sediment interface change. Trace metals (Cd, Pb, Cu, Cr, Co, Ni, Hg, Zn) are the smallest group constituting less than 0.1 % of the sediments. But they are the active agents in the geochemical processes and hence given special contemplation in this study.

4.2 Results

The different parameters in the surficial sediments of the study region are subdivided in to 5 major groups and their monthly and spatial variations are given below. The monthly data of total carbon, nitrogen and sulphur are presented in Appendix D. The monthly data on heavy metal concentration at different stations are tabulated in Appendix E. The pre-monsoon and monsoon sampling of station 2 was done within the regularly dredged National Waterway and the post-monsoon samples were taken from outside the waterway. The wide variation in post-monsoon data from the other seasons is due to this.

4.2.1 Sediment Texture

Textural characteristics of the sediments are given in Table 4.1 and in Fig. 4.1. The substratum generally represented a combination of clay, sand and silts. The composition of the sediment showed distinct spatial variation, but the seasonal variations were minimal. Coarser fractions were found at stations 1,2 and 5 while the stations 7, 8 and 10 were dominated by finer fractions. By applying Folk (1974) classification, sediments at stations 2 and 5 were sandy, where as it was muddy at stations 8 and 10. Sandy mud nature was seen at station 1 and sandy silt at station 7.

Table 4.1 Textural characteristics of the surficial sediments

Stations	Sand (%)	Silt (%)	Clay (%)	Nature*
1	82.5	7.3	10.2	Sandy Mud
2	91.0	1.6	7.4	Sand
5	97.4	0.7	1.9	Sand
7	27.4	51.0	21.6	Sandy silt
8	0.4	67.2	32.4	Mud
10	0.0	54.0	46.0	Mud

* Folk, 1974

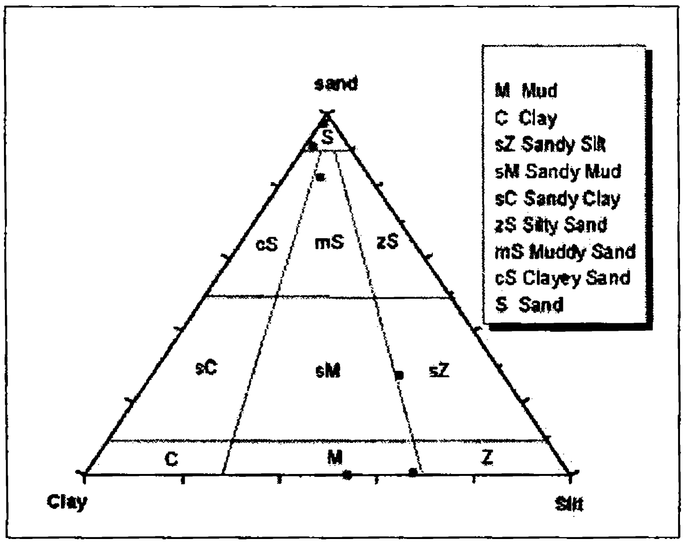

Figure 4.1 Ternary diagram showing the grain size distribution in the surficial sediments Sediment nomenclature after (Folk, 1974)

4.2.2 Mineralogy

X-ray diffraction (XRD) is an important tool in mineralogy for identifying, quantifying and characterising minerals in complex mineral assemblages (Moore & Reynolds, 1997). Powder X-ray diffraction analyses of the representative sediments of the study region showed that illite, kaolinite + chlorite, smectite and gibbsite were the dominant clay mineral components. Quartz and feldspar were the dominant non-clay minerals (Table 4.2 and Fig. 4.2). Quartz and smectite were present at all stations. Stations 2 and 5 (sandy nature) were deficient in clay minerals whereas station 7 and 10 (muddy nature) were characterized by the presence of higher number of clay minerals.

Table 4.2 Major minerals present in the surficial sediments

Stations	Clay Minerals				Non-Clay Minerals	
	Smectite	Illite	Kaolinite + Chlorite	Gibbsite	Quartz	Feldspar
1	√	√	√	-	√	√
2	-	-	-	-	√	√
5	√	-	-	-	√	-
7	√	√	√	√	√	√
8	√	-	√	-	√	√
10	√	√	√	-	√	√

4.2.3 Major elements and Carbonate elements

Since the major elements are conservative in nature and unlikely to be affected by diagenesis, only the representative samples were analysed to access their background levels. The composition of Al and Ca in the study region during pre-monsoon is presented in table 4.3 and fig. 4.3. Aluminium and Calcium content varied considerably between the stations and the range was from 0.18 to 8.22 % and 0.036 to 0.92 % of dry weight respectively. In both cases, higher concentration was found at station 10 and lower at station 2.

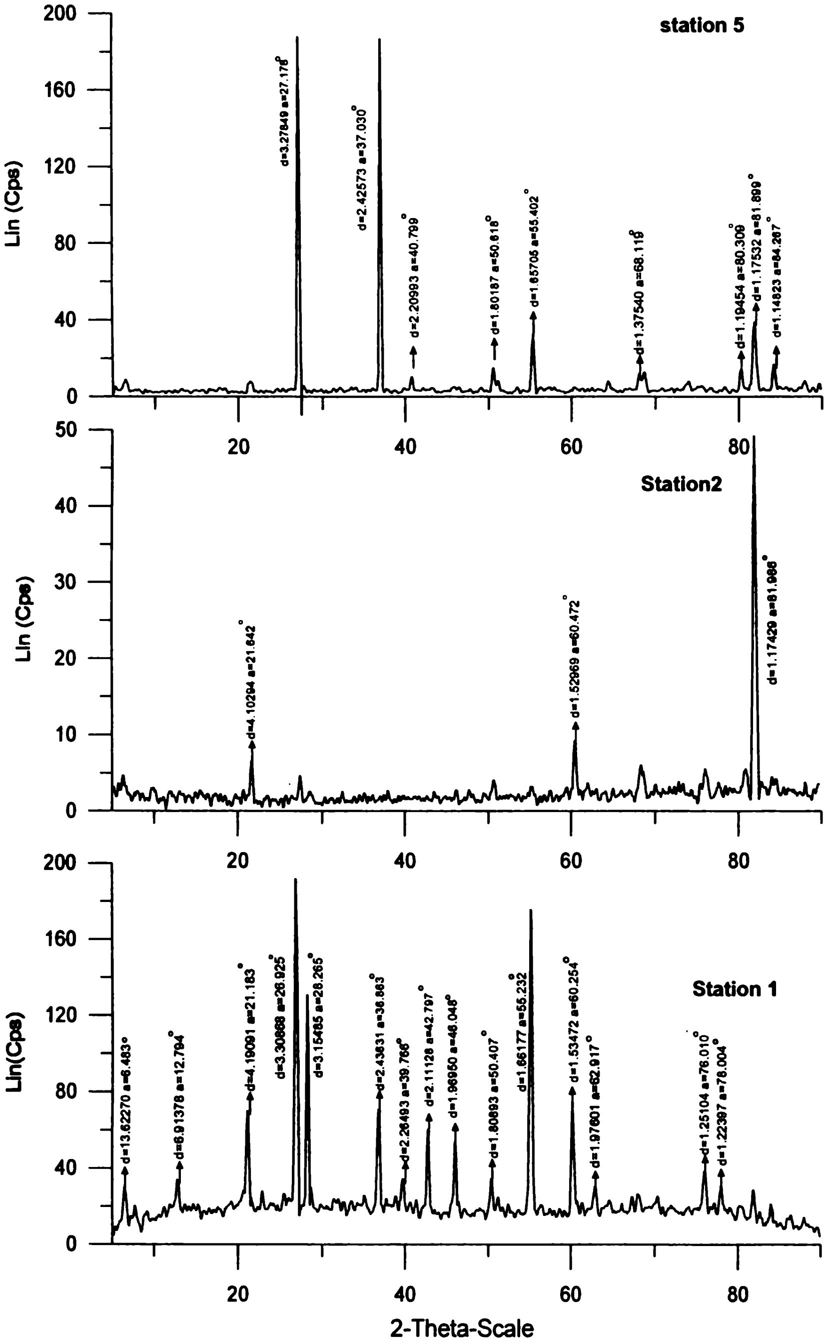

Figure 4. 2 XRD spectra of the sediments in the study region

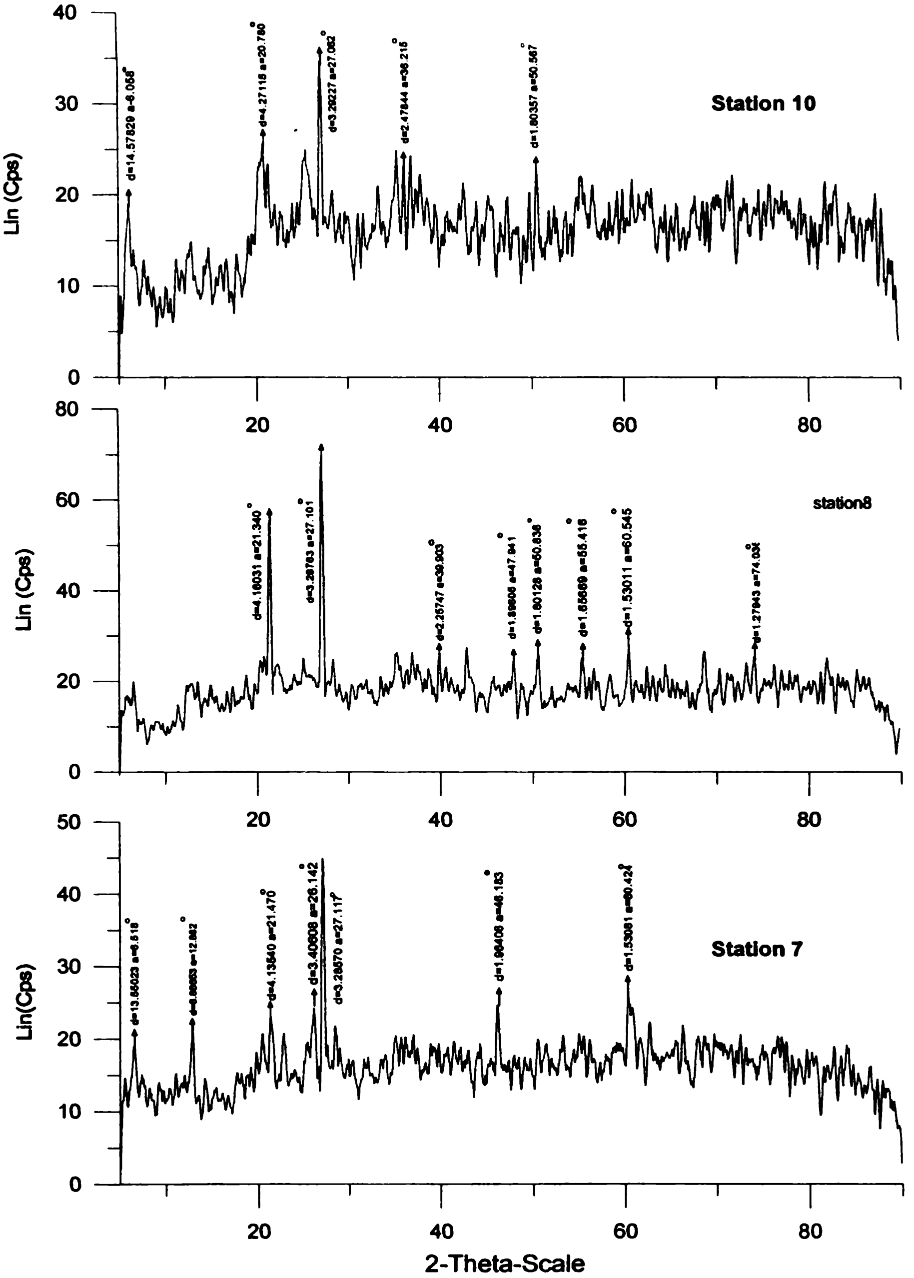

Figure 4. 2 (Contd.)

Seasonal variations of Carbon and Magnesium in the study region are presented in Table 4.4 and in Fig. 4.4. Total carbon in the study region showed a wide variation, ranging from 0.06 % dry weight at station 2 during July to 4.05 % dry weight at station 8 during September. On seasonal basis, it ranged from 0.08 to 3.7 % dry weight in pre-monsoon. During monsoon, it showed an increase and the range was from 0.06 to 4.05 % dry weight. It ranged between 0.06 and 3.77 % dry weight during post-monsoon. ANOVA (Table 4.10) established significantly higher and lower levels at stations 8 and 2 respectively, but monthly variations were insignificant in the study region. Magnesium in the study region was highest (1.36 %) during August at station 10 and lowest (0.015 %) at station 5 during July. Magnesium ranged between 0.049 and 1.33 % dry weight during pre-monsoon and between 0.015 and 1.36 % dry weight during monsoon. During post-monsoon Mg ranged from 0.03 to 1.27 % dry weight. ANOVA (Table 4.10) showed that significantly higher values were observed at station 10 and lower values at stations 2 and 5. Like carbon, monthly variations were not statistically significant.

Table 4. 3 Aluminium and Calcium compositions in the study region.

Stations	Al (%)	Ca (%)
1	2.118	0.143
2	0.179	0.036
5	0.291	0.056
7	5.642	0.287
8	7.078	0.366
10	8.221	0.915

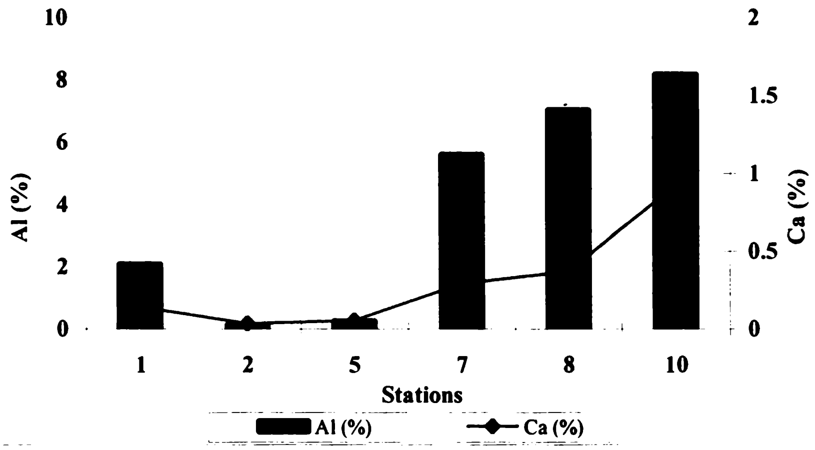

Figure 4. 3 Compositions of Aluminium and Calcium in the study region

Table 4. 4 Seasonal variations of Carbon and Magnesium in the study region.

Season	Stations	Carbon (%)	Magnesium (%)
Pre-monsoon	1	0.68 ± 0.10	0.42 ± 0.047
	2	0.10 ± 0.03	0.05 ± 0.007
	5	0.21 ± 0.17	0.11 ± 0.056
	7	2.65 ± 0.83	0.85 ± 0.35
	8	3.61 ± 0.08	0.79 ± 0.091
	10	2.83 ± 0.91	1.03 ± 0.083
Monsoon	1	0.69 ± 0.05	0.40 ± 0.03
	2	0.07 ± 0.01	0.03 ± 0.005
	5	0.09 ± 0.02	0.03 ± 0.01
	7	2.68 ± 0.20	0.74 ± 0.094
	8	3.86 ± 0.13	0.78 ± 0.047
	10	3.50 ± 0.14	1.34 ± 0.019
Post-monsoon	1	0.81 ± 0.24	0.39 ± 0.07
	2	2.53 ± 1.87	0.33 ± 0.25
	5	0.10 ± 0.04	0.03 ± 0.001
	7	2.35 ± 0.21	0.64 ± 0.053
	8	3.74 ± 0.03	0.74 ± 0.057
	10	3.37 ± 0.12	1.28 ± 0.036

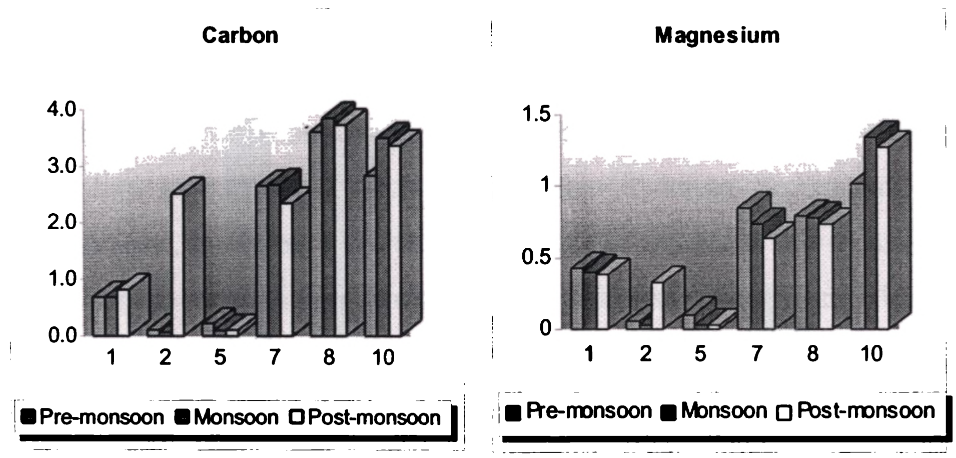

Figure 4. 4 Seasonal variations of Carbon and Magnesium

4.2.4 Nutrient elements

Organic carbon constituted about 60 % of total carbon in carbon rich sediments, where as it was about 80-95 % for low carbon sediments (Table 4.5 and Fig. 4.5). The percentage of organic carbon to total carbon did not show any seasonal trend. Organic carbon showed a clear spatial variation and it was higher at stations 7, 8 and 10 and very low at stations 1,2 and 5. Total nitrogen in the sediment ranged from 0.04 to 0.42 % dry weight during pre-monsoon and 0.02 to 0.46 % dry weight during monsoon. It ranged between 0 and 0.55 % dry weight during post-monsoon. Highest concentration was found at station 10 during December and lowest at stations 2 and 5 during October and November respectively. ANOVA (Table 4.10) shown that total nitrogen was significantly lower at station 5 and higher at station 10. Monthly variations were not statistically significant. Phosphorus ranged between 0.03 and 0.19 % dry weight during pre-monsoon and between 0.04 and 0.28 % dry weight during monsoon. The post-monsoon range was from 0.04 to 0.23 % dry weight. Higher levels were found at station 10 and lower at stations 2 and 5 (Fig. 4.6).

Table 4.5 Seasonal variations of TOC (in weight %) in the study region
(% of TOC to total carbon content is shown in parenthesis)

Stations	Pre-monsoon	Monsoon	Post-monsoon
1	0.54 (94.7)	0.5 (80.6)	0.42 (76.4)
2	0.09 (64.3)	0.06 (96.3)	3.57 (86.6)
5	0.29 (70.7)	0.07 (87.5)	0.06 (66.7)
7	1.72 (97.7)	1.86 (69.4)	1.62 (69.2)
8	2.51 (70.1)	2.47 (64.5)	2.36 (63.4)
10	2 (61.9)	1.98 (54.8)	1.99 (59.8)

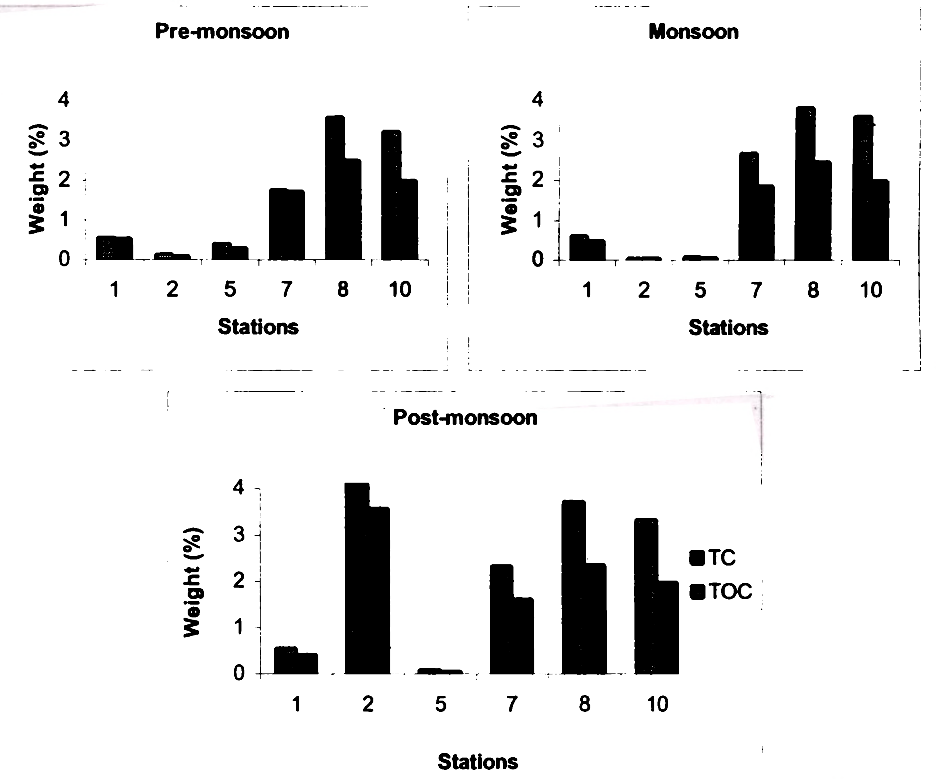

Figure 4.5 Seasonal variations of total carbon and organic carbon

Table 4. 6 Seasonal variations of Nitrogen and Phosphorus

Season	Stations	Nitrogen (%)	Phosphorus (%)
Pre-monsoon	1	0.12 ± 0.02	0.08 ± 0.02
	2	0.06 ± 0.03	0.03 ± 0.00
	5	0.08 ± 0.02	0.04 ± 0.01
	7	0.32 ± 0.10	0.18 ± 0.05
	8	0.33 ± 0.02	0.17 ± 0.04
	10	0.27 ± 0.18	0.19 ± 0.06
Monsoon	1	0.10 ± 0.06	0.08 ± 0.03
	2	0.09 ± 0.04	0.04 ± 0.00
	5	0.09 ± 0.01	0.08 ± 0.03
	7	0.29 ± 0.05	0.19 ± 0.08
	8	0.35 ± 0.04	0.19 ± 0.03
	10	0.42 ± 0.03	0.28 ± 0.05
Post-monsoon	1	0.15 ± 0.09	0.09 ± 0.04
	2	0.26 ± 0.24	0.09 ± 0.05
	5	0.03 ± 0.05	0.10 ± 0.04
	7	0.30 ± 0.06	0.18 ± 0.08
	8	0.36 ± 0.08	0.13 ± 0.01
	10	0.46 ± 0.09	0.23 ± 0.05

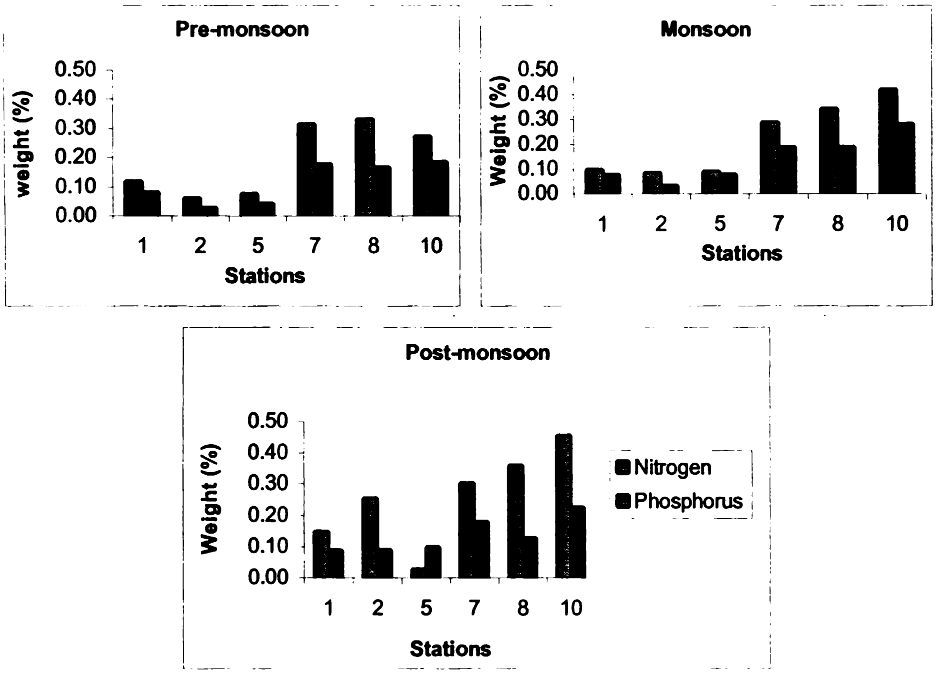

Figure 4.6 Seasonal variations of nitrogen and phosphorus

4.2.5 Mobile elements

Iron ranged between 0.28 and 7.79 % dry weight during pre-monsoon and between 0.21 and 7.74 % dry weight (Table 4.7). During post-monsoon, the range was from 0.28 to 8.27 % dry weight. Sulphur was in the range of 0.02 to 1.32 % dry weight during pre-monsoon and between 0 and 1.63 % dry weight during monsoon. Post-monsoon range was from 0.01 to 1.75 % dry weight. Manganese ranged between 9.99 and 352.72 µg/g during pre-monsoon and between 7.26 and 361.65 µg/g during monsoon. Mn ranged from 15.74 to 348.80 µg/g during post-monsoon. Monthly variations of all the mobile elements were not statistically significant (ANOVA, Table 4.10). But significant spatial variations were observed with higher values at stations 7, 8, and 10 and lower values at stations 1, 2 and 5.

Table 4. 7 Seasonal variations of mobile elements in the study region

Season	Stations	Fe (%)	Sulphur (%)	Mn (µg/g)
Pre-monsoon	1	2.40 ± 0.23	0.27 ± 0.01	91.12 ± 5.69
	2	0.45 ± 0.15	0.04 ± 0.03	12.44 ± 2.92
	5	0.72 ± 0.39	0.09 ± 0.06	20.71 ± 11.39
	7	4.80 ± 1.08	0.82 ± 0.18	170.50 ± 112.91
	8	7.52 ± 0.12	1.17 ± 0.22	178.95 ± 26.17
	10	5.91 ± 2.17	0.88 ± 0.27	221.68 ± 125.48
Monsoon	1	2.34 ± 0.32	0.60 ± 0.69	91.09 ± 7.46
	2	0.34 ± 0.14	0.02 ± 0.00	9.29 ± 2.87
	5	0.28 ± 0.08	0.08 ± 0.12	13.04 ± 2.90
	7	5.29 ± 0.53	0.79 ± 0.52	127.30 ± 11.16
	8	7.37 ± 0.29	1.04 ± 0.70	174.28 ± 8.43
	10	7.19 ± 0.27	1.13 ± 0.06	316.85 ± 57.23
Post-monsoon	1	2.33 ± 0.52	0.32 ± 0.08	81.10 ± 15.77
	2	2.08 ± 1.15	0.92 ± 0.74	76.83 ± 50.42
	5	0.68 ± 0.65	0.02 ± 0.01	18.62 ± 3.83
	7	5.12 ± 0.996	0.83 ± 0.07	113.66 ± 5.52
	8	6.98 ± 0.21	1.52 ± 0.20	163.77 ± 8.04
	10	7.54 ± 0.79	1.09 ± 0.08	334.12 ± 30.09

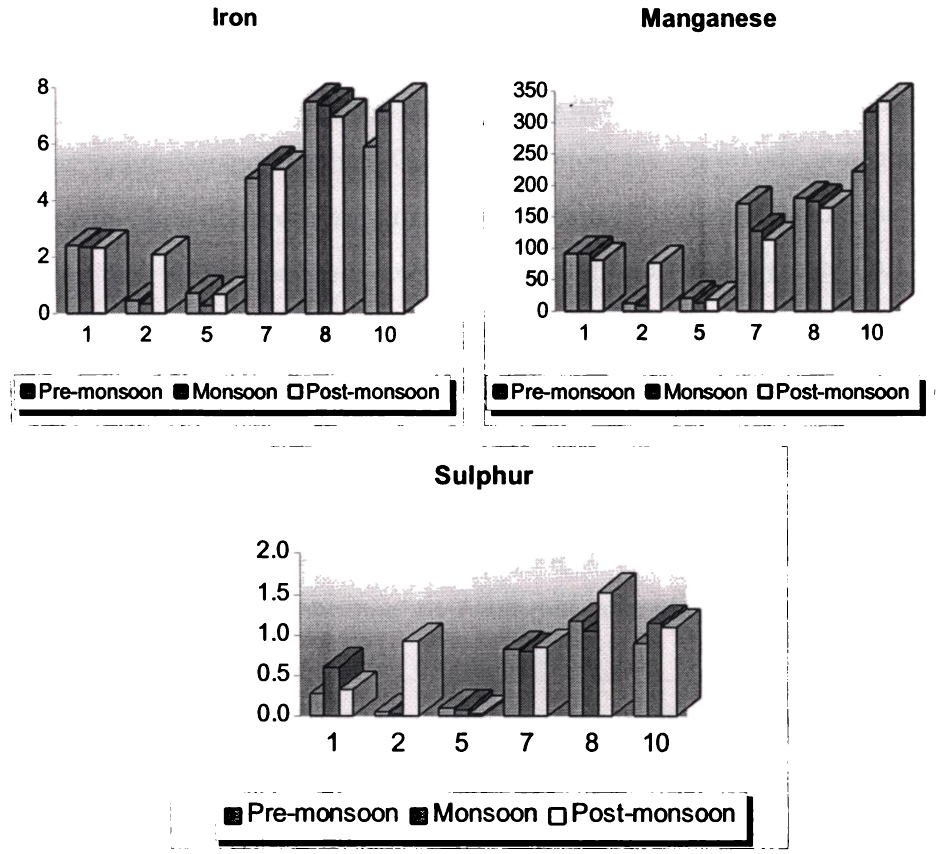

Figure 4. 7 Seasonal variations of mobile elements in the study region

4.2.6 Trace elements

The elements analysed during the present study were Cr, Co, Cu, Pb, Ni and Zn (Table 4.8 and Fig. 4.8). Pre-monsoon values of chromium were in the range from 2.16 to 101.14 µg/g. During monsoon Cr ranged between 0.35 and 102.79 µg/g and from 6.64 to 110.48 µg/g during post-monsoon. Cobalt ranged between 3.07 and 37.77 µg/g during pre-monsoon and from 3.18 to 29.40 µg/g during monsoon. It ranged from 0.00 to 29.63 µg/g during post-monsoon. Copper in the study region ranged between 0.22 and 41.18 µg/g during pre-monsoon and between 0.39 and 42.19 during monsoon. During post-monsoon the range was from 0.08 to 44.14 µg/g. Lead was in the range from 5.96 to 54.20 µg/g during pre-monsoon and from 9.09 to 76.23 µg/g during monsoon. During post-monsoon season, Pb ranged between 11.36 and 81.56 µg/g. Nickel ranged between 8.12 and 87.17 µg/g and between 3.24 and 110.60 µg/g respectively during pre-monsoon and monsoon seasons in the study region. It ranged from 6.68 to 100.56 µg/g during the post-monsoon period. Zinc ranged between 2.71 and 181.84 µg/g during pre-monsoon period and from 3.97 and 172.65 µg/g during monsoon. The post-monsoon range for Zn was from 4.63 to 156.93 µg/g.

Like other geochemical parameters, trace metals did not show statistically significant monthly variations in the study region (ANOVA, Table 4.10). All the trace elements showed significant spatial variations with lower and higher values at sandy and muddy stations respectively.

4.2.7 Benthos

In the present study, the benthic groups obtained were polychaetes, molluscs and crustaceans (Table 4.9). Crustaceans constituted mainly of amphipods, tanaidaceans and crabs. There were a few other groups, which were in small numbers and these include penaeid prawns, benthic fishes, isopods and cumaceans. These are clubbed under "others". Seasonal average of benthic density showed that post-monsoon season is most productive. During monsoon, sharp decline in number was noticed. During pre-monsoon, benthic density ranged between 547.5 and 1699 no./m^2 and during monsoon it ranged between 253 and 737.7 no./m^2. During post-monsoon, the range was from 703.6 to 2100 no./m^2.

Table 4. 8 Seasonal variations of trace elements in the study region

Season	Stations	Trace Metals (Avg. ± SD µg/g)					
		Co	Cr	Cu	Ni	Pb	Zn
Pre-monsoon	1	10.66 ± 2.69	23.01 ± 0.84	9.96 ± 0.75	38.26 ± 3.97	25.08 ± 10.62	41.48 ± 12.18
	2	4.05 ± 1.09	3.73 ± 1.78	0.87 ± 0.82	9.08 ± 1.59	14.19 ± 7.43	4.00 ± 1.93
	5	4.81 ± 1.54	6.41 ± 3.72	2.04 ± 1.87	14.66 ± 5.29	11.10 ± 2.45	13.36 ± 6.31
	7	20.72 ± 2.63	70.75 ± 27.00	26.90 ± 7.74	54.37 ± 14.73	42.85 ± 5.11	88.50 ± 38.22
	8	28.07 ± 8.46	66.57 ± 12.15	39.10 ± 2.36	82.06 ± 3.49	51.80 ± 6.96	91.35 ± 17.52
	10	19.24 ± 8.64	62.96 ± 26.40	30.22 ± 10.73	66.82 ± 24.96	41.69 ± 8.59	134.60 ± 56.70
Monsoon	1	8.35 ± 2.88	23.43 ± 4.12	8.25 ± 0.38	32.93 ± 9.42	30.62 ± 15.39	39.37 ± 6.59
	2	3.61 ± 0.08	8.32 ± 4.33	0.70 ± 0.40	5.10 ± 2.64	17.78 ± 8.94	10.11 ± 2.16
	5	3.77 ± 0.75	3.58 ± 2.76	0.48 ± 0.14	16.75 ± 16.12	14.67 ± 6.97	7.42 ± 5.14
	7	17.67 ± 6.77	40.07 20.76	26.10 ± 1.69	76.08 ± 18.90	54.66 ± 9.13	75.08 ± 3.87
	8	26.02 ± 4.65	74.66 ± 10.27	41.09 ± 0.95	85.16 ± 6.04	56.68 ± 8.50	97.35 ± 17.07
	10	25.24 ± 4.11	87.08 ± 12.84	41.05 ± 0.47	85.07 ± 32.62	62.44 ± 14.48	134.50 ± 34.54
Post-monsoon	1	6.37 ± 1.33	32.83 ± 1.95	9.27 ± 2.33	27.74 ± 9.88	24.57 ± 17.54	46.38 ± 7.11
	2	11.07 ± 5.57	32.87 ± 19.13	9.50 ± 6.78	32.62 ± 18.12	25.57 ± 11.01	35.95 ± 17.93
	5	3.19 ± 0.21	7.17 ± 1.04	0.25 ± 0.22	9.15 ± 2.38	23.29 ± 19.95	8.17 ± 3.11
	7	12.79 ± 2.39	57.93 ± 4.85	24.43 ± 0.89	68.53 ± 10.87	53.79 ± 16.00	91.65 ± 20.89
	8	25.25 ± 3.82	86.90 ± 21.50	41.52 ± 2.90	87.17 ± 10.88	52.14 ± 6.64	86.54 ± 7.34
	10	23.43 ± 4.43	97.56 ± 2.59	40.80 ± 0.96	93.27 ± 10.02	71.38 ± 9.52	132.91 ± 21.56

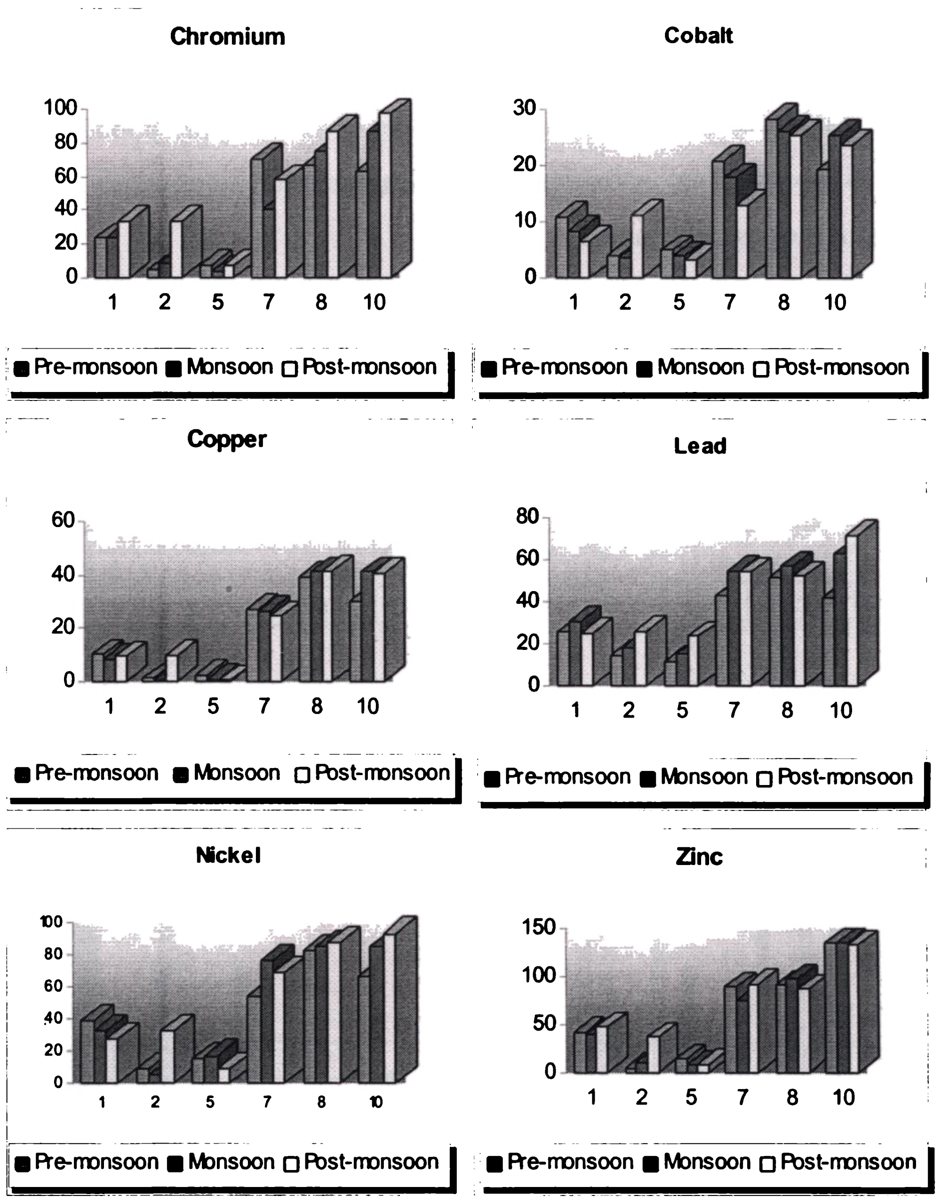

Figure 4. 8 Seasonal variations of trace elements in the study region

Monthly and spatial variability of benthos was examined using analysis of variance (Table.4.10). There was significant variation ($p<0.05$) between stations and stations 5,8 and 10 were of low benthic population. Unlike all geochemical parameters, significant monthly variations were observed in the case of benthos.

