CHEMICAL OCEANOGRAPHIC STUDIES OF THE COASTAL WATERS OF COCHIN

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By

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August, 2001

DECLARATION

I hereby declare that this thesis entitled "**Chemical Oceanographic Studies of the Coastal Waters of Cochin**" is an authentic record of research work carried out by me, in the Regional Centre of National Institute of Oceanography, Cochin-14, under the supervision of Dr. V.N.Sankaranarayanan, Former Scientist-in-Charge, National Institute of Oceanography, Regional Centre, Cochin-14 in partial fulfillment of the requirement of the Ph.D. degree of the Cochin University of Science and Technology and that no part thereof has been previously formed the basis for the award of any degree, diploma or associateship in any University.

Cochin-682 014,
August, 2001.

(K.K.BALACHANDRAN)

CERTIFICATE

This is to certify that this thesis entitled "**Chemical Oceanographic Studies of the Coastal Waters of Cochin**" is an authentic record of the research work carried out by Sri. K.K. Balachandran, under my supervision and guidance in the Regional Centre of National Institute of Oceanography, (Council of Scientific and Industrial Research), Cochin-14 and that no part thereof has been previously formed the basis for the award of any other degree, diploma or associateship in any University.

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PREFACE

Cochin is the second largest city along the west coast of India and one of the finest natural harbours in the country. In recent years, great concern has been expressed with regard to deterioration of Cochin backwaters and consequent loss of supportive functions of this wetland system, especially due to urbanization, industrialization and agricultural activities. The impact of changes in the backwater system on the coastal waters are however, not fully known. Considering the economic importance of Cochin, these activities are expected to increase in future. The resultant increased marine transport of nutrients and other toxic metals through the backwaters are likely to upset the coastal ecosystem. Moreover, the Arabian Sea, which has been identified as one of the highly vulnerable region following its mid-depth oxygen deficiency and associated denitrification, is bordering this coast. Located between these two environmentally sensitive zones, the coastal waters are vulnerable to the changes in the backwaters as well as the Arabian Sea. Thus, the coastal waters necessitate a critical evaluation of the nature and quantum of inputs to the Arabian Sea as well as their assimilative capacities.

With a view to delineate environmental changes of such a vulnerable region, a series of chemical oceanographic studies in the coastal waters of Cochin covering seasonal signals and also that of the adjoining backwaters have been carried out. A comparison of the water quality of these two different entities based on the behaviour of some of the major environmental tracers such as phosphate and nitrate could provide valuable information regarding probable changes that may occur in the coastal waters in future.

The thesis is presented in 6 chapters. The first chapter gives a general introduction to the topic, coastal environmental issues, background information on oceanographic investigations carried out along the west coast of India, the shortfall, the need for an exhaustive study, scope and objective of the present study. The second chapter is on the materials and methods, which cover description about the study region and methodology, adopted for sample collection and analysis of chemical oceanographic parameters of water and sediment samples.

The third chapter comprises the results and discussion of the hydro-chemical parameters of coastal waters of Cochin during different seasons with statistical analysis. The parameters dealt with are salinity, temperature, pH, dissolved oxygen, nitrite-N, nitrate-N, ammonia-N, silicate-Si, phosphate-P, chlorophyll 'a' and suspended solids, dissolved trace metals and sediment characteristics including sediment metals. The fourth chapter furnishes an account of water quality and trace metal levels in the Cochin backwater system and delineate the environmental conditions of the system.

A long-term scenario of environmental quality of the Cochin backwaters, coastal waters and the stability of coastal region is presented in chapter 5.

The sixth chapter gives the summary of the thesis. This chapter is followed by the list of references cited in the text and published papers of the candidate.

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CHAPTER 1

INTRODUCTION

Coastal waters form a multi-dimensional system where the dynamic processes are rarely in equilibrium. Compared to the open ocean systems, the coastal region exhibits environmental gradients occurring spatially and temporally on micro or macro-scale. The study of the chemical and physical aspects of the nearshore environment provides background information necessary for the understanding of the coastal oceanographic processes. There is a greater potential in applying the tools of modern oceanography and chemistry to unravel the geological, biological and anthropogenic coastal processes.