Table 4.9 Average benthic organisms in the study region

Groups	Jan	Feb	Mar	Apr	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Polychaetes	523.6	384.8	555.6	556	104	103.1	149	236	448	621.5	973.8
Molluscs	190.3	83.32	-	-	59.5	71.42	87.29	89.3	143	323.7	385.6
Amphipods	198.3	323.9	202.3	143	55.5	59.51	57.13	76.2	138	171.5	290.5
Tanaids	204.8	250	273.7	349	87.3	123.7	158.7	99.2	145	259.4	428.5
Crabs	95.22	107.3	47.6	71.4	-	23.8	-	23.8	95.2	95.24	23.8
Others	59.52	59.51	59.52	71.4	23.8	39.68	23.8	23.8	27.8	23.8	39.68
Total (no./m^2)	1272	1209	1139	1190	330	421.2	476	548	996	1495	2142

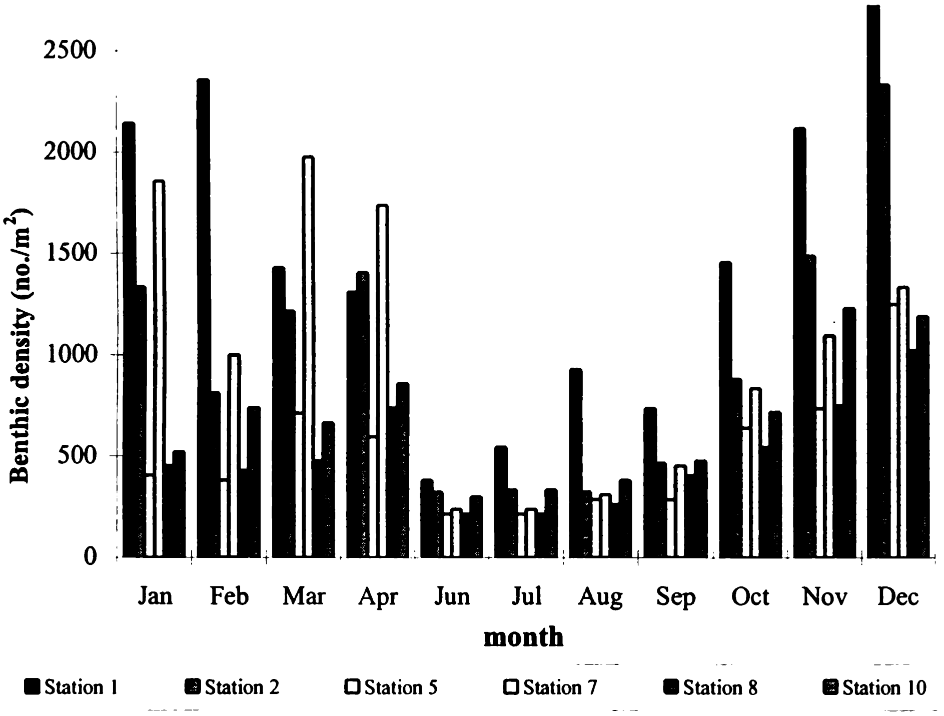

Figure 4.9 Monthly variations of benthic density in the study region

Table 4. 10 Analysis of variance (Two-way without replication) of different geochemical parameters

Carbon	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Months	4.514507	9	0.501612	0.834504	0.588425	2.83012
Stations	102.7039	5	20.54078	34.17255	2.97E-14	3.454431
Error	27.04905	45	0.60109			
Total	134.2675	59				

Mg	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Months	25097384	9	2788598	0.970475	0.476678	2.83012
Stations	3.99E+10	5	7.98E+09	2775.816	7.95E-55	3.454431
Error	1.29E+08	45	2873436			
Total	4E+10	59				

Nitrogen	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Months	0.161682	9	0.017965	2.642476	0.01508	2.83012
Stations	0.892355	5	0.178471	26.25188	2.61E-12	3.454431
Error	0.305928	45	0.006798			
Total	1.359965	59				

Iron	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Months	1580117	9	175568.6	0.058716	0.999948	2.83012
Stations	9.9E+08	5	1.98E+08	66.2249	1.3E-19	3.454431
Error	1.35E+08	45	2990126			
Total	1.13E+09	59				

Sulphur	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Months	1.048333	9	0.116481	1.044813	0.42079	2.83012
Stations	11.26175	5	2.252351	20.20309	1.62E-10	3.454431
Error	5.016847	45	0.111485			
Total	17.32693	59				

Mn	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Months	7525.043	9	836.1159	0.350689	0.952065	2.83012
Stations	526979.1	5	105395.8	44.20575	2.89E-16	3.454431
Error	107289.5	45	2384.211			
Total	641793.6	59				

Cr	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Months	3563.687	9	395.9652	1.877938	0.08015	2.83012
Stations	53302.56	5	10660.51	50.55943	2.36E-17	3.454431
Error	9488.299	45	210.8511			
Total	66354.54	59				

Co	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Months	179.1561	9	19.90623	1.007506	0.448308	2.83012
Stations	4397.164	5	879.4328	44.51038	2.55E-16	3.454431
Error	889.1067	45	19.75793			
Total	5465.427	59				

Cu	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Months	97.7173	9	10.85748	0.580705	0.805731	2.83012
Stations	15335.81	5	3067.162	164.045	1.04E-27	3.454431
Error	841.3683	45	18.69707			
Total	16274.9	59				

Pb	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	2852.604	9	316.956	3.101493	0.005543	2.83012
Columns	18061.36	5	3612.272	35.34698	1.64E-14	3.454431
Error	4598.759	45	102.1946			
Total	25512.72	59				

Ni	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Months	941.3506	9	104.5945	0.409835	0.923233	2.83012
Stations	53911.29	5	10782.26	42.24836	6.65E-16	3.454431
Error	11484.51	45	255.2113			
Total	66337.15	59				

Zn	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Months	654.4009	9	72.71121	0.165009	0.996574	2.83012
Stations	118646.6	5	23729.32	53.85073	7.12E-18	3.454431
Error	19829.25	45	440.65			
Total	139130.3	59				

Benthos	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Station	10047080.35	5	2009416.0	13.97	4.706E-09	2.37
Month	14152046.06	12	1179337.1	8.20	7.462E-09	1.92
Error	8628698.557	60	143811.64			
Total	32827824.97	77				

4.3 Discussion

The geochemical data of the study region were statistically analysed to find their inter-dependence and the correlation matrix was shown in Table 4.11. All the parameters showed highly significant inter-correlations, except benthos. Silt and clay showed highly significant positive correlations with sedimentary parameters, while it was negative for sand.

4.3.1 Texture and Mineralogy

The determination and interpretation of particle grain size has a fundamental role in hydraulics, geomorphology and sedimentology (Friedman & Sanders, 1978). The texture of the sediments has a significant role on the physico chemical processes as well as on the species diversity of the depositional environment (Badarudeen *et al.*, 1996). The grain size of the sediments influence the sedimentation processes, the capacity for entrainment as well as the capacity of the materials to bind pollutants. Grain size is also related to other properties (e.g. permeability), which have major economic implications and thus is an important aspect of sedimentologic research.

Sediment textures are highly variable in estuaries and this particular system is not an exception. Grain size is related to hydrodynamics and it generally showed an increase from the inner areas towards the bar mouth direction. High water column currents and local eddies in the starting stations (as reported in chapter 3) keep the finer fractions suspended in the water column and the reverse happens for the end stations. Comparatively higher sand fractions near bar mouth in this estuary were also reported earlier (Seralathan *et al.*, 1993; Nair *et al.*, 1993; Balachandran *et al.*, 2001). Surficial sediments in Cochin estuary indicated variations in texture resulting from detritus settlement influenced by mixing conditions (Nair *et* *al.*, 1993). Seralathan & Padmalal (1994) also reported highly complicated surficial sediment textual pattern in this estuary, owing to the fluctuation in the physico-chemical conditions prevailing in the system. Menon *et al.*, (2000) reviewed that the sediments are a mixture of clay and silt (70–85%) and sand.

The direct influence of river discharge and land run-off were not reflected on the texture of the present study region, though Nair *et al.*, (1993) reported abundance of sand during monsoon due to estuarine bed load movements. This was supported by the TSS data, mentioned in chapter 3. Hence sediment retained its nature through out study period. The particle size has a significant role in the accumulation and exchange process of elements between sediments and water in fresh water-sea water mixing. Correlation analysis showed that silt and clay fractions have high positive correlations with all the analysed sedimentary parameters except benthic density. Sand fractions showed similar negative behaviour. It is well documented that fine particles often concentrate metals due to their greater surface area and amounts of organic carbon, clay, iron, or aluminium (Santschi *et al.,* 2001) and also proportionally higher concentrations of associated trace elements (Myers & Thorbjornsen, 2004). Because organic matter content generally decreases with increasing grain size, it seemed that coarse-grained sandy deposits lack the substrate to sustain significant biological activity. Sands were therefore considered to be biogeochemical deserts that did not significantly contribute to the cycling of organic matter (Boudreau *et al.*, 2001). Hence the geochemistry of the sediments is usually normalized on the basis of the textural characteristics, which was followed in the factor analysis of the present study.

Table 4.11 Correlation of seasonal averages of different sedimentary parameters in the study region (n=18)

	Cu	Zn	Ni	Pb	Mn	Cr	Co	Mg	Fe	TN	TC	TS	TP	Sand	Silt	Clay	Benthos
Cu	1.000	.926(**)	.979(**)	.940(**)	.892(**)	.967(**)	.980(**)	.916(**)	.994(**)	.946(**)	.952(**)	.918(**)	.861(**)	-.976(**)	.960(**)	.920(**)	-.203
Zn	.926(**)	1.000	.920(**)	.909(**)	.952(**)	.938(**)	.882(**)	.980(**)	.937(**)	.904(**)	.866(**)	.799(**)	.911(**)	-.942(**)	.885(**)	.963(**)	-.094
Ni	.979(**)	.920(**)	1.000	.961(**)	.878(**)	.938(**)	.950(**)	.913(**)	.986(**)	.942(**)	.941(**)	.919(**)	.866(**)	-.952(**)	.941(**)	.890(**)	-.200
Pb	.940(**)	.909(**)	.961(**)	1.000	.890(**)	.926(**)	.889(**)	.913(**)	.952(**)	.929(**)	.892(**)	.860(**)	.898(**)	-.923(**)	.902(**)	.879(**)	-.201
Mn	.892(**)	.952(**)	.878(**)	.890(**)	1.000	.925(**)	.861(**)	.984(**)	.893(**)	.891(**)	.814(**)	.739(**)	.869(**)	-.868(**)	.786(**)	.942(**)	-.087
Cr	.967(**)	.938(**)	.938(**)	.926(**)	.925(**)	1.000	.934(**)	.935(**)	.957(**)	.956(**)	.918(**)	.874(**)	.845(**)	-.939(**)	.911(**)	.910(**)	-.046
Co	.980(**)	.882(**)	.950(**)	.889(**)	.861(**)	.934(**)	1.000	.886(**)	.972(**)	.922(**)	.953(**)	.914(**)	.828(**)	-.942(**)	.933(**)	.876(**)	-.208
Mg	.916(**)	.980(**)	.913(**)	.913(**)	.984(**)	.935(**)	.886(**)	1.000	.923(**)	.908(**)	.850(**)	.782(**)	.911(**)	-.905(**)	.841(**)	.943(**)	-.080
Fe	.994(**)	.937(**)	.986(**)	.952(**)	.893(**)	.957(**)	.972(**)	.923(**)	1.000	.935(**)	.943(**)	.904(**)	.871(**)	-.975(**)	.959(**)	.921(**)	-.181
TN	.946(**)	.904(**)	.942(**)	.929(**)	.891(**)	.956(**)	.922(**)	.908(**)	.935(**)	1.000	.962(**)	.930(**)	.864(**)	-.907(**)	.884(**)	.871(**)	-.142
TC	.952(**)	.866(**)	.941(**)	.892(**)	.814(**)	.918(**)	.953(**)	.850(**)	.943(**)	.962(**)	1.000	.983(**)	.833(**)	-.915(**)	.912(**)	.841(**)	-.216
TS	.918(**)	.799(**)	.919(**)	.860(**)	.739(**)	.874(**)	.914(**)	.782(**)	.904(**)	.930(**)	.983(**)	1.000	.767(**)	-.872(**)	.884(**)	.776(**)	-.236
TP	.861(**)	.911(**)	.866(**)	.898(**)	.869(**)	.845(**)	.828(**)	.911(**)	.871(**)	.864(**)	.833(**)	.767(**)	1.000	-.868(**)	.840(**)	.845(**)	-.215
Sand	-.976(**)	-.942(**)	-.952(**)	-.923(**)	-.868(**)	-.939(**)	-.942(**)	-.905(**)	-.975(**)	-.907(**)	-.915(**)	-.872(**)	-.868(**)	1.000	-.983(**)	-.944(**)	.251
Silt	.960(**)	.885(**)	.941(**)	.902(**)	.786(**)	.911(**)	.933(**)	.841(**)	.959(**)	.884(**)	.912(**)	.884(**)	.840(**)	-.983(**)	1.000	.868(**)	-.261
Clay	.920(**)	.963(**)	.890(**)	.879(**)	.942(**)	.910(**)	.876(**)	.943(**)	.921(**)	.871(**)	.841(**)	.776(**)	.845(**)	-.944(**)	.868(**)	1.000	-.211
Benthos	-.203	-.094	-.200	-.201	-.087	-.046	-.208	-.080	-.181	-.142	-.216	-.236	-.215	.251	-.261	-.211	1.000

**Correlation is significant at the 0.01 level (2-tailed)   * Correlation is significant at the 0.05 level (2-tailed)

Mixing of riverine with marine sediments could be explained by different mineralogical composition of clay minerals (Chamley, 1989). In a similar fashion, mineralogical fingerprints might be employed as tools to explore the dynamics and transport of particle and sediments associated with local environments. Feldspars are the most common minerals in the Earth's crust and are the major component in nearly all igneous rocks on the earth. Quartz is the second most abundant mineral in the Earth's crust, present in many rocks. Feldspars are aluminosilicate minerals with the general formula AT_4O_8 in which A = potassium, sodium, or calcium (Ca); and T = silicon (Si) and aluminum (Al). Quartz consists of silica, or silicon dioxide (SiO_2). Both are non clay minerals. Clay minerals are hydrous aluminium phyllosilicates, with variable amounts of iron, magnesium, alkali metals, alkaline earths and other cations. Clay minerals are common weathering products and are very common in fine-grained sedimentary rocks such as shale, mudstone. Clay minerals include the following groups (Bailey, 1980):

- Kaolinite group which includes the minerals kaolinite, dickite, halloysite etc.
- Smectite group which includes pyrophyllite, talc, vermiculite, sauconite, saponite, nontronite and montmorillonite.
- Illite group which includes the clay-micas. Illite is the only common mineral.
- Chlorite group includes a wide variety of similar minerals with considerable chemical variation.

The structural formula of smectites of the dioctahedral aluminous species may be represented by $(Al_{2-y}Mg^{2+}/_{y})(Si_{4-x}Al_{x})O_{10}(OH)_{2}M^{+}/_{x+y}$ □ nH_2O, where M^{+} is the interlayer exchangeable cation expressed as a monovalent cation and where x and y are the amounts of tetrahedral and octahedral substitutions, respectively (0.2 □ $x + y$ □ 0.6). The smectites with $y > x$ are called montmorillonite and those with $x > y$ are known as beidellite. In the latter type of smectites, those in which ferric iron is a dominant cation in the octahedral sheet instead of aluminum and magnesium are called nontronite. Kaolinite has the general formula $Al_2Si_2O_5(OH)_4$ and Al $(OH)_3$ for Gibbsite. The general formula of Chlorite may be stated as A^5-6T^4O^10-Z^8, where A = Al, Fe^{2+}, Fe^{3+}, Li, Mg, Mn, or Ni, while T = Al, Fe^{3+}, Si, or a combination of them, and Z = O and/or OH. Illite has the formula $K_{0.65}A_{2.0}$ [] [Al $_{0.65}Si_{3.35}O_{10}](OH)_{2}$.

Clay minerals present acidic catalytic and redox properties that promote the polymerization of organic residual substrates, which strongly contribute to their humification. Mineralogy of the study region showed that, in general, there was variability of major minerals and the geology of the basin is not homogeneous. Similar mineralogy in the in the surficial sediments of Cauvery estuary, East Coast of India was reported by Ramanathan *et al.,* (1993). Smectite, illite, kaolinite and chlorite were the major clay mineral groups present in the sediments of the western continental shelf and slope of India with the dominance of kaolinite in sediments off Cochin (Rao & Rao, 1995). Kaolinite and smectite together constituted over 95% of clay mineral population in Ashtamudi estuary and illite represented the remaining (Sajan, 1988). The sand fraction in Ashtamudi estuary exhibits dominance of quartz with minor amounts of feldspars and fragments of molluscan shells, similar to this some stations in the study region also showed shell remaining.

Quartz and feldspar occurred in the coarse-grained fraction (sand and silt) and decreased in abundance with decreasing particle size. Minerals like chlorite + kaolinite and smectite consistently increased in abundance with decreasing particle size and dominated the clay fraction. Among the clays, chlorite+kaolinite was the predominant mineral. Complete absence of clay minerals was observed at stations 2 and 5, which were sandy in nature. Stations 7, 8 and 10 showed the predominance of clay minerals. This grain-size dependence on mineralogy indicates the importance of chemical weathering in the estuary. Also it was reported that high contents of kaolinite and gibbsite are indicative of intense chemical weathering (Rao & Rao, 1995). The low degree of crystallinity, based on asymmetric, low intensity and broad reflections in XRD patterns, suggest an allochtonous origin for most of the clay minerals.

Good orientation of clay minerals requires the removal of nonplaty minerals such as quartz, and organic matter, which can produce broad X-ray diffraction peaks, increase the background and inhibit dispersal of other minerals (Moore & Reynolds, 1997). Since XRD analysis was carried out with the untreated samples, the high background noises for stations 7, 8 and 10 indicate the presence of higher amount of organic carbon.

4.3.2 Nutrient elements

Nutrient elements in the study region did not show any seasonal trend as reported in the case of other Indian estuaries (Ghosh & Choudhury, 1989; Babu *et al.*, 2000). Seasonal changes are difficult to observe in surface sediments of estuaries due to periodic resuspension by tidal currents, bioturbation, and post-depositional chemical reactions (Zwolsman *et al.*, 1993; Vale *et al.*, 1998). As primary production increases, respiration and thus recycling of nutrients in water column also increases (Oviatt *et al.*, 1986).

The nutrient concentrations in the study region are comparable to that of different aquatic systems (Table 4.12). They varied widely with respect to the granulometric compositions of sediments; decreased with increase in grain size of the sediment. Fine-grained sediments are richer in organic matter than coarse sand (Tam & Wong, 2000). The maximum values of nutrients were recorded in the muddy stations (stations 7,8 and 10), while minimum in the sandy stations (stations 2 and 5). This is evident from the high positive correlations of nutrient elements with the silt and clay and the their high negative correlations with sand. The positive correlation of sediment carbon with total nitrogen and phosphorus indicates a common source (organic matter) to these elements.

The tropical vegetation in the catchment areas of rivers and estuary, presence of mangrove patches on estuarine banks, high rate of primary production (chapter 3), prevailing anoxic condition and fine particle size of sediments are important factors responsible for the higher concentration of organic matter in this estuary. Organic carbon content in recently deposited sediments has received much attention in environmental monitoring because of their bearing on the physical, chemical and biological processes to which the sediments have been subjected. Organic carbon plays an important role in the dispersal pattern of many major and trace elements. The sedimentation followed by diagenetic decomposition of organic matter can alter the pH and Eh of aquatic environments. Abundant supply of organic matter in the overlying water column, rapid rate of accumulation of organic matter and the low oxygen content of the water immediately above the surface sediment favour the preservation of organic matter in sediments.

Biological utilization of detrital matter leads to lower organic carbon values.

Table 4. 12 Nutrient levels in the sediments of different aquatic systems

Aquatic systems	Nutrients	Reference
Ashtamudi estuary	TOC 0.74- 3.86 % TN 0.082- 0.27 % TP 88-279 µg/g	Babu *et al.*, 2000
Hooghly estuary	TOC 1.53 –5.41 % TN 0.08-0.58 % TP 0.16- 0.46 %	Ghosh & Choudhury, 1989
Vellar estuary	TOC 0.028 –2.84 % TN 0.003-0.665 % TP 3.45 -288.16 µg/g	Chandran, 1987
Thames estuary	TOC 0.26-3.59 %	Trimmer *et al.*, 2000
Bay of Concepcion, Chile	TOC 3.55-3.83 % TN 0.36- 0.52 % TOC 0.5 -5.3%	Farias, 2003
Grandfather Lake, Southwestern Alaska	TN 0.04 - 0.6% TOC 0.04 –8.89 %	Hu *et al.*, 2001
Lake Orta, Italy	TN 0.01 - 0.88 % TP 0.05- 0.24 % TOC 1–3 %	Baudo & Beltrami, 2001
Saguenay Fjord	TC 0.37- 2.70 %	Mucci *et al.*, 2000
Lake Illawarra, Australia	TN 0.04- 0.27 % TOC 2.16 – 4.96 %	Qu *et al.*, 2005
Oman Margin of Arabian Sea	TN 0.27- 0.64 %	Alagarsamy, 2003
Seto Inland Sea, Japan	TOC 0.62-1.17 %	Magni *et al.*, 2006
Cochin estuary	TOC 0.06 –3.57 % TN 0.02-0.55 % TP 0.03- 0.28 %	***Present study***

Stoichiometric ratios of nutrients have been utilized in many stuarine studies to determine the origin of organic matter sources and ocumenting organic transformation (Thornton & McManus, 1994; 'amamuro, 2000). The range of C: N values are typically lower for aquatic organic matter than for terrestrial organic matter (Meyers & Lallier-Verges, 1999) and the ranges were 6.0-9.0 for planktonic organisms and 20.0–100.0 for terrestrial plant tissue and soil (Meyers, 1994; Tyson, 1995). Conventionally, the value of 10 is assumed as an index to distinguish between autochthonous and allochthonous material.

Stoichometric ratios of nutrients in the study region are presented in Fig. 4.10. Monthly variations of C/N ratios were lower than 10 during most of the time and seasonal averages were 6.6, 7.8 and 7.3 respectively during pre-monsoon, monsoon post-monsoon. The data indicate that organic matter in the sediments is labile, originates mainly from the water column suspended matter, and phytoplankton-derived matter is presumably a major fraction of this material (autochthonous). According to Russel-Hunter (1970), organic matter should have a C/N ratio lower than 17 in order to be of nutritional use to invertebrates. Hence this organic matter input is characterised by a high nutritional value (i.e. protein content) and represents a high- energy source for benthic organisms (Albertelli *et al.*, 1998). Though contents of C and N increased with decreasing particle size, C/N ratios were 6-8 on all of fractions, indicating the common origin (autochthonous).

In shallow coastal areas, such as the study region, sediments exhibit higher biological mixing intensities while a shallow water column and increased productivity (chapter 3) provide a greater supply of highly labile organic matter to the sediment–water interface, as mentioned earlier. Since the euphotic zone extends down to the sediment–water interface, the primary production of benthic microalgae is high (Sreekumar & Joseph, 1997), hence an important source of sedimentary organic matter.

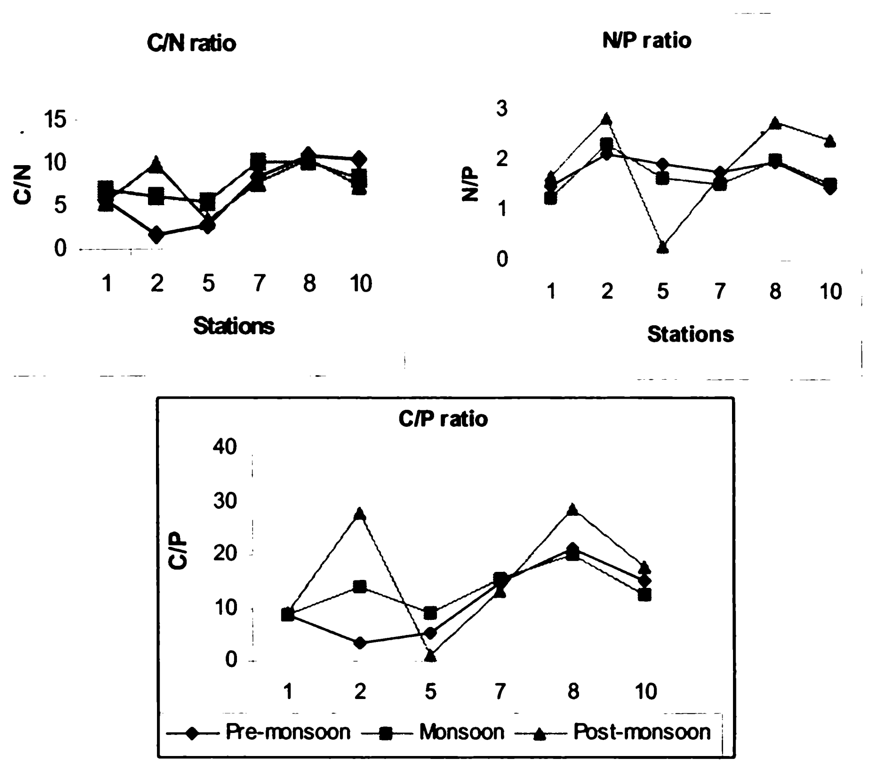

Figure 4.10 Stoichometric ratios nutrients in the study region

By mass, Redfield (1958) predicts a C: P ratio of 40, and N: P ratio of 7 for algal material, while Hecky *et al.,* (1993) indicated that a wider range of C:P and N:P ratios in lakes can still be considered to obey Redfield (C:P = 28 to 56 and N:P = 4 to 9). The C: P ratio varies widely in the study region (~1 to 28) and was higher in the muddy stations than in sandy ones. But N: P ratio did not show considerable variations among stations and ranged between 0.3 and 2.7. Both these ratios did not show any seasonal variations and were far below than Redfield ratio. Hence there is a possibility of phosphorus enrichment in this estuary. Hydrodynamical studies (chapter 3) also suggested the lack of phosphorus limitation. However, from these proportions it can also be assumed that the organic carbon and nitrogen could be rapidly oxidized in the water column and surface sediments. This possibility was discussed in chapter 3 also.

Tests for post-depositional alteration have been performed chiefly on sediments where only two end members were recognized autochthonous, including primary production by surrounding vegetation, phytoplankton, microphytobenthos and chemoautotrophs, or allochthonous, including marine and/or riverine input, as well as anthropogenic runoff (Thornton & McManus, 1994). Studies showed that this ratio could be altered by many processes, including ammonification, nitrification and denitrification (Thornton & McManus, 1994; Cifuentes *et al.,* 1996; Yamamuro, 2000). According to Day *et al.,* (1989) the nutrient transformation processes, such as the redox reactions, enhance the energy flux and, therefore, the chemical dynamics of sediment. These processes are fundamental aspects of understanding estuarine ecology. Biological productivity in aquatic ecosystems is highly influenced by the cycling of essential nutrients, especially nitrogen and phosphorus (Vitousek *et al.*, 1997; Carpenter *et al.,* 1998). The determination of the transfer of nutrients across sediment-water interface definitely gives insight into the sequence of oxidation, nature of oxidants and ultimately the mobility of elements during the diagenetic decomposition of organic matter-rich sediments (Manheim, 1976; Nath & Mudholkar 1989; Padmalal & Seralathan 1991).

Little change in C/N ratio between living (sources) and decaying organic matter pools suggests that C and N are mineralized or preserved at the same rate. Decreases in C/N ratios may be as a result of the absorption of organic or inorganic N onto silicate clay surfaces (Macko *et al.,* 1993) or the incorporation of N by bacteria in decaying organic matter (Cifuentes *et al.,* 1996). It must be kept in mind, however, that any determination of organic matter source in the sediment will only reflect the component of the organic matter that is preserved and not the original flux to the sediment. High primary production contributed to the increase in organic carbon (Nair *et al.*, 1975). Organic carbon values would be significantly larger if loss through microbial decomposition was not occurring. Thus, the continuous pedogenic addition and loss of organic matter is in part responsible for the development of sediment surface layers with stable, organic carbon levels (Demas & Rabenhorst, 1999). The decomposition of organic matter consumes all oxygen. After its depletion, the remainder of the organic matter is successively degraded by denitrification, manganese reduction, iron reduction, sulfate reduction and methane production (Aller, 1982). The average N/P ratios indicate that benthic nitrogen recycling is in excess of phosphorous. The lower N/P ratio shows that denitrification and the benthic release of nitrogen might play a role in sustaining the productivity of the system, as suggested in chapter 3.

Naturally occurring heterotrophic bacteria typically are more abundant and grow faster than nitrifying bacteria (Prosser, 1989) and thus should out compete nitrifying bacteria for available NH in N-limited environments. As a result, nitrification rates should decline. High quality (more easily decomposed) organic carbon should provide a better substrate for heterotrophic activity, which would then increase the demand and competition for inorganic N and reduce nitrification rates. Poor quality (more refractory) organic carbon should have less of an effect on nitrification because lower heterotrophic activity will limit competition for inorganic nitrogen. Thus, the critical C:N ratio for nitrification should vary among systems depending on the quality of the ambient organic carbon., which is often considered to be inversely related to the C: N ratio of the matter as discussed earlier (Russel-Hunter,1970), although certain non nitrogenous carbon compounds also may be very labile (e.g., glucose and acetate) if a separate source of N is present to facilitate decomposition.

Estuarine sediments are essentially anaerobic below a few surface millimeters, and the mineralization of organic matter proceeds via alternate electron acceptors such as NO_3^- and $SO4^{2-}$. Sulphur concentration in the sediment mainly depends on mineralisation of organic matter producing organic S, such as amino acids and ester sulphate, and reduction of SO_4^{2-} to S^{2-}caused by oxygen depletion in bottom water and in the sediment. It has been found that sulfate reduction is typically the predominant process responsible for the mineralization of organic carbon in anaerobic marine sediments (Jorgensen & Sorensen, 1985; Seitzinger & Giblin, 1996) and generally accounts for 5–50% of the total mineralization of organic matter in shallow coastal sediments (Jorgensen & Sorensen, 1985; Berelson *et al.*, 1996).

The S/C value in sediments did not show any significant variations; values were in the range 0.3-0.5 during most of the cases. This ratio, which is very much higher than the average ratio in abyssal plain sediments (0.13), showed no spatial variations, maintaing same levels in sandy and muddy sediments. Very high levels of sulphur (about 1% dry weight) indicated an anthropogenic source. This can be by the active transport of sulphur to FACT, Cochin Division through the National Water Way, which passes through the study region. Presence of such a higher level of sulphur can also cause higher accumulation of metals in sediments, through complexation.

4.3.3 Heavy metals

The determination of the transfer of nutrients across sediment-water interface definitely gives insight into the sequence of oxidation, nature of oxidants and ultimately the mobility of elements during the diagenetic decomposition of organic matter-rich sediments (Manheim 1976; Nath & Mudholkar 1989; Padmalal & Seralathan 1991). Salinity controls flocculation and sedimentation mechanisms in estuarine environments, changing the availability of metals. Clays have high specific surface area and can directly trap heavy metals, but they also may act as a substrate for organic matter flocculation (Keil *et al.*, 1994) that in turn adsorbs metals. The chemical and mineralogical compositions of the substrate can influence concentrations and distributions of metals (Marchand *et al.*, 2006).

The metal recovery using the tri-acid mixture digestion was checked with the standard reference material for marine and estuarine sediments (BCSS-1) obtained from National Research Council of Canada. The recovery was very good and ranged between 82.7 % for Mn and 103.9 % for Zn (Table 4.13) and this has been considered when assessing the concentrations. The extractable component is the mobile one and of environmental concern. The metals contained in the silicate structure of the sediments, which can be released only through weathering over geological time is of little importance.

General abundance for the elements analyzed were: Al >Fe > Mg > Ca > Mn > Zn > Ni > Cr > Pb> Cu > Co. This abundance order suggests that the organic chelates and oxyhydroxides of aluminum and iron are dominant components. All the elements showed highly significant positive correlations with the organic content, nutrients and clay and silt fractions, where as they were correlated negatively with the sand fraction. It is well known that the smallest and lightest particles are often most enriched in trace metals (Salomons *et al.*, 1987). Because the surface area of sediments is grain-size dependent and controls the adsorption of metals in the sediment (Mayer & Fink, 1980) and finer particles provides the greatest surface area for the adsorption of metals (Jickells & Knap, 1984). Further, the metal-scavenging phases like Fe/Mn hydrolisates, organic carbon, clay minerals, etc., are more in silt and clay fractions than in sand. However, interpretation of metal concentrations in sediments is compounded by the metal's natural concentration in different minerals and by the relationship of metals to sediment grain-size characteristics (Mostafa *et al.,* 2004). Positive correlations of trace metal contents with the silt and the clay content and Fe and the negative correlations with sand suggest that the trace metals are associated with Fe oxides and hydroxides of the finest fraction or co-precipitated by these oxides.

Comparison of the metal concentrations with other aquatic systems of the world (Table 4.14) showed that the metal concentrations were similar in magnitude with some exceptions. The metal content were also compared with the previous studies in and around the cochin estuarine system and presented in chronological order (Table 4.15). These show that the heavy metal contents in the study region is comparable to the previous studies around Cochin estuary and there is no significant enrichment for any of the metals analyzed, during last two decades. These also neglect the chances of higher levels of anthropogenic contamination in the study region.

Table 4.13 Analysis of standard reference material (BCSS-1)

Metal (µg/g)	Certified BCSS-1	Obtained BCSS-1 (n=3)
Cu	18.5 ± 2.7	18.2 ± 0.25
Zn	119 ± 12	123.64 ± 2.51
Ni	55.3 ± 3.6	49.16 ± 2.01
Mn	229 ± 15	189.47 ± 10.75
Pb	22.7 ± 3.4	24.9 ± 0.01
Co	11.4 ± 2.1	10.67 ± 2.68
Cr	123 ± 1.4	112 ± 0.25
Mg (%)	2.44 ± 0.23	2.32 ± 0.41
Fe (%)	4.7± 0.14	4.64± 0.41

The concentrations of major elements in sediments depend mainly on the geochemistry of the estuary, and the differences among stations reflect the sedimentation pattern produced by hydraulic factors, as well as variability in the geochemistry. Since these elements are present in the sediments in high concentrations, variations over time are usually quite low. Mineralogy and sediment chemistry dictate that naturally occurring elements in sediment exist in predictable proportion to other elements. Trace element concentrations are expected to covary with major element concentrations, and such correlations can be effectively used to distinguish between naturally occurring and anthropogenic concentrations (Myers & Thorbjornsen, 2004).

Table 4.14 Levels of heavy metals in the surficial sediments of different aquatic systems

Location	Metals (µg/g)										
	Al (%)	Ca (%)	Cr	Co	Cu	Fe (%)	Pb	Mg (%)	Mn	Ni	Zn
Brisbane and Logan Estuaries[1]	0.27-3.3	NR	1-85	NR	0-67	0.12-3.93	7-107	NR	57-751	6-75	1-246
Lake Orta, Italy[2]	6.46-10.22	0.43-1.61	136-2877	NR	72-2440	2.83-8.95	24-660	0.63-1.99	259-1767	30-303	134-1004
Tinto river estuary[3]	NR	NR	61-151	26-42	1760-2700	5.96-11.9	1110-2380	NR	NR	12-36	1050-5280
44 estuaries in Galicia (NW Spain)[4]	12.02	NR	64.56	13.19	62.48	3.38	219.7	NR	375.5	47.87	193.3
Cauvery estuary[5]	3.89-11.28	1.46-2.82	6-85	NR	2-46	0.58-2.93	12-47	1.20-1.76	264-1800	NR	14-120
Alexandra Western Harbour[6]	0.19-5.92	NR	33-649	NR	27-378	0.99-3.69	21-1070	0.13-1.68	91-317	5.0-52.8	33-1221
African Margin of Arabian Sea[7]	6.2-7.9	NR	NR	NR	NR	3.43-4.08	NR	NR	320-1270	NR	NR
The Tyume River, South Africa[8]	NR	NR	NR	.102-.312	.082-0.496	NR	.042-.067	NR	NR	.401-.891	.080-.491
Riberia Bay[9]	2.33-10.88	0.49-2.71	24-110	NR	3-32	1.06-4.97	.042-.067	0.54-1.65	202-981	27-73	.29-189
Jacarepagu Basin, *Brazil*[10]	NR	NR	25-163	NR	32-108	4.25-4.94	41-130	NR	194-600	32-87	121-507

NR Not reported

[1]Cox & Preda, 2005 [2]Baudo & Beltrami, 2001 [3]Morillo *et al.*, 2002 [4]Villares *et al.*, 2005 [5]Ramanathan *et al.*, 1993 [6]Mostafa *et al.*, 2004 [7]Morford & Emerson, 1999 [8]Awofolu *et al.*, 2005 [9]Cardoso *et al.*, 2001 [10]Fernandes, 1997

A comparison of the metal concentration in the sediments with the world shale is generally taken as a quick and practical method for tracing heavy metal enrichment. The "average geochemical background" or average shale (Table 4.16) represents the standard level of the metals in argillaceous sediments. One way to account the characteristics of the sediments when evaluating bioavailability is to normalize the concentrations for different geochemical factors (Bryan & Langston, 1992; Montouris *et al.*, 2002). Normalization is accomplished by graphical and/or mathematical comparison of the trace -metal concentration in a particular sediment to the concentration of some conservative element that is also present in the system (Trefry & Presley, 1976; Klinkhammer &. Bender 1981; Horowitz, 1985; Windom *et al.*, 1989; Summers *et al.*, 1996). This element, often referred to as a reference element, acts as a proxy for both mineralogic and grain-size variability.

Table 4.15 Levels of heavy metals in the surficial sediments in and around Cochin estuary (in chronological order)

Location	Metals (µg/g)										
	Al (%)	Ca (%)	Cr	Co	Cu	Fe (%)	Pb	Mg (%)	Mn	Ni	Zn
Cochin Estuary (N)[1]				10.0 - 43	17-71				73-318		103-664
Cochin Estuary (N)[2]					5-61	4.4 - 29.1			15-640		116-1385
Cochin Estuary (N)[3]				2-42	8-63	3.1-9.06	3-46		44-1439		10-417
Cochin Estuary (N)[4]			7-130				10-90				35-750
Cochin Estuary[5]					3.14-11.4		14.2-46.5				
Cochin Estuary (N)[6]			4-100	1-25	1-50	2.8-20.2	3-50		7-170		14-259
Cochin Estuary[7]					5.5-51.3	1.5-5.5	33.2-117.1		123-280		29.3-290.5
Kerala Coast[8]					5.5-18.1	0.5-5.5	17.9-80.9		44-318		7.4-148.75
Cochin Estuary[9]			`10-160	`12-25	5-53	1.4-6.2	21-71		151-337	`20-70	92-126.6
Cochin inner shelf[10]			195			8.93	164	3.34		81	124
Cochin estuary (N)[11]			140			6.97	37	2.2		56	588
Cochin estuary (S)[12]			173			8.03	69	2.66		72	125
Periyar river[13]			55			2.95	27	0.63		13	211
Muvattupuzha river[14]	4.41-18.33	0.17-2.58	48-216	3-25	6-56	2.03-10.16	10-342	0.51-3.33	200-800	14-93	18-316
Chitrapuzha river[15]			101	13.39	28.47	2.56	22.4		245.18		177.01
South-West coast[16]			0.1-205	0-37.4	0-40	0.8-5.6	0-71.3		0.2-773	0.1-174.6	0.1-132
Cochin Estuary[17]	0.18-8.22	0.036-0.92	0.35-110.5	3.05-37.8	0.08-44.14	0.21-8.26	5.96-81.56	0.015-1.36	7.3-361.6	3.24-110.6	2.71-181.84

[1]Venugopal *et al.*, 1982 [2]Paul & Pillai, 1983 [3]Malik & Suchindan, 1984 [4]Ouseph, 1987 [5]Babukutty, 1991 [6]Nair, 1992 [7,8]Rajammani Amma, 1994 [9]Balachandran *et al.*, 2002 [10-14]Shajan, 2001 [15]Joseph, 2002 [16] Balachandran *et al.*, 2003 [17]**Present study**

Table 4.16 World average shale values for different heavy metals

Metals	World average shale (μg/g)			
	a	**b**	**c**	**d**
Al*	8			8.8
Ca*				1.6
Co	68			
Cr	90	90	100	90
Cu	45	39	57	39
Fe*	4.57			4.8
Pb	20	23	20	20
Mg*				1.6
Mn	850			850
Ni	68	68		68
Zn	95	120	80	120

* (in weight %)

(a) Turekian & Wedepohl, 1961 (b) Krauskpof, 1967 (c) Leckie & Parks, 1968 (d) Bowen, 1979.

Aluminum is typically used in sediment studies as a normalizer of trace element concentrations because it is naturally abundant, anthropogenic contribution is rare, and it is a primary component of clay minerals, which concentrate many trace elements (Windom *et al.*, 1989; Hanson *et al.*, 1993; Daskalakis & O'Connor, 1995). Iron is also an important reference element because of the relative abundance of iron oxide minerals, with which many trace elements associate, and thus it has also been used as a normalizer in sediment studies (Daskalakis & O'Connor, 1995; Schiff & Weisberg, 1997). Normalization of metal concentration to aluminum concentration proved superior to granulometric normalizations and normalizations to total organic matter, total carbon, and total nitrogen (Trimble *et al.,* 1999). This method was successfully used by Pereira *et al.,* (2005) to depict the differences in the elemental composition of sediments from different areas in Mondego River estuary.

In this study, Sediment enrichment factors (SEF) were used to obtain indications on the degree of trace metal anthropogenic enrichment. According to the formula proposed by Kemp & Thomas (1976), the SEF was calculated as follows,

$$\mathrm{SEF} = \frac{(C_z/\mathrm{Al}_z) - (C_b/\mathrm{Al}_b)}{(C_b/\mathrm{Al}_b)}$$

Where C_z is the content of the element in the sample z, C_b the content of the element in world average shale, Al_z the content of Al in sample z, and Al_b the content of Al in world average shale.

Normalisation to Aluminium content takes into account the changes in particle grain size and provides better estimates of trace metal pollution compared with the simple ''contamination factor'' defined as C_z/C_b (Pereira *et al.,* 2005). The values showed that Ca, Cu, Cr, Mn, Mg and Zn were not enriched at any stations. Ni showed enrichment only at sandy stations with SEF 1.27, 6.84 and 3.67 respectively for stations 1,2 and 5 respectively. Lead showed higher enrichment at sandy stations (SEF 3.18, 48.93 and 12.26 respectively for stations 1, 2 and 5 respectively) while it was lower (SEF~2) for muddy stations. Cobalt showed slight enrichment (SEF 1.75) at station 2. Iron showed slight enrichment at stations 2 and 5 (SEF 1.85 and 1.53 respectively). Thus the normalization studies showed that though most of the metals are in the normal ranges, Ni and Pb showed enrichment particularly at stations 2 and 5, suggesting a different source of input.

The adsorption of cations on clay minerals occurs according to the Freundlich adsorption isotherm. The factors like valence of ions, hydration behaviour, electron negativity and ionization potential (Forstner & Wittmann, 1983) influence the affinity of clay minerals for trace metals. Pb has a special affinity for the clay mineral structures due to its ionic radius, which is similar to that of potassium (a metal primarily incorporated onto clay minerals). Sorption and complexation of metals by organic compounds was in the sequence Pb> Cu> Ni> Co>Zn>Cd>Fe> Mn>Mg (Forstner & Wittmann, 1983).

The main non-natural source of Ni is the burning of fuel and residual oils. Smaller quantities can be released through coal combustion and use of fertilisers (McGrath & Smith, 1990). Higher values are most likely related to vehicle emission and phosphate use in agricultural regions. The high Pb concentration may be related to the runoff of residential wastewater as well as the atmospheric emissions (leaded gasoline) from urban and industrial areas. Williams (1995) suggested that anthropogenic lead is mostly associated with the slowest settling fraction of particulate matter, and so has a potential to be transported far from its source and not settle to the sediment until reaching areas of high water stability. Considering that a survey of 13,000 published results from international literature (Ure & Berrow, 1982) gave a world average of 93 µg/g of Ni in soils, the concentrations found in the study region are generally lower. Proposed sediment quality guidelines for Ni (MacDonald *et al.*, 2000) are 22.7 µg/g for TEC[♣] and 48.6 µg/g for PEC and the concentration were

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[♣] Threshold effect concentration (TEC): The concentration above which toxicity may be observed.

higher than proposed PEC during many observations in the study region, particularly at muddy stations. However, Ni represents only a moderate to very low toxicity for many aquatic plants and fish (Moore, 1991). Nickel concentration in the study region was above ERM[♣] values (Long & Morgan, 1990; Long *et al.*, 1995) and those for Pb was between ERL and ERM values. Hence they possess possible detrimental effects to benthic organisms.

Trace metal enrichment in estuarine and marine sediments also results from the presence of metal scavenging phases like Fe/Mn hydroxides during estuarine mixing and the process are described in next section. Fe/Mn hydroxides help in the removal of several trace elements from natural waters by lattice substitution and surface adsorption process. It was reported that the higher content of some of the trace metals in Cochin inner shelf (Paropkari, 1990) and estuary (Padmalal et al., 1997) were resulted from the physico- chemical flocculation of Fe and Mn hydroxides.

The major changes that occur in redox conditions between oxic waters and anoxic sediments had profound influences on the speciation and bioavailability of many trace metals. Sulfate is the major electron acceptor driving organic matter oxidation in anaerobic marine sediments, after oxygen utilization in the top few millimeters (Gaillard *et al.*, 1989). Anoxic conditions in sediments often result in the microbially mediated production of major amounts of hydrogen sulfide in marine and estuarine environments. As soon as sulphate-reduction began, dissolved Fe

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Probable effect concentration (PEC): The concentration above which toxicity is frequently observed.

[♣] ERL and ERM delineate concentrations at with adverse biological effects occur rarely (<ERL, <10% occurrence), occasionally (between ERL and ERM, 10-50%occurrence), and frequently (>ERM, 50% occurrence).

concentrations will decrease, reflecting the co-precipitation of Fe and S in the form of framboidal pyrite (Marchand *et al.,* 2003) and probably also greigite. Pyrite is an important sink for trace metals since many of them are incorporated during its formation (Boule`gue *et al.,* 1982). Huerta-Diaz & Morse (1992), in their study of the pyritization in anoxic marine sediments, found that incorporation into pyrite was high for Hg, moderate for Co, Mn, Cu, and Ni and low for Cr, Pb and Zn.

Trace metal-sulfide interactions can have a profound influence on the bioavailability of toxic metals in sediments (Di Toro *et al.,* 1990; 1992; Morse, 1994). The source of free sulfides is presumed to be the solid-phase iron sulfides which dissolve in response to the depletion of pore-water sulfides as those become bound to other metals, the overall reaction being expressed as: $Me^{2+} + FeS_{(s)}^{-} > MeS_{(s)} + Fe^{2+}$. The above reaction implies that divalent metal may displace the iron in FeS(s) and form insoluble metal sulfide (MeS(s)) and soluble ferrous iron (Fe^{2+}) as sediment metal concentrations increases (Di Toro *et al.,* 1990; 1992). This reaction occurs quite rapidly and yields a non-bioavailable solid metal sulfide (Casas & Crecelius, 1994). Under oxic conditions, Pb, Ni and Co can be easily adsorbed on oxide fractions (Lienemann *et al.,* 1997; Zwolsman & van Eck, 1999; Dong *et al.,* 2000). On the contrary, in anaerobic conditions, active sulphide co-precipitation rapidly removes Co, Cu, Ni, Pb and Zn from the dissolved phase (Balistrieri *et al.,* 1994; Clark *et al.,* 1998; Schlieker *et al.,* 2001). Chances of decrease of redox potential due to organic matter or the depletion of dissolved oxygen content are minimal at the sandy stations 2and 5, due to higher dynamics (chapter 3). This may be the reason for the enrichment of Pb and Ni at these stations.

4.3.4 Benthos

The sediment-water interface in estuarine ecosystems often is highly dynamic and resident organisms are faced with erosion, transport, and deposition events of various magnitudes over various time scales, as mentioned earlier. Estuarine benthic organisms are frequently subjected to these disturbances caused by hydrodynamic processes that disrupt and move the sediment in which the animals reside, however the mechanisms by which physical disturbance processes affect infaunal and epifaunal populations and communities remain poorly resolved (Hinchey *et al.*, 2006). In addition, anthropogenic activities such as dredging and dredged material disposal are common and cause significant, although localized, sediment disturbance (Maurer *et al.*, 1986; Hall, 1994). Sediment deposition resulting from terrestrial run-off is also emerging as a threat to shallow estuarine and coastal benthic communities worldwide (Edgar & Barrett, 2000; Norkko *et al.*, 2002). Some benthic species had mechanical and possibly physiological adaptations to survive deposition events of the magnitude commonly encountered in estuarine environments (Hinchey *et al.*, 2006). It is accepted that significant spatial and temporal variability is characteristic of benthic faunal assemblages in estuarine sediments (Morrisey *et al.*, 1992; Chapman, 1998). Significant increase of acid volatile sulphide in both surface and subsurface sediments corresponded to the most remarkable changes among macrofaunal assemblages (Magni *et al.*, 2006). Confounding natural variables, especially organic content, salinity and sediment granulometry, often influence community structure and mask the effects of low levels of contamination (Gray *et al.*, 1988; Wilson & Elkaim, 1992). Pore water transfer of chemicals in the upper 1 cm of the sediment layer is controlled by molecular diffusion and benthic activity (Hennies, 1997).

The benthic data of the present study are in good agreement with the earlier investigations carried out in the Cochin estuary in the species composition, density and seasonal variations (Desai & Krishnankutty, 1967; Ansari, 1974; Kurian *et al.*, 1975; Pillai, 1977; Saraladevi & Venugopal, 1989; Sunilkumar, 1995). Salinity is the most significant hydrographic parameter influencing the benthic fauna in the study region and the nature of substratum could also be important. Though station 5 showed the lowest benthic density, it was higher for stations other sandy stations 1 and 2. In a similar way, off the muddy stations, though station 7 showed maximum density, it was lower for stations 8 and 10. Correlation analysis also reflects this anomaly, showing no significant correlations with any of the other sedimentary parameters. This also indicates the dominance of salinity in regulating the benthic fauna in the study region. This was further supported by their significant positive correlation (r=0.683) with salinity. Further the distribution of organisms within estuaries is influenced more highly by variation than by absolute salinity regimes (Wolff, 1983; Attrill, 2002). Higher heavy metal concentrations in muddy stations may also affect the benthic population inversely, as discussed earlier.

Though the importance of sediment composition in determining (spatial) distribution patterns of estuarine benthic fauna has long been recognized (Snelgrove & Butman, 1994), the nature of the sediment (in terms of granulometric characterization, organic matter) did not fully explain the substantial spatial and temporal (seasonal) variability in the benthos (Ysebaert *et al.*, 2005), as found in the present study. Hennies (1997) also remarked that relationship between the distribution of benthic flora and fauna and sediment parameters is difficult to determine. Though correlation between benthic species richness and organic enrichment has been reported in numerous studies (Majeed, 1987; Weston, 1990), very high concentrations of organic matter drive the benthos to an afaunal state. Oxygen concentrations in water are therefore a major factor in the structuring and functioning of benthic communities. In the case of permanent anoxia, the macrofauna is eliminated from benthic communities. In addition to physiological stressors such as reduced or variable salinity and hypoxia, sediment instability may be a major physical stressor affecting the composition and abundance of benthic communities in some estuaries (Schaffner *et al.,* 2001). It is still unclear that how functional changes could alter rates of nutrient regeneration and bioturbation in benthic systems (Weston, 1990). When the water body is shallow, the residence time is long and the suspension feeding biomass is high, the secondary trophic level is dominated by benthic ecosystems and can even regulate pelagic primary production (Cloern, 1996).

4.4 Factor Analysis

The geochemical parameters in the present study were further analysed using principal component analysis (PCA) to find the major biogeochemical processes in this estuary and their spatial variations. This data set is large and complex and does not offer a direct interpretation. The main aim of PCA is to reduce the number of variables that needed to be considered into a smaller number of indices, principal components (PCs), which can be more easily interpreted (Manly, 1997; Panigrahy *et al.*, 1999; Spencer, 2002). Principal component analysis (PCA), a multivariate statistical technique, is generally employed to reduce the dimensionality of a data set while attempting to preserve the relationships present in the original data. Factor analysis is a powerful statistical technique, which delineates simple patterns distributed among complex data by evaluating the structure of the variance-covariance matrix and extracting a small number of hypothetical variables (R mode) or samples (Q mode), referred to as factors (Klovan & Imbrie, 1971). Duman *et al.*, (2006) successfully used PCA analysis to describe the geochemistry and sedimentology of Black Sea.

Major biogeochemical processes in estuaries

Massive biological and chemical recycling of nutrient and metal constituents occurs in most estuaries (Burton & Liss, 1976; Paulson *et al.*, 1993). Chemical removal of trace metals from water to sediments occurs frequently when fresh and saline waters are mixed (Paulson *et al.*, 1993; Millward & Glegg, 1997; L'Her Roux *et al.*, 1998). The variations in physical mixing and local inputs (Paulson *et al.*, 1993; Owens & Balls, 1997), the domination of biological processes (Paulson *et al.*, 1993) and the domination of riverine and anthropogenic inputs (Millward & Glegg, 1997; Owens & Balls, 1997) in different estuaries make the generalization impossible in estuarine trace metal cycling. Trace metal removals by biological processes are comparatively lower in estuaries (Church, 1986).

In estuarine environments, the chemical form in which metals are present during physical mixing is assumed to play an important role in their geochemical cycle (L'Her Roux *et al.*, 1998). Complexation with dissolved organic (van den Berg *et al.*, 1987) and inorganic (Comans & van Dijk, 1988) species, and interactions with particulate material (Turner *et al.*, 1993; Owens & Balls, 1997) and sediments were demonstrated to play a major controlling role in the trace metal behaviour. It has been shown that the partitioning of metals between the dissolved and particulate phase, due to adsorption, desorption, precipitation and flocculation, takes place frequently within the estuarine zone (Sholkovitz, 1976; Li *et al.*. 1984; Stumm, 1987; L'Her Roux *et al.*, 1998), and that the rate and extent to which this occurs depend on many factors including metal reactivity and the estuarine hydrodynamics (Morris, 1990; Millward & Turner, 1995).

Gibbs (1973) suggested four groups of heavy metal associations in aquatic solid substances characterized by the bonding processes viz. adsorptive bonding, coprecipitation by hydrous iron and manganese oxides, complexation by organic molecules and incorporation into crystalline minerals. Precipitation, primarily of hydroxides, sulphides and carbonates occurs with in a water body when the corresponding solubility product is exceeded. Carbon and sulphur are the most important elements controlling solubilities of metal ions in natural waters.

A number of sediment-forming materials with a large surface area- particularly clay minerals, freshly precipitated iron hydroxides, amorphous silicic acids, as well as organic substances-are capable of sorbing cations from solution and releasing equivalent amounts of other cations into the solution by cation exchange. This exchange is based on the sorpive properties of the negative charged anionic sites in the above groups towards positively charged cations. Further, these fine-grained materials with large surface area are capable of accumulating heavy metal ions at the solid-liquid interface by adsorpion. The redox sensitive Fe and Mn hydroxides and oxides under oxidizing conditions constitute significant sinks of heavy metals in aquatic systems. These hydroxides and oxides readily sorb or coprecipitate cations and anions; even a low percentatge of $Fe(OH)_3$ and MnO_2 has a controlling influence on the heavy metal distribution in an aquatic system. Under anoxic conditions, the sorbed heavy metals are readily mobilized. Accumulations of hydrous Fe/Mn oxides can therefore act as a source of dissolved metals in natural waters. In aquatic environment, Fe and Mn hydroxides and oxides commonly occur as coating on minerals and finely dispersed particles. The active forms exhibit higher specific surface areas (Förstner & Wittmann, 1983).

When the dissolved oxygen level is low, iron sulphide minerals like greigite will form and these thermodynamically unstable minerals will transform to pyrite during early diagenesis (Berner, 1970). Coagulation and inorganic precipitation are the possible processes responsible for the inclusion of trace metals in anaerobic sediments. There are three major processes leading to the incorporation of particular metal-organic species into sediments (Förstner & Wittmann, 1983). They are reaction between metal ion and organic ligand in solution, leading to a species which can either precipitate directly or be absorbed on sedimentary material; incorporation in a sedimentary pile of all or part of an organism containing biologic coordination compounds and adsorption on a sediment of molecules resulting from the solubilisation of minerals (sulphides, carbonates, etc.) by natural waters containing organic ligands.

Sorption of trace metals on carbonates and phosphates are also important process in aquatic environment. Coprecipitation with carbonate minerals may be an important mechanism for a number of metals like Zn and Cd (Deurer *et al.,* 1978). Calcite minerals are important nucleation centers for manganese oxides since there is a microzone of higher pH on the surface of the carbonates (Förstner & Wittmann, 1983). Sorption of phosphates and polyphosphates on to clay minerals involves chemical bonding of the anions to positively charged edges of the clays as well as substitution of phosphates for silicates in the clay structure (van Olphen, 1963). Characteristic sorption of phosphate anions occurs on freshly precipated ferric and aluminium hydroxides (Förstner & Wittmann, 1983). Natural silicates provide catalytic surfaces to organic molecules influencing transformations such as polymerization, isomerization, hydrogenation and conversion to cyclic compounds (Degens, 1965). There is an increasing tendency of dissolved organic compounds to adsorb onto solid substances as the molecular mass of the organic compounds increases (Mortland, 1970).

The transition of sediments from the water to the estuarine sediment by the above mentioned processes like flocculation, adsorption and precipitation may give rise to diagenetic processes associated with the depletion of the dissolved oxygen content in the sedimentary environment as a result of microbiological activity. Idealized diagenetic reactions in aquatic sediments are aerobic respirations, nitrification, denitrification, manganese reduction, iron reduction, sulphate reduction and methane production (Aller, 1982). Oxygen penetration and thus aerobic decomposition processes in coastal marine sediments are usually limited to the upper few millimeters (Revsbech *et al.*, 1980; Howarth & Jørgensen, 1984). Estuarine sediments are essentially anaerobic below a few surface millimeters, and the mineralization of organic matter proceeds via alternate electron acceptors such as NO_3^- and SO_4^{2-}. It has been found that sulfate reduction is typically the predominant process responsible for the mineralization of organic carbon in anaerobic marine sediments (Jorgensen & Sorensen, 1985; Seitzinger & Giblin, 1996) and generally accounts for 5–50% of the total mineralization of organic matter in shallow coastal sediments (Jorgensen & Sorensen, 1985; Berelson *et al.*, 1996). Anaerobic sulfate reduction is particularly important in marine environments due to the high abundance of sulfate (Jørgensen, 1982; Skyring, 1987).

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 84.8\ NO_3^- \longrightarrow 84.2\ HCO_3^- + HPO_4^- + 16\ NH_3 + 65.6\ H_2O + 42.4\ N_2 + 23.2\ CO_2$$

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 53\ SO_4^{2-} \longrightarrow 106\ HCO_3^- + 16\ NH_3 + H_3PO_4 + 53\ H_2S$$

It is well known that NO_2–N and NO_3–N will be released during oxidation of NH_3 (Suess *et al.,* 1980; Nath & Mudholkar, 1989; Sharma & Kaur, 1996), which is produced as a result of the diagenetic decomposition of organic matter rich estuarine sediments (De Lange 1986; DiToro *et al.,* 1990) and brought to the sediment-water interface during sediment compaction (Manheim, 1976; Hakanson & Jansson, 1983; Padmalal & Seralathan, 1991). This process together with decomposition of organic matter drastically lowers the DO levels of the micro layer at the sediment-water interface and thus setting up an anoxic situation within a few centimeters of the sediment substratum. This naturally favours the release of more and more NH_3–N and PO_4–P through the biologically mediated breakdown of organic matter rich sediments. Under this reducing condition, a part of Fe will be released as Fe^{2+}, which is the most soluble form of Fe and concentrates in the interstitial water (Padmalal & Seralathan, 1995). Another portion will be trapped in sediments as iron sulphide minerals under this supposed anoxic condition (Berner, 1970). During sediment compaction, the pore fluids rich in these ingredients (and its partially oxidised forms produced in the sediment micro layer at the sediment-water interface) will be welled out/ bubbled out to the bottom waters where NH_3 rapidly oxidizes to NO_2–N and finally to NO_3–N through biologically mediated reactions.

$$2\ NH_3 + 3O_2 \xrightarrow{\text{Nitrosifying bacteria}} 2\ HNO_2 + 2H_2O + 158\ \text{k.cals}$$

$$2HNO_2 + O_2 \xrightarrow{\text{Nitrifying bacteria}} 2\,HNO_3 + 38\ \text{k.cals}$$

The benthic fauna through their feeding, bioturbation, burrow construction and burrow irrigation activities influence the rates of organic matter inputs to the sediment, their vertical distribution, rates and pathways of mineralization within the sediment compartment and the fluxes of the regenerated dissolved nutrients back to the overlying water (Aller, 1988; Christensen *et al.,* 2000; Kristensen, 2000). The degree of these effects is in large part dependent upon the comportment of the individual species and in particular, their feeding mode. Therefore, the biomass, population density and community structure of the benthic fauna is a significant determinant of local nutrient recycling rates and hence influences primary production in the overlying water column, which in turn, ultimately represents the organic matter input to the sediment and the food source for the benthic community (Welsh, 2003). Three principal mechanisms were suggested by (Welsh, 2003). Firstly the macrofauna influence organic and inorganic nutrient fluxes to the water column through their effects on organic matter deposition rates and the depth distribution of this organic matter in the sediment. Secondly, the macrofauna directly influence benthic fluxes of oxygen and dissolved nutrients through their metabolism. Thirdly, the benthic macrofauna also stimulate sediment-water column fluxes of dissolved species through bioturbation and the construction of burrow structures.

The bottom dynamic conditions are highly significant in the geochemistry and accordingly three areas can be defined (Håkanson, 1977). Areas of erosion (E) are having no apparent deposition of fine materials but, rather, a removal of such materials, consisting of sand and gravel. Areas of transportation (T), where fine materials are periodically deposited generally dominate where wind/wave action regulates the bottom dynamic conditions. Areas of accumulation (A) prevail where the fine materials are deposited continuously (soft bottom areas). These are the areas, the 'end stations', where high concentrations of pollutants might appear. The sedimentological behaviour of the friction material is closely linked to the grain size of the individual particles (Hjulström 1935). Brownian motion governs the sedimentological behaviour of the very fine materials. These latter particles are so small that they will not settle individually, but will do so if they form larger flocs or aggregates dense enough to settle according to Stokes' law (Lick *et al.* 1992). The cohesive materials that follow Stokes' law are very important as they have a great affinity for pollutants. This group includes many types of detritus, humic substances and plankton, all of which play significant roles in aquatic ecosystems (Wetzel 1983; Salomons & Förstner 1984).

The generally hard or sandy sediments within the areas of erosion and transport (E, T) often have low water content, low organic content and low concentrations of nutrients and pollutants. For natural reasons, the conditions within the T-areas are variable, especially for the most mobile substances (phosphorus, manganese, iron), which might react rapidly to alterations in the chemical 'climate' of the sediments (given by the redox potential). Fine materials might be deposited for long periods during stagnant weather conditions. In relation with a storm or a mass movement on a slope, this material might be resuspended and transported up and away, generally towards the A-areas in the deeper parts, where continuous deposition occurs. Therefore, resuspension is a most natural phenomenon on T-areas.

In the present study, factor analysis is attempted using the data on all the analysed sedimentary parameters. The parameter with factor loadings of greater than 0.4 and factors with eigen values greater than 1 are considered for interpretation. Although the system characteristics vary widely between stations; factor analysis method was applied out to find the dominant process in the study region. For this, the principal component analysis was carried out by taking the seasonal averages of the biogeochemical parameters of all the six stations together (Table 4.15a).

Factor analysis of the system characteristics as a whole showed two dominant factors with a total variance of 92.49 %. Principal component, which has 86.26 % of variance, has high positive loadings for trace elements, mobile elements, nutrient elements and silt and clay components and negative loadings for sand. Component 2 with high positive loadings for benthic density accounts for 6.23 % of the total variance. Hence it can be inferred that geochemical processes are the dominant factor controlling the geochemistry of the study region, along with a low dominance of benthic activities.The anthropogenic influence is seemed to be of little significance as discussed earlier.

Table 4.15 Factor matrix for seasonal averages of all sedimentary parameters in the study region

Total Variance Explained

Component	Initial Eigen values			Extraction Sums of Squared Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	14.664	86.260	86.260	14.664	86.260	86.260
2	1.059	6.229	92.488	1.059	6.229	92.488

Extraction Method: Principal Component Analysis

Component Matrix [a]

	Component	
	1	2
Cu	.990	-2.40E-02
Zn	.961	.136
Ni	.980	-2.44E-02
Pb	.959	-7.16E-03
Mn	.926	.171
Cr	.971	.152
Co	.963	-4.44E-02
Mg	.952	.164
Fe	.989	-7.70E-04
TN	.964	4.155E-02
TC	.953	-7.31E-02
TS	.911	-.123
TP	.907	-5.89E-03
Sand	-.976	6.939E-02
Silt	.949	-.117
Clay	.941	2.158E-02
Benthos	-.198	.958

Extraction Method: Principal Component Analysis.

a. 2 components extracted.

The geochemical distribution patterns of various elements in the study area indicate that the texture of the sediments is the major controlling factor on sediment geochemistry. The contribution of bottom dynamics, as discussed above in forming erosional and depositional zones were also seems to be significant. Stations 1, 2, and 5 with coarse substratum showed almost same chemical composition and trends. Stations 7, 8 and 10 have fine sediments with a different chemical composition than that of former stations.. Hence, factor analysis was separately carried for these two groups in order to eliminate the differences that are attributable entirely to the variations in grain size (Table 4.16a,b).

Table 4.16a Factor matrix for Group 1 (stations 1, 2 and 5)

Total Variance Explained

Component	Initial Eigen values			Extraction Sums of Squared Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	8.608	66.213	66.213	8.608	66.213	66.213
2	1.700	13.078	79.291	1.700	13.078	79.291

Extraction Method: Principal Component Analysis

Component Matrix [a]

	Component	
	1	2
Cu	.975	-.145
Zn	.917	-.260
Ni	.823	-.216
Pb	.386	-.196
Mn	.959	-.225
Cr	.943	-5.85E-02
Co	.869	6.946E-02
Mg	.951	-.251
Fe	.942	-.243
TN	.587	.677
TC	.715	.669
TS	.679	.662
Benthos	.559	-2.64E-02

Extraction Method: Principal Component Analysis.

a. 2 components extracted.

Factor analysis showed that 79.29 % of variance due to two factors for group 1. Principal component that has 66.21 % of variance showed significant positive loadings for all components except lead, which has a comparatively low positive loading. Factor 2 has significant positive loadings for TC, TN and TS and insignificant negative loadings for all trace metals and benthos.

Sediments were low in organic content and the prevailing condition in this region in oxic. The low C:N ratio and the freshness of the sediments indicate that the major biogeochemical process in these stations is autochthonous addition, the deposition of materials generated in the water column. This is in agreement with the earlier discussions, constituting the first factor. All the metals are having significant positive loadings with in fact supports the addition. Though lead showed a clear enrichment in this region, there was only low lading for Pb. This indicates that lead is not added through the above process. Benthos also showed significant positive loading in this component, which supports the autochthonous addition in to the sediments.

Generally in the systems like the present one, diagenesis is the major biogeochemical process, which release organic carbon by mineralisation. The organic associated metals shall also exhibit a decrease in concentration. In the present case C,N and S, the indicators of diagenesis showed positive loadings there by assigning the component 2 to diagenesis. But in the case of metals, an opposite loading pattern is observed. The inorganic adsorption of the metals by silicates may be the possible reason. This, being an erosional zone, the deposited particles are not being stored, evident by low carbon content. The organic carbon content was about 80-95% of the total carbon and the low sulphur content testify to a slack proceeding of diagenetic processes.

Table 4.16b Factor matrix for Group 2 (stations 7, 8 and 10)

Total Variance Explained

Component	Initial Eigen values			Extraction Sums of Squared Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	6.769	52.071	52.071	6.769	52.071	52.071
2	2.156	16.582	68.654	2.156	16.582	68.654
3	1.044	8.032	76.685	1.044	8.032	76.685

Extraction Method: Principal Component Analysis

Component Matrix[a]

	Component		
	1	2	3
Cu	.947	-.182	.143
Zn	.668	.497	-.209
Ni	.681	-.174	-.325
Pb	.427	.118	-.459
Mn	.782	.498	-9.75E-02
Cr	.751	.333	.316
Co	.661	-.279	.453
Mg	.768	.494	-.135
Fe	.899	-.167	2.730E-02
TN	.815	.238	.164
TC	.833	-.449	9.581E-02
TS	.516	-.721	6.015E-02
Benthos	-.379	.587	.539

Extraction Method: Principal Component Analysis.

a. 3 components extracted.

Principal component analysis of the monthly data established 3 components for the second group with a total variance of 76.68 %. Factor 1 with 52.07 % variance has significant positive loadings for most of the parameters except benthic density. Factor 2 has significant positive loadings for Zn, Mn, Mg and benthos and negative loadings for TS and TC with 16.58 % of variance. Factor 3 (8.03 % variance) has significant positive loadings for benthos and Co and negative loadings for Pb and Ni.

This region in being the depositional zone and organic rich and anoxic condition is prevailing here. From the loading patterns, the principal geochemical process in this region may be the diagenetic decomposition. This process release organic carbon by mineralisation and also the organic associated metals. Second dominant factor seems to be the storage processes like pyritization, coprecipitation and adsorption. But carbon and nitrogen showed difference in behaviour in this component. This may be because of higher accumulation of sulphur by anthropogenic addition. An enhanced input of sulphur may stimulate reduction, substantially altering the cycling of elements such as carbon, nitrogen, phosphorus and iron. Clay minerals present acidic catalytic and redox properties that promote the polymerization of organic residual substrates, which strongly contribute to their humification. Hence metal selectivity is shown in this region, where carbon is comparatively refractory than the sandy stations (higher C:N ratio than the former). Because of the metal selective processes, no uniform regulatory process can be seen for the metals. Third dominant process seems to be the benthic activity. The negative loadings for Ni and Pb indicate the contribution from anthropogenic sources.

Summary and Conclusion

The geochemical data of showed that sediment textures and mineralogy were highly variable in the study region and were related to hydrodynamics. The nutrient elements in the study region did not show any seasonal trend and varied widely with respect to the granulometric compositions of sediments. Stoichometric ratios of nutrients indicated the autochthonous origin of organic matter and also a possibility of phosphorus enrichment in this estuary. Very high levels of sulphur (about 1% dry weight) indicated an anthropogenic source. Sediment enrichment factor (SEF) analysis showed the chances of Ni and Pb enrichment, particularly at sandy stations, suggesting a different source of input. The benthic fauna was influenced by salinity and the nature of substratum. PCA analysis indicated that the major biogeochemical process in the sandy stations was autochthonous addition, where as diagenesis dominated in the muddy stations.

The essentiality of metal speciation in organic rich sediments is evident from the factor analysis by grain size normalization, since metals are on independent behaviour in the clay sediments and general criteria were not useful. It is known that besides the input from natural and anthropogenic sources, heavy metal distribution in sediments can be affected by factors such as sediment chemical composition and diagenesis (Salomons & Forstner, 1984). Since total concentration does not yield information on mobility, origin or bioavailability of metallic elements, metals in sediments have to be associated with the different fractions (Li *et al.,* 2000; Zhang *et al.,* 2001; Cobelo-García & Prego, 2004). The chemical species, rather than the metal itself, that plays the important role in the transfer of metals along the water–soil–plant–animal–human chain (Shrivastava & Banerjee, 1998). The determination of potentially available metals by sequential chemical extraction offers a more realistic estimate of actual environmental impact.

From the analysis of the surficial sediments, phosphorus was found to be suitable for giving a better index of the biogeochemical processes in the study region. Hence phosphorus was further examined using sequential extraction scheme in the next chapter. Fundamental understanding of phosphorus behavior is a key to solving environmental problems of nutrition, eutrophication and geochemistry.

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Chapter 5

NUTRIENT DYNAMICS

5.1 Introduction

Phosphorus is the eleventh-most common element in the earth's crust. The German alchemist H. Brandt probably discovered phosphorus about 1669 in Hamburg. The word phosphorus is derived from the Greek "phos" meaning "light" and "phorus" meaning "bringing". Phosphorus occurs primarily as phosphate in deposits of apatite [$Ca_5F(PO_4)_3$], a mineral found in igneous, sedimentary and metamorphic rocks. Rocks containing apatite, when exposed to weathering, release the phosphate into the environment. Phosphorus is an important nutrient affecting the ecological balance of aquatic and terrestrial habitats and can influence species composition. The most important function of phosphorus in plants is the storage and transfer of energy, and cell division (Troeh & Thompson, 1993). Phosphorus is the mineral with the most known biological functions in animals (Beede & Davidson, 1999). In addition to providing the phosphate-ester backbone of DNA and RNA, phosphorus is critical in the transmission of chemical energy (via the ATP molecule) and in structural components such as phospholipids (in cell membranes), teeth, and bones. Whole blood contains 6-8 times more phosphorus than plasma.

Phosphorus is an important nutrient that plays a limiting role in terrestrial productivity (Schlesinger, 1997). It is perhaps one of the most critical nutrients to ecosystems on longer time scales (Howrath *et al.,* 1995; Tyrell, 1999) because its only natural source is typically derived from the slow process of rock weathering, compared to vast atmospheric source of nitrogen. Phosphorus plays a key role in oceanic biogeochemical cycles (Holland, 1978; Broecker, 1982; Smith, 1984; Codispoti, 1989; Howarth *et al.,* 1995; Tyrell, 1999). The importance of P limitation in the modern ocean has also been highlighted recently in the north Atlantic (Sanudo-Wilhelmy *et al.*, 2001) and north Pacific (Karl *et al.*, 2001). Thus decrease in the availability of dissolved P may reduce the surface productivity, which may lead to reduction in export fluxes of carbon, eventually resulting in lower burial of organic carbon in sediments. Changes in the oceanic burial of organic carbon affect the sedimentary pyrite formation (Berner, 1984) and control the partial pressure of atmospheric oxygen and carbon dioxide (Holland, 1984; Berner, 1989; Berner & Canfield, 1989). Thus understanding the phosphorus cycle in the oceanic realm aids in understanding the geochemical cycling of P, C, S and oxygen on a geological time scale (Babu & Nath, 2005). Phosphate can be used to immobilize metals primarily through the formation of metal phosphates with reduced solubility and enhanced geochemical stability in a wide range of environmental conditions (Cao *et al.*, 2003).

Increases in anthropogenic activities, such as agricultural (prolonged application of superphosphate fertilizers) and urban development, and the diffuse nature of its associated nonpoint source pollution from surface runoff and/or ground water contamination have become a major water quality concern. Phosphorus occurs in a sedimentary cycle with no significant gaseous loss mechanism, so it tends to accumulate in wetland systems. Depending on limnological conditions, sediments can function either as sources or sinks for P (Fisher *et al.*, 1982; Koop *et al.*, 1990; Olila & Reddy, 1995). The adsorption and desorption of P by sediments mainly depend on their physical, chemical, and biological properties. In general, sediments retain inorganic P at considerably greater concentrations than those observed in sediment porewater, whereas at low water column P concentrations, sedimentary P can function as an internal load to the overlying water column for a long period (Froelich, 1988; Afif *et al.*, 1993; Ravan & Hossner, 1993;Lijklema, 1993; Reddy *et al.*, 1996). Fundamental understanding of phosphorus behavior is a key to solving environmental problems of plant, animal and microbe nutrition, eutrophication, corrosion and geochemistry (Morton & Edwards, 2005).

There is much interest in the capability of sediments to sequester P because of its effect on oceanic P budget (Ruttenberg & Berner, 1993; Howarth *et al.*, 1995) and productivity of estuaries (Caraco *et al.*, 1990). The challenge of addressing the issue of P transfer to water bodies is, however, complex. Relatively little is known about the concentrations, turnover rates, transport, and fate of P in the aquatic system and practically nothing is known about the composition and changes in composition of this pool with age/depth and location. Accordingly, identification of P compounds in estuarine sediments and knowledge of changes in the makeup of the phosphorus pool in space and time are relevant for understanding the origin, transformations, and regeneration of phosphorus. Also the control of tropic status requires limitation of phosphate inputs (Morton & Edwards, 2005). The exchange of nutrients across the sediment–water interface in shallow coastal and estuarine systems has been the focus of number of studies (Hargrave, 1973; Koop *et al.*, 1990). Since phosphorus behaviour in soil, in water and at the interface between these two media is very complicated, P management is a challenge that requires a multi-disciplinary approach. Phosphorus cycling and bioavailability in estuaries also depend upon P speciation (de Jonge & Villerius, 1989; Lebo, 1991; Paludan & Morris, 1999; Andrieux-Loyer & Aminot, 2001). Sequential chemical extraction techniques have been a useful tool to examine these processes (Psenner & Puckso, 1988; Ruttenberg, 1992;

Jensen & Thamdrup, 1993). The range of conditions such as salinity, pH or redox potential present in estuarine systems determines the relative importance of each fraction (de Jonge & Villerius, 1989; Lebo, 1991; Paludan & Morris, 1999). This is important for understanding the P cycle, for defining processes of P regeneration in the water column, and for better interpretation of sedimentary P burial as a proxy for past nutrient burial and as a paleoproductivity indicator.

This chapter attempts to evaluate the phosphorus dynamics and bioavailability in the surficial sediments of this estuary. It intents to quantify the significance of the different phosphorus fractions and the temporal trends in distribution to elucidate their relative importance in the phosphorus dynamics. It also envisages understanding the diagenetic transformations of organic phosphorus in the estuarine sediments. An attempt to evaluate the physical significance was also made by measuring the different species in fine and coarse fractions of the sediment.

5.2 Phosphorus dynamics in the environment

Earth's crust contains an average of about 0.1% phosphorus and it exists primarily as calcium phosphate, mostly in phosphate rocks (van Wazer, 1961; Klein & Hurlbut, 1999). Approximately 300 naturally occurring minerals contain the PO_4^{3-} structural unit (Jahnke, 2000). Apatite is the most common, accounting for over 95% of P in the crust (Jahnke, 2000). It occurs as an accessory phase in igneous rock (0.02-1.2%) and in sedimentary environments such as marine phosphorite deposits (biogenic carbonate-apatite minerals), which are mined, for rock phosphate to make fertilizer (Jahnke, 2000; Welch *et al.*, 2002). The diagenesis of sediments containing bird or bat guano can also lead to the crystallization of apatite and other P-minerals (Tiessen *et al.*, 1996). Additionally, the minerals strengite and variscite have been identified as important soil constituents (Karathanasis, 1991; Tiessen *et al.*, 1996; Golden *et al.*, 1997). Apatite, strengite, and variscite are widely regarded as weathering end-member phases in soils (Armstrong & Helyar, 1993; Ghosh *et al.*, 1996) and therefore represent the least bioavailable forms of inorganic Ca, Fe and Al phosphate. Over time and because of weathering of rock surfaces, phosphates became available to organisms (Duley, 2001), with a very slow turnover rate of more than 1 Gy (10^9 years) as restricted by diagenesis (Pierrou, 1979). The primary anthropogenic nonpoint sources of phosphorus include runoff from land areas, which are mined for phosphate deposits, agricultural areas, and urban/residential areas. Phosphorus also originates from the use of industrial products, such as toothpaste, detergents, pharmaceuticals, and food-treating compounds. Eutrophication is often caused by excessive inputs of phosphate through the above sources, and it is well known that control of tropic status requires limitation of phosphate inputs (Morton & Edwards, 2005).

Phosphorus forms within the environment are classified in terms of organic and inorganic composition. Phosphorus in the environmental compartments, in relation to organic and inorganic forms is shown in Fig. 5.1. Phosphorus is known to occur in at least 7 oxidation states, including the phosphides (-3), diphosphide (-2), tetraphosphide (-0.5), elemental phosphorus (0), hypophosphite (+1), phosphite (+3), and phosphate (+5). Phosphorus species with an oxidation state lower than (+5) are generally termed as "reduced phosphorus." (Morton & Edwards, 2005)

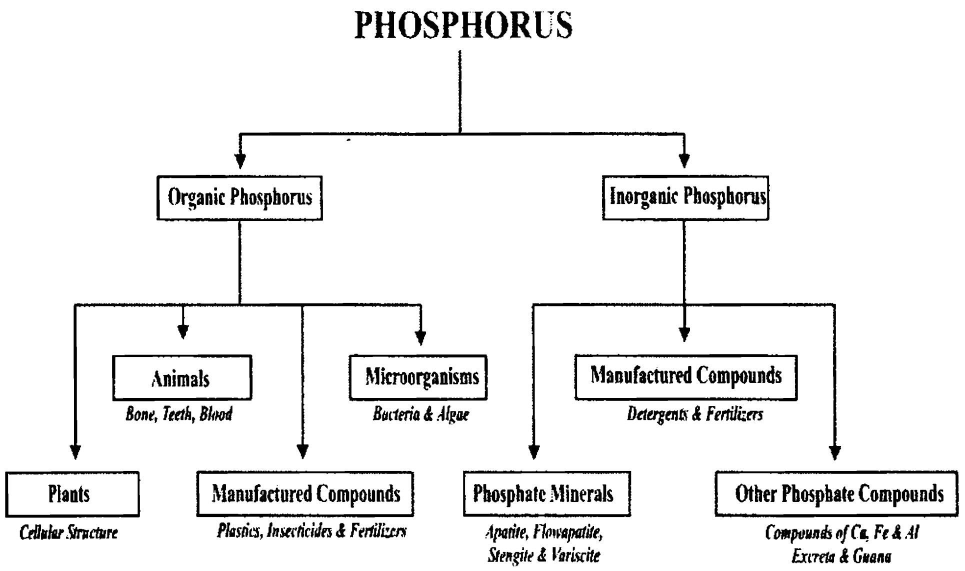


Figure 5.1 Different forms of P in the environment

The forms of soil P include P in apatite minerals, P co-precipitated with and/or adsorbed onto iron, manganese, and aluminum oxyhydroxides (termed "occluded" P), P in soil pore spaces (as dissolved phosphate), and adsorbed onto soil particle surfaces (these forms are termed "non-occluded" P), as well as P in soil organic matter. With time and soil development, however, P is increasingly released from apatite form and incorporated in the others. The most frequent soluble forms of phosphorus are orthophosphate ($H_2PO_4^-$and HPO_4^{2-}) under the pH conditions normally encountered in natural waters and organic phosphorus compounds. Orthophosphates are readily available for assimilation by organisms; they may, however, be removed from the dissolved phase by chemical precipitation with Al^{3+}, Fe^{3+} and Ca^{2+}(Spivakov *et al.,* 1999). Particulate and dissolved organic phosphorus forms undergo bacterial decomposition (mineralization) and the phosphorus is transferred into the soluble orthophosphate pool. The major quantity of the phosphorus that enters the aquatic systems does so in particulate form. Rock weathering releases a number of so-called accessory minerals, apatite being one of the most abundant in silicate rocks. Rock weathering also produces as reaction products a number of clay minerals with large adsorptive capacities (Bostrom *et al.,* 1982), and orthophosphates as well as some organic phosphorus compounds might be sorbed on the surface of such particles and reach the lake bottom. The association of both orthophosphates and organic phosphorus compounds with iron, manganese and aluminum occurs as surface sorption on freshly precipitated oxyhydrate gels of these metals; post-depositional processes (diagenesis), however, produce a large number of well-defined chemical species, the most often encountered ones being vivianite and ludlamite; others such as dufrenite, graftonite, phosphoferrite, klinostrengite and anapaite (Strunz, 1972) are to be expected as well according to the local redox conditions.

The potential importance of atmospheric phosphorus loading to aquatic systems was well established (Schindler *et al.,* 1976; Lewis *et al.,* 1985; Chambers & Dale, 1997; Benitez-Nelson, 2000). Pierrou (1979) estimated that atmospheric fallout of phosphorus is in the range of 3.6–9.2 Tg P/yr (Tg= 1012 g) for terrestrial ecosystems and Graham & Duce (1979) estimated P flux from land to the atmosphere to be 4.3 Tg P/yr. Fertilizers account for 80% of overall phosphorus chemical production, with the balance used in detergents (12%), animal feeds (5%), and special applications (3%) (CEFIC, 1997). Since the first commercial modern phosphate industry began to produce fertilizer in the mid-19th century, demand increased continuously, especially after the 1950s, and reached a range of 25–35 million metric tons after the 1970s (IFIA, 2002).

There has been a number of previous global phosphorus budgets proposed (Froelich *et al.,* 1982; Richey, 1983; Froelich, 1984; Ruttenberg, 1993; Filippelli & Delaney, 1994; Baturin *et al.,* 1995; Reddy *et al.,* 1999) as well as reviews of our current understanding of the phosphorus cycle (Bentor, 1980; Arthur & Jenkyns, 1981; Glenn *et al.,* 1994; Föllmi, 1996). A brief overview of quantitative understanding of the reservoirs and fluxes of the global phosphorus cycle was presented by Compton *et al.,* (2000), with an emphasis on recent results and remaining key uncertainties. The book 'Phosphorus in the Global Environment' by SCOPE (Tiessen, 1995) also explained the minute details of global phosphorus cycle.

There is a net transport of phosphorus to the oceans (Tiessen, 1995) and it enters the ocean mainly by rivers in the form of both dissolved and particulate phases (Froelich *et al.,* 1982; Meybeck, 1982; Froelich, 1988; Berner *et al.,* 1993). Estimates of yearly P transport to the oceans vary between 21 and 39 Tg per year with 23 Tg per year as the best estimate (Howarth *et al.,* 1995). The dissolved inorganic phosphorus (DIP) flux of rivers (orthophosphate, H_2PO4^-, HPO_4^{2-}, PO_4^{3-}) is estimated to be 0.26 to 0.46 Tg /yr (Meybeck, 1982; 1993; Savenko & Zakharova, 1995). Pollution is estimated to increase the present-day DIP river flux to between 0.8 and 1.4 Tg /yr (Meybeck, 1982). The dissolved organic phosphorus (DOP) and particulate organic phosphorus (POP) river flux can be calculated as 0.55 to 0.68 Tg /yr and 8 Tg /yr respectively (Meybeck, 1982). The particulate inorganic phosphorus (PIP) flux, which includes detrital phosphorus and adsorbed phosphorus was calculated to be 9.8–16.8 Tg /yr (Milliman & Zyvitski, 1992). The eolian phosphorus flux to the ocean was estimated to be 1 Tg /yr, mostly particulate phosphorus, by Graham and Duce (1979).

Chemical weathering would make up 21–26% of the total weathering flux (Berner & Berner, 1987).

The phosphorus is then removed from the ocean by primary production, sorption to Fe-(oxy)hydroxides and formation of authigenic minerals (Froelich *et al.*, 1982; Berner *et al.*, 1993). Burial with sediment is the ultimate mechanism for removal of P from the ocean (Ruttenberg & Berner, 1993) although a small amount of the total P (0.3 Tg y^{-1}) is harvested in fish catch (Senez, 1992). Preservation of phosphorus in sediments depends on several factors including the nature of phosphorus compounds supplied to the sediment/ water interface, sedimentation rate, bioturbation, or irrigation by bottom current, bottom-water oxygen content, diagenetic processes (Ingall & Van Cappellen, 1990; Ruttenberg & Berner, 1993; Schenau & De Lange, 2001). Fig. 5.2 summarizes the current best estimates of global ocean P fluxes. Imbalances in the budget reflect the uncertainty and are most likely due to underestimating burial, with riverine input being the second largest uncertainty (Howarth *et al.*, 1995).

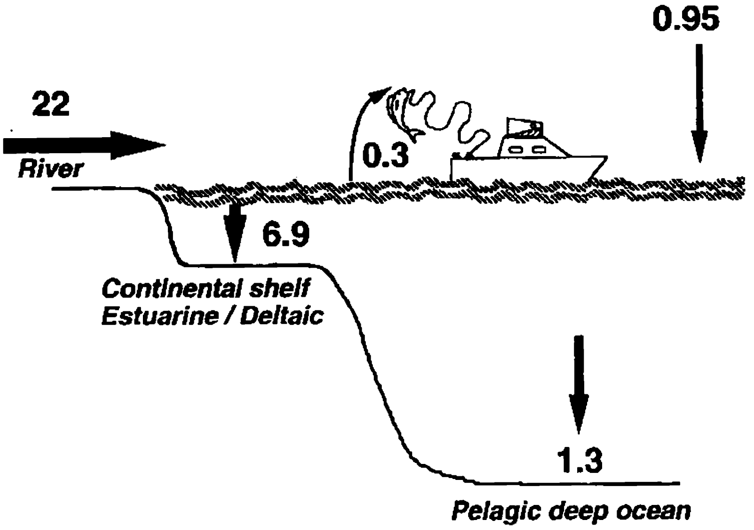


Figure 5.2 Global ocean P fluxes (Tg y^{-1}), from Howarth *et al.*, (1995).

Phosphorus is unique among the major nutrients in that it is often assumed to lack a gaseous species for atmospheric transport. However, the works of Glindeman *et al.,* (1996, 1999) and Han *et al.,* (2000) unambiguously confirmed that volatile phosphine gas (i.e., hydrogen phosphide or PH_3) could be detected in the earth's atmosphere at trace levels. These authors have also identified several sources of phosphine. Unfortunately, study of total transport through this mechanism has received minimal attention because of the erroneous assumption that phosphorus is nonvolatile, (Morton & Edwards, 2005).

5.2.1 Phosphorus dynamics in estuaries

Estuaries normally mediate the phosphorus transfer from the land into the ocean, where considerable processing of P occurs, altering both the immediate biological availability and the flux of P to coastal seas and oceans. The highly variable biological and physical dynamics of estuaries make it difficult to estimate the net phosphorus river flux to the ocean (Wollast, 1983; Froelich, 1984). Phosphorus is assimilated by phytoplankton, bacteria, and benthic plants and is remineralised by the heterotrophic activity of animals and microorganisms (Grobbelaar & House, 1995). The mixing of river water with salt water in estuaries creates some unique chemical characteristics, which affect the adsorption of inorganic phosphate on particles. The physical mixing of estuaries also creates some unique properties for trapping particles, including particulate P. The conservative mixing behavior of DOC in estuaries would suggest that most DOC and associated DOP is delivered to the sea and perhaps 5–10% is trapped in estuaries by flocculation of primarily humic compounds (Sholkovitz, 1976; Sholkovitz *et al.,* 1978; Burton, 1983).

The river water DIP flux appears to be enhanced by desorption of iron-bound PIP in estuaries. Chase & Sayles (1980) observed as much as 3% phosphate desorption associated with an increase in pH during mixing. Froelich (1984) found that the DIP river flux may increase by 50% during passage through estuaries. Extrapolation of these results suggests a global desorption flux to estuaries of 0.05–0.23 Tg/yr. A phosphorus mass balance of the Scheldt estuary indicates that much of the phosphate entering the estuary is deposited rather than being directly transported to sea (Wollast, 1983). Considering the above estimates, estuaries may trap approximately one-quarter of the total potentially reactive phosphorus river flux as DOP and POP, as well as a significant but unknown amount of the iron-bound PIP flux (Compton *et al.*, 2000). Efficient phosphorus trapping by estuaries is supported by Holocene reactive phosphorus accumulation rates of 1,000–11,000 μmol/cm^2/kyr, which are an order of magnitude greater than the typical phosphorus accumulation rates on continental margins (Filippelli, 1997).

Particulate matter in rivers can carry a significant amount of inorganic adsorbed phosphate (Fuller *et al.*, 1993; Waychunas *et al.*, 1993), although it has been suggested that such phosphate may not be truly adsorbed but may be present as mixed crystalline iron-phosphate phases (Fox, 1989; 1991). The adsorbed phosphate in rivers can be considered in equilibrium with dissolved phosphate in the river water (Froelich, 1988). When riverine particulate matter meets the higher salinity water of an estuary, the nature of this equilibrium changes, and much of the adsorbed phosphate is potentially released to solution (Sharp *et al.*, 1982; Pilson, 1985; Edmond *et al.*, 1985; Fox *et al.*, 1986; Froelich, 1988). This release in estuarine waters is primarily a result of competition for sorption sites with other anions, since ionic strength alone would be expected to increase, not decrease, adsorption of phosphate (Nair *et al.*, 1984; Froelich, 1988).

The desorption of phosphate from particles in many estuaries tends to buffer the concentration of dissolved phosphate at concentrations of 30 to 60 µg/l (Pomeroy *et al.*, 1965; Liss, 1976; Chase & Sayles, 1980; Wollast, 1983; Fox *et al.*, 1985, 1986; Froelich, 1988; Lebo, 1991), much higher concentrations than are typically found in freshwaters (Froelich, 1988). While several mechanisms, including benthic regeneration (Nixon *et al.*, 1980; Pilson, 1985), may contribute to this concentration increase, desorption of phosphate from riverine particulate matter is often the significant factor (van Bennekom *et al.*, 1978; Sharp *et al.*, 1982; Edmond *et al.*, 1985; Fox *et al.*, 1985, 1986; Froelich, 1988). Large phytoplankton blooms can lower the phosphate concentration to the limit of detection, below 1 to 2 µg/l (Sharp *et al.*, 1984; Lebo, 1990, 1991). Another important factor controlling P fluxes in some estuaries is the flocculation and subsequent precipitation of river-borne, humic-complexed Fe at low salinities (2 to 3 ‰). This can coprecipitate P (Sharp *et al.*, 1982), and therefore works in the opposite direction of the desorption seen in many estuaries.

Phosphorus retention by estuaries is considerably less than the storage of sediment, due to both the desorption of phosphate from suspended particles (Liss, 1976; Froelich, 1988; Billen *et al.*, 1991), the chemical and biological reactivity of P in sediments (Berner & Rao, 1994) and also by diagenetic processes within the bottom sediments (Sundby *et al.*, 1992).

In sediments, P bound to particles is mobilized into dissolved form in desorption, dissolution, ligand exchange and enzymatic hydrolysis

(Boström *et al.*, 1982). The main physical factors enhancing the exchange of P between sediment and water are diffusion, temperature, water turbulence, gas ebullition and bioturbation (Boström *et al.*; 1982). Temperature can have a major effect on the release rate of P from sediment to water (Holdren & Armstrong, 1980; Psenner, 1984). An increase in temperature accelerates the diffusion rate as a result of increased Brownian movement. However, temperature also has an indirect effect on P release, because an increase in temperature raises the metabolic rate of bacteria and subsequently the mineralization rate and microbial redox reactions in sediments. Physical water movement is a much faster transport mechanism than diffusion. Physical pore water movement is increased by water currents at the sediment-water interface and by gases formed in microbial reduction processes in sediments.

Bioturbation has a three-way effect on the cycling of P in sediments: first, the transport of water increases the concentration of O_2 in the burrows, thereby improving the P-binding capacity of sediment, but it also promotes the transport of pore water P from sediment to water; second, an abundance of macroinvertebrates increases the rate of mineralization (Hansen *et al.*, 1998) and the acceleration of their digestive and excretory processes furthers the dissolution of P; and third, burrowing animals move particulate oxidized compounds down to the reduced zone and reduced compounds up to the oxic zone, thus affecting Fe(III) oxide reduction and re-oxidation in sediments (Canfield *et al.*, 1993). Periphyton can assimilate P, alter hydrodynamics, and modify the local chemical environment in ways that ultimately influence P retention by an aquatic system (Adey *et al.*, 1993).

5.2.2 Phosphorus speciation

Sediment phosphorus is particularly important in shallow lakes and wetlands as various forms of bioavailable P in the upper sediments can be a major source of P to the water column biota via numerous physically, chemically and biologically mediated processes (Reddy & D'Angelo, 1994; Kufel *et al.,* 1997). Analysis of total phosphorus loading alone does not provide information regarding phosphorus availability to biota or the potential for recycling through sediment-water interactions as it is transported to downstream locations (James *et al.,* 2001). An exact stochiometric and structural identification and quantification of inorganic P species is very complicate (Lüderitz & Gerlach, 2002). A common route to estimate the stock of potentially accessible forms is to fractionate phosphorus based on the extractability by leaching reagents of increasing aggressiveness (Golterman, 1996; Ting & Appan, 1996; Perkins & Underwood, 2001; Tiyapongpattana *et al.,* 2004).

Sequential leaching extractions were proposed to understand the association of phosphorus with various sedimentary components and to estimate its mobility, solubility, or biological availability. The phase in the sediment with which phosphorus is associated will affect its mobility, and hence availability to the water column (Reynolds & Davies, 2001). Although leaching procedures are operationally defined, they provide an insight to understand the distribution of elements in different phases and the mode of fixation in the sediment column (Babu & Nath, 2005). Chemical fractionation, involving sequential extraction procedures, is based on differences in reactivity of solid phases to different extractant solutions. Sequential extraction techniques have also been utilized to understand the diagenetic transformations of organic P in sediments (Ruttenberg & Berner, 1993; Filippelli & Delaney, 1996; Slomp *et al.,* 1998; Anderson & Delaney, 2000; Latimer & Filippelli, 2001; Slomp *et al.,* 2002; Tamburini *et al.,* 2002; van der Zee *et al.,* 2002; Faul *et al.,* 2003; Filippelli *et al.;* 2003). When considering P-franctions and their mobilization, there is a need to know how much (or what fraction) of the sediment can be available to algae and/or bacteria (Fytianos & Kotzakioti, 2005). According to Bostrom *et al.*, (1982), a good approach would be to consider all P that can be released within the occurring ranges of temperature, pH and redox as bioavailable.

Although many different extraction schemes may exist, the underlying extraction mechanisms are the same. The four most common extraction mechanisms are ion exchange, acid and base dissolution and reduction.

Ion exchange

Elements bound to sediment by electrostatic attraction do so at sites on clay minerals, organic materials and amorphous solids. These elements can easily be replaced since there is no specific bond to the adsorption site. Ion exchangeable phosphorus extraction involves displacement by another anion of similar mass or by the formation of an alkaline phosphate complex (Ruttenberg, 1992).

Acid dissolution

Many minerals in the sediment are, to some extent, acid soluble (Williams & Mayer, 1972). Acid dissolution involves dissolving these minerals, therefore releasing the phosphorus bound to them. Acid dissolutions have been used to extract phosphorus bound to apatite minerals, and iron and aluminum oxides (Williams & Mayer, 1972). Acid extractions are typically used last in sequential fractionation schemes as they extract a wide range of phosphorus.

Base Dissolution

Base solutions are perhaps the most widely used chemical extraction technique. Base extractions work on the same dissolution principle as the acid extractions discussed above. It has been shown that base extractions will release a wide range of phosphorus from the sediment, including that bound to humic substances (Deurer *et al.,* 1978).

Reduction

Reduction extractions are based on reducing minerals in the sediment, thereby releasing phosphorus. Reduction solutions are most often used to extract metal oxides (Fe and Mn), which are important to binding trace elements to sediments (Pickering, 1986). Iron oxides are particularly important in the binding of phosphorus (Emsley, 1980).

Such extraction of different forms of P has been the subject of great interest ever since the first attempt reported by Mulder (1844). Even extraction schemes developed for the specification of different metals are applicable to the extraction of different P species because of their association with both redox-dependent metals (Fe and Mn) and other metals like Ca (Tessier *et al.,* 1979). Some of the commonly used extraction schemes are summarized in Table 5.1.

Sequential fractionation schemes are not an exacting science (Dean, 1938; Chang & Jackson, 1957; Williams *et al.,* 1967). It must be kept in mind that these are rather crude methods; with many extractants causing the dissolution of more than one type of P solid phase as various extractants are unlikely to be either exhaustive or unique with respect to the target compounds (Turner *et al.,* 2005). For example, sodium hydroxide is often used to extract Al and Fe-bound P (van Eck, 1982; Hieltjes & Lijklema, 1980). However, this compound will also extract organic P fractions, particularly in soils that have been heavily manured in the past. Sequential extraction techniques are traditionally conducted in a batch end-over-end fashion, which is rather laborious, tedious, time consuming and it is subjected to several potential errors including risks of contamination due to sample manipulation and underestimation of given fractions due to re-adsorption phenomena (Buanuam *et al.*, 2006). Hence the awareness of the pitfalls and fallibility of the methods are essential and also the choice of the best procedure available.

A number of research groups have developed a flow-based system for sequential extraction of metals in soil and sediment, which has the benefits of less risk of contamination, less vulnerability to change in extraction conditions and rapidity (Shiowatana *et al.*, 2001; Tiyapongpattana *et al.*, 2004; Jimoh *et al.*, 2005). Since the contact time between the extractant and soil sample is minimal, less opportunity for re-distribution to occur (Chomchoei *et al.*, 2002). In addition, the continuous-flow system can be made partially automated. ^{31}P-NMR is a well established and widely used spectroscopic technique that exploits the magnetic properties of the atomic nucleus, thereby providing information about the bonds of P and therefore the P species present in the sample (Magid *et al.*, 1996; Condron *et al.*, 1997).

Table 5.1 Some of the commonly used sequential extraction schemes

Scheme	Extractants	Phosphorus Fraction
1. SEDEX procedure Ruttenberg, (1992) Modified by **Anderson & Delaney (2000)**	a) CDB (citrate-dithionite-bicarbonate)	Labile and oxide-associated P
	b) 1 M sodium acetate buffered to pH 4	Authigenic CFA
	c) 1 N hydrochloric acid	Detrital Apatite P
	d) 50% magnesium nitrate to sediments, drying in oven at 80°C, and ashing at 550°C, 1 N HCl	Organic P
2. Psenner *et al.* (1984) Modified by **Hupfter *et al.* (1995)**	a) NH4Cl- at neutral pH	Labile, loosely bound or adsorbed P
	b) Buffered dithionite	Reductant soluble P, bound to Fe oxides and hydroxides
	c) NaOH	P adsorbed to metal oxides and bound to humic substances
	d) HCl	P bound to carbonates, apatite-P and released by the dissolution of oxides
	e) Digestion	Organic and refractory P
3. Filippelli & Delaney (1996)	a) Citrate–dithionite–bicarbonate reducing agent and magnesium chloride	Occluded fraction
	b) Sodium acetate + acetic acid solution and hydrochloric acid	Mineral fraction
	c) Ashing followed by dissolution with hydrochloric acid	Organic fraction
4. Hieltjes & Lijklema (1980) and **Nürnberg (1988)**	a) 1 M Ammonium Chloride	Loosely bound P
	b) 0.11 M Sodium bicarbonate and Dithionate	Iron bound P
	c) 0.1 N Sodium Hydroxide	Aluminium bound P
	d) 0.5 N Hydrochloric acid	Calcium bound P
	e) Persulphate digestion of NaOH extraction	Labile organic/Polyphosphate P
	f) Persulphate digestion of remaining sediment	Refractory Organic P
5. Chang & Jackson (1957) modified by **Hartikainen (1979)**	a) 1 M Ammonium Chloride	Loosely bound P
	b) 0.05 M Ammonium Fluoride	Aluminium bound P
	c) 0.1 N Sodium Hydroxide	Iron bound P
	d) KCl-$C_6H_8O_6$-EDTA	Occluded P
6. Jensen & Thamdrup (1993)	a) $MgCl_2$	Loosely sorbed P
	b) Buffered dithionite extraction	Iron bound P
	c) NaOH	Al/clay mineral and humic bound
	d) HCl	Calcium bound P
	e) Digestion	Refractory organic P
7. De Groot & Golterman (1993)	a) Buffered CaEDTA/dithionite	Iron bound P
	b) Na_2EDTA	Calcium bound P
	c) H_2SO_4	Acid solubile P
	d) 2M NaOH	Alkali solubile P
	pH 1 with H_2SO_4	Humic& Fulvic P
	e) Digestion	Residual Organic P

While solid-state ^{31}P-NMR allows samples to be examined directly with little preparation, solution ^{31}P-NMR gives a much better spectral resolution, thereby allowing the identification of more P species (Paytan et al., 2003). However, it has generally required 10–30 g of material for extraction (Sundareshwar *et al.*, 2001), making it impractical for very small samples such as sediment trap material. The Gel Permeation Chromatography (GPC) technique is an advantageous technique in order to study the fractions of organic phosphorus, especially those linked to the humic substances Gilbin *et al.*, (2000). Non-destructive techniques used along with the chemical extraction would allow the interpretation of the role of the organic matter in the fate of phosphorus in aquatic ecosystems Gilbin *et al.*, (2000).

In spite of these shortcomings these fractionation schemes are used widely since these schemes use only small soil samples (≤0.5 g), are relatively simple to perform, and require only basic laboratory equipment. To avoid disadvantages like the uncertainty in the bioavailable and the nonspecific nature of the extraction solutions, an extraction scheme using chelating agents was developed by Golterman, (1996). This "EDTA method" is useful for the extraction of inorganic phosphorus pools with lesser modifications of the organic pool. The Ca-EDTA solution has an advantage over the CDB and NaOH to extract both Fe(OOH) and Fe(OOH)_P with optimal efficiency and EDTA solutions are recommended for inorg-P extractions without disturbing the org-P(Golterman, 1996). Ca-saturated EDTA (avoids Cabound phosphate removal) renders the iron soluble at the same time as the phosphate and the pH avoids re-precipitation. Then, Na-EDTA renders calcium and bound phosphate soluble, minimising the extraction of organic materials. Ca-saturated EDTA (avoids Ca bound phosphate removal) renders the iron soluble at the same time as the phosphate and the pH avoids re- precipitation. Then, Na-EDTA renders calcium and bound phosphate soluble, minimising the extraction of organic materials. A modification of this scheme by Diaz- Espejo *et al.*, (1999) was used in this study. Though drying has been shown to have an influence on the P-distribution (Golterman, 1998), dried samples were used here.

5.3 Results

Total phosphorus in the surficial sediments ranged between 319.54 and 2229.45 µg/g dry weight during pre-monsoon and between 620.42 and 3225.26 µg/g during monsoon. The post-monsoon range was from 649.55 to 2765.06 µg/g. As described in chapter 4, higher levels were found at station 10 and lower at stations 2 and 5. Phosphorus was also found to be generally enriched at the finer fractions of the sediment.

The different chemical fractions of phosphorus in the surficial sediments of the study region and their seasonal and spatial variations are presented in Table 5.2 and figures 5.4, 5.5 and 5.6. The different forms of phosphorus obtained were iron bound inorganic (Fe-IP) and organic fractions (Fe-OP), calcium bound inorganic (Ca-IP) and organic fractions (Ca-OP), acid soluble organic fraction (Acid-OP), alkali soluble organic fraction (Alkali-OP) and residual organic phosphorus (ROP). The iron bound inorganic, calcium carbonate bound inorganic and acid soluble organic fractions of phosphorus were considered as a source of bio available phosphorus for phytoplankton growth (Diaz- Espejo *et al.*, 1999).

Among the bio available fractions of phosphorus, Fe-IP ranged between 5.04 and 507.35 µg/g dry weight. It was found to be higher at the fine fractions of the sediment compared to the coarse. In the pre-monsoon, Fe-IP ranged from 5.04 to 507.35 µg/g dry weight of the sediment and between 14.53 and 151.02 µg/g dry weight during monsoon. During the post-monsoon season, the variation was from 8.55 to 366.64 µg/g dry weight. Fe-IP constituted about 8-25 % of the total phosphorus concentration during pre-monsoon and it was 3-16 % and 3-10 % for monsoon and post-monsoon seasons, respectively.

Ca-IP varied widely in the study region and ranged from 11.16 to 913.28 µg/g dry weight. It was also found to be higher at the finer fractions in general; enrichment was also seen for coarser fractions in organic rich samples. During pre-monsoon it ranged from 11.16 to 913.28 µg/g and between 33.01 and 779.18 µg/g dry weight during monsoon. Ca-IP ranged between 83.34 and 676.68 µg/g during post-monsoon. It was a major fraction, constituting >1 to 37 % of total phosphorus content during pre-monsoon. During monsoon it constituted 4-39 % and 8-34 % during post-monsoon.

Acid-OP varied between 22.22 and 410.95 µg/g dry weight in the study region and showed the same trend as Ca-IP in grain size distribution. It ranged between 1 and 23 % of total phosphorus concentration during pre-monsoon and between 4 and 19 % during monsoon. The post-monsoon variation was from 6 to 26 % of total phosphorus content. During pre-monsoon their concentration ranged from 22.22 to 315.18 µg/g while it was from 29.65 to 410.95 µg/g during monsoon. During post-monsoon Acid-IP ranged between 55.04 and 350.37 µg/g.

Among the non bioavailable fractions, Fe-OP varied between 2.26 and 580 µg/g dry weight in the study region. It varied from 2.26 to 50.27

µg/g and from 24.23 to 97.08 µg/g respectively during pre-monsoon and monsoon periods. During post-monsoon it showed an increase and ranged between 20.27 and 580 µg/g. The percentage of contribution was between 0 and 9 % during pre-monsoon and between 1 and 5 % and between 2 and 21 % respectively during monsoon and post-monsoon seasons.

Ca-OP varied widely in the study region and ranged between 11.40 and 965.72 µg/g. Ca-OP was comparatively lower during pre-monsoon and varied from 11.58 to 244.14 µg/g and the range was from 35.69 to 648.17 µg/g during monsoon. It ranged from 11.40 to 965.72 µg/g during post-monsoon. This fraction constituted 1-55 % of the total phosphorus during pre-monsoon and 4-46 % and 1-46 % respectively during monsoon and post-monsoon seasons.

Alkali-OP ranged between 44.09 and 1100.37 µg/g in the study region. It was one of the major fraction contributing 14-28 %, 20-75 % and 3-79 % respectively during pre-monsoon, monsoon and post-monsoon seasons. It varied from 57.65 to 526.93 µg/g during pre-monsoon and between 135.76 and 1100.37 µg/g during monsoon. During post-monsoon, the variation was from 44.09 to 783.38 µg/g.

Residual organic phosphorus ranged between 25.25 and 304.04 µg/g. ROP varied from 39 to 242 µg/g and from 33.67 to 304.04 µg/g respectively during pre-monsoon and monsoon seasons. The range was from 25.25 to 131.69 µg/g during post-monsoon. Its percentage to total was 8-25, 3-16 and 3-10 respectively for pre-monsoon, monsoon and post-monsoon seasons.

Table 5.2 Seasonal variations of different fractions of phosphorus

Stations	Fraction	Fe-IP	Fe-OP	Ca-IP	Ca-OP	Acid-OP	Alkali-OP	ROP	Total P
Pre-monsoon									
1	Fine	77.27	50.27	291.61	11.58	205.12	177.05	73.00	885.90
	Coarse	83.69	2.26	184.50	11.99	124.23	173.16	97.50	677.32
2	Fine	-	-	-	-	-	-	-	-
	Coarse	5.04	20.61	11.16	159.87	22.22	57.65	43.00	319.54
5	Fine	93.31	13.05	49.51	51.43	61.96	62.20	59.00	390.46
	Coarse	39.87	9.25	53.41	137.13	29.69	118.81	39.00	427.16
7	Fine	507.35	25.09	652.56	244.14	258.31	356.00	186.00	2229.45
	Coarse	441.12	15.38	310.59	112.05	176.06	217.15	136.50	1408.83
8	Fine	359.66	11.62	362.35	111.18	237.75	267.11	150.00	1499.67
	Coarse	321.91	18.19	564.52	35.26	315.18	367.02	142.50	1764.56
10	Fine	325.26	31.06	913.28	58.81	218.10	526.93	142.00	2115.44
	Coarse	323.58	24.63	738.90	47.03	266.64	446.97	92.25	1940.00
Monsoon									
1	Fine	28.78	43.10	41.06	506.73	203.70	227.81	33.67	1084.86
	Coarse	24.42	24.33	239.11	51.10	113.39	135.76	83.49	671.61
2	Fine	-	-	-	-	-	-	-	-
	Coarse	14.53	29.64	33.01	35.69	29.65	602.49	53.41	798.42
5	Fine	-	-	-	-	-	-	-	-
	Coarse	16.29	34.92	23.40	25.78	43.06	424.67	52.30	620.42
7	Fine	137.73	97.08	197.93	316.25	309.26	532.73	183.92	1774.91
	Coarse	102.88	87.52	453.26	322.99	215.93	626.41	170.80	1979.78
8	Fine	71.03	61.60	114.54	457.90	262.85	675.18	255.62	1898.72
	Coarse	60.22	50.49	266.62	177.00	333.23	731.76	304.04	1923.36
10	Fine	151.02	50.34	625.25	648.17	410.95	1100.37	239.14	3225.26
	Coarse	86.23	27.65	779.18	294.83	320.76	904.52	239.22	2652.40
Post-monsoon									
1	Fine	35.95	99.83	209.02	62.54	239.61	223.66	33.29	903.90
	Coarse	29.30	205.53	111.21	358.44	102.29	65.40	25.25	897.42
2	Fine	160.84	223.88	108.78	660.66	176.50	44.09	59.89	1434.65
	Coarse	68.47	89.36	104.06	211.60	89.24	59.74	27.09	649.55
5	Fine	-	-	-	-	-	-	-	-
	Coarse	8.55	20.27	83.34	11.40	55.04	783.38	33.30	995.28
7	Fine	366.64	32.49	630.74	37.56	252.96	463.81	60.01	1844.19
	Coarse	196.93	199.95	468.58	325.18	291.78	216.35	79.24	1778.01
8	Fine	83.40	93.37	89.63	263.90	276.37	271.38	114.52	1192.58
	Coarse	63.55	128.59	259.86	124.42	350.37	275.06	131.69	1333.53
10	Fine	138.75	580.00	471.77	965.72	289.85	217.22	101.74	2765.06
	Coarse	102.64	353.81	676.68	236.20	310.90	217.22	119.09	2016.54

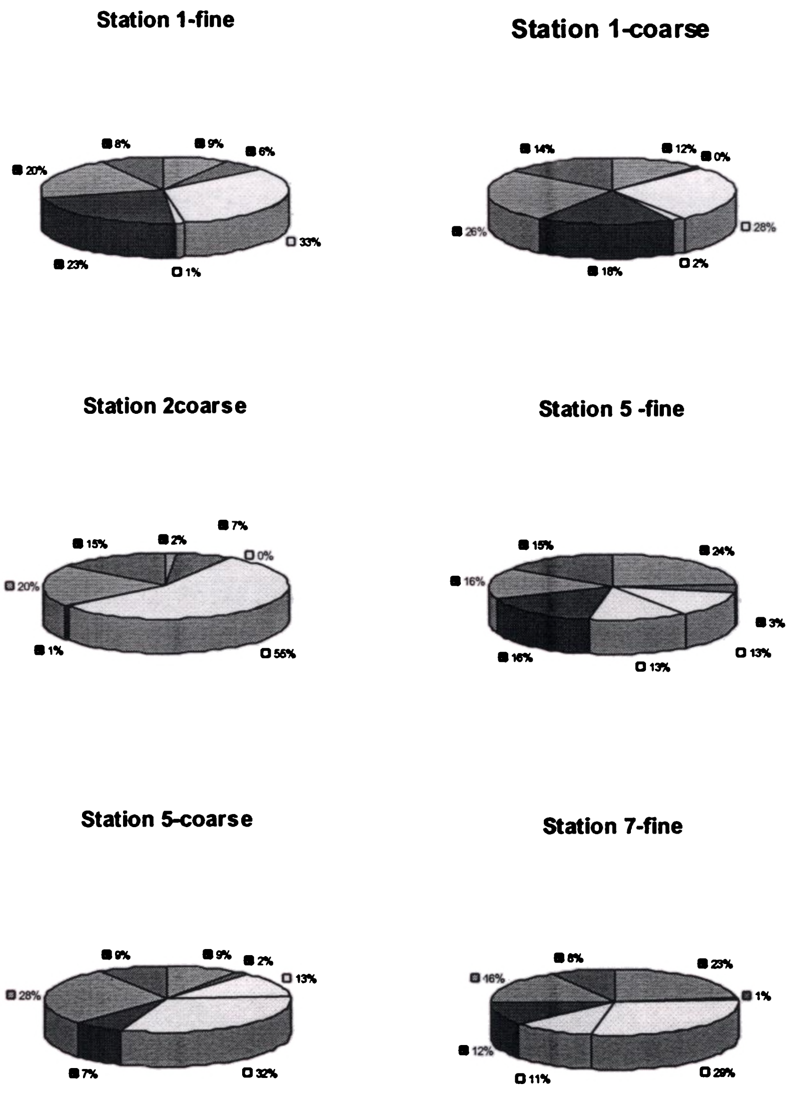


Figure 5.4 variations of different P-fractions during pre-monsoon

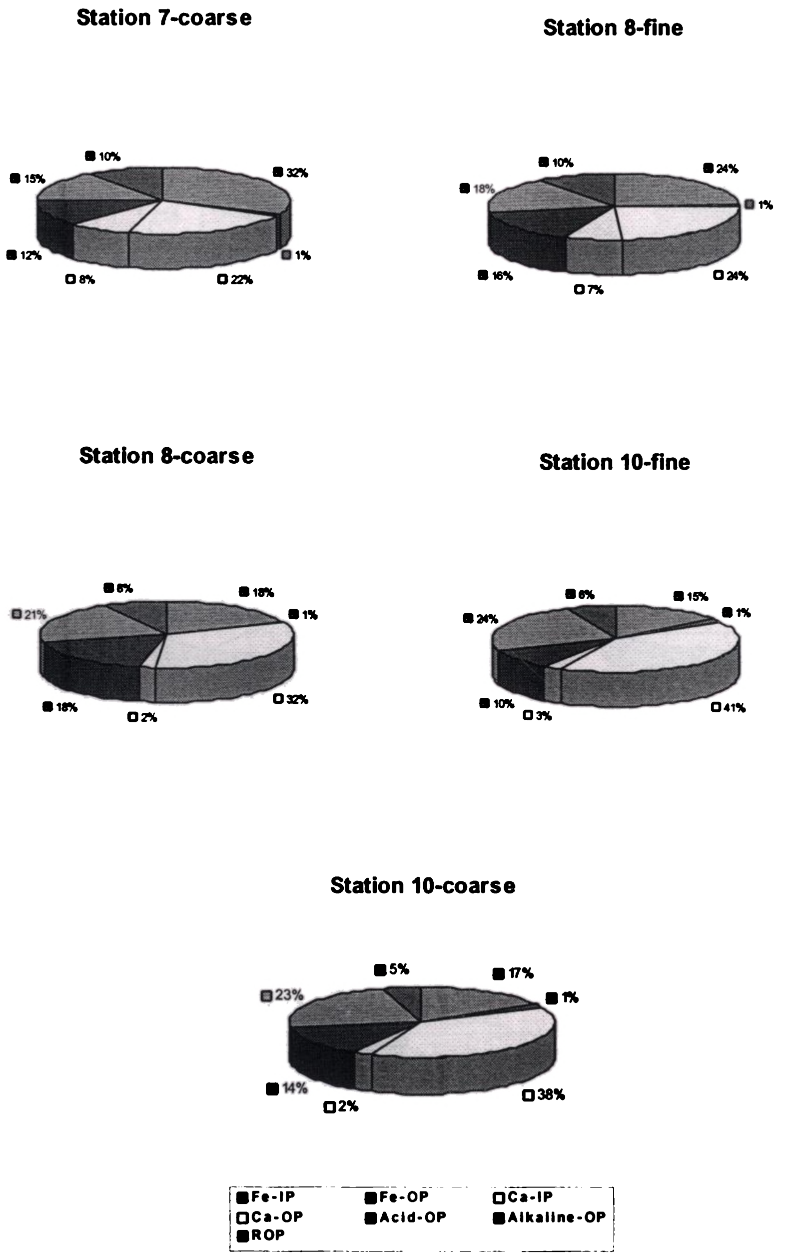
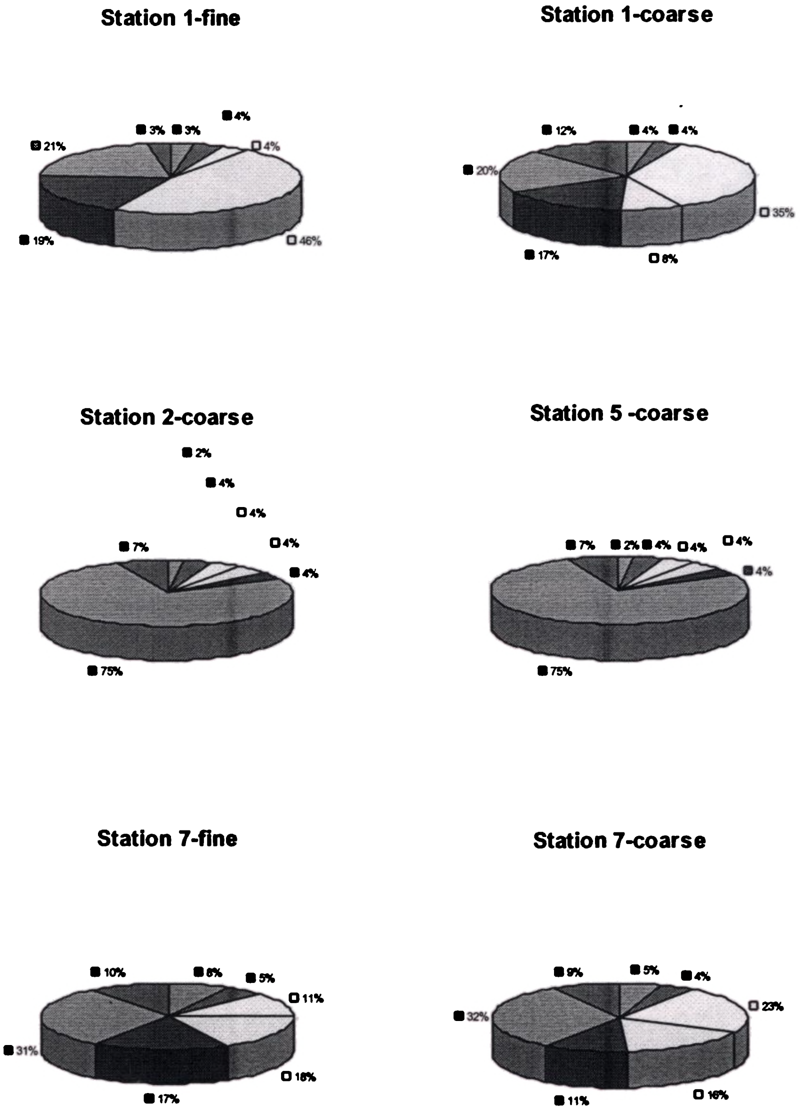


Figure 5.4 (Contd.)


Station 1-fine

Station 1-coarse

Station 2-coarse

Station 5 -coarse

Station 7-fine

Station 7-coarse

Figure 5.5 variations of different P-fractions during monsoon

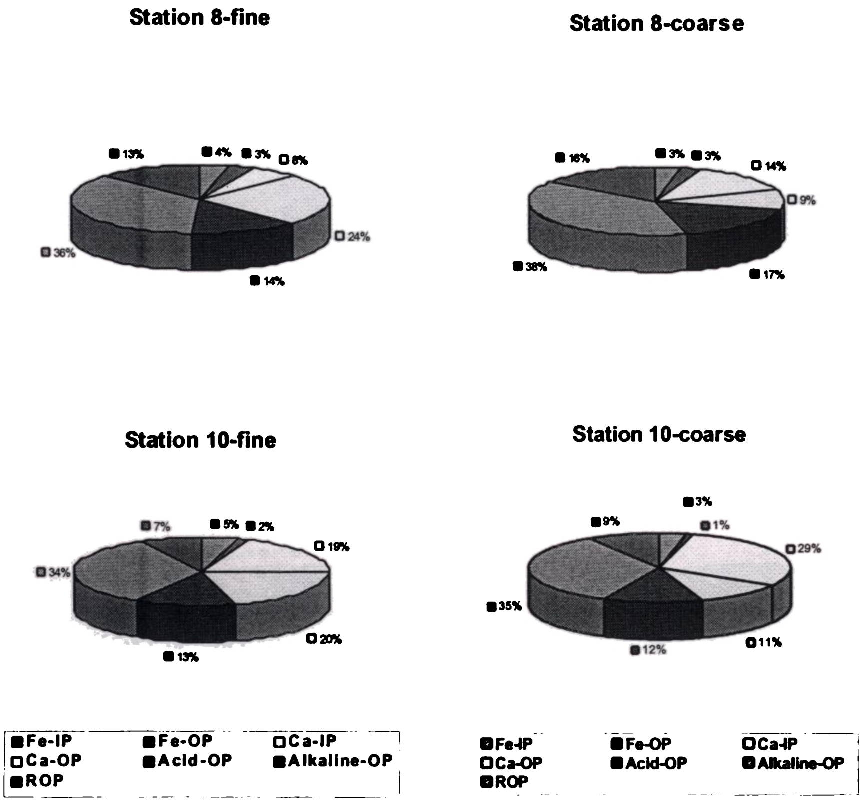
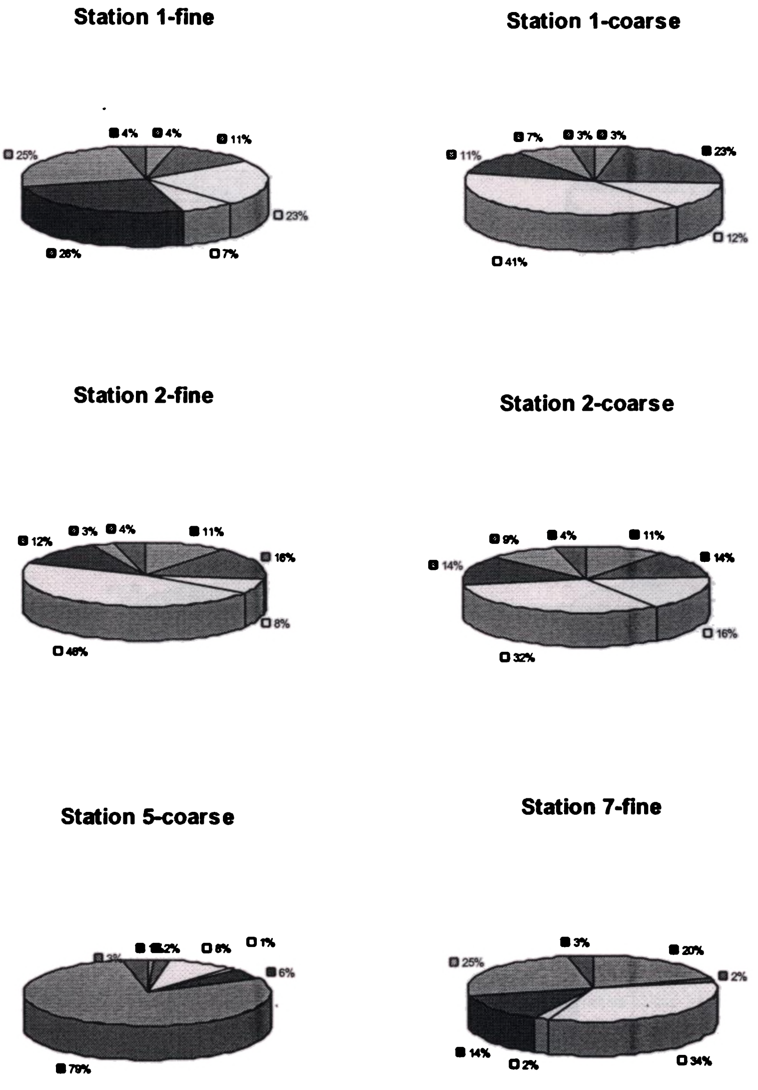


Figure 5.5 (Contd.)


Station 1-fine

Station 1-coarse

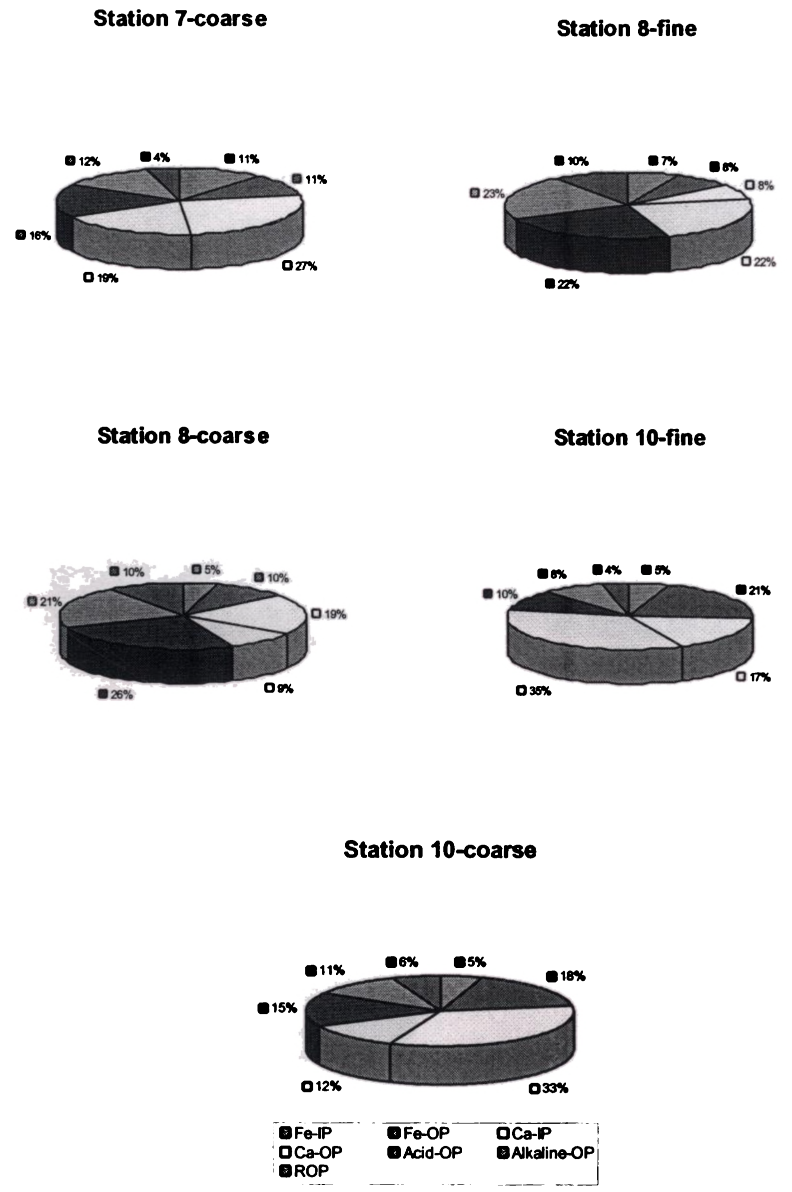
Station 2-fine

Station 2-coarse

Station 5-coarse

Station 7-fine

Figure 5.6 variations of different P-fractions during post-monsoon



Station 7-coarse

Station 8-fine

Station 8-coarse

Station 10-fine

Station 10-coarse

Figure 5.6 (Contd.)

5.4 Discussion

The dynamicity of aquatic systems is well proven and the presence, forms and concentration of any element will be a result of the dynamics. The biogeochemical processes operating in the system will lead to chemical transformations of the element and will ultimately decide on the bioavailability of the element with the required chemical character. The chemistry of the element will also have a definite role in this. The addition of any element in any chemical form, thus will initiate a variety of chemical reactions, which finally ends in a more or less steady state.

Biogeochemical processes define a system and identification of the biogeochemical processes requires monitoring of all the contributions including that from the physical processes. In aquatic systems, an *in situ* identification and monitoring of individual processes and their contribution to the total dynamicity is an unreachable task, one that can never be made a reality with the presently available technology. The only possibility is to identify the possible products and reactants. The speciation study thus can be considered as an indexing of various biogeochemical processes to get a thorough understanding of the processes.

The index should be developed in such a way that it will have the signals of all the possible processes. If we consider the chemical transformations as redox reactions, a better index can be developed by potential elements, which exhibit a definite redox character and sufficient concentration to monitor the transformations. Two elements that can generally be considered as having these qualities are iron and sulphur, with varying oxidation states and high environmental reactivity. At the same time the growth inhibiting character of sulphide, which is a result of the oxygen limiting condition and the high depositional character of iron in the form of oxide and sulphide makes these elements inadequate in considering as index elements.

Another possibility is the nutrient elements nitrogen and phosphorus. The growth limiting condition of nitrogen in this estuary (chapter 3) makes phosphorus as the only alternate for such a study. The advantage with phosphorus is that it is available in various oxidation states (Morton & Edwards, 2005) and the monitoring of phosphorus in various forms can be easily done. Hence phosphorus is taken as the element to identify the geochemistry of the system.

The various processes which are operating in the system and which can contribute to geochemical transformations are chemical weathering, autochthonous and allochthonous additions, co precipitation, flocculation, adsorption, desorption, diagenesis etc. the dominant form of phosphorus, which will exhibit a stable identity is orthophosphate and the effective concentration of phosphorus is the addition from land and the removal to the marine system. Sedimentary storage also is a path of removal of phosphorus from the water column. But the incorporation in to the sediment is retaining the phosphorus within the system and the stored phosphorus will be available for bogeochemical processes and for the availability of orthophosphate in the water column when there is an essentiality. The net result will be maintenance of a steady concentration of the sedimentary phosphorus and so the discussion on the geochemical reactivity of phosphorus essentially requires the possible interface dynamics.

When the dynamics of phosphorus is the consideration, the different forms of phosphorus available in the water column have to be indexed. In an estuarine system, phosphorus will be available both in the dissolved and particulate forms. The bioavailable species, orthophosphate is the major form that is present in the dissolved and particulate forms, which will take part in active geochemical processes. The different forms of phosphorus, which will be present in the sedimentary compartment as a result of biogeochemical processes, are

1) Free or exchangeable orthophosphate, which generally associated with major ions.
2) Orthophosphate which is associated with Fe and Ca, which have only very low solubility in water.
3) Organic phosphate which will have an organic component restricting a direct dissolution in water and will be available for the system after the demineralization processes.
4) Phosphate which are associated with humic materials, which can be available only in a rigorous condition of exchange of phosphorus with a strong anion.
5) Phosphorus compounds with C-P bond as phospholipids. This form will not be available through any of the normal biogeochemical processes and hence treated generally as residual fraction.

The present study is organized in such a way to identify all the geochemical forms with an intention to assess the interrelations for the identification of the extend of the geochemical processes. The speciation scheme, so, is selected in such a way that the maximum variability and species diversity can be estimated. The species identified in this scheme are iron bound inorganic (Fe-IP) and organic fractions (Fe-OP), calcium bound inorganic (Ca-IP) and organic fractions (Ca-OP), acid soluble organic fraction (Acid-OP), alkali soluble organic fraction (Alkali-OP) and residual organic phosphorus (ROP). The species designated as Fe-OP and Ca-OP is derived and expressed so to quantify any organic phosphorus which may be present in the sedimentary component and which will be released in the presence of an organic ligand. The source of these species may be the precipitation of organic phosphorus during the estuarine mixing process. Although this characterisation has a valid and solid argument, the geochemical conditions available in the system make it difficult to attribute these fractions totally to the designation given. With sufficient population of the benthic community along with the available chemical conditions in the sediment, the possibility of such entities cannot be fully explained. A detailed identification procedure is required in this case. These reservations in designating these species have restricted the further discussions to the inorganic forms of Fe and Ca.

Some of very recent and important works on the fractionation of phosphorus in the sediments of different aquatic systems and some reported works in India, especially near the Cochin area are tabulated in Table 5.3. Comparisons are difficult because of the difference in the extraction schemes. All these works underlined the role of chemical speciation of phosphate as an indicative of the processes controlling the pathways of phosphorus in the aquatic environment and its importance in maintaing the fertility and the health of these systems. These were also helpful in understanding the diagenetic transformations of organic P in sediments.

Table 5.3 Important works on the fractionation of phosphorus in the sediments of different aquatic systems

Aquatic system and reference	Extraction scheme	Results
1.Eastern Arabian Sea (Babu & Nath, 2005)	SEDEX procedure Ruttenberg, (1992) Modified by Anderson & Delaney (2000)	Total phosphorus ranged between 920 and 2496 ppm, while it was 1070 -1632 ppm in off Cochin region. Porg was low in shelf (6%,) and relatively high in deep-sea sediments (12–17%). In sediments overlain by OMZ, Porg proportion is relatively high in the SE Arabian Sea (10–26%) when compared to the NE Arabian Sea (8–13%), which have less Porg than the deep-sea sediments
2.Volvi and Koronia lakes in Northern Greece (Fytianos & Kotzakioti, 2005)	Psenner *et al.*, (1984) Modified by Hupfter *et al.*, (1995)	P_{Tot} ranged from 0.9 to 1.30 mg/g DW, with higher values in the fine fraction of sediments compared to coarse. P mainly consisted of HCl-P and Res-P, which accounted for 12 and 82% and 24 and 75% of TP for Koronia, and Volvi respectively.
3.Different oceanic regimes (Faul *et al.*, 2005)	SEDEX procedure Ruttenberg, (1992) Modified by Anderson & Delaney (2000)	Org. P was the largest contributor to total P, especially in the Ross Sea (average 53% of total P). Detrital P is a more significant contributor to total P on the California Coast (Monterey Bay, average 16% of total P; Northern California Coast, average 22% of total P), where lithogenic contributions, presumably from riverine, or at least continental, sources, are known to be significant and in the Palmer Deep (average 40% of total P).
4. Japan Sea (Cha *et al.*, 2005)	Ruttenberg (1990) modified by Rao (1994)	The total P ranged 13.0–35.5 μmol/g. The concentrations of Det-P were very low (0.7–2.6 μmol/g) accounting less than 10% (by weight) of total P. The Fe-P concentration was 0.9–23 μmol/g, accounting for 7–63% of the total P. The CFA-P concentration was 3.1–6.1 μmol/g (9–44% of the total P), while Org-P was the major form (3.6–10 μmol/g), accounting for more than 40% of the total P.

5.Mattaponi River, Virginia, USA (Morse *et al.*, 2004)	Paludan & Jensen (1995)	Al-Po and Fe-Pi comprising 64% and 53% of total Pat the upstream and downstream sites, respectively. organic P represented a larger percentage of total P – 88% versus 59% for the upstream marsh and 70% versus 50% for the downstream marsh. Sediment HA-P was slightly higher at the upstream marsh (11% vs. 5%), and Ca-P was higher at the downstream marsh (9% vs. 2%). Aluminum-bound organic P (49%) was clearly the most important fraction in surface soils at the upstream marsh, followed by HA-P (23%), Fe-Pi (9%), and Res-P (9%). Iron-bound organic P, high only in CM locations at the upstream marsh (27%), represented the most important soil P fraction at the downstream marsh (40%) followed by Fe-Pi (20%) and Al-Po (20%). The percentage of bioavailable P in sediments) was significantly higher at the upstream marsh.
6. Lake Agmon, Israel (Hambright & Eckert, 2001)	Modification of Hieltjes & Lijkema (1980) and Karl & Tien (1992)	Total P averaged 1041 ± 97 µg/g dw. P bound to calcium accounted for the largest fraction (49%). metal-bound p accounted for ca. 12%, ca. 21% was bound to humic acids, and the remaining 18% was bound to other organic compounds. Loosely bound p was undetectable.
7. Mediterranean French coastal lagoons (Thau and Méjean) (Paing *et al.*, 1999)	De Groot & Golterman (1993)	Fe-P constituted about 25% of P, Ca-bound (30%)was the most important inorganic fraction. Organic-P represented a substantial proportion of the Total-P (38% of Total-P in Thau and 28% in Méjean). This Organic-P pool was subdivided in three fractions: Fulvic-P attaining 60% of Organic-P whereas Humic-P and Organic- Pac represented the remaining 40%.
8. Southwest coast of India (Nair *et al.*, 1993)	8 different schemes	The major forms of P namely exchangeable P, Carbonate bound P, labile and resistant organic P, Fe-, Al- and Ca bound P etc

9.Cauvery Estuary and Pichavaram mangroves (Ramanathan, 1999)	Ramanathan *et al,* (1996)	In the estuary P was mainly associated with Al-P followed by Ca-P and Fe-P suggesting origin by natural weathering. In the mangroves the Al-P was dominant in the outer channels and in the interior channel increase in the Fe-P, Organic P and total P. P is widely distributed in all the fraction of the sediments. In the estuary p was higher in the coarse sand and silt fractions as compared to fine fractions suggesting the anthropogenic input to the Cauvery estuary. In the mangroves the P was generally abundant in the coarser fractions in comparison to finer fractions in the outer channels and reverse trend was noticed in the interior channels.
10. Cochin estuary Balchand & Nair (1994)	8different schemes	The major forms of P namely exchangeable P, Carbonate bound P, labile and resistant organic P, Fe-, Al- and Ca bound P etc. The changes in the exchangeable P together with the marked regional variation in the calcium bound P exemplified the complex variability of phosphorus in this estuary.
11. Kuttanad region, Vembanad Lake (Lizen, 2000)	Hieltjes & Lijkema (1980) and van Eck (1982)	Residual P (40.06-91.65%) dominated in the region with very low contribution of exchangeable P (0.06-0.6%). Fe- and Al-bound P (2.76- 37.25%) and Ca bound P (1.49-33.50%) were the other dominant forms.
12. Mangrove ecosystems around Cochin (Shaly, 2003)	Golterman (1996) modification by Pardo *et al.*, (1998)	Total P in surficial sediments was in the range from 480.72 to 1967.60 µg/g. Fe-IP was the dominant fraction (21.82-28.31%), followed by Ca-IP (15.55-20.47%) and Alk-OP (14.22-21.35%)

The mobility of phosphorus in the sediment is probably controlled by its speciation (Selig & Schlungbaum, 2003). Phosphorus dynamics in the study region were found to be influenced by three dominant characteristics, viz. the geochemical character of the sediment, exchangeable/bioavailable phosphorus and the significance of individual species. Hence the further discussions on phosphorus dynamics in the study region are limited in to these three categories.

1) Geochemical character of the sediment

The significant correlations of the geochemical parameters with total P suggest the possibility of evaluating the biogeochemical processes outlined in the previous chapter through phosphorus speciation. Like all the other geochemical parameters, total phosphorus was found to be higher at muddy stations and lower at sandy stations. Since the biogeochemistry and sediment composition of the study region was found to be distinctively different (chapter 4), same grouping was followed here also for discussing the phosphorus speciation and dynamics in this section.

Stations 1, 2, and 5 with coarse substratum, which are in the erosional zone, autochthonous addition were the major biogeochemical process. Low carbon and the low sulphur content testify to a slack proceeding of diagenetic processes in this region. Ca-IP was the dominant fraction during pre and post-monsoon seasons, while Ca-OP was the major fraction during monsoon in the fine fraction at station 1.Coarse fraction of station 1 was dominated by Alkali-OP, while a higher concentration of Ca-OP was seen during post-monsoon. At station 2, Ca-OP was the principal fraction during pre-monsoon and post-monsoon seasons, while a very high percentage Alkali-OP was noticed during monsoon season. Alkali-OP was the main fraction in the coarser sediments of station 5,though Ca-OP was the chief component during pre-monsoon season.

Stations 7, 8 and 10 had fine sediments and anoxic condition is prevailing in this organic rich depositional zone. Principal geochemical process in this region might be the diagenetic decomposition. Ca-IP was dominant during pre-monsoon and post-monsoon seasons, whilst Alkali-OP constituted the major portion during monsoon. Higher levels of Fe-IP were also seen during pre-monsoon and post-monsoon seasons. Fe-IP, Alkali-OP and Acid-OP were the key fractions during pre-monsoon, monsoon and post-monsoon seasons respectively at station 8. Ca-IP was the chief component during pre-monsoon at station 10 and Alkali-OP dominated during monsoon. During post-monsoon, Ca-IP was the most prevailing the fraction in the fine sediments, whereas Ca-OP dominated in the coarse fraction.

Analysis of the results shows that the overall geochemical structure and character is maintained in the micro evaluation of the system. The sandy and muddy stations showed distinctively different species composition in the speciation study. This also gives the signature of diagenesis, as the organic fractions like Alkali-OP were comparatively lower in the muddy stations.

2) Exchangeable/bioavailable phosphorus

The percentage of bioavailable fractions was ranged between 12.02 and 64.79 during pre-monsoon at sandy stations and between 63.61 and 68.86 at muddy stations. These fractions varied from 9.67 to 56.12 % and from 23.62 to 44.72 % respectively at these stations during monsoon. Sandy stations showed a variation between 14.76 and 53.61 % and muddy stations between 32.56 and 67.80 % in the bioavailable fractions during post-monsoon. The variations were not prominent in the different size fractions of sediments.

Total inorganic fraction varied from 5.07 to 41.64 % during pre-monsoon at sandy stations and from 48.14 to 58.55 % at muddy stations. These were very low during monsoon and ranged between 5.95 and 39.24 % at stations with coarser substratum and from 9.77 to 32.63 % at fine textured stations. The inorganic fraction was in the range from 9.23 to 27.10 % and from 14.51 to 54.08 % respectively at these stations during post-monsoon season. No apparent differences between finer and coarser fractions of sediments were noticed.

·Total organic fraction showed a range from 58.36 to 94.93· % during pre-monsoon at sandy stations and between 41.45 and 51.86 % at muddy stations. These stations showed a variation from 60.76 to 94.05 % and from 67.37 to 90.23 % respectively during monsoon. The post-monsoon range was from 72.90 to 90.77 % at sandy stations, whereas it was from 45.92 to 85.49 % at muddy stations. Differences between finer and coarser fractions of sediments were not clear.

These results suggest that the percentage of bioavailable fractions is maintained in all the seasons in this estuary. Hence phosphorus limitation never conversely affects in the productivity. If the limitations of nitrogen and other physiological parameters were properly managed, the fertility and the health of the ecosystem can be effectively increased. Meanwhile it should be bone in mind that since the system has a buffering capacity of phosphorus, the trophic nature of the system can be damaged by the over production, when the other conditions favour. So a proper management is essential for sustainability.

3) Significance of individual species

Phosphorus chemistry in sediments is greatly influenced by the oxidation-reduction status (redox potential). The classic model of P-release from anoxic sediments is the reduction of FeOOH-phosphate complexes (Einsele 1936, 1938; Mortimer 1941, 1942). Although Org-P is the primary source of P to the sediment, the redox cycle of Fe greatly affects P geochemistry after burial (Cha *et al.,* 2005). Under oxidized conditions, ferric and manganic oxides and hydroxides are important adsorption sites for P (Krom & Berner, 1980; Slomp *et al.,* 1996). In addition, ferric and manganic phosphate minerals, such as strengite ($FePO_4.2H_2O$), and trivalent Mn phosphate ($MnPO_3$ $.1.5H_2O$) can form and persist under oxidized conditions. However, under reducing conditions these minerals are unstable, resulting in dissolution and release of soluble P into the water (Patrick *et al.*, 1973; Emerson, 1976; Emerson & Widmer, 1978; Krom & Berner, 1980; Boyle & Lindsay, 1986; Sundby *et al.*, 1992;Moore & Reddy, 1994; Lucotte *et al.*, 1994; Louchouarn *et al.*, 1997).

The Fe:P ratio is considered to be a measure of free sorption sites for phosphate ions on iron hydrohydroxide surfaces (Jensen *et al.*, 1992; Jensen & Thamdrup, 1993; Paludan & Jensen, 1995). The lower Fe:P ratios propose saturation of sorption sites or less capability to adsorb phosphate, resulting in phosphate efflux to the overlying water. Jensen *et al.*, (1992) suggested that when the total Fe:P ratio above 15 (w:w) is enough Fe to control the benthic flux of P from sediment to oxic water. Rydin & Brunberg (1998) described the formation of an effective oxic barrier with a Fe:P ratio (by weight) of above 15. In the study region, Fe:P ratio was about double of the critical value for muddy stations throughout the year, while less in the sandy stations 2 and 5 during monsoon and post-monsoon seasons. Therefore, there seems to be enough Tot-Fe in surface sediments to bind P along the estuarine gradient, except for sandy stations.

However, Tot-Fe concentration does not reveal the pool of Fe^{3+} oxides, which can efficiently bind P.Thamdrup *et al.*, (1994) showed that only about 20% of total Fe in the surface sediments of the transition zone between the Baltic Sea and the North Sea were in the form of Fe^{3+} oxides, since Fe is mainly bound to sheet silicates. On the basis of extractions of P and Fe from sediments collected from the Canadian and Portuguese continental margins and the Chesapeake Bay in the USA, Anschutz *et al.*,

(1998) estimated that 20 to 30% of the sedimented P had been remobilized and exported to the overlying water, mainly due to the reductive dissolution of poorly crystalline iron oxides. In addition, a further distinction must be made between Fe^{3+} oxides like Fe_2O_3, not active for P, and Fe (OOH), efficiently P binding. The P sorption capacity of amorphous, *i.e.* poorly crystallized, $Fe(OH)_3$ and lepidocrocite (ã-FeOOH), is about 20 times that of crystalline Fe(III) oxides such as goethite (.-FeOOH) and hematite (.-Fe_2O_3; McLaughlin *et al.*, 1981).The increase in pH with salinity increase may prevent phosphate adsorption onto iron-oxyhydroxides, by shifting the speciation of phosphate from $H_2PO_4^-$ to HPO_4^{2-}, and by changing the surface charge on the iron-oxyhydroxides (Lebo, 1991; Zwolsman, 1994). An increase in pH can also increase the negative charge of the sorbing oxides (Hartikainen 1981, Hartikainen & Yli-Halla, 1996). A significant decrease in P sorption to Fe(III) oxides occurs at pH > 6.5 (Stumm 1992), values that are often observed in the sediments of the Baltic Sea. It was found that Fe^{3+} oxides were depleted in sulphide environments by the formation of solid iron sulphides like monosulphide (FeS) and pyrite (FeS_2)] (Krom & Berner, 1980; Thamdrup *et al.*, 1994; Paludan & Morris, 1999). Higher total sulphur content in this study region because of anthropogenic addition (chapter 4) might also be the reason for lower iron bound fraction even after a higher Fe content.

In marine sediments, however, most of the total Fe (60–80%) is bound to sheet silicates (Chlorite; Canfileld 1988, Thamdrup *et al.*, 1994). Adsorption of P by silicate-bound Fe is insignificant compared to that by Fe(III) oxides, which are considered to be the main Fe compounds in P binding. Sediments contain a multitude of Fe(III) oxides, often in complexed mixtures, that range widely in degree of crystallinity, particle size, available surface area, reactivity and oxidation state (Lovley, 1991). Although most of the Fe(III) is in the form of insoluble oxides, organically complexed and colloidal forms may also be abundant in sediments (Lovley, 1991).

Other negatively charged anions can also compete with the PO_4^{3-} of adsorption sites in sediments. For example, the effect of pH can be related to competition for adsorption sites, because desorption of P from clay minerals and Fe and Al (hydr) oxides is based on ligand exchange, in which P is substituted for by OH^- (Bolt, 1982). It has also been suggested that competition between SO_4^{2-} and PO_4^{3-} for Fe(III) oxide surface binding sites could promote P release at high SO_4^{2-} concentrations (Caraco *et al.*, 1989). However, no difference has been found in the P concentration of pore water between low SO_4^{2-} and SO_4^{2-} amended sterile treatments (Roden & Edmonds, 1997). Nor has any decrease been found in the adsorption capacities of clays determined in seawater Cl^- and SO_4^{2-} concentrations (Edzwald *et al.*, 1974). Silicate (SiO_4) and P are sorbed onto the surfaces of hydrated Al and Fe oxides by the same specific mechanism (Obihara & Russell, 1972) and, thus, SiO_4 may chemically compete with PO_4^{3-} for adsorption sites (Hartikainen *et al.*, 1996, Tuominen *et al.*, 1998, Tallberg, 2000).

Bacteria have been generally considered as "catalysts" that accelerate the solubilisation of P (Gachter & Meyer, 1993). They act to decompose material and P is then released from particulate matter and recycled by phytoplankton and bacteria themselves (Currie & Kalf, 1984). Sediment resuspension is one alternative mechanism of recycling P from the sediments to the water column. Incorporation of P into heterotrophic bacteria may be an important mechanism maintaining P availability in the water column after resuspension events. Although bacteria can compete with phytoplankton for P (Currie & Kalff, 1984; Cotner & Wetzel, 1992; Vadstein *et al.,* 1993), and thus, decrease productivity; the study region is found to be relatively P-rich with internal concentrations. The C: P ratio varies widely in the study region (~1 to 28) and was higher in the muddy stations than in sandy ones (Chapter 4).

It is need to take the redox-sensitive P pool into account when considering management strategies for controlling P transport from agricultural fields to surface waters, especially in fine-textured catchments (Uusitalo & Turtola, 2003). In oxidizing sediments most of the P released into interstitial water during organic matter decomposition is adsorbed by Fe-oxides, carbonates and clay minerals in processes similar to those in the overlying oxygenated waters. Further in areas of high $CaCO_3$, P may precipitate as apatite (Calvert, 1976). These processes might be occurring in this estuary. Ca–P was found to be the main P pool in the estuary. This can result from several processes. Solid calcium carbonates are also influenced by salinity and pH. Calcite is produced at high salinities through precipitation reactions and biological activity, both in estuarine and marine environments, forming an adsorption substrate for dissolved phosphate. Calcium associated minerals were found in the study region (chapter 4). $CaCO_3$ can be considered an important pool in P dynamics not only in tropical areas but also in temperate estuaries, where it functions as a P immobilization agent in the higher salinity area (Moutin *et al.,* 1993; Paludan & Morris, 1999; Andrieux-Loyer & Aminot, 2001). The high organic P content may be the result of flocculation and precipitation processes involving humic acids, Fe/Al oxides and DRP complexes from advective mixing of saltwater with the nutrient rich freshwater input from the river (Paludan & Jensen, 1995; Paludan & Morris, 1999).

The total flux of dissolved compounds across the sediment-water interface includes advection, bioturbation, irrigation, physical wave activity and current effects. Microbially induced changes in pH and redox potential affect the ability of sediments to retain inorganic phosphorus (Roden & Edmonds 1997; Gachter & Muller 2003). Although these changes are driven by organic matter decomposition, the direct role of sediment bacteria by the release of organically bound phosphorus needs special reference. Many studies have shown that a substantial proportion of phosphorus in settling seston originates from biomass (Hupfer *et al.,* 1995; Kleeberg, 2002).

Golterman (2001) discussed that apart from Fe-bound P-release under anoxic conditions, the possibility that an organic constituent forms a part of the adsorbing complex in oxidised muds. Other processes for anoxic P-release includes solubilization of apatite by a drop of the pH-value (Golterman, 1998), mineralisation of sedimentary organic matter by bacterial activity (Gächter *et al.*, 1988; Sinke *et al.*, 1990), mineralisation of phytate (Golterman *et al.*, 1998) and the release of polyphosphate by sediment bacteria (Hupfer *et al.*, 1995).

Given the high diversity of benthic organisms and considering that the surface of sediments often represents an aerobic/anaerobic transition layer with variable redox conditions, it has been speculated that poly-P-accumulating organisms might also be present in lake sediments (Uhlmann & Bauer, 1988; Khoshmanesh *et al.,* 2002). Redox-controlled poly-P metabolism has been proposed to contribute to benthic P fluxes in marine

(Ingall & Jahnke, 1997) and in lacustrine sediments (Gachter *et al.*, 1988; Davelaar, 1993).

Phosphorus associated with humic acids has been considered either as an integral part of humic acids or as a phosphate/metal/organic matter complex (Stevens & Stewart, 1982). NaOH–NRP fraction may to some unknown extent contain phytate, an organic phosphate that is common in plants (Hess, 1975) and soils (Stevenson, 1982). De Groot & Golterman (1993) found phytate concentrations ranging 24–149 µg/g DW for a number of sediments from marshes and a shallow brackish water lake in the Camargue (France).

As a result of the diagenetic reorganization of P within sediments, organic P concentrations usually decrease with time as it is ultimately transformed to authigenic P during diagenesis (Ruttenberg & Berner, 1993; Filippelli & Delaney, 1996; Delaney & Anderson, 1997; Anderson *et al.*, 2001). The conversion of more labile forms of P (organic and oxide-associated) to authigenic P is time dependent (Filippelli & Delaney, 1996; Faul *et al.*, 2003), therefore, the conversion is likely ongoing in young sediments.

Statistical techniques are employed to deduce the diagenetic interrelationships among the organic and inorganic forms of P and other sediment components like Fe, Mn, Mg, S, C, N and benthic density (Table 5.4). The bio available fractions Fe-IP, Ca-IP and Acid-OP showed significant interrelations and also significantly correlated with metals, C, N and S. These testify that the principal geochemical processes governing these species are same and they behave in a similar way to the changes in redox and pH conditions. ROP showed significant positive correlations with all parameters except Fe-IP and benthos. Alkali-OP showed significant negative correlation with benthos. This is also expected, as Alkali-OP fraction mainly consists of phosphorus associated with humic acids and also phytate, which are not of nutritional values.

Table 5.4 Inter correlations between seasonal averages of different fractions of phosphorus in the study region (n=18)

ameter	Fe-IP	Ca-IP	Acid-OP	Alkali-OP	ROP	Fe	Mn	Mg	S	C	N	Benthos
e-IP	1.000	.718(**)	.469(*)	-.025	.336	.525(*)	.456	.543(*)	.435	.523(*)	.502(*)	.113
a-IP	.718(**)	1.000	.748(**)	.304	.502(*)	.745(**)	.836(**)	.876(**)	.549(*)	.649(**)	.704(**)	-.035
cid-OP	.469(*)	.748(**)	1.000	.303	.755(**)	.964(**)	.882(**)	.926(**)	.875(**)	.901(**)	.914(**)	-.082
lkali-OP	-.025	.304	.303	1.000	.572(*)	.288	.293	.298	.257	.279	.253	-.560(*)
ROP	.336	.502(*)	.755(**)	.572(*)	1.000	.783(**)	.683(**)	.725(**)	.739(**)	.776(**)	.745(**)	-.410
Fe	.525(*)	.745(**)	.964(**)	.288	.783(**)	1.000	.893(**)	.923(**)	.904(**)	.943(**)	.935(**)	-.181
Mn	.456	.836(**)	.882(**)	.293	.683(**)	.893(**)	1.000	.984(**)	.738(**)	.814(**)	.891(**)	-.087
Mg	.543(*)	.876(**)	.926(**)	.298	.725(**)	.923(**)	.984(**)	1.000	.781(**)	.850(**)	.908(**)	-.080
S	.435	.549(*)	.875(**)	.257	.739(**)	.904(**)	.738(**)	.781(**)	1.000	.983(**)	.929(**)	-.237
C	.523(*)	.649(**)	.901(**)	.279	.776(**)	.943(**)	.814(**)	.850(**)	.983(**)	1.000	.962(**)	-.217
N	.502(*)	.704(**)	.914(**)	.253	.745(**)	.935(**)	.891(**)	.908(**)	.929(**)	.962(**)	1.000	-.142
Benthos	.113	-.035	-.082	-.560(*)	-.410	-.181	-.087	-.080	-.237	-.217	-.142	1.000

** Correlation is significant at the 0.01 level (2-tailed).
* Correlation is significant at the 0.05 level (2-tailed).

The overall dynamics of phosphorus in this estuary can be schematically represented as depicted in Fig. 5.7. The input is mainly from the land run off and there will be other contributions from atmospheric precipitation and seawater intrusion. Precipitation/flocculation and sedimentation transfer the P in water to the sedimentary compartment. There it undergoes biogeochemical processes such as diagenesis and bioturbation, leading to the conversion of P into organic and reactive phosphorus. Fe-P undergoes cycling in water and exchange layer of sediment by a mechanism like redox pump and Ca-P cycles around the exchange and deposition layers of sediment. Organic P undergoes diagenesis, being converted to bioavailable and residual fractions.

Water column showed marked seasonal fluctuations and spatial variations. Phosphate showed significant positive correlations with current and TSS, indicating the significance of particulate associated phosphorus in the estuary. During post-monsoon period rapid removal of DIP by some mechanisms like adsorption and sedimentation were noticed. Tidal analysis also established significant diurnal variations in phosphate levels in this highly fertile ecosystem, although it lacks a clear tidal rhythm. It also showed significant positive correlations with river runoff and negative correlation with salinity. Maximum values were obtained during southwest monsoon and the annual range was from ND to 17.80 µmol/l. The percentage of contribution from the water column is not shown as it is of different scale to that in sediments.

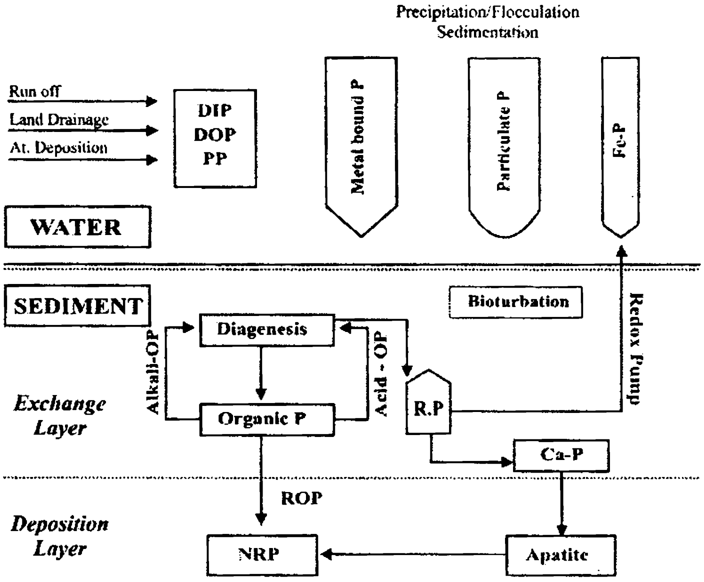


Figure 5.7 Phosphorus dynamics in the study region

Summary and Conclusion

Phosphorus dynamics is employed for biogeochemical characterisation and to identify the possible promotion of bioavailability and productivity. Phosphorus is taken as the representative element because of its nutrient character and geochemical reactivity and the micro level speciation is taken as a tool for this. The scheme using chelating agents developed by Golterman (1996) modified by Diaz-Espejo *et al.,* (1999) was employed to differentiate the higher possible number of species viz. iron bound inorganic) and organic fractions, calcium bound inorganic and organic fractions, acid soluble organic fraction, alkali soluble organic fraction and residual organic phosphorus. The results indicated that sedimentary character such as grain size has no role in micro speciation, when the percentage of species is considered. Seasonal changes do not reflect on the bioavailability and the inter-correlations of species along with the residual concentrations indicate more or less steady state maintenance in the estuary. The speciation study warrants a multi compartment and interdisciplinary management strategy for the sustainable development of this aquatic system.

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Chapter 6

ECOHYDROLOGY

6.1 Introduction

Ecohydrology is an environmental problem-solving concept, which is based upon the assumption that sustainable development of water resources is dependent on the ability to maintain evolutionarily established processes of water and nutrient circulation, and energy flows at the basin scale (Zalewski *et al.*, 1997; Zalewski, 2000). Pedroli (1990) first used the term “ecohydrology” in an underground water study and quickly adopted by fields of study ranging from plant physiology to aquatic geochemistry (McClain, 2002). This concept developed during UNESCO’s International Hydrological Programme, promotes the integration of hydrology and ecology, and the control of these processes to enhance the adsorption and assimilation capacity of ecosystems (Fig. 6.1 and 6.2). This depends on a profound understanding of the whole range of processes involved that have a two-dimensional character. The first dimension is temporal: spanning a time frame from past paleohydrological conditions to the present, with due consideration of future global change and variability scenarios. The second dimension is spatial: understanding the dynamic role of aquatic and terrestrial biota over a range of scales, from molecular to basin scales. According to the ecohydrology concept, elimination of threats without consideration of increased opportunities, cannot lead to success. Thus, ecohydrology incorporates the use of ecosystem properties as a management tool in implementing a program of water resource management. Scientific knowledge supplies the analytical tools that water managers use to shape and evaluate management practices (Nuttle, 2002).

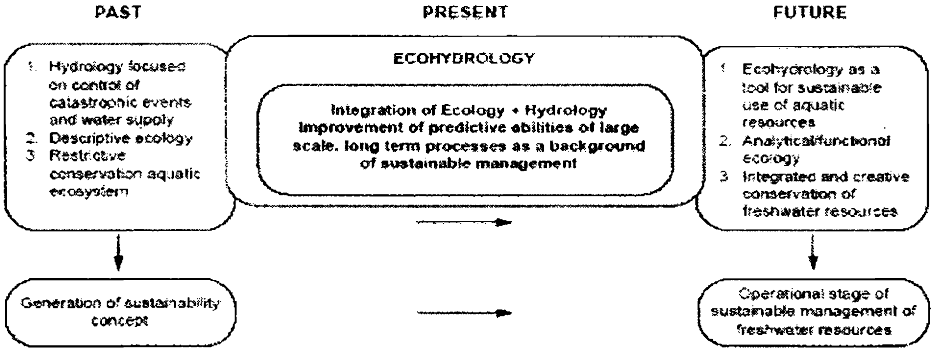

Figure 6. 1 Evolution of Ecohydrology (Zalewski, 1997)

Water management is now an essential component in the management of natural resources. In addition to traditional roles of assuring adequate supplies of clean, fresh water and reducing the risks of flooding, water managers protect endangered species and restore failing ecosystems. Achieving the expanded goals for water management and integration with other natural resources requires new information from the Earth sciences and ecology. The paradigm of sustainable water resource management recognizes implicitly that the primary resource is the natural endowment of climate, geology and ecosystem processes in each region. These attributes determine the quantity, quality, timing and spatial distribution of water readily available to us. Ecohydrology, the science, seeks knowledge that we need to understand the influence of human activities on this resource. As such, ecohydrology embraces a range of topics as varied as the Earth's ecosystems and the human activities that will determine their, and our, future (Nuttle, 2002). GIS tools are probably amongst the best ones to make a link between hydrology and ecology: valuable ecohydrological results are provided without the scale differences generally used in both specific domains. Evaluation of how and to what extent biological processes might modify the flow of water, nutrients, sediments and pollutants in aquatic ecosystems and the surrounding landscape is a logical further step in the development of ecohydrology (Zalewski, 1995; Schiemer *et al.*, 1995)

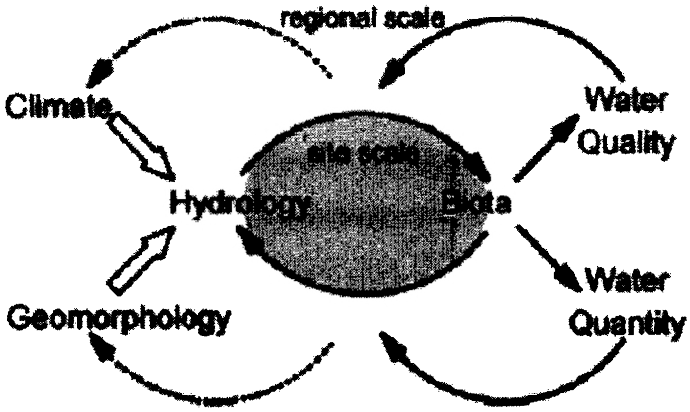

Figure 6. 2 Concept and components of Ecohydrology (Zalewski, 1997)

This is based on three steps: The preliminary study of a catchment starts with an in-depth ecological understanding of the environment (climate, soil science, vegetation, human occupation). The prevention of pollution, basement of a sustainable development, represents the second step. This implies to establish a catchment model in view to precise sources and to assess pollutants fluxes. From this model, a sustainable land-use management programme will be constituted for the catchment. Bio-engineers implement several technologies to strengthen the ecosystems, like phytoremediation and biomanipulation. They consider long-term management scenarios, in particular through the model previously established. It is advisable to insist on phytoremediation and biomanipulation, both important innovative research axes for ecohydrology.

The current geological epoch has been dubbed the "Anthropocene," because nowadays it is man that will probably be most responsible for shaping natural processes that transpire on a global scale. The conscious harnessing, based on interdisciplinary knowledge, of an ecosystem's own properties as tools for increasing the environmental "carrying capacity" is becoming a necessity. Without a doubt, our understanding of the interactions between abiotic and biotic processes is becoming crucial for curbing this human impact. This pertains in particular to the most dynamic abiotic factor of all: water. UN bodies as UNESCO and UNEP, as well as of the EU, have recognized that water quality is a crucial factor for meeting mankind's needs and for achieving sustainable development, and that it depends on the condition of the ecosystem. Developing environmental protection systems that improve the state of natural resources while generating positive socioeconomic feedback is made possible by an integrative combination of earth sciences, biology, mathematical modeling, and socioeconomics.

Eagleson (1978, 1982) investigated the interaction of hydrology, vegetation and soil properties in water-limited ecosystems and generated fundamental insights into the relationship among the dynamic and interdependent properties of soil, vegetation, and climate. Ecohydrologyis was defined as Darwinian expression of vegetation form and function (Eagleson, 2002). Groundwater, surface water, and sediment transport interaction was examined to find the influence the structure and functioning of river and stream ecosystems (Petts & Bradley, 1997). The influence that river flow and its variation exert on estuarine and near shore ecosystems was also covered in these studies (Livingston et al., 1997; Loneragan & Bunn, 1999). Baird & Wilby (1999) studied the plant-water interactions and the hydrological processes related to plant growth. Ecohydrological implications of woody plant encroachment in semiarid and arid grassland ecosystems were studied by Huxman *et al.*, (2005). An important aspect is the quantitative prediction of the linkages among climate, soil-moisture dynamics, and vegetation in natural water limited ecosystems (Guswa *et al.*, 2004). Ecosystem dynamics in arid and semiarid climates are strongly dependent on the soil water availability, which, in turn, is the result of a number of complexes and mutually interacting hydrologic processes (Porporato *et al.*, 2005). Monitoring of basic hydrological and ecological characteristics of the Guadiana Estuary before the construction of the Alqueva dam was carried out in ecohydrological approach (Chícharo *et al.*, 2001). Kemp *et al.*, (2000) examine the influence of channel geomorphology and geology on the diversity of functional habitats, identified by distinct invertebrate assemblages. Biswas & Boruah (2000) explained the dramatic decline of highly diversified Himalayan Mountain Brahmaputra River fish fauna by accelerated deforestation and land degradation due to 'careless' agricultural practices of the river basin.

Over the coming decades, greater than 90% of population growth is expected to occur in the tropics. Currently, the human populations occupying tropical river basins vary greatly in density and the extent to which they have altered the river basins. Throughout the world, estuaries and coastal waters have experienced degradation. Presently proposed remedial measures based on engineering and technological fixes are not likely to restore the ecological processes of a healthy, robust estuary and, as such, will not reinstate the full functioning of the estuary ecosystem. Traditionally, the management of estuaries and coastal areas was carried out through the implementation of engineering solutions. However, this approach commonly generated other impacts, such as decrease in fisheries and other ecosystem services. This phenomenon in the Cochin estuary was well discussed in the introductory chapter. Even where freshwater discharge is artificially regulated, managing such discharge considering ecosystem needs can provide an important basis for maintenance or restoration of system health and ecological services in rivers, estuaries and coastal areas. The successful management of estuaries and coastal waters requires an ecohydrology-based, basin-wide management approach. This necessitates changing present practices by official institutions based on municipalities or counties as an administrative unit, or the narrowly focused approaches of managers of specific activities (e.g. farming and fisheries, water resources, urban and economic development, nature conservationists). Without this change in thinking and management concept, estuaries and coastal waters will continue to degrade; whatever integrated coastal management plans are implemented.

To help in this process of change there is need to develop a profound understanding of the effects of biota and biotic processes on mediating estuary response to changing hydrology, sediment and nutrient fluxes etc.; develop science-based remediation measures to strengthen the ability of the biota to sustain and adapt to human-induced stresses; develop public awareness and expand collaboration between coastal zone managements and other scientists with the aim of diffusing world-wide the scope of application of the ecohydrology concept. This chapter is also an attempt towards that.

The main drawback of the present concept of ecohydrology is that chemical parameters are not having significant contribution in the modeling. The indispensable contribution of water chemistry, geochemistry and the nutrient dynamics to the estuarine ecology was well described in the previous chapters. This study is an attempt to propose a sustainable management scheme by the re-definition of the "ecohydrology" concept by the application of aquatic chemistry.

6.2 Estuarine Dynamics

Predictions based on extrapolation of observations from representative samples are well approved. But the validity of such predictions has to be meticulously confirmed. In an open, positive aquatic system like Cochin estuary, where the number of parameters contributing to the estuarine processes are large, such approximations may not give valid predictions. So tidal observations were carried out in the entire southern arm of Cochin estuary between barmouth and Thanneermukkam bund during pre-monsoon period to examine the hydrodynamics, geochemistry and nutrient dynamics in order to envisage the estuarine dynamics. Pre-monsoon was chosen to minimize the external influence, as it will reveal the real system characteristics. The locations were near Cochin port, Thevara, Kumbalam, Perumbalam, Panavally, Kattachira and Thanneermukkam bund (chapter 2).

6.2.1 Hydrodynamics

Observations were made at seven different parts of the estuary for complete tidal cycle. On each day of observations, two stations were covered by continuously moving between stations so that data at an interval of two hours are obtained from each station. In the case of the station near Cochin port, hourly data were collected and the tidal variations are described in detail (Fig. 6.3).

6.2.1.1 Tidal variations near Cochin port

The station selected is in the middle of Cochin port and Marine drive, away from the deep Ernakulam ship channel and the maximum depth of the station was 1.5 m. Tidal range reported at Cochin Port was 49cm. Ebb lasted for 7 hours. Maximum flood and ebb currents were 30 cm/sec and 47 cm/sec, respectively. The slack periods more or less coincided with high and low waters. Depth wise difference of currents was negligible. Salinity varied between 29.2 and 35.6 ‰. Vertical salinity gradient did not exist, due to the predominance of tides over fresh water flow, indicating well-mixed condition. Salinity variations followed tidal rhythm. Temperature ranged between 30.7 and 32.6°C and the variation appears to be mainly due to diurnal heating cycle. The maximum was recorded during midday and it decreased subsequently. As in the case of salinity, the vertical temperature gradient was also not seen. Turbidity varied between 1.9 and 18.3 NTU and bottom waters were more turbid. Suspended sediments varied between 25.8 to 59.5 mg/l. Both these, in general, were higher when current speed was more. In the case of nutrients, fluctuations were noticed. Variation of phosphate was from 0.6 to 3.65 µmol/l, of nitrite was from 0.11 to 0.59 µmol/l, of nitrate was from 1.15 to 4.88 µ mol/l and of silicate was from 1.57 to 15.72 µmol/l. Silicate showed minimum during low tide. Nutrients in bottom waters showed more fluctuations. Dissolved oxygen ranged between 4.92 and 9.39 mg/l and did not show depth wise variations. Rather than following the tidal rhythm, it showed a diurnal pattern; an increase till evening followed by a sharp decrease. Gross and net primary productions, averaged over a few estimates were 110 and 68 mg C/m^3/hr respectively.

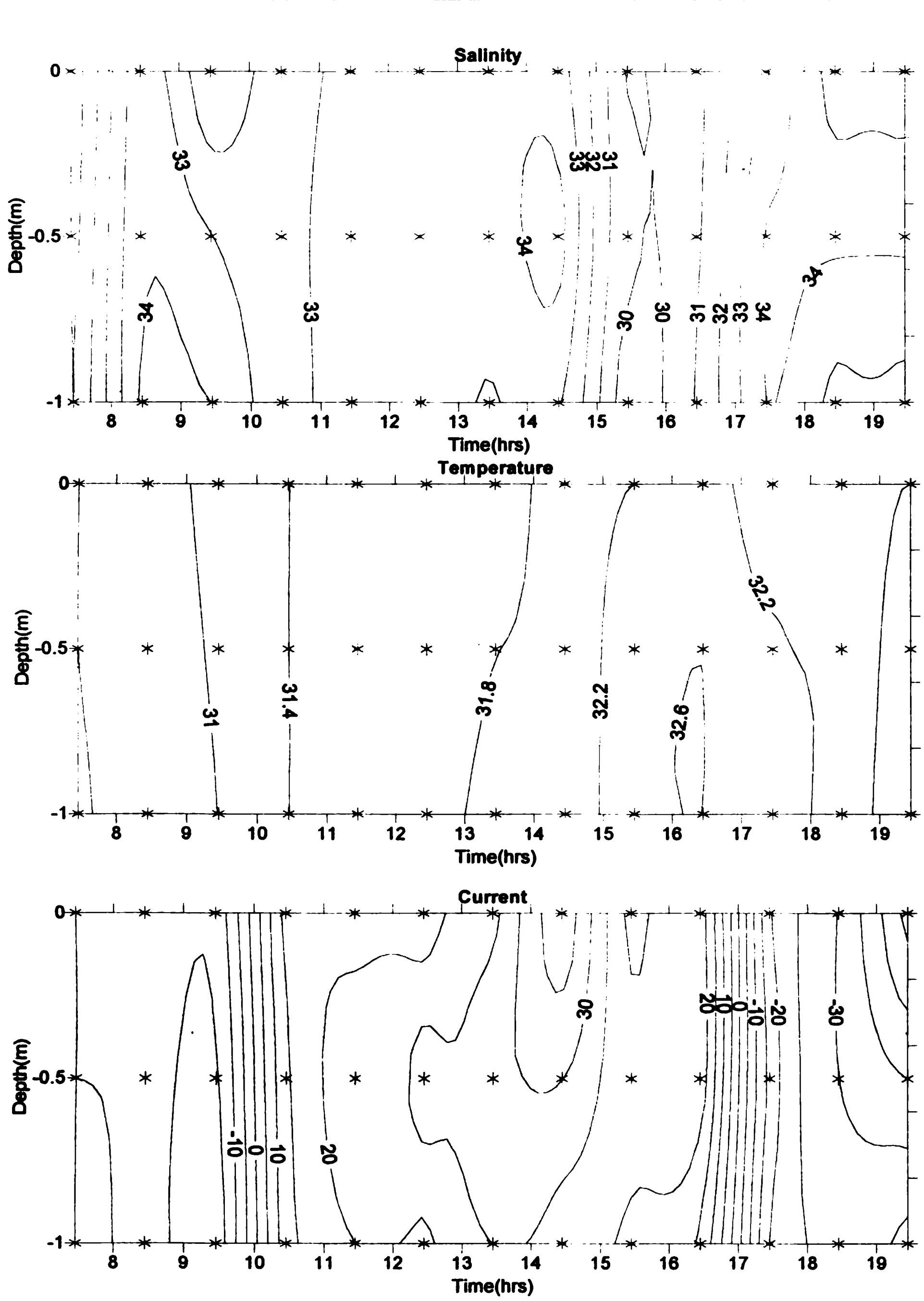

Figure 6.3 Tidal variations of different hydrographical parameters near Cochin port

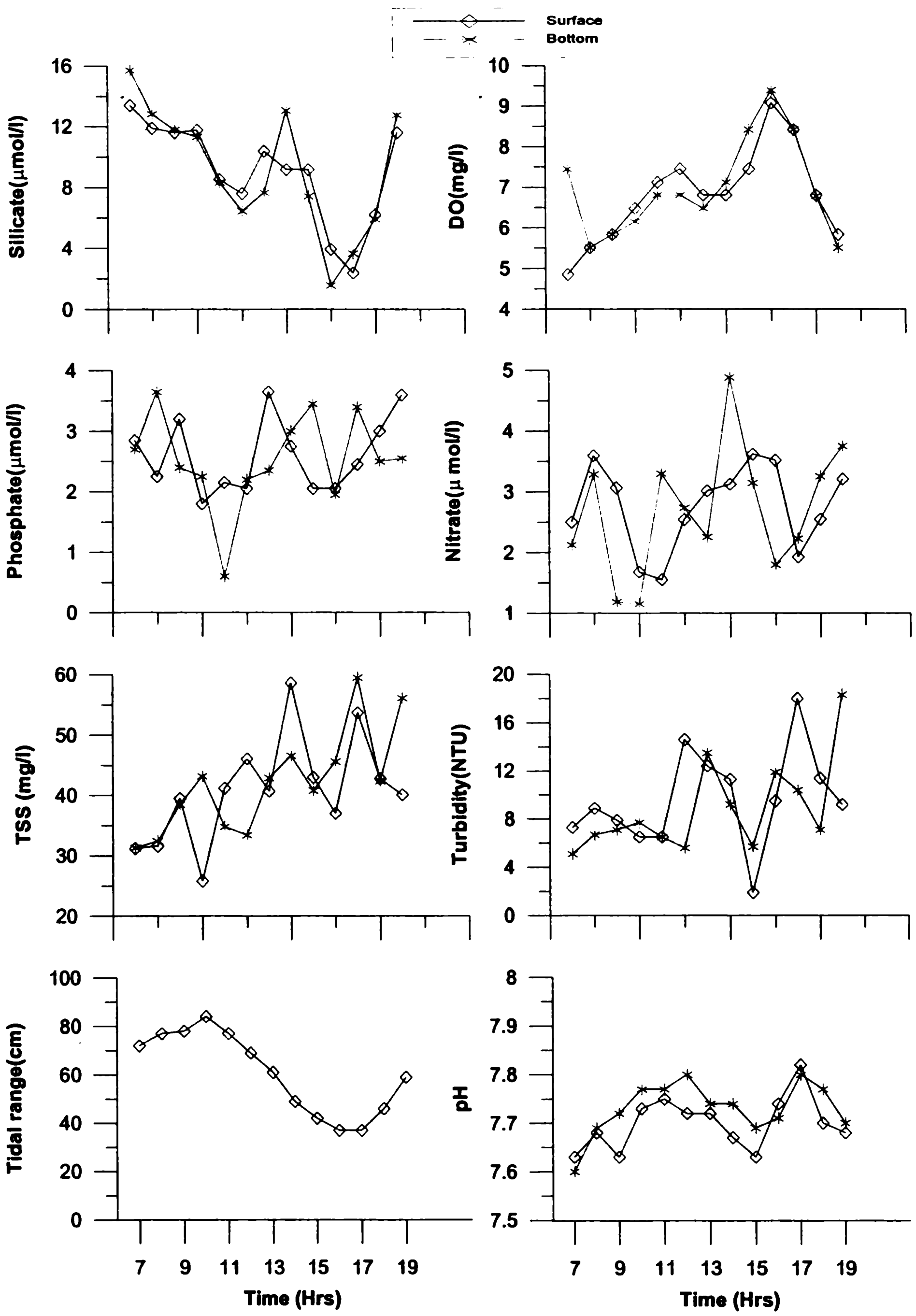

Figure 6.3 (contd.)

6.2.1.2 Variation of hydrographical parameters

The tidal range and averages of all parameters in the water column are shown in Table 6.1 and Fig. 6.4. Since there was variations during tidal cycle as discussed earlier, tidally averaged values were used in order to compare their variations. Tidally averaged salinity varied from 32.7 ‰ near the mouth to 16.5 ‰ at Thannermukkam and generally did not show any depth wise variation. A sharp gradient zone between 10 and 15 km from the mouth was seen, where a drop of about 10 ‰ was noticed. In the next 5 km, the drop was about 5 ‰ and thereafter the decrease was gradual. Temperature did not show any significant change in this tropical estuary and the depth wise variation was also low. Suspended sediment load were higher near the mouth and decreased considerably towards the upper reaches, the range being 14.4-65.8 mg/l. Turbidity also showed similar trend with higher values up to Kumbalam region and decreasing gradually.

pH was also higher near the barmouth region. The alkaline nature continued to decrease towards upper part of estuary and almost neutral pH prevailed near the bund. Higher nutrients were noticed near the mouth. This trend continued up to 10 km in the case of phosphate with gradient zone corresponding to that of salinity. Nitrate decreased more rapidly. Towards the head of the estuary, all nutrients except phosphate increased and a conspicuous increase is seen in the case of silicate, which is a totally land derived nutrient. Dissolved oxygen, however, slightly varied from this pattern. Higher concentration was seen near the mouth and after decreasing, it increased again. Primary production was higher at the mouth and decrease to about half at the head of the estuary. Zooplankton density and diversity also decreased from the mouth towards 10 km and there after showed a rapid increase in the next 10 km. Total density obtained was

Table 6.1 Tidal variations in the southern arm of Cochin estuary (Tidal average is shown in parenthesis)

Station	Depth	Salinity (ppt)	Temp (°C)	Current (cm/s)	TSS (mg/l)	Turbidity (NTU)	pH	Phosphate (µmol/l)	Nitrite (µmol/l)	Nitrate (µmol/l)	Silicate (µmol/l)	DO (mg/l)	GP (mg C/ m³/hr)	NP (mg C/ m³/hr)
Cochin Port	S	29.2-34.5 (32.42)	30.8-32.4 (31.61)	10-47 (22.15)	25.8-58.6 (40.87)	1.9-18 (9.65)	7.63-7.82 (7.70)	1.8-3.65 (2.60)	0.13-0.59 (0.37)	1.55-3.62 (2.76)	2.38-13.40 (9.05)	6.57-9.08 (6.11)	80.14 - 128.13 (110.08)	31.25-83.13 (68.65)
	B	29.2-35.6 (32.69)	30.7-32.6 (31.68)	8-27 (18)	31.3-59.5 (42.12)	5.1-18.3 (8.83)	7.60-7.80 (7.73)	0.6-3.65 (2.54)	0.11-0.59 (0.35)	1.15-4.88 (2.70)	1.57-15.72 (9.11)	5.50-9.39 (6.98)		
Thevara	S	29.7-33.7 (32.2)	32.1-32.6 (32.33)	19-119 (65.86)	31.5-46.5 (41.86)	8.5-21.3 (9.5)	7.66-7.82 (7.72)	2.15-3.05 (2.61)	0.56-0.69 (0.64)	0.24-0.74 (0.54)	9.16-22.56 (15.77)	4.88-6.17 (5.44)	70.83 - 103.13 (92.36)	43.54- 77.08 (57.57)
	B	31.1-33.8 (32.32)	31.4-32.6 (32.18)	21-85 (48.43)	33.1-54.2 (40.86)	5.5-25.1 (10.91)	7.66-7.75 (7.71)	1.9-4 (2.71)	0.55-0.78 (0.62)	0.19-0.65 (0.48)	9.74-22.91 (16.02)	4.56-5.85 (5.09)		
Kumbalam	S	27.9-33.5 (30.8)	32.2-32.9 (32.61)	40-101 (73)	25.7-39.3 (32.23)	3.3-17.3 (9.8)	7.54-7.8 (7.67)	2.1-4.15 (2.89)	0.42-0.90 (0.67)	0.06-0.66 (0.35)	12.53-24.24 (20.63)	4.56-6.17 (5.57)	103.02 - 104.17 (103.47)	50.94- 51.04 (51.01)
	B	30.4-33.3 (32.03)	32.1-32.6 (32.4)	9-71 (45.57)	27-65.8 (39.53)	4.8-24.6 (12.11)	7.64-7.78 (7.7)	2.45-3.9 (2.96)	0.50-0.74 (0.63)	0.13-1.00 (0.62)	11.77-23.20 (18.62)	4.56-5.85 (4.92)		
Perumbalam	S	23.2-26.2 (24.3)	31.3-33.8 (32.85)	9-85 (51.67)	15.6-22.8 (19.65)	1.2-3.3 (2.3)	7.45-7.56 (7.51)	0.60-1.50 (1.09)	0.15-0.34 (0.24)	0.06-0.44 (0.24)	2.61-7.25 (4.15)	7.12-7.45 (7.40)	102.92 - 103.13 (102.99)	61.98- 77.19 (68.40)
	B	23.6-28.8 (25.83)	31.6-33.8 (33.82)	3-38 (22.17)	23-31.3 (26.5)	0.2-5.9 (2.38)	7.43-7.63 (7.52)	0.65-3.45 (1.76)	0.15-0.42 (0.29)	0.05-0.33 (0.18)	0.87-4.99 (3.23)	5.50-7.12 (6.59)		
Panavally	S	19.2-21.9 (20.82)	32-33.8 (33.22)	2-77 (45.5)	14.4-21.8 (18.3)	0.3-2.1 (0.89)	7.37-7.74 (7.42)	0.6-0.9 (0.77)	0.13-0.19 (0.15)	0.08-0.41 (0.21)	1.91-5.91 (3.24)	7.12-8.43 (7.83)	102.71 - 103.13 (102.92)	51.46-77.08 (64.86)
	B	21.4-26.8 (23.28)	32.7-33.7 (33.3)	2-51 (29)	15.8-26.1 (20.02)	0.52-7.7 (2.66)	7.36-7.53 (7.43)	0.65-1.15 (0.92)	0.13-0.39 (0.19)	0.04-0.23 (0.18)	1.91-5.92 (3.24)	5.83-8.10 (7.07)		
Kattachira	S	18.1-18.3 (18.2)	32.8-33.4 (33.05)	0-26 (17.5)	15.4-19.6 (17.45)	0.3-1.5 (0.48)	7.15-7.21 (7.17)	0.25-0.35 (0.29)	0.13-0.21 (0.16)	0.46-1.38 (0.75)	25.46-28.36 (26.55)	6.81-7.77 (7.29)	51.46 - 77.19 (60.04)	25.73- 47.86 (32.53)
	B	17.9-18.4 (18.08)	30.7-33 (32.33)	3-20 (9.25)	17-22.2 (20.05)	0.2-2.3 (0.66)	7.08-7.21 (7.18)	0.25-0.4 (0.3)	0.09-0.25 (0.18)	0.76-1.66 (1.00)	18.50-29.17 (24.90)	6.48-7.77 (7.17)		
Thanneer-mukkam	S	15.4-17.1 (16.54)	31.8-33 (32.54)	8-48 (27.14)	15-20.8 (17.08)	0.17-0.51 (0.33)	6.98-7.11 (7.05)	0.25-0.39 (0.29)	0.42-0.61 (0.53)	0.78-2.15 (1.16)	40.48-46.69 (43.30)	6.48-7.12 (6.81)	51.46 - 77.19 (68.61)	25.73-51.46 (34.31)
	B	15.8-17.2 (16.62)	30.6-32.8 (31.76)	2-33 (14.67)	15.3-22.4 (17.9)	0.04-0.59 (0.33)	7.07-7.13 (7.10)	0.20-0.30 (0.26)	0.40-0.59 (0.51)	0.79-1.26 (1.02)	40.19-46.63 (43.89)	5.83-7.12 (6.67)		

46720, 21670, 15700, 32870, 34880, 34220 and 22180 respectively for the seven stations. Major groups obtained were copepods, nauplius, zoea, chaetognaths, appendicularians, tintinnids, polychaete larvae, molluscs, fish egg and fish larvae. The southern side of the bund also showed same environmental conditions since the bund was open during the time of observations, indicating that estuarine conditions prevailed even beyond the bund when it is open.

6.2.2 Geochemistry

Textural characteristics of the sediments along the main channel of the southern arm of Cochin estuary are given in Table 6.2 and Fig. 6.5. The substratum generally represents a combination of clay, sand and silts. The composition of the sediment showed spatial variation. By applying Folk (1974) classification, sandy mud nature was dominant in the estuary, while sediments near Thevara showed muddy nature.

Table 6.2 Textural characteristics of the surficial sediments in the southern arm of Cochin estuary

Stations	Sand (%)	Silt (%)	Clay (%)	Nature*
Cochin Port	49.88	19.57	30.55	Sandy mud
Thevara Ferry	0.29	48.76	50.95	Muddy
Kumbalam	45.79	18.41	35.80	Sandy mud
Perumbalam	43.46	21.38	35.16	Sandy mud
Panavally	49.76	17.22	33.02	Sandy mud
Kattachira	53.17	5.29	41.54	Silty sand
Thanneermukkam bund	48.90	16.24	34.86	Sandy mud

* Folk, 1974

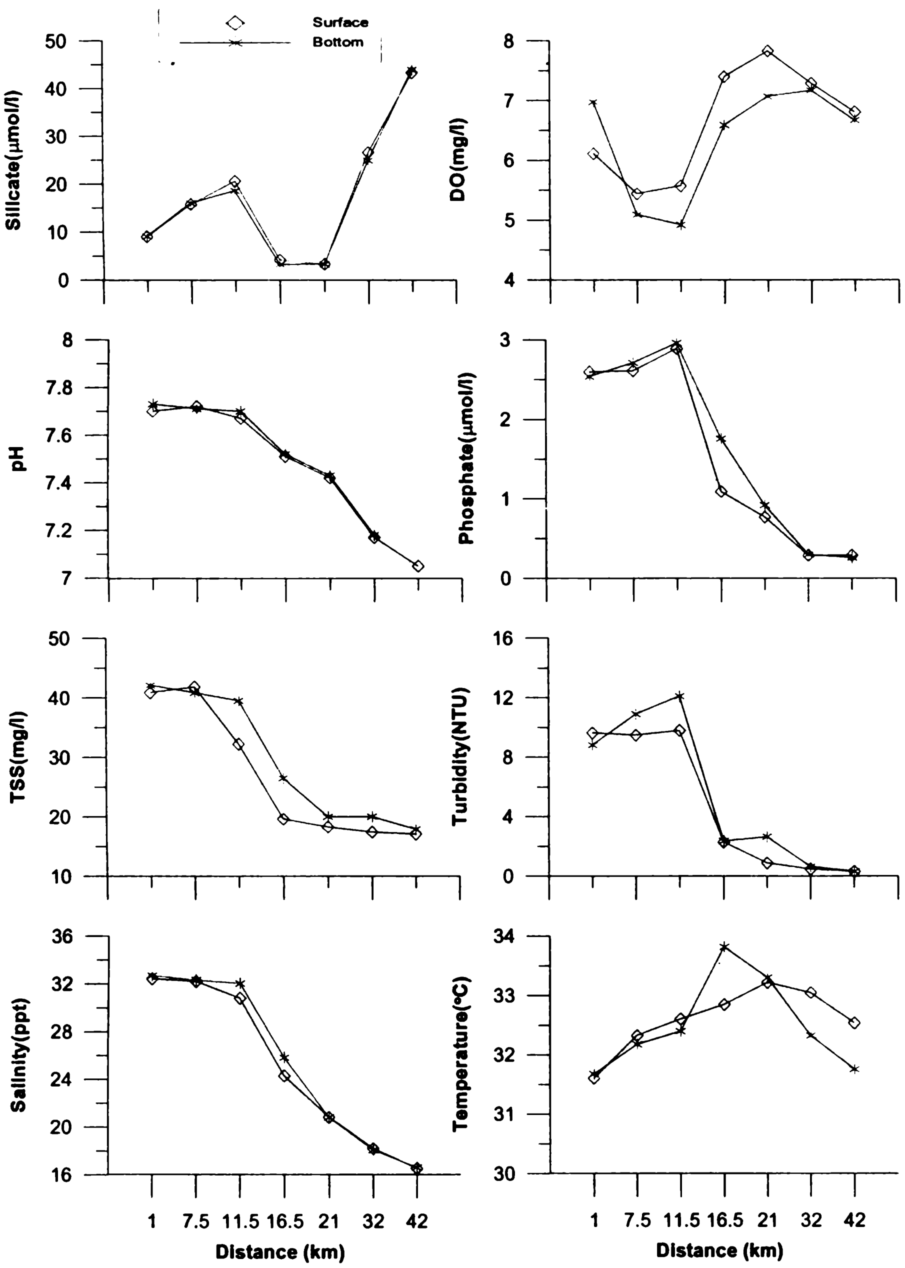

Fig. 6.4 Variations of hydrographical parameters in the southern arm of Cochin estuary

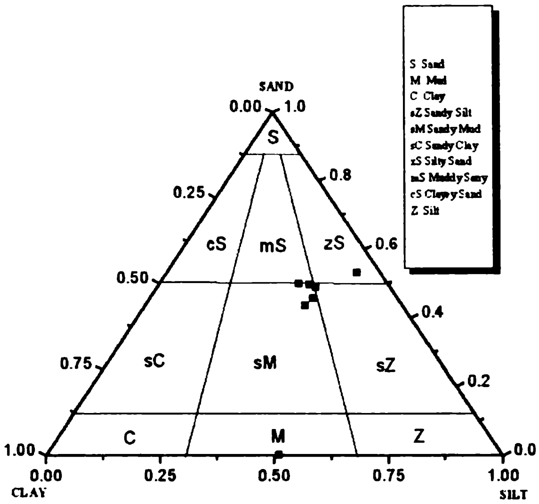

Figure 6.5 Ternary diagram showing the grain size distribution in the surficial sediments of the southern arm of Cochin estuary. Sediment nomenclature Folk, (1974)

Powder X-ray diffraction analyses of the surficial sediments showed the presence of clay minerals like illite, kaolinite + chlorite, smectite and gibbsite. Quartz and feldspar were the non-clay minerals found (Table 6.3 and Fig. 6.6). Quartz was present at all stations. Thevara was found to be rich in clay minerals, while sandy sediments near bar mouth was deficient with the clay minerals.

Table 6.3 Major minerals present in the surficial sediments of the southern arm of Cochin estuary

Stations	Clay Minerals				Non-Clay Minerals	
	Smectite	Illite	Kaolinite + Chlorite	Gibbsite	Quartz	Feldspar
Cochin Port	-	-	-	-	√	√
Thevara Ferry	√	√	√	-	√	√
Kumbalam	-	√	√	-	√	√
Perumbalam	-	√	√	-	√	-
Panavally	-	√	-	√	√	-
Kattachira	-	√		-	√	√
Thanneermukkam	√	√	√	-	√	-

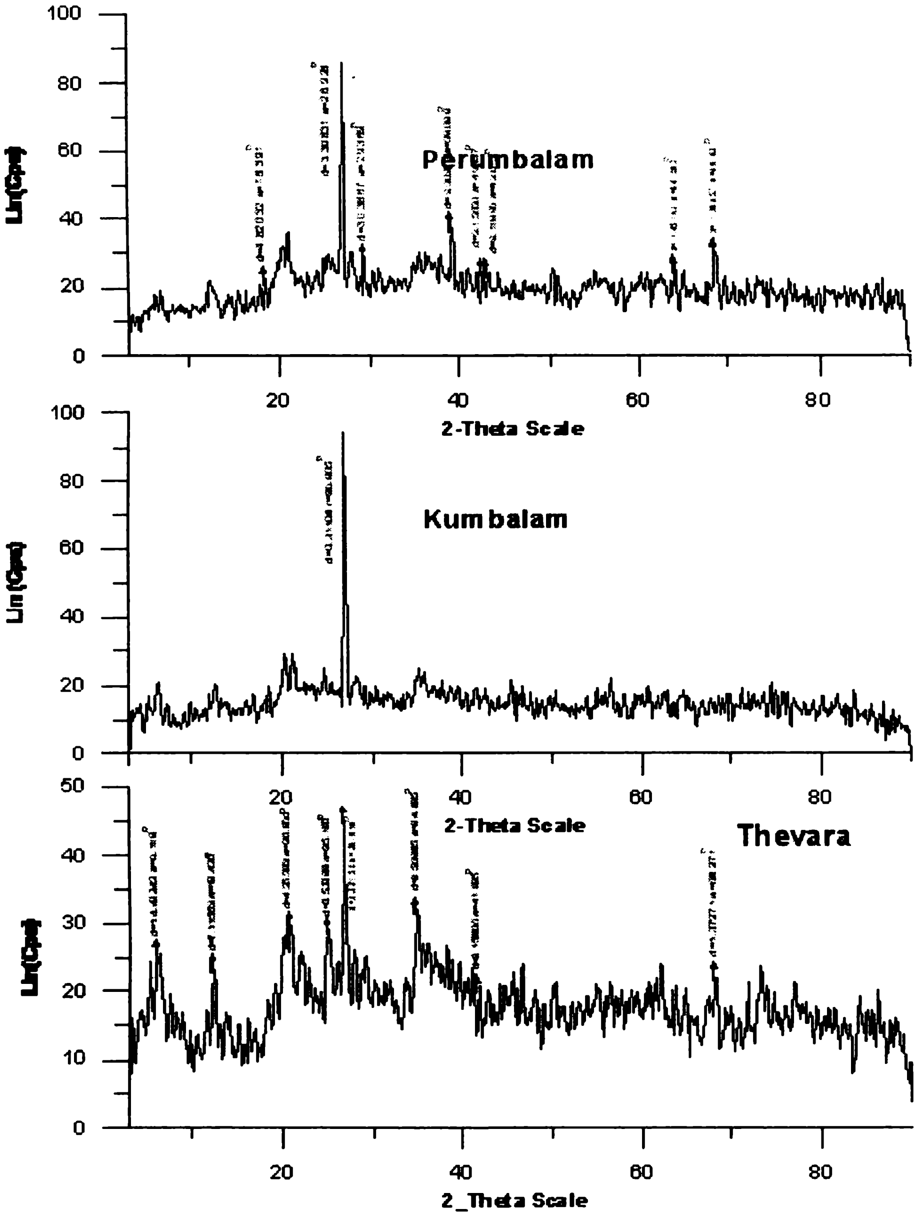

Figure 6.6 XRD spectra of the sediments in the southern arm of Cochin estuary

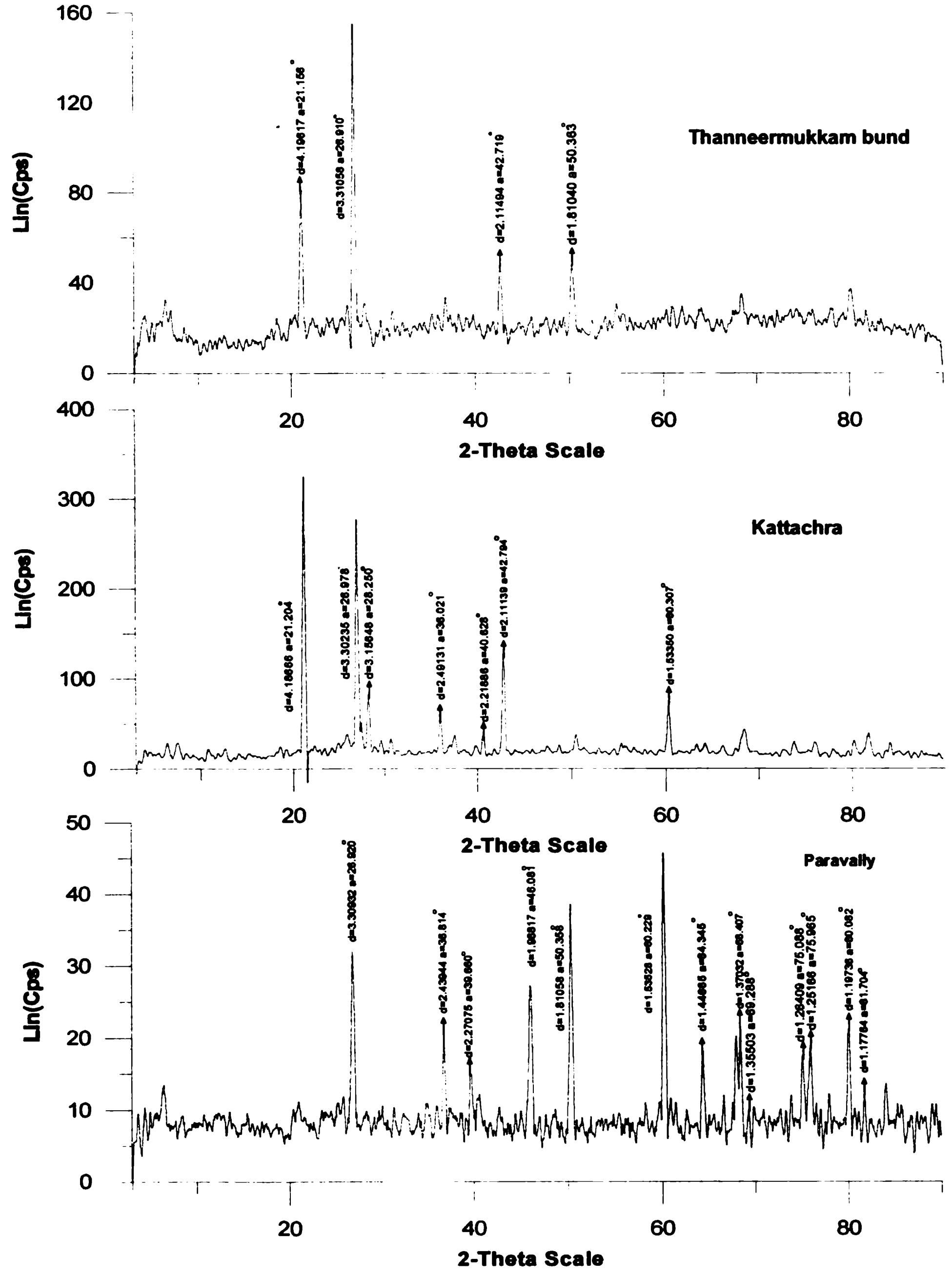

Figure 6. 6 (Contd.)

Among the carbonate elements, total carbon in the southern arm of Cochin estuary (Fig. 6.7) showed a wide variation, ranging from 0.08 % dry weight at Kattachira to 3.33 % dry weight at Thevara. Magnesium varied from 0.18 % dry weight at Kattachira to 1.44 % dry weight at perumbalam. Organic carbon varied between 0.62 and 2.21 % and was higher at muddy station near Thevara. The percentage of organic carbon to total carbon was in the range 60.12-85. Total nitrogen in the sediment ranged from 0.11 to 0.39 % dry weight. Total sulphur varied between 0.24 and 1.21%. Iron ranged between 2. 56 and 7.42 % dry weight and for Manganese the range was from 107.45 to 304.30 µg/g dry weight. Lower values were generally seen near the head of the estuary.

In the case of trace elements, Chromium varied from 33.59 and 94.21 µg/g dry weight and Cobalt varied between 10.10 and 26.28 µg/g dry weight. Copper showed a range from 10.51 and 37.54 µg/g dry weight and Lead varied between 31.40 and 68.59 µg/g dry weight. The variations for Nickel and Zinc were from 24.57 to 94.90 and from 26.07 and 220.13 µg/g dry weight respectively (Table 6.4). The trends were somewhat irregular in the case of trace metals. Benthic density, like zooplankton, decreased from the mouth towards 10 km and there after showed a rapid increase in the next 10 km.

Table 6. 3 Variations of geochemical parameters in the southern arm of Cochin estuary

Parameter	Cochin Port	Thevara	Kumbalam	Perumbalam	Panavally	Kattachira	Thanneer-mukkam
C (%)	3.11	3.33	3.25	3.23	0.78	0.8	1.64
Org. C (%)	1.87	2.21	2	1.99	0.62	0.68	1.02
TN (%)	0.32	0.39	0.39	0.38	0.12	0.11	0.2
TS (%)	1.21	1.2	1.09	1.09	0.24	0.27	0.36
Co (μg/g)	22.63	25.99	19.87	26.28	10.1	12.23	22.6
Cr (μg/g)	93.03	94.21	81.89	86.21	48.88	33.59	38.58
Cu (μg/g)	31.9	37.54	37.18	36.02	10.51	11.21	18.92
Fe (%)	5.66	7.42	5.84	7.36	2.56	3.36	4.94
Pb (μg/g)	55.37	61.07	49.2	68.59	56.66	31.4	63.84
Mn (μg/g)	173.89	228.41	304.3	248.22	107.45	121.75	221.32
Mg (%)	1.36	1.41	1.31	1.44	0.33	0.18	0.32
Ni (μg/g)	83.23	89.52	94.9	92.92	34.32	24.57	38.26
Zn (μg/g)	148.53	220.13	106.54	130.28	38.8	26.07	49.73

6.2.3 Nutrient Dynamics

Phosphorus fractionation using the sequential extraction scheme was employed to study the variations of different phosphorus fractions in the southern arm of Cochin estuary and its dynamics. Total phosphorus showed a sharp decline (Table 6.5 and Fig. 6.8) towards the head of the estuary and the variation was from 252.60 to 1980.40 μg/g dry weight. All the fractions of phosphorus showed the same trend. Fe-IP varied from 28.88 to 130.25 μg/g and Fe-OP from 12.05 to 42.98 μg/g. Ca-IP showed the highest fluctuation, ranging from 8.66 to 874.89 μg/g, while Ca-OP varied between 34.45 and 224.69 μg/g. Acid-OP vas in the range from 26.08 to 278.91 μg/g and Alkali-OP ranged from 56.84 to 281.26 μg/g. the residual organic fraction ranged between 27.24 and 106.83 μg/g. Ca-IP was the dominant fraction near the mouth regions of the estuary, but Alkali-OP dominated in the head of the estuary.

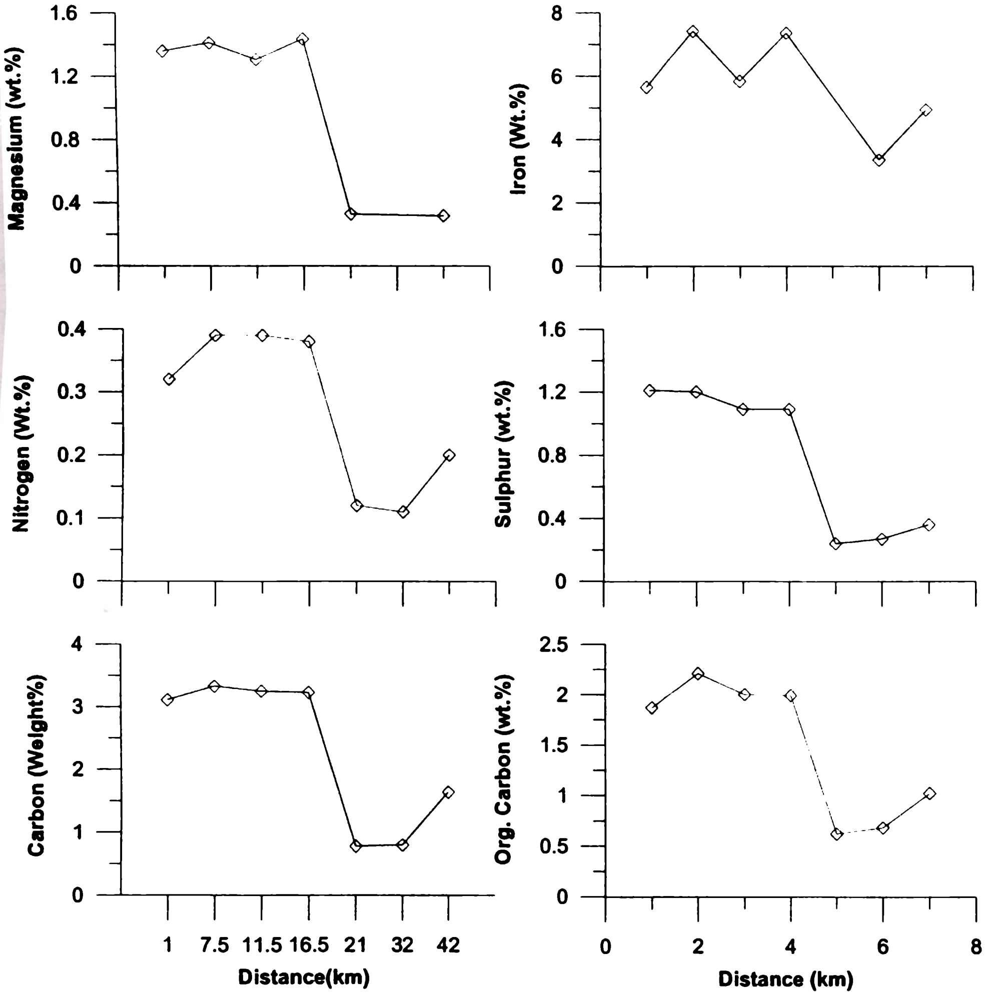

Figure 6.7 Variation of geochemical parameters in the southern arm of Cochin estuary

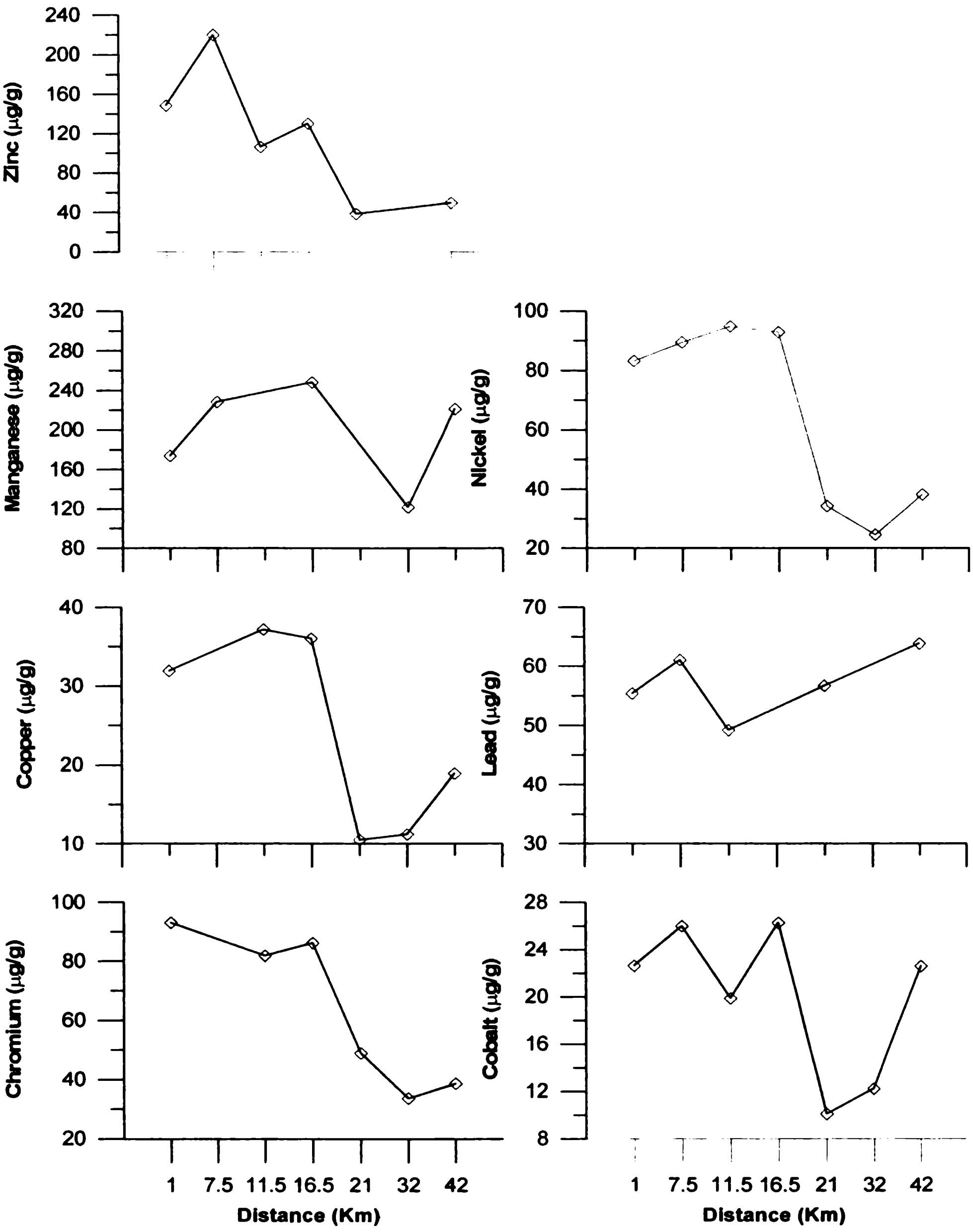

Figure 6.7 (contd.)

Table 6. 5 Variations of different fractions of phosphorus in the southern arm of Cochin estuary

Stations	P Fractions (µg/g)							Total P
	Fe-IP	Fe-OP	Ca-IP	Ca-OP	Acid-OP	Alkali-OP	ROP	((µg/g)
Cochin Port	92.63	23.62	808.61	190.18	240.33	245.35	86.36	1687.09
Thevara	126.93	42.98	874.89	224.69	247.77	266.32	106.83	1890.40
Kumbalam	91.91	35.41	807.51	154.84	278.91	278.91	90.40	1737.89
Perumbalam	130.25	38.97	849.83	121.41	269.46	281.26	91.76	1782.93
Panavally	28.88	12.05	98.85	34.45	57.77	91.10	28.86	351.96
Kattachira	32.20	14.87	8.66	35.89	56.95	76.80	27.24	252.60
Thanneermukkam	56.77	33.45	31.73	45.13	26.08	56.84	40.10	290.11

6.3 Discussion

Hydrodynamical analysis results showed that there is a general conformity of the hydrographical conditions in the Panangad region with the nearby places in the main channel of the estuary. Also a progressive decrease in tidal amplitude was noted from the barmouth with distance. The longitudinal variations of parameters from the mouth to the head of the estuary indicate a gradient region around 10-15 km from the mouth, including the study region. These suggest that there is a generation of counter currents in this region that opposes the propagation of tides further in the estuary. For confirming these phenomena, the tidal variations of salinity and currents of all transects were drawn (Fig. 6.9 and 6.10). These figures showed the general features of water flow, with a drag on either banks of the estuary.

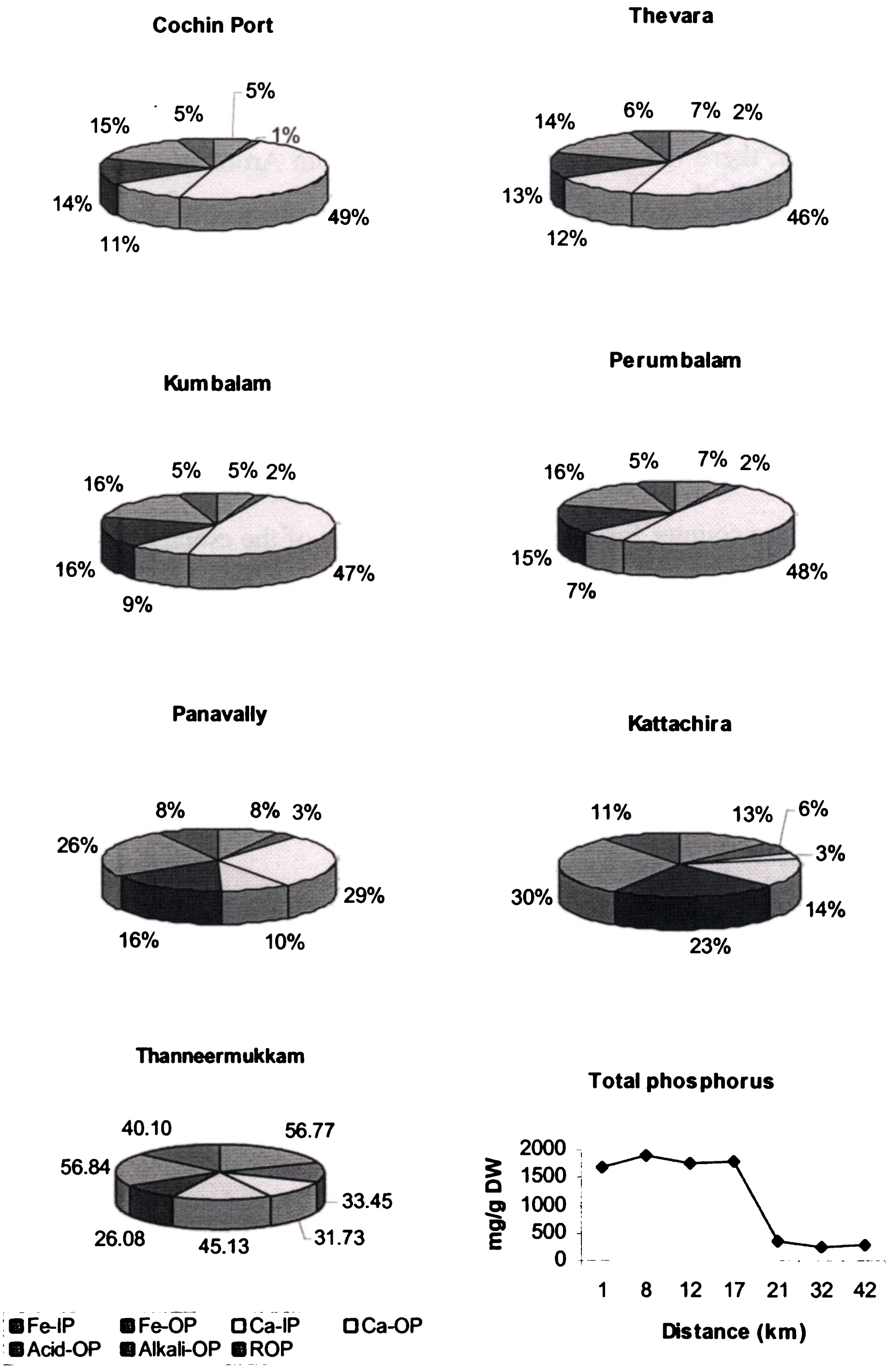

Figure 6.8 Phosphorus fractions in the southern arm of Cochin estuary

But the circulation pattern of Arrokutty-Perumbalam transect (Fig 6.11). confirms the possibility of a counter current mechanism prevailing in the region. Though the width of the estuary at the transect point is less than one kilometer, there was a significant tidal lag from Arookutty area to the other two, separated by only about 300m. Current speed was of less amplitude in the Arookutty area, compared to the other two. Shallowness of the Arookutty side and the big Arookutty and Perumbalam Islands disturbs the easy propagation of tidal energy. Also there are chances of wave refraction, which results in the tidal propagation through the more open area to the right of Preumbalam Island. Freshwater input from the rivers may also exert a counter force in the narrow region of the estuary to the left of the Perumbalam Island. Similarity in salinity pattern of the stations in the main channel of the study compartment also supports this argument. Stations 10 and 11, which are in the locations, where this tidal deviation is expected, showed the same salinity pattern of the stations in the main channel, indicating a possibility of this region to be the main channel for tidal propagation.

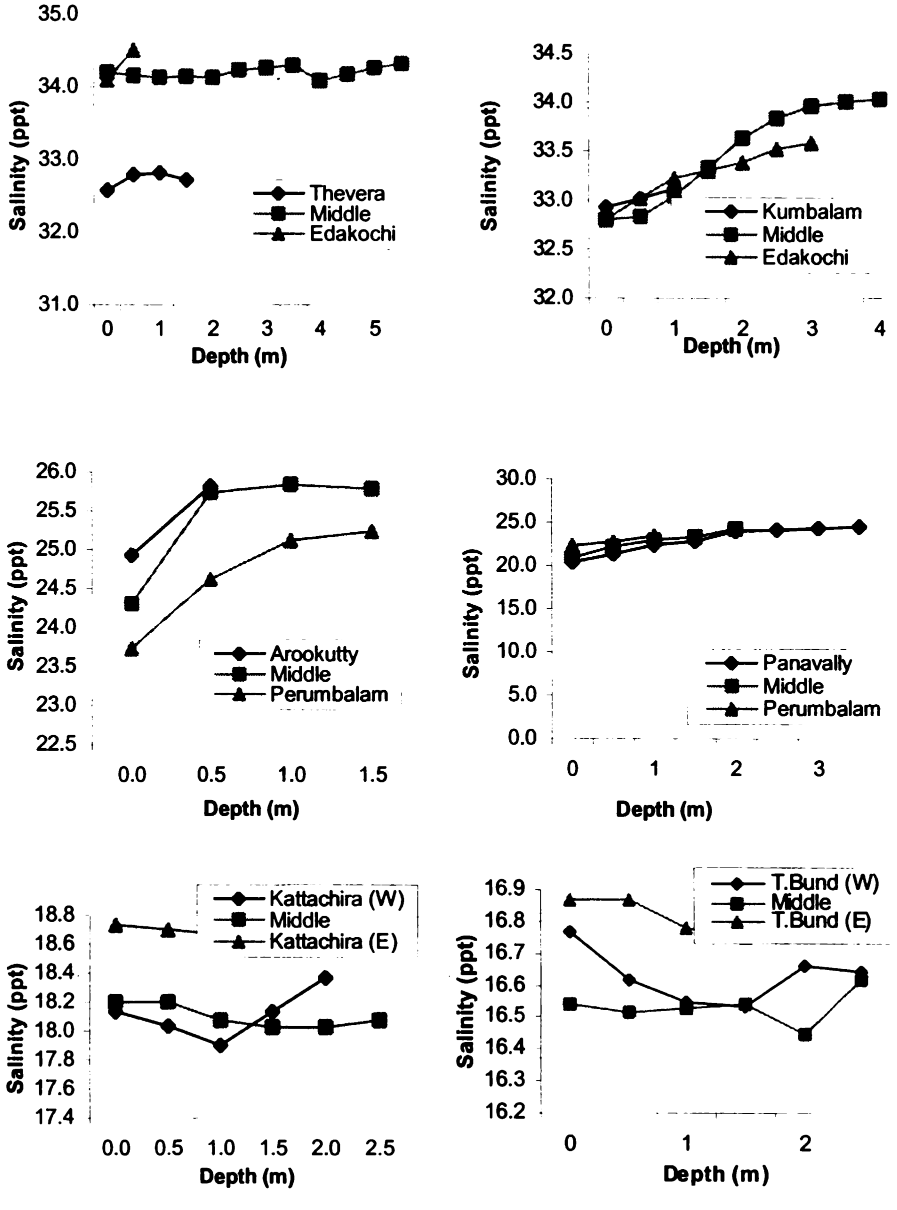

Figure 6.9 Variation of salinity in different transects

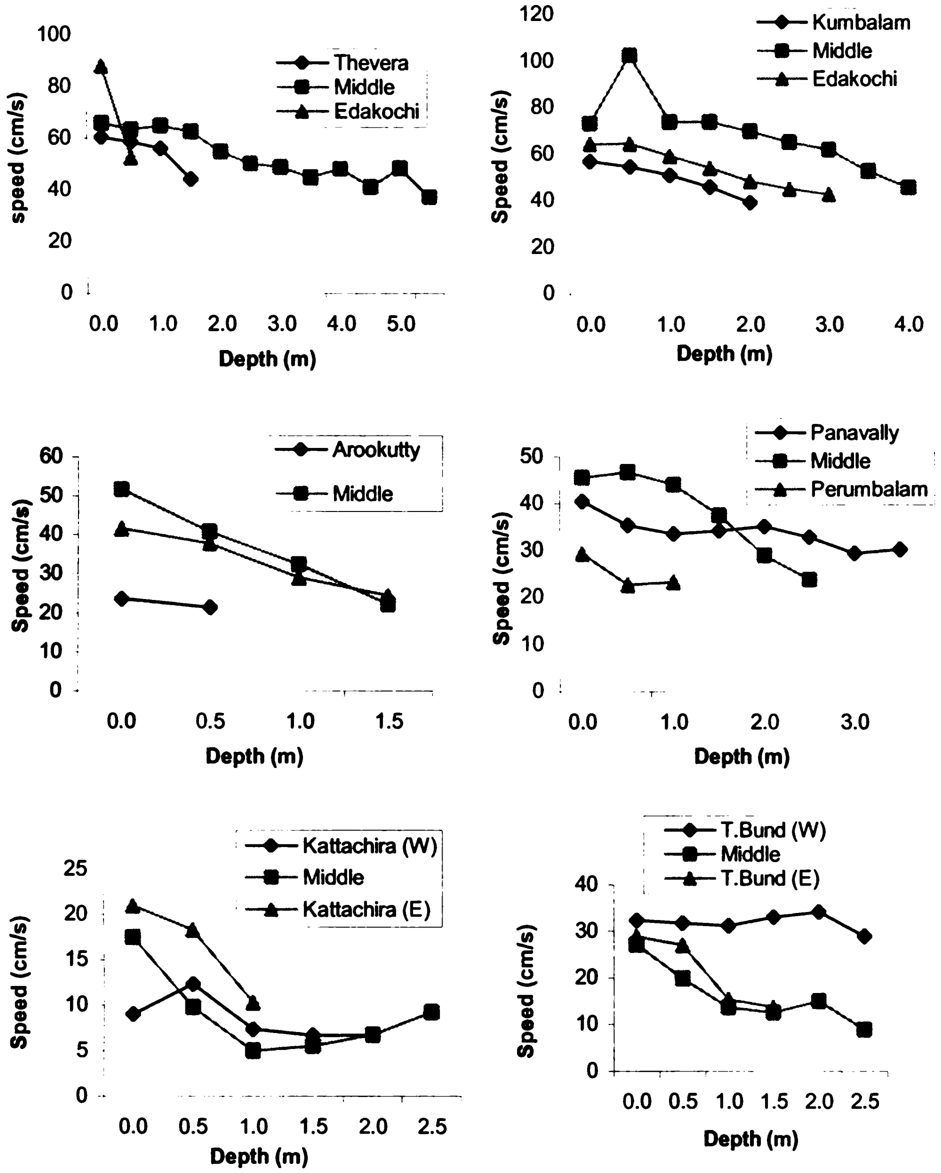

Figure 6.10 Variation of current in different transects

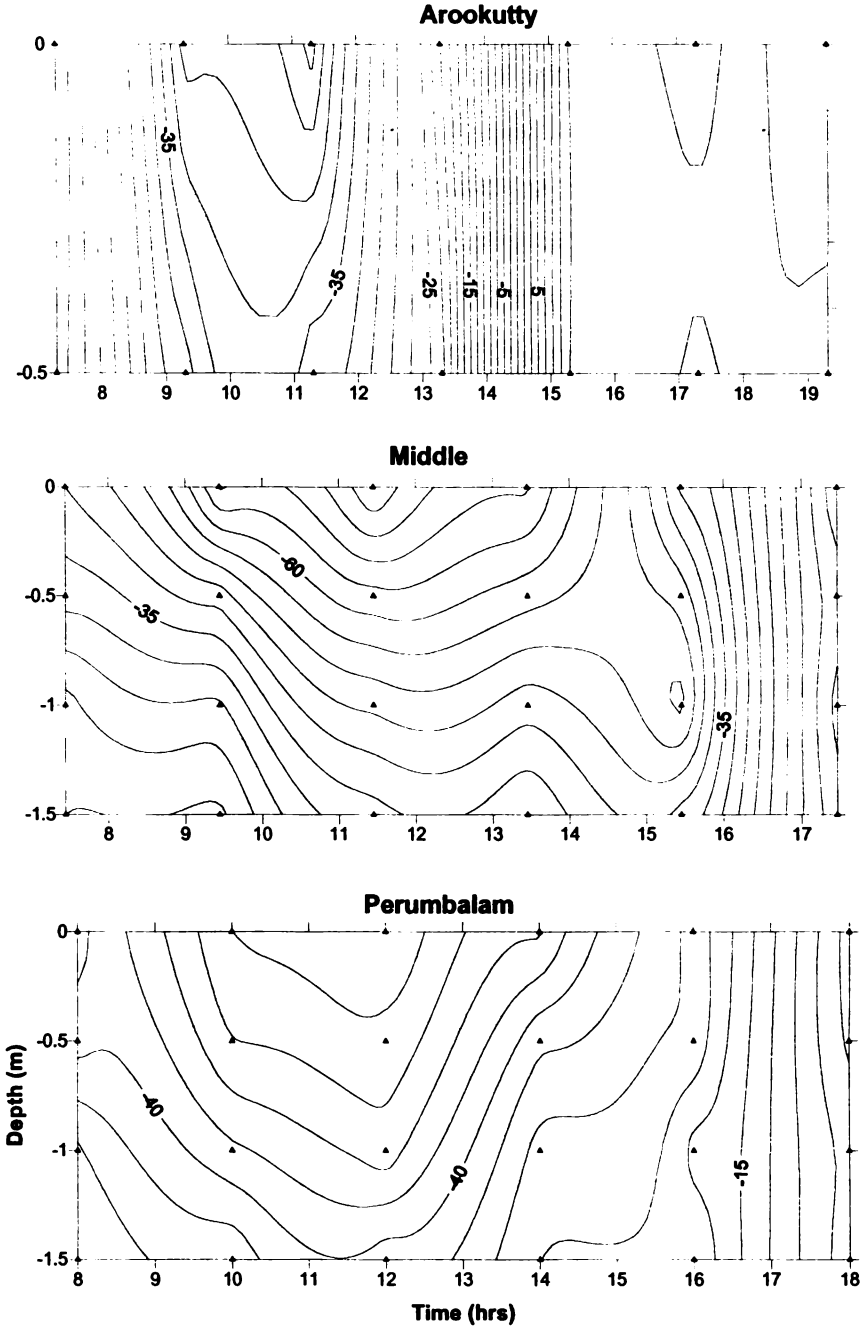

Figure 6.11 Circulation pattern in the Arookutty- Perumbalam transect

If there is disturbance in tidal propagation, possibilities for settling are high. The geochemical analysis of the southern arm confirmed this possibility. Regions up to the Perumbalam region showed almost uniform distribution in geochemical character. After that a steep decrease was noticed for all geochemical parameters, suggesting the lack of transport. Since the texture of the study region was found to be highly variable, spatial comparison is meaningless. Mineralogy was also found to be rather similar in nature. The trend of mineral distribution was similar to that of the study compartment of the estuary, as muddy sediments have higher clay minerals. Higher nutrients were found up to the Perumbalam region and after that a sudden decrease was seen. Higher levels of sulphur because of the transport through National Waterway, was also seen up to Perumbalam only. Stoichometric analysis showed that the variation in C:N ratio was not large in the estuary (6.5 to 9.7), signaling to the autochthonous origin of organic matter, due to higher production as found in the case of study compartment. The C: P ratio varies widely in the estuary (17.6 to 56.5) and was very high in the head of the estuary. N: P ratio followed the same trend and ranged between 0.3 and 2.7. Both these ratios were far below than Redfield ratio up to the Perumbalam region. Hence there is a possibility of phosphorus enrichment in lower reaches of estuary. The obeying of Redfield ratio in the head of the estuary suggests that phosphorus is not being enriched there. The S/C value in sediments did not show any significant variations from head to mouth; values were in the range 0.22-0.39 during most of the cases, much higher than the average ratio in abyssal plain sediments. Very high levels of sulphur (about 1% dry weight) up to the Perumbalam region can also cause higher accumulation of metals in sediments, through complexation.

Most of the heavy metals followed the distribution pattern of other geochemical parameters. Iron and zinc was found to be higher than the average shale value at the lower reaches of the estuary, while lead was found to be higher throughout the southern arm of this estuary. This supports the earlier possibility that lead is having anthropogenic addition in this estuary. The previous argument that the distribution of benthic organisms within the estuary is influenced more highly by variation than by absolute salinity regimes is followed in their longitudinal distribution pattern, with higher population in the mouth and decreasing gradually. But a conspicuous drop was seen in the Kumbalam region. Iron, zinc, cobalt and lead also showed a decrease there. Further analysis is required to get a clear picture, which is beyond the scope of present study.

Total phosphorus also showed the pattern of other geochemical parameters and varied widely. Ca-IP was the dominant fraction in the lower reaches, contributing about half of the total fractions. This might be because of higher alkaline nature of the water column in the lower reaches of the estuary. Lowering of calcium minerals through the estuarine gradient may also resulted in the low concentration in the head of the estuary. Alkali-OP was the major fraction in the upper reaches, where ROP also showed higher percentage. As a reason, bioavailable fractions were lower at the upper reaches and showed increase from Perumbalam (66-70%). This might be contributing towards higher productivity in the lower reaches of the estuary. In the estuary, while Fe:P ratio was about double of the critical value in the lower reaches, it was very high in the head of the estuary. Therefore, there seems to be enough Fe in surface sediments to bind P along the estuarine gradient, especially at the upper reaches. This might be the reason for comparatively higher percentage of iron bound phosphorus in the upper reaches.

From the tidal anaysis of the southern arm of Cochin estuary, it can be concluded that there is a sharp gradient of physico-chemical and biological characters from the mouth towards the Thannermukkam bund. The estuarine region up to Perumbalam showed a general character and from there a sharp decrease was noticed. The tidal propagation is seemed to be affected by the big islands in these regions and also by the fresh water flow from the opposite side, generating a kind of counter current. The study region lies in this transitional zone and hence is ideal to be taken as a representative to study the dynamics of this estuary. This analysis also gives an indication of declination of true estuarine character beyond the Perumbalam region, changing the southern part of estuary gradually in to a freshwater habitat. Batcha & Damodaran (1987) also reported that both the Idukki hydroelectric project and Thanneermukham bund brought about a reduction in salinity of the estuary, the former causing a reduction at the southern side and latter at the northern side of the bund. These are also chances for further advancement of this freshwater dominance in the future, drastically affecting the estuarine ecology.

6.4 Ecohydrology

The improvement and development of an ecosystem for a better production requires the identification of different environmental compartments and the various processes operating in these compartments. The convergence of these processes to defining the ecosystem as a whole is the basic consideration in the ecohydrological approach. There can be many ways to reach the goal, of which the most common is to bring this system to a mathematical model, which can accommodate and integrate all these processes. Generally in environmental systems the model concept is in terms of a mass balance, the difference will be only on the identification of interlinked parameters.

The limitation to such a processes is that the integration of this to the biological realm was always more or less empirical. The attempt here is to consolidate the various processes that contribute the chemical environment of a particular system to a chemically modulated biological system or rather to an ecosystem. The tool identified in this particular case is the dynamics of one of the most important nutrient, phosphorus. The various physical, geological and chemical processes, which can contribute to the bioavailability of this particular nutrient and its significance to the observed biological conditions is the attempt done here.

The total analysis of the system in terms of the climatologic conditions and physical processes such as current, tide and river influx along with the geochemical processes such as precipitation, flocculation, mineralization, adsorption/desorption etc. have indicated that the system has the following characteristics,

1) Geographically significant, as it covers the inner areas of the estuary, where circulation pattern is complex by the generation of local eddies. Hence a general tidal rhythm is absent. Geomorphology of the estuarine bed also contributes to the complexity of circulation.
2) Hydrodynamically variable by the profound influence of southwest monsoon and accordingly exhibit seasonal characteristics. During monsoon this part is in the tidal section of the rivers and subsequently transformed to a partially mixed estuary. During pre-monsoon, when river run off is least, well-mixed condition exists.

Physico-chemical parameters also showed these seasonal variations and the local effects has also significant influence.

3) Highly variable in sediment nature, but has limited influence on the overall biogeochemical processes. The geochemical parameters showed a similar distributional character. Absence of noticeable levels of anthropogenic contamination, except for sulphur and lead.
4) Sedimentary character such as grain size has no role in micro speciation and the seasonal changes do not reflect on the bioavailability. Phosphorus dynamics indicate more or less steady state maintenance in the estuary.
5) The study region lies in the transitional zone of the southern stretch of Cochin estuary and shows a considerable geochemical reactivity.

All the above signifies the selection of the study region for an ecohydrological evaluation of the Cochin estuary.

In the case of the prevailing biological character, primary production in this study area is found to be higher than that reported for many coastal areas and other estuaries in India, with a sufficient stock of standing crop. Nutrients, especially nitrogen limitation plays a major role in phytoplankton production in this estuary and light limitation is only of minor importance. Also, the fresh water condition prevailed during monsoon also does not seem to affect primary production as the euryhaline and stenohaline species would negate the salinity variation and maintain the production rate more or less constant. The system is also rich in zooplankton and benthic density as well as diversity. Benthic primary production in this estuary accounts for about 1.4 g C/m^2/day, almost equal to the planktonic production (Sreekumar & Joseph, 1997). The grazing effects of zooplankton species never exceed the daily production in the estuary and a large surplus of basic food is available in the estuary for transfer to higher trophic levels. The study area also showed higher fishery potential, based on the observations on primary production.

An attempt is made to identify the ecological character with respect to the chemical/hydrological character. The comparison of the identified observations on the hydrological, geological and chemical processes explained above with biological character exhibited by the system has shown that the prediction on the productive character on the basis of hydrological condition can be well proved.

It is in context that for the development of a management scheme, the chemical speciation of phosphorus was conducted. As stated in the pervious chapter, the selection of phosphorus was based on the basis that it is not showing any limiting nutrient character and has high environmental reactivity.

The bioavailability of phosphorus was found to be not limited by the physical characteristics of the substratum. The productivity trend was appeared to be parallel with the bioavailability of phosphorus except that the system was never at its productivity maximum. There is scope for further betterment of the productivity, without reaching to the eutrophic status. Moreover it implies that by monitoring/regulating the chemical environment, sustainability of an aquatic system can be achieved. The importance of water quality has been recognized as a high priority factor by the UN bodies for the socio-economic endorsement of the mankind.

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Summary

The amplified human role in shaping natural processes makes it imperative to understand the interactions between abiotic and biotic processes, which pertain particularly to the most dynamic abiotic factor, water. Estuaries are the integral part of hydrological cycle and provide us with numerous resources, which cannot be easily evaluated. Estuaries rank along with tropical rainforests and coral reefs as the world's most productive ecosystems and undergo daily, seasonal and long-term changes, defying generalization. In recent times, many estuaries are subjected to over exploitation and also destruction due to industrialization and urbanization. Ecosystem restoration in highly complex, human-dominated estuaries rests on a strong conceptual foundation of sustainability, ecosystems, and adaptive management of human-induced environmental impacts. The conscious harnessing, based on interdisciplinary knowledge, of an ecosystem's own properties as tools for increasing the environmental "carrying capacity" is becoming a necessity to rectify the serious threats to estuaries and coastal areas.

Vembanad-Kol wetlands (09°50' N, 76°45' E), the largest brackish water, humid tropical ecosystem in the Southwest coast of India had been identified as a Ramsar Site. This lies parallel to the coastline extending between Thannermukkam at south and Azheekode at north. There are six rivers debouching into the estuary on either side of the mouth. With the construction of Thannermukkam bund in 1976, an area of about 68 Km^2 of brackish water system lying south of the bund has been ecologically cut off from the salt intrusion during the months of it's closure. This aquatic system is also facing tremendous environmental stress, mainly due to the rapid expansion of the Cochin City, encroachment of low-lying areas and the industrial developments. Many new projects that are planned to come up in the lower reaches of this estuary and off shore like Vallarpadam container terminal, Mareena Park and LNG terminal, moored buoy terminal etc. are likely to affect the dynamics and ecology of this estuary. The inner arms of the estuary were not seriously attended in the earlier studies. Hence, it is imperative that detailed studies on the hydrography of the Cochin estuary covering the inner areas only can derive a long-term sustainable management scheme for this important ecosystem.

The main objectives of the present study were to characterize the chemical dynamicity in relation to the bio, geo and physical conditions in the Cochin estuary and to propose a management scheme for its sustainable development. Detailed studies on the hydrodynamics, geochemistry and the nutrient dynamics were carried out to unravel the estuarine dynamics. Ecohydrological concept, developed during UNESCO's International Hydrological Programme is redefined in a chemical perspective and used as a new paradigm for the sustainable management of this important aquatic system.

The study area is the Panangad region of the Cochin estuary and is situated about 10 km from the barmouth. It is mainly in the inner arms of the estuary surrounding Nettoor and Panangad islands and the approximate area is about 6.25 km^2. This region is shallow and the presence of canals affects the general circulation pattern. Monthly surveys were carried out from January to December 2003. Data collections were organized on days of higher tidal range (near spring tide). Generally the observations were made immediately after low water slack period. Salinity, temperature and water current data were collected from all stations at a depth interval of 0.5m. Secchi disc transparency was also noted. Water samples were collected from surface using a clean bucket and near bottom using Van Dorn sampler. Sediment samples were collected using a van Veen grab. Suspended sediments and turbidity were also determined. Standard methods were used for the chemical analysis (Grasshoff *et al.,* 1983) and for primary production and Chlorophyll-a (Strickland & Parsons, 1972). For collecting zooplankton, 60 liters of water was filtered through plankton net (No 25) and samples were counted under a stereoscopic binocular microscope. Texture analysis was also carried out (Krumbein & Pettijohn, 1938). Powder XRD technique was used for the identification of minerals. Organic carbon, total carbon, nitrogen and sulphur were analyzed using CHN analyzer. Metals in the sediment were analyzed using flame AAS and ICP-AES. For benthos, organisms retained on a 0.5mm mesh sieve were identified and counted. Sequential extraction scheme using chelating agents developed by Golterman (1996), modified by Diaz-Espejo *et al.,* (1999) was carried out to understand the association of phosphorus with various sedimentary components and to estimate its mobility, biological availability and the diagenesis.

To study the tidal variations of the physico-chemical parameters in the study area, hourly observations covering one complete tidal cycle (13 hours) were made from two representative stations (Stations 1 and 5). Observations were also made for two different seasons viz. pre-monsoon and post-monsoon. In order to envisage the estuarine dynamics and to compare the results from the study area with the features in the main arm of the estuary, tidal observations were carried out between the barmouth and the Thannermukkam bund during pre-monsoon period. Observations were made at seven different transects of the estuary for complete tidal cycle (13 hours).

The hydrodynamics of the study region is very complex and unique. The hydrography of this estuary is under the profound influence of the southwest monsoon and the seasonal variations are very prominent. From the observed salinity pattern, it can be concluded in general that during southwest monsoon this part is in the tidal section of the rivers. It gets transformed subsequently to a partially mixed estuary. During pre-monsoon, when river run off is least, this part becomes well mixed. There was a significant increase in nutrients and suspended matter in the study region with the onset of monsoon. Nutrient concentration in this estuary follows marked seasonal rhythm induced by the local precipitation and land run off. The hydrographical parameters showed spatial variation, which is attributed to the complex circulation patterns and to the geomorphology. Stoichiometric analysis of the major nutrients showed the possibility of nitrogen limitation during pre-monsoon and monsoon seasons. Light limitation is only of minor importance in this estuary and primary production was found to be higher than that reported for many coastal areas and other estuaries in India, with a sufficient stock of standing crop. Though post-monsoon was found to be higher in production, the seasonal changes was not seem to affect primary production as the euryhaline and stenohaline species would negate the salinity variation and maintain the production rate more or less constant. Zooplankton density appeared to be controlled by the change in the salinity and many marine forms were brought into the estuary along with the seawater during pre-monsoon period, enriching the density. The picture of abundance reversed totally with this drastic change in the environmental conditions during monsoon and during post-monsoon, when the fresh water influx decreases and salinity started to increase, the organisms got repopulated. The grazing effects of zooplankton species never exceed the daily production in the estuary and a large surplus of basic food is available in the estuary for transfer to higher trophic levels. The study area also showed higher fishery potential, based on the observations on primary production.

Tidal cycle observations provided information on the variation of hydrographical parameters in relation to tides; the relative importance of tides was evident from the seasonal changes. Natural factors including meteorological variations, diel effects and tidal variations affect the hydrodynamics of the estuary. There was little influence of the tidal cycle on physical parameters such as stratification and water residence time when freshwater discharge was low, but when discharge is high, the tidal cycle has a pronounced effect on physical circulation and therefore on GPP. Tidal asymmetry of weaker longer duration of ebb and stronger shorter duration flood was occurred generally. The tidal rhythm of salinity during post-monsoon indicated the predominance of progressive type component of tide and the tidal lag during pre-monsoon was typical of mixed tide having components of both progressive and standing waves. Hence the changing nature of the tidal components with seasons can be observed by the tidal observations. Dissolved oxygen followed diurnal rhythm than the tidal variations and clear tidal rhythm was not seen for all nutrients. The distinct variations between the two stations in the inner because of the geomorphology of the locations were established by the tidal cycle observations. This is due to the peculiarity of the location of the station, where depth variation is seen across the width of the estuary. Another peculiar behaviour of the study region, *i.e.* the effect of local rains and runoffs, was also established with the tidal cycle observations. This can change the general seasonal pattern in the estuary at least for short durations, as indicated by the above tidal analysis. During the present observations, the entire tidal cycle could not be covered because of the mixed nature of the tides in the study region. Hence, a detailed work covering longer duration would give a complete picture of the complex dynamics of the estuary.

The geochemical data of the study region showed that sediment textures were highly variable and were related to hydrodynamics. Mineralogy of the study region showed that, in general, there was variability of major minerals and the geology of the basin is not homogeneous. Illite, kaolinite + chlorite, smectite and gibbsite were the dominant clay mineral components, while quartz and feldspar were the dominant non-clay minerals in the study region. The nutrient elements in the study region did not show any seasonal trend and varied widely with respect to the granulometric compositions of sediments. The tropical vegetation in the catchment areas of rivers and estuary, presence of mangrove patches on estuarine banks, high rate of primary production, prevailing anoxic condition and fine particle size of sediments contributed to the higher concentration of organic matter in this estuary. Stoichometric ratios of nutrients indicated the autochthonous origin of organic matter and also a possibility of phosphorus enrichment in this estuary. Very high levels of sulphur (about 1% dry weight) indicated an anthropogenic source.

General abundance for the elements analyzed were: Al >Fe > Mg > Ca > Mn > Zn > Ni > Cr > Pb> Cu > Co. All the elements showed highly significant positive correlations with the organic content, nutrients and clay and silt fractions, where as they were correlated negatively with the sand fraction. Comparison with the previous studies in and around the Cochin found no significant enrichment neglecting the chances of higher levels of anthropogenic contamination. Sediment enrichment factor (SEF) study· showed the chances of Ni and Pb enrichment, particularly at sandy stations, suggesting a different source of input. Salinity was the most significant hydrographic parameter influencing the benthic fauna in the study region and the nature of substratum could also be important. Principal component analysis (PCA), which was used to find the major biogeochemical processes, established the significance of two groups to eliminate the differences that are attributable entirely to the variations in grain size. This indicated that the major biogeochemical process in the sandy stations was autochthonous addition, where as diagenesis dominated in the muddy stations. The role of bioturbation was also evident and these results also suggested the necessity of speciation analysis to give a realistic estimate of actual environmental reactivity.

Phosphorus is taken as the representative element to identify the geochemistry of the system because it is not showing any limiting nutrient character and has high environmental reactivity. The mobility of phosphorus in the sediment is probably controlled by its speciation and speciation scheme, so, is selected in such a way that the maximum variability and species diversity can be estimated. The species identified by the sequential extraction scheme (Golterman, 1996), modified by Diaz-Espejo *et al.*, (1999) were iron bound inorganic (Fe-IP) and organic fractions (Fe-OP), calcium bound inorganic (Ca-IP) and organic fractions (Ca-OP), acid soluble organic fraction (Acid-OP), alkali soluble organic fraction (Alkali-OP) and residual organic phosphorus (ROP). Ca–P was found to be the main P pool in the estuary. Low iron bound fraction was obtained even after a higher Fe content. Analysis of the results shows that the overall geochemical structure and character is maintained in the micro evaluation of the system. The sandy and muddy stations showed distinctively different species composition in the speciation study. This also gives the signature of diagenesis, as the organic fractions like Alkali-OP were comparatively lower in the muddy stations. The bio available fractions Fe-IP, Ca-IP and Acid-OP showed significant interrelations and also significantly correlated with metals, C, N and S. These testify that the principal geochemical processes governing these species are same and they behave in a similar way to the changes in redox and pH conditions. The results also showed that the percentage of bioavailable fractions is maintained in all the seasons in this estuary. Hence phosphorus limitation never conversely affects in the productivity. If the limitations of nitrogen and other physiological parameters were properly managed, the fertility and the health of the ecosystem can be effectively increased.

The tidal anaysis of the southern arm of Cochin estuary showed that there is a sharp gradient of physico-chemical and biological characters from the mouth towards the Thannermukkam bund. The estuarine region up to Perumbalam showed a general character and from there a sharp decrease was noticed. The tidal propagation is seemed to be affected by the big islands in these regions and also by the fresh water flow from the opposite side, generating a kind of counter current. These trends were also noted in the geochemistry of the surficial sediments and in the speciation analysis of phosphorus. Ca-IP was the dominant fraction in the lower reaches and Alkali-OP was the major fraction in the upper reaches. Bioavailable fractions were lower at the upper reaches and showed increase from Perumbalam region, contributing towards higher productivity in the lower reaches of the estuary. The study region lies in this transitional zone and hence is ideal to be taken as a representative to study the dynamics of this estuary. This analysis also gave an indication of declination of true estuarine character beyond the Perumbalam region, changing the southern part of estuary gradually in to a freshwater habitat.

Ecohydrology is an environmental problem-solving concept developed during UNESCO's International Hydrological Programme, promotes the integration of hydrology and ecology, and the control of these processes to enhance the adsorption and assimilation capacity of ecosystems. Ecohydrology incorporates the use of ecosystem properties as a management tool in implementing a program of water resource management. Hence an attempt to redefine of the "ecohydrology" concept by the application of aquatic chemistry is made here. The indispensable contribution of water chemistry, geochemistry and the nutrient dynamics to the estuarine ecology was well established by this study. It is in context that the chemical speciation of phosphorus was considered. The bioavailability of phosphorus was found to be parallel with the productivity trend and not limited by the physical characteristics of the substratum. There is scope for further betterment of the productivity, without reaching to the eutrophic status. Moreover it implies that by monitoring/regulating the chemical environment, the sustainability of an aquatic system can be achieved.

Appendix A

Monthly data of physical parameters

1) Salinity

Station 1

Depth	Jan	Feb	Mar	Apr	Jun	Jul	Aug	Sep	Oct	Nov	Dec
0	25.4	28.7	25.6	26.2	0.2	0.8	0.9	21	3.6	22.4	25.6
0.5	26.9	28.8	25.7	26.3	0.2	0.8	0.9	21.5	4.2	23.5	26.4
1	27.1	29	26	26.5	0.2	0.8	0.9	21.6	5.4	27.5	25.5
1.5	27.2	29.2	25.8	25.9	0.2	0.8	0.9	21.6	5.5	28	26

Station 2

Depth	Jan	Feb	Mar	Apr	Jun	Jul	Aug	Sep	Oct	Nov	Dec
0	22.5	26.6	30.5	26	0.2	2.3	1.1	19.1	2.8	19.8	24.3
0.5	23.2	26.7	30.2	26.2	0.2	2.4	1.1	21.4	2.8	21.7	24.4
1	24	27.1	28.9	26.3	0.2	2.5	1.1	24.5	4.7	22	24.8
1.5	24.1	27.1	28.2	26.3	0.2	2.7	1.1	24.9	5.3	22.6	24.7

Station 3

Depth	Jan	Feb	Mar	Apr	Jun	Jul	Aug	Sep	Oct	Nov	Dec
0	19.5	25	24.7	24.4	0.2	1.4	1.1	21.2	1.7	17.8	22.2
0.5	21	25.5	25.3	24.6	0.2	1.4	1.1	21.4	1.9	19.2	22.3
1	21.4	27.2	25.3	25	0.2	1.5	1.1	22	3	22.3	22.4
1.5	21.6	27.4	25.9	25.1	0.1	1.5	1.1	22.4	3.7	22.7	22.6
2	21.8	27.6	25.9	25.3	0.1	1.5	1.1	22.7	4.1	23.1	22.6
2.5	21.8	27.6	26	25.2	0.1	1.6	1.1	22.7	5.1	25.7	22.5

Station 4

Depth	Jan	Feb	Mar	Apr	Jun	Jul	Aug	Sep	Oct	Nov	Dec
0	19.4	24.6	24.2	20.6	0.2	0.8	1.1	17.9	1.1	15	19.8
0.5	19.6	25	24.7	20.7	0.2	0.7	1.1	19.4	1	15.5	19.9
1	19.8	25.7	25	21.2	0.2	0.7	1.1	20.6	1.2	18.1	19.9
1.5	19.9	25.8	25.1	21.5	0.2	0.8	0.9	22	1.2	18.9	20
2	19.9	25.8	25.1	21.7	0.1	0.8	0.9	21.9	1.2	19.3	20

Station 5

Depth	Jan	Feb	Mar	Apr	Jun	July	Aug	Sep	Oct	Nov	Dec
0	18.9	23	23	22.8	0.4	1.4	1.5	10	1.5	13.8	19
0.5	19.1	23	23	22.7	0.4	1.3	1.6	9.9	1.2	14	19.1
1	19.1	23.1	23.1	22.7	0.4	1.3	1.6	10	1.3	14.1	19.1
1.5	19.1	23	23	22.7	0.4	1.3	1.6	9.9	0.8	14.3	19.2

Station 6

Depth	Jan	Feb	Mar	Apr	Jun	July	Aug	Sep	Oct	Nov	Dec
0	18.2	22.7	22.6	23	0.4	1.3	1.7	9.7	0.6	13.1	19.4
0.5	18.5	23.1	23	22.9	0.4	1.2	1.6	9.8	0.5	13.3	19.4
1	18.5	23.5	23.1	22.9	0.3	1.3	1.5	9.8	0.6	13.6	19.5
1.5	18.8	23.8	23	23	0.3	1.3	1.6	9.8	0.6	14.1	19.5
2	18.8	23.9	23.1	23	0.3	1.3	1.5	9.8	0.6	14.4	19.5

Station 7

Depth	Jan	Feb	Mar	Apr	Jun	Jul	Aug	Sep	Oct	Nov	Dec
0	17.2	15.3	22.3	22.7	0.4	1.2	1.5	11	0.4	14.8	18.4
0.5	17.7	15.5	22.5	22.7	0.4	1.2	1.5	11	0.4	14.9	18.5
1	17.8	15.5	22.8	22.7	0.3	1.2	1.5	12.8	0.4	16.4	19

Station 8

Depth	Jan	Feb	Mar	Apr	Jun	Jul	Aug	Sep	Oct	Nov	Dec
0	17.6	21.2	22	22.9	0.2	0.8	0.9	9.2	0.1	11.9	17.3
0.5	16.6	21.6	22	22.8	0.1	0.8	0.9	9.2	0.2	11.9	18.2
1	20	22.3	22.3	22.8	0.1	0.9	0.9	10.6	0.2	12.5	19.1

Station 9

Depth	Jan	Feb	Mar	Apr	Jun	Jul	Aug	Sep	Oct	Nov	Dec
0	16.8	22.3	22.1	24.2	0.1	0.6	1	9	0.1	11.6	17.2
0.5	17.4	22.4	22	24.1	0.1	0.6	0.9	9.3	0.1	11.8	18.6
1	22.1	22.5	22.3	24	0.1	0.7	0.9	14.7	0.2	12.1	20.2

Station 10

Depth	Jan	Feb	Mar	Apr	Jun	Jul	Aug	Sep	Oct	Nov	Dec
0	17.9	20.6	20.2	22.5	0.1	0.4	0.9	9.3	0.1	13.2	17.8
0.5	18.6	22.6	20.6	22.7	0.1	0.4	0.9	11.2	0.1	13.4	19.3
1	18.7	23.4	21.1	22.8	0.1	0.5	0.8	13.3	0.4	17.2	19.7
1.5	19.2	24.9	21.7	23.1	0.1	0.5	0.8	18.8	0.5	18.1	20.4
2	20.3	26.4	22.6	23.3	0.1	0.5	0.8	23.3	0.6	20.6	22.2
2.5	22.9	26	22.7	23.5	0.1	0.5	0.8	24.4	0.8	24.2	24.2
3	24.7		22.7	24	0.1	0.5	0.8	24.6	5.2	27.5	22.2

Station 11

Depth	Jan	Feb	Mar	Apr	Jun	Jul	Aug	Sep	Oct	Nov	Dec
0	21.2	29	25	25	0.1	0.7	0.9	16.8	1.7	15.7	21.4
0.5	24.2	29.1	25.2	25.3	0.1	0.7	0.9	17	1.9	22.3	24.5
1	27.9	29.2	25.2	25.5	0.1	0.7	0.9	17.1	5.3	25.8	26.3
1.5	28.2	29.3	25.3	25.5	0.2	0.7	0.9	17.2	6.7	25.8	27.2
2	28.1	29.6	25.5	25.7	0.2	0.7	0.9	17.3	6.9	27.1	27.4

Station 12

Depth	Jan	Feb	Mar	Apr	Jun	Jul	Aug	Sep	Oct	Nov	Dec
0	26.6	28	25.4	26.8	0.1	0.8	1.4	17.3	0.6	21	26.8
0.5	26.8	28.2	25.6	26.7	0.1	0.8	0.6	17.4	5	23.8	27
1	27.7	28.2	25.9	27	0.1	0.8	1.2	17.3	5.4	26.1	27
1.5	28.3	28.5	25.9	27.2	0.1	0.9	1.2	17.5	6.5	29.5	27.1
2	28.4	28.6	26.2	27.2	0.1	0.9	1.2	17.6	7.8	30	27.3
2.5	28.4	28.6	26.6	27.3	0.1	0.9	1.2	18	8.8	30.2	28

2) Temperature

Station 1

Depth	Jan	Feb	Mar	Apr	Jun	Jul	Aug	Sep	Oct	Nov	Dec
0	29.8	32	32.8	32.7	29.6	29.9	29	30.1	31	31.5	31.2
0.5	29.9	32.2	32.7	32.8	29.6	30	29.2	30.2	30.8	31.8	31.2
1	29.8	32	32.6	32.9	29.6	29.9	29.2	30.1	30.5	31.4	31
1.5	29.8	31.9	32.6	33	29.6	29.9	29.2	30.1	30.2	30.8	31

Station 2

Depth	Jan	Feb	Mar	Apr	Jun	Jul	Aug	Sep	Oct	Nov	Dec
0	30.2	32.8	32.8	32.4	29.9	30.2	30	32.9	32.5	31.7	31.7
0.5	30.2	32.8	32.8	32.6	30.2	30.2	30	32.5	32.6	31.7	31.5
1	30.1	32.4	32.8	32.8	30.2	30.2	30	30.7	32.1	31.6	31.4
1.5	30.1	32.2	32.8	32.9	30.2	30.1	29.9	29	31.7	31.5	31.3

Station 3

Depth	Jan	Feb	Mar	Apr	Jun	Jul	Aug	Sep	Oct	Nov	Dec
0	30	32.7	33.5	32.4	30.4	30.3	30.2	31.6	32	31.6	30.6
0.5	30	32.8	33.5	32.9	30.5	30.3	30.1	31.6	32.2	31.7	31.1
1	30	32.7	33.4	33.1	30.5	30.2	30	31.1	32	31.4	31.2
1.5	29.9	32.6	33.2	33.2	30.5	30.2	30	30.4	31.6	31.2	31.1
2	29.8	32.2	33.1	33.1	30.5	30.2	30	30	31.3	31.2	31
2.5	29.8	32.1	33.1	33.2	30.5	30.1	30	29.9	31.1	30.9	30.9

Station 4

Depth	Jan	Feb	Mar	Apr	Jun	July	Aug	Sep	Oct	Nov	Dec
0	29.9	31.8	32.6	32.9	30.3	30	30.7	31.9	32.2	31.2	31.6
0.5	30	32	33.2	33.2	30.5	30.3	30.6	31.9	32.4	31.6	31.5
1	29.9	32	33.3	33.4	30.5	30.4	30.5	31.4	32.1	31.4	31.3
1.5	29.9	31.8	33.2	33.4	30.5	30.4	29.7	31.1	31.8	31.2	31.2
2		31.8		33.4	30.5	30.3	29.7	30.9	31.5	31.1	31.2

Station 5

Depth	Jan	Feb	Mar	Apr	Jun	July	Aug	Sep	Oct	Nov	Dec
0	29.5	31.4	32.3	31.5	30	30.2	29.6	32	30.6	30.9	30.4
0.5	29.4	31.5	32.2	31.9	29.9	30.2	29.8	32	30.9	30.9	30.4
1	29.4	31.5	32.1	32	29.9	30.2	29.8	32	30.7	30.9	30.4
1.5	29.3	31.5	32	32	29.9	30.1	29.8	32	30.5	30.8	30.4
2	29.3	31.5	32	32				32		30.8	30.4

Station 6

Depth	Jan	Feb	Mar	Apr	Jun	Jul	Aug	Sep	Oct	Nov	Dec
0	29.7	31.4	32.5	31.1	29.8	30	29.2	32.1	30.9	31.1	30.8
0.5	29.6	31.4	32.2	31.5	29.9	30.2	29.2	32.1	30.7	31	30.5
1	29.5	31.3	32.1	31.8	29.9	30.1	29.2	32	30.6	31	30.4
1.5	29	31.2	32	31.9	29.8	30.1	29.3	32	30.6	30.9	30.4
2	29.5	31.2	32	31.9	29.8	30.1	29.2	32.1	30.6	30.9	30.2
2.5	29.4	31.2	32		29.8	30.1	29.3	32.1	30.5	30.8	30.3

Station 7

Depth	Jan	Feb	Mar	Apr	Jun	July	Aug	Sep	Oct	Nov	Dec
0	30.2	30.8	33	31.6	30.1	30.1	29	32.2	30.1	31.1	30.8
0.5	29.5	31.4	32.5	31.8	30	30.1	29.1	32.1	30	31	30.7
1	29.4	31.3	32.3	31.9	30	30.1	29.1	31.8	30	30.9	30.5

Station 8

Depth	Jan	Feb	Mar	Apr	Jun	Jul	Aug	Sep	Oct	Nov	Dec
0	30.1	30.8	32.5	31.4	29.7	30	28.8	31.4	30.9	30.5	31.1
0.5	29.2	30.8	32.3	31.8	29.6	30.1	28.8	31.6	30.6	30.5	30.9
1	29.5	30.9	31.9	31.8	29.3	30.1	28.7	31.5	30.2	30.4	30.9
1.5			31.8					31.6	30	31	31.3

Station 9

Depth	Jan	Feb	Mar	Apr	Jun	Jul	Aug	Sep	Oct	Nov	Dec
0	29.2	31.1	32.8	32	29.9	30.2	30.3	31.3	30.7	31.9	32.1
0.5	29.3	31.6	33	32.6	29.8	30.3	29.5	31.3	30.1	31.5	30.9
1	29.3	31.4	32.2	32.4	29.5	30.1	29.1	31.5	29.8	31.5	31
1.5		31.7	32	32.2			29.1	31.5	29.8	31.5	31.1

Station 10

Depth	Jan	Feb	Mar	Apr	Jun	Jul	Aug	Sep	Oct	Nov	Dec
0	30.1	32.4	32.5	32	29.4	29.8	29.3	32.1	31.1	31.8	32.5
0.5	29.8	32.1	32.8	32.6	29.2	29.8	29.1	31.3	30.8	31.6	31.7
1	29.8	31.1	32.8	32.4	29	29.7	28.9	31.3	30.4	31.4	31.4
1.5	29.8	31.4	32.6	32.2	28.8	29.7	28.9	30.6	30.3	31.2	31.2
2	29.7	31.4	32.3	32.1	28.7	29.6	28.6	30.7	30.1	31.2	30.9
2.5	29.7	31.5	32.2	32	28.6	29.6	28.5	29	29.9	31.1	30.7
3	29.6		32.1	31.9	28.5	29.6	28.4	28.8	29.8	31	30.5

Station 11

Depth	Jan	Feb	Mar	Apr	Jun	Jul	Aug	Sep	Oct	Nov	Dec
0	30.2	32.4	32.3	31.9	29.6	30	29.4	30.7	31.4	32.1	31.8
0.5	30	32	32.5	32.2	29.5	29.9	29.2	30.8	31.1	31.8	31.4
1	29.7	31.1	32.5	32.4	29.4	29.8	29	30.8	30.6	31.3	31.2
1.5	29.6	31.6	32.4	32.3	29.5	29.8	28.9	30.8	30.4	31.2	31
2	29.6	31.6	32.4	32.3	29.6	29.8	28.9	30.7	30.2	30.8	30.8

Station 12

Depth	Jan	Feb	Mar	Apr	Jun	Jul	Aug	Sep	Oct	Nov	Dec
0	30.5	32.5	33	32.2	29.6	30.2	30.4	31.2	31.7	31.7	31.2
0.5	30.4	32.2	33.1	32.9	29.6	30.2	29.6	31.2	31.6	31.5	31.6
1	30.2	32.1	33.1	33	29.6	30.1	29.2	31.4	31.2	31.1	31.5
1.5	30	32	33	33	29.5	30	29	31.4	30.7	30.8	31.4
2	29.9	31.9	33	33	29.5	30	28.8	31.3	30.3	30.6	31.1
2.5	29.9	31.9	33	32.8	29.4	30	28.8	31.2	30.1	30.5	30.8

3) Secchi Disc Transparency (m)

Station	Jan	Feb	Mar	Apr	June	Jul	Aug	Sep	Oct	Nov	Dec
1	0.65	0.5	0.75	0.5	0.5	0.75	0.75	1	1.25	1.1	1
2	0.8	1.05	1	0.75	0.5	0.5	0.75	1.5	1	1.1	1
3	0.73	0.85	0.75	1	0.5	0.5	0.5	1.25	1	1	1.5
4	0.95	1.05	0.75	1	0.5	0.75	0.5	0.75	0.5	1	1
5	0.79	0.6	0.75	1	0.75	0.75	1	1.75	0.75	1.2	0.9
6	0.96	0.6	0.75	0.75	0.75	0.75	0.5	1.25	0.75	1.2	0.6
7	1.05	0.8	0.8	1	1	0.75	0.5	1	0.75	1.2	1
8	1	0.9	1	1	0.5	0.5	0.5	1.5	0.75	1.25	1.65
9	0.75	1.16	1.15	1	0.5	0.75	0.75	1.4	0.5	1.25	1.4
10	0.75	0.9	1.35	1.25	0.6	1	0.8	2	0.75	1.4	1.5
11	0.72	0.95	1	1.25	0.6	0.5	1	1.5	0.75	1.4	1.25
12	0.76	1	1	0.5	0.7	0.75	1	2	0.75	1.1	1.4

4) Turbidity

Station	Level	Turbidity (NTU)										
		Jan	Feb	Mar	Apr	June	Jul	Aug	Sep	Oct	Nov	Dec
1	Surface	5.5	4.3	5.5	11.6	10.9	27.6	20.6	1.4	8.5	0.03	3.4
	Bottom	5.2	5.2	5.2	11.5	13.2	34.1	26.5	2.6	9.3	0.23	4.2
2	Surface	2.6	4.5	2.6	10.6	13.8	22.2	24.7	2.5	7.7	0.6	4
	Bottom	3.5	5	3.5	6.8	16.9	28.2	22.8	4.7	8.5	2	2.8
3	Surface	2.8	4	2.8	9.9	7.6	16.8	13.5	1.2	5.7	0.4	4.5
	Bottom	8.6	6.5	3.6	12.7	8.6	36.9	21.6	0.56	6.7	2.3	3.4
5	Surface	7.1	6.2	7.1	12.1	16.5	11	17.9	1.4	13.3	0.2	2.5
	Bottom	9.4	10.2	9.4	11.9	17.3	14.4	21.4	1.4	15.3	0.45	5
7	Surface	1.6	5	1.6	7.7	14.3	12	24.7	1	11.8	0.1	0.3
	Bottom	1.4	7.7	1.4	6.2	21.3	16.6	32.6	1.3	13.7	0.6	2.4
8	Surface	1.3	1.2	1.3	4.2	17.9	16.6	28.7	0.49	11.2	0.6	0.19
	Bottom	10.5	3.3	10.5	6.5	16.8	14.8	32.7	3.4	12.6	1.4	1.4
10	Surface	0.9	2.7	0.9	5.2	5.4	8	5.8	4.8	11.8	0.22	2.1
	Bottom	6.2	4.9	6.2	7.8	6.9	8.6	12.8	4.5	15.6	0.56	0.65
11	Surface	3.6	9	3.6	15.5	12.9	15	12.1	1.6	4.2	0.01	3
	Bottom	9.6	9.1	9.6	11.4	16.2	30.5	20.5	1.6	5.3	1.9	4.4

5) Suspended sediments

Station	Level	Suspended sediments (mg/l)										
		Jan	Feb	Mar	Apr	June	Jul	Aug	Sep	Oct	Nov	Dec
1	Surface	28	33.6	13	8	16.8	50	29.3	18.2	17	29	20.1
	Bottom	8.7	18.5	20.3	2	18.5	41	29.7	12.3	10.5	26.6	17.1
2	Surface	14.6	11.2	12.3	8	21.3	48.6	37.6	16.8	17.1	26.8	19.2
	Bottom	23.1	29.7	33	41	23.5	37.4	27	14.6	16.5	25	14.3
3	Surface	14.5	27.7	23.7	11	15.6	30	20.2	11.6	27.7	26.6	17.1
	Bottom	33	23.8	16	28	23.2	48.3	24.1	24.4	25	25	18.2
5	Surface	29.1	10	22.1	46.9	22.1	23.9	34.2	16.2	24.3	24.4	26.2
	Bottom	30.7	39.1	20.3	14	25.5	25.7	39.9	13.4	16.3	25.4	21.2
7	Surface	9	35	17.2	11	33.7	22.2	34.6	14	16.8	19.4	22.4
	Bottom	20.1	11	34	4	36.8	23.1	37	9.3	26.3	15.2	14.5
8	Surface	9.6	14.1	15	25.4	20.3	26.9	26	13.5	18.2	16	14.2
	Bottom	7	41	20.5	9.2	19.7	25.3	31.6	11	12.4	17.4	13.2
10	Surface	6	10.7	28	6	6.5	13.7	8.3	17.3	14	10.4	19.6
	Bottom	14.3	29.9	26	24.1	8.4	15.5	13.1	23.7	11.9	19.8	13.9
11	Surface	12.7	18	13.6	4	19.6	26.6	14.5	16.3	17.6	18.2	20.4
	Bottom	43	34.9	27	28.1	19.7	30.5	22.3	15.6	14.8	36.8	21.9

Appendix B

Monthly data of chemical parameters

1) Phosphate

Station	Level	Phosphate (µmol/l)										
		Jan	Feb	Mar	Apr	June	Jul	Aug	Sep	Oct	Nov	Dec
1	Surface	0.76	0.20	1.02	1.73	2.45	1.34	3.16	1.43	0.19	0.58	0.96
	Bottom	0.23	0.36	1.49	0.00	2.15	2.01	3.74	0.82	0.05	ND	0.72
2	Surface	ND	2.28	3.00	0.62	10.50	1.77	4.17	2.21	4.37	ND	2.45
	Bottom	ND	0.56	2.61	1.68	9.70	3.16	4.56	1.20	1.25	ND	2.93
3	Surface	0.96	2.84	3.53	4.85	17.30	3.84	3.88	0.72	5.62	1.10	8.30
	Bottom	0.10	1.49	3.37	4.46	17.80	2.83	5.04	1.01	3.31	1.78	7.73
5	Surface	1.65	3.96	2.54	2.78	5.25	16.46	5.28	1.15	3.98	3.26	7.58
	Bottom	0.56	4.09	2.54	2.83	5.60	5.71	5.13	1.15	4.75	4.03	7.30
7	Surface	0.07	0.46	0.89	0.53	4.00	7.00	3.98	0.82	0.00	2.16	0.82
	Bottom	0.10	0.83	1.25	0.67	4.25	6.09	3.69	0.62	1.44	1.34	1.78
8	Surface	ND	ND	0.43	0.00	3.10	0.91	3.98	0.05	0.43	ND	0.05
	Bottom	ND	ND	1.02	0.10	3.25	0.72	3.69	ND	0.43	ND	0.58
10	Surface	ND	ND	ND	ND	1.75	ND	1.58	ND	ND	ND	0.05
	Bottom	ND	0.17	1.32	0.14	1.25	0.00	2.14	0.38	0.05	ND	ND
11	Surface	ND	0.79	1.42	0.00	2.05	1.20	2.31	0.72	0.10	ND	0.53
	Bottom	ND	0.96	1.62	1.06	2.55	0.82	3.36	1.30	0.29	ND	0.53

2) Nitrate

Station	Level	Nitrate (µmol/l)										
		Jan	Feb	Mar	Apr	June	Jul	Aug	Sep	Oct	Nov	Dec
1	Surface	3.13	1.47	1.32	3.06	10.64	11.24	12.42	2.14	4.95	2.22	5.75
	Bottom	2.55	1.86	1.86	2.06	7.90	15.56	16.63	0.46	8.05	1.70	5.99
2	Surface	3.07	1.51	1.45	0.26	6.34	17.79	7.96	0.81	8.52	20.40	5.57
	Bottom	1.68	2.39	2.08	2.09	8.86	21.34	15.56	0.71	9.47	1.73	6.04
3	Surface	5.64	1.44	0.54	2.12	7.52	18.29	15.17	0.96	4.67	2.11	5.74
	Bottom	2.04	1.14	1.77	5.08	7.43	17.16	16.24	0.88	5.64	3.06	6.15
5	Surface	3.69	2.00	2.34	1.85	3.21	11.24	5.19	1.65	4.66	3.18	4.23
	Bottom	6.07	4.01	1.93	1.83	7.85	9.06	6.91	2.78	5.83	3.65	6.04
7	Surface	3.18	1.67	0.19	0.25	5.36	9.41	6.23	0.78	6.21	2.37	5.36
	Bottom	1.99	1.45	0.31	1.51	6.93	7.87	7.16	0.35	6.72	2.74	3.03
8	Surface	1.92	1.38	0.28	0.07	7.39	13.75	7.14	0.60	4.62	1.81	4.44
	Bottom	1.83	1.05	0.32	0.12	9.56	11.71	7.05	0.45	6.32	1.58	5.25
10	Surface	1.44	2.39	2.84	1.78	5.48	14.42	12.24	0.73	6.54	1.32	5.26
	Bottom	1.80	0.54	0.35	1.78	9.16	22.17	11.37	0.75	10.45	2.81	4.52
11	Surface	1.56	1.82	1.52	1.01	8.23	10.87	16.24	1.50	9.21	2.03	4.93
	Bottom	3.30	1.51	1.64	0.41	8.44	17.23	2.42	1.42	8.85	1.71	5.91

3) Nitrite

Station	Level	Nitrite (µmol/l)										
		Jan	Feb	Mar	Apr	June	Jul	Aug	Sep	Oct	Nov	Dec
1	Surface	0.05	0.54	0.42	1.08	0.46	0.87	2.07	0.02	1.08	0.90	0.46
	Bottom	0.06	0.42	0.68	0.00	0.44	0.75	1.72	0.12	1.01	0.85	0.35
2	Surface	0.02	0.19	0.53	0.76	0.74	0.48	1.91	0.21	1.59	0.90	0.85
	Bottom	0.03	0.58	1.28	0.97	0.78	1.03	2.13	0.16	0.85	0.67	0.83
3	Surface	0.06	2.61	0.60	1.33	0.97	1.17	2.16	0.00	1.54	0.94	1.79
	Bottom	0.03	1.93	1.23	1.40	0.95	0.47	2.32	0.05	1.20	0.90	1.77
5	Surface	0.24	4.18	0.69	0.85	0.74	1.47	2.66	0.18	1.50	1.17	1.77
	Bottom	0.32	4.30	0.86	0.00	0.82	1.11	2.48	0.35	1.31	1.06	1.79
7	Surface	ND	0.40	0.11	0.44	0.82	3.24	2.13	0.21	0.90	0.90	0.16
	Bottom	0.02	0.56	0.26	0.53	0.84	2.11	2.43	0.37	1.29	1.10	0.21
8	Surface	ND	ND	0.02	0.44	0.61	0.92	2.57	ND	1.08	0.44	0.14
	Bottom	ND	0.03	0.13	0.37	0.69	0.89	2.69	ND	1.04	0.55	0.55
10	Surface	ND	0.16	0.10	0.62	0.25	0.46	1.71	0.02	0.90	0.48	0.14
	Bottom	ND	0.63	0.13	0.44	0.23	0.51	1.58	0.18	0.92	0.51	0.55
11	Surface	ND	0.34	0.37	0.64	0.38	0.82	2.11	0.00	1.20	0.55	0.41
	Bottom	ND	0.83	0.22	0.92	0.46	0.52	2.02	0.02	0.78	0.90	0.30

4) Silicate

Station	Level	**Silicate (µmol/l)**									
		Feb	Mar	Apr	June	Jul	Aug	Sep	Oct	Nov	Dec
1	Surface	27.44	34.57	37.53	119.07	124.64	99.06	135.02	105.62	3.36	31.78
	Bottom	40.37	46.63	36.89	120.70	58.87	19.02	101.33	100.62	4.06	30.16
2	Surface	20.94	28.94	36.89	113.74	186.87	12.64	182.99	115.48	3.02	31.90
	Bottom	33.00	33.18	37.76	113.97	157.81	61.31	58.17	102.02	2.61	36.66
3	Surface	33.40	82.24	33.29	97.50	131.54	10.15	97.27	113.85	3.65	42.05
	Bottom	27.61	28.42	30.62	109.16	162.16	52.25	68.03	102.20	3.31	37.64
5	Surface	30.33	62.58	32.77	123.48	118.95	83.23	197.08	124.29	4.70	48.14
	Bottom	23.55	35.61	34.39	113.80	101.91	112.69	197.08	129.28	5.51	47.62
7	Surface	38.34	55.56	35.50	124.29	118.95	12.99	186.88	130.15	5.34	52.20
	Bottom	30.74	76.79	37.41	122.90	95.35	18.91	197.08	128.88	10.90	49.94
8	Surface	55.33	27.72	38.05	113.74	66.75	84.21	28.48	122.26	6.96	49.18
	Bottom	40.37	66.47	35.84	112.69	147.21	21.81	191.46	121.92	11.66	53.24
10	Surface	40.19	73.78	46.34	117.86	107.01	8.17	84.56	120.12	5.05	48.72
	Bottom	47.10	142.97	45.47	124.82	99.82	16.12	162.17	112.46	4.12	45.36
11	Surface	33.58	26.85	43.91	113.91	69.65	19.02	130.15	104.81	7.66	36.66
	Bottom	19.78	50.81	43.85	119.13	82.65	13.63	174.00	98.31	2.44	33.00

5) Dissolved oxygen

Station	Level	Dissolved oxygen (mg/l)									
		Feb	Mar	Apr	June	Jul	Aug	Sep	Oct	Nov	Dec
1	Surface	5.51	5.67	5.29	3.97	7.62	6.78	4.51	6.77	7.65	5.80
	Bottom	4.54	5.67	4.63	3.63	5.84	6.33	4.51	5.77	7.08	5.80
2	Surface	7.50	6.58	5.27	4.51	6.01	6.28	5.63	5.84	8.59	6.10
	Bottom	6.60	6.58	6.39	3.30	6.01	6.28	4.51	5.51	4.96	4.54
3	Surface	5.89	6.01	6.94	4.96	7.70	5.65	5.15	4.87	7.28	5.84
	Bottom	5.50	6.01	5.95	2.99	6.75	4.00	4.51	3.57	4.96	5.18
5	Surface	5.70	7.00	4.96	4.95	8.84	7.17	4.51	4.87	5.95	5.51
	Bottom	5.50	4.67	4.96	3.31	8.09	5.27	5.18	4.21	5.29	4.54
7	Surface	8.30	7.00	6.28	4.63	10.15	9.81	6.12	6.48	8.93	8.22
	Bottom	8.70	5.18	7.28	4.54	6.39	9.27	5.48	5.84	8.59	7.78
8	Surface	7.10	5.34	5.29	3.97	7.97	8.51	4.18	5.18	8.93	8.10
	Bottom	5.80	4.67	4.63	3.63	7.33	7.91	3.87	4.21	7.93	7.78
10	Surface	8.60	6.68	6.61	3.63	7.90	6.40	6.12	6.81	8.88	8.22
	Bottom	5.80	5.34	6.61	2.31	5.84	5.27	5.15	6.48	6.40	7.78
11	Surface	7.30	8.46	6.40	4.51	6.68	6.94	3.97	5.84	7.93	7.12
	Bottom	5.30	5.08	4.90	3.23	6.33	6.28	3.30	4.21	7.28	5.85

Appendix C

Monthly data of biological parameters

1) Primary Production

Station	Production (mg C/m^3/hr	Production (mg C/m^3/hr										
		Jan	Feb	Mar	Apr	June	Jul	Aug	Sep	Oct	Nov	Dec
5	GP	134.38	89.58	120.83	96.88	78.13	159.06	101.25	73.33	77.19	162.50	128.13
	NP	110.42	45.83	87.50	66.04	52.08	106.56	75.00	52.50	51.46	93.75	62.50
7	GP	151.04		108.23	128.13	78.13	132.50	103.75	78.75	51.46	183.33	103.13
	NP	111.46		90.63	103.13	52.08	106.04	81.25	26.25	25.73	105.21	26.04
8	GP	151.04	76.04	79.17	128.13	78.13	132.51	91.88	78.75	91.67	159.38	79.17
	NP	71.88	68.75	33.75	103.13	52.08	79.49	65.63	52.50	51.04	83.13	53.13
10	GP	151.04	59.38	62.50	123.96	52.08	159.06		52.50	77.19	79.17	72.92
	NP	111.46	44.79	29.17	103.13	26.04	93.02		26.25	51.46	52.08	52.08

2) Chlorophyll-a

Station	Chlorophyll-a (µg/l)							
	Mar	Apr	July	Aug	Sept	Oct	Nov	Dec
5	21.12	10.67	34.61	11.34	3.19	2.92	26.89	8.98
7	8.14	7.86	7.75		3.33	4.83	13.76	7.67
8	21.53	14.52	29.14		2.37	7.76		
10	8.14	7.86	7.75	1.03	3.33	4.83	13.76	7.67

3) Zooplankton

Groups	Jan	Feb	Mar	Apr	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Copepods	2700	9100	5200	5700	1583	1400	1200	1800	2000	4080	5420
Nauplius	700	1900	900	600	500	400	200	700	300	4330	1030
Zoea	-	100	300	100	-	-	-	-	-	-	-
Cladocerans	500	-	160	330	-	-	-	-	-	-	-
Chaetognaths	-	460	70	300	-	-	-	-	-	-	-
Appendicularians	100	350	480	-	-	250	330	-	-	-	-
Fish egg	-	-	-	-	216	660	1160	500	-	-	-
Fish larva	-	-	-	-	-	160	250	160	420	1000	3160
Total (No./m3)	8000	11910	7110	7030	2300	2870	1980	5140	2720	9410	9610

4) Benthos

Groups	Jan	Feb	Mar	Apr	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Polychaetes	523.6	384.8	555.6	556	104	103.1	149	236	448	621.5	973.8
Molluscs	190.3	83.32	-	-	59.5	71.42	87.29	89.3	143	323.7	385.6
Amphipods	198.3	323.9	202.3	143	55.5	59.51	57.13	76.2	138	171.5	290.5
Tanaids	204.8	250	273.7	349	87.3	123.7	158.7	99.2	145	259.4	428.5
Crabs	95.22	107.3	47.6	71.4	-	23.8	-	23.8	95.2	95.24	23.8
Others	59.52	59.51	59.52	71.4	23.8	39.68	23.8	23.8	27.8	23.8	39.68
Total (no./m^2)	1272	1209	1139	1190	330	421.2	476	548	996	1495	2142

Appendix D

Monthly data of Carbon, Nitrogen and Sulphur

Stations	Total Carbon (%)									
	Feb	Mar	Apr	June	Jul	Aug	Sep	Oct	Nov	Dec
1	0.77	0.57	0.70	0.71	0.62	0.69	0.72	1.02	0.55	0.87
2	0.08	0.14	0.09	0.08	0.06	0.07	2.05	0.47	4.12	2.99
5	0.15	0.41	0.08	2.59	0.08	0.09	0.12	0.14	0.09	0.06
7	3.41	1.76	2.79	3.75	2.68	2.49	2.95	2.56	2.34	2.14
8	3.70	3.58	3.56	3.60	3.83	3.80	4.05	3.72	3.72	3.77
10	1.79	3.23	3.48		3.61	3.47	3.32	3.50	3.33	3.27

Stations	Total Nitrogen (%)									
	Feb	Mar	Apr	June	Jul	Aug	Sep	Oct	Nov	Dec
1	0.14	0.12	0.10	0.11	0.15	0.12	0.02	0.07	0.14	0.24
2	0.09	0.06	0.04	0.11	0.10	0.12	0.04	0.00	0.29	0.48
5	0.07	0.10	0.06	0.28	0.08	0.09	0.08	0.00	0.00	0.09
7	0.42	0.23	0.30	0.29	0.23	0.31	0.34	0.28	0.26	0.37
8	0.36	0.32	0.32	0.42	0.37	0.36	0.36	0.30	0.33	0.45
10	0.06	0.38	0.38		0.46	0.41	0.40	0.38	0.44	0.55

Stations	Total Sulphur (%)									
	Feb	Mar	Apr	June	Jul	Aug	Sep	Oct	Nov	Dec
1	0.28	0.27	0.26	0.24	0.21	0.32	0.25	0.40	0.24	0.33
2	0.03	0.08	0.02	0.00	0.02	0.02	1.23	0.23	1.70	0.83
5	0.05	0.16	0.06	1.18	0.00	0.03	0.04	0.01	0.02	0.02
7	0.95	0.61	0.89	1.63	0.92	1.05	1.15	0.91	0.82	0.77
8	0.91	1.27	1.32	1.06	1.24	1.53	1.38	1.75	1.38	1.42
10	0.58	1.10	0.97		1.09	1.19	1.06	1.17	1.02	1.08

Appendix E

Monthly data of Heavy metals

Station 1

Months	Metals (µg/g)								
	Cu	Zn	Ni	Pb	Mn	Cr	Co	Mg	Fe
Feb	10.77	55.50	34.84	17.81	94.34	22.05	7.56	4651.62	25257.32
Mar	9.83	33.51	42.62	37.27	94.47	23.53	12.27	3708.58	25376.51
Apr	9.29	35.43	37.33	20.15	84.55	23.46	12.15	4331.09	21354.67
June	7.87	29.94	42.15	52.33	85.71	18.72	6.46	3889.31	26235.15
Jul	8.00	45.14	22.45	30.65	101.93	21.25	11.42	4318.58	25513.45
Aug	8.70	40.39	39.51	21.00	86.69	27.14	10.14	4294.55	22713.39
Sep	8.42	42.00	27.63	18.50	90.03	26.61	5.39	3601.79	19091.48
Oct	11.96	54.58	38.44	11.59	99.30	31.45	7.90	4675.60	29253.56
Nov	7.80	42.69	18.95	44.53	72.26	31.99	5.60	3308.82	20486.11
Dec	8.04	41.88	25.84	17.59	71.74	35.06	5.60	3624.75	20043.78

Station 2

Months	Metals (µg/g)								
	Cu	Zn	Ni	Pb	Mn	Cr	Co	Mg	Fe
Feb	1.80	6.22	8.20	16.17	9.99	2.16	3.08	522.19	5760.94
Mar	0.22	3.05	8.12	5.96	15.67	5.66	5.24	627.11	5035.52
Apr	0.59	2.71	10.91	20.43	11.64	3.36	3.83	496.70	2833.28
Aug	0.41	11.64	3.24	24.10	7.26	11.38	3.55	298.02	4353.69
Sep	0.98	8.58	6.97	11.46	11.31	5.26	3.67	374.04	2396.20
Oct	3.21	18.41	17.29	17.26	25.85	14.38	4.64	1065.77	8238.60
Nov	16.68	54.24	52.62	21.39	126.67	52.58	14.25	5924.88	30811.52
Dec	8.62	35.20	27.96	38.05	77.96	31.66	14.32	2880.55	23361.52

Station 5

Months	Metals (µg/g)								
	Cu	Zn	Ni	Pb	Mn	Cr	Co	Mg	Fe
Feb	0.93	18.02	12.91	13.62	13.78	3.44	5.36	835.91	5990.71
Mar	4.20	15.88	20.60	10.94	33.86	10.59	5.99	1684.16	11482.94
Apr	0.99	6.19	10.47	8.74	14.50	5.22	3.07	649.87	3983.28
June	0.43	3.97	6.60	12.61	14.22	0.35	3.68	268.38	2274.56
Jul	0.39	6.73	40.67	9.09	9.19	2.36	3.36	153.50	3751.60
Aug	0.69	14.89	7.64	12.12	12.75	5.14	4.85	447.98	2055.44
Sep	0.42	4.09	12.08	24.86	16.01	6.48	3.18	418.25	3247.28
Oct	0.49	9.38	9.31	11.36	22.96	6.50	3.05	317.34	3301.49
Nov	0.08	4.63	11.44	46.32	17.15	8.36	3.43	300.48	2835.79
Dec	0.18	10.50	6.68	12.19	15.74	6.64	3.09	310.47	14366.19

Station 7

Months	Metals (µg/g)								
	Cu	Zn	Ni	Pb	Mn	Cr	Co	Mg	Fe
Feb	33.713	131.373	70.428	48.2861	298.939	101.14	19.4232	12289	57051.5
Mar	18.489	57.9743	41.4791	42.1222	86.881	49.5498	18.9871	5369.77	36028.9
Apr	28.498	76.1629	51.2043	38.1504	125.666	61.5462	23.7406	7722.01	50951.5
June	27.794	69.6102	74.7812	56.1854	125.298	10.4415	18.0241	8576.97	45917.9
Jul	25.901	78.4469	102.219	58.439	135.747	48.5341	7.97345	7428.68	58686.6
Aug	23.838	75.3101	57.3968	62.4884	112.294	42.955	22.4264	6318.27	53878.9
Sep	26.867	76.9627	69.9427	41.5319	135.842	58.3652	22.2361	7130.26	53054.2
Oct	25.389	103.033	81.0653	47.0451	119.946	52.3328	14.8328	6998.44	62675
Nov	24.294	104.383	61.6642	72.0654	111.478	60.8841	10.1597	6110.7	46508.2
Dec	23.62	67.5452	62.8626	42.2675	109.564	60.5835	13.3847	6050.06	44505.2

Station 8

Months	Metals (µg/g)								
	Cu	Zn	Ni	Pb	Mn	Cr	Co	Mg	Fe
Feb	39.60	106.26	79.89	43.78	208.23	56.77	24.25	8903.97	76372.49
Mar	41.18	95.73	86.09	56.20	170.78	80.17	37.77	7807.84	75144.22
Apr	36.53	72.05	80.21	55.43	157.85	62.76	22.19	7103.83	73985.17
June	40.51	87.55	78.20	61.36	180.03	66.23	29.00	7085.12	73724.19
Jul	42.19	122.78	91.96	57.68	182.89	68.52	28.22	8033.95	77434.90
Aug	41.54	91.68	87.94	63.27	168.35	89.06	27.78	8027.72	73454.72
Sep	40.11	87.39	82.52	44.42	165.86	74.83	19.09	8030.07	70263.11
Oct	38.41	78.64	75.16	45.45	155.45	68.39	22.61	6839.24	71890.04
Nov	44.14	87.84	89.99	58.72	171.51	81.82	29.63	7242.12	67699.16
Dec	42.02	93.15	96.37	52.26	164.34	110.48	23.52	7968.99	69935.55

Station 10

Months	Metals (µg/g)								
	Cu	Zn	Ni	Pb	Mn	Cr	Co	Mg	Fe
Feb	17.86	71.72	38.97	40.69	102.62	32.72	9.34	4706.90	35396.55
Mar	35.64	150.23	87.17	50.74	209.69	81.46	23.09	12803.23	63877.44
Apr	37.17	181.84	74.34	33.65	352.72	74.69	25.29	13311.23	77883.26
June	41.72	172.65	101.99	51.75	241.80	73.32	29.40	13166.33	74052.02
Jul	40.69	100.78	37.84	73.53	361.37	102.79	22.55	13357.84	68235.29
Aug	40.75	109.49	89.86	48.26	302.60	91.40	28.04	13605.03	71390.92
Sep	41.04	155.08	110.60	76.23	361.65	80.81	20.97	13504.09	73771.56
Oct	40.33	126.53	97.40	62.69	354.05	98.24	24.83	13188.07	76414.37
Nov	41.90	115.26	81.85	81.56	348.80	94.70	26.98	12746.63	82657.75
Dec	40.17	156.93	100.56	69.88	299.50	99.74	18.47	12472.67	67086.98