Bigelow, (1930) initiated studies in this direction by observing temperature cycle on the continental shelf, Cape Cod to Chesapeake Bay. Ketchum (1955) examined the interaction of freshwater and seawater in coastal regions, which was treated as a "gigantic estuary". This approach must be considered as one of the major advancements in the study of the coastal ocean environment. Currently the coastal water body is receiving close attention especially with respect to hydrography, biological production and fertility. The structure of the physical and chemical environment is commonly expressed in terms of water quality parameters such as temperature, salinity, dissolved oxygen, nutrients, metal concentration, pigments etc. Hydrogeochemical factors can influence the colour, odour, taste, temperature and degree of mineralisation of water derived from surface runoff, underground springs etc. (Clark and Snyder, 1970). Studies on the distributional and biogeochemical characterisitics of nutrients in coastal waters can provide satisfactory assessment on the bioavailability of various nutrients.

The coastal areas of the tropics are productive except turbid near river mouths, where light penetration is poor. In shallow areas, the high productivity is accounted by the increased regeneration rate of nutrients due to high temperatures accelerating all bacterial processes at the bottom (Nair et al., 1973). One of the major findings of the International Indian Ocean Expedition during 1962-65 was the extremely high rates of primary production and large standing crops of phytoplankton and zooplankton along the western regions of the Arabian Sea (IIOE, 1972). The values of primary production and standing crops in the central Arabian Sea are higher than the average values encountered in the world oceans (Wooster et al., 1967). The maximum production was reported nearer to the coasts, within 50 m depths and gradually decreasing seaward (Nair et al., 1973). High rate of production was also noted in the shallow waters of the coastal regions of Laccadive and Minicoy islands (Prasad and Nair, 1960).

The west coast of India experiences a time dependent wind stress due to monsoons (Pankajakshan and Rama Raju, 1987); so also the phenomenon of upwelling (Sastry and D'souza, 1972; Ramamritham and Rao, 1973; Basil, 1983). Charney (1955) showed that in presence of stratification and thermocline displacements, due to upwelling or downwelling, affect only a strip of a few kilometers adjacent to the shore. Upwelling may be coupled with undercurrents, which move the mud deposits from deeper areas to shallow regions (Gopinathan and Qasim, 1974). One effect of upwelling is to force fish and prawns to move closer to the shore to avoid the oxygen deficient waters (Sankaranarayanan and Qasim, 1969). The width of the continental shelf along the southwest coast of India is found to vary from place to place. It is narrower on the southern side and wider on the northern side (Gopinathan and Qasim, 1974). In upwelling region the downward transport of nutrient elements is reversed seasonally and the surface waters get replenished with nutrients (Spencer, 1975).

Man-made changes of the marine transitional systems like coastal marine areas and estuaries have increased rapidly worldwide over the last decades affecting the natural dynamic equilibria and the biotic composition of the respective ecosystems. The main causes for such changes are introduction of untreated and partly treated sewage rich in organic substances and plant nutrients from human settlements, urban areas and certain industries, leaching of nutrients from soils and agricultural fields and animal husbandry.

In global terms, the quality of coastal water is declining, particularly in estuary, with estimated stocks of species decreasing and vitally important habitats being destroyed or being degraded. It is estimated that the world's fleet of 35,000 commercial ships release several thousands m^3 of water every hour, which have been taken on board at a distant port, thus introducing thousands of new species to another port on the globe (Gilbert Barnabe and Regine Barnabe, 2000). It is also estimated that 600,000 tonnes of hydrocarbons are released into the sea each year, although oil pollution from ships decreased by 60% between 1981-89. In addition to these impacts, marine coastal waters receive fresh water from rivers and urban waste, either treated or untreated. These inputs often upset the coastal water ecology.

The west coast of India is environmentally more sensitive than the east coast primarily because it is bordering one of the most sensitive ecosystems in the world, the Arabian Sea. The environmental property of the northern Arabian Sea is unique which manifests in rich biological production throughout the year through different processes and thus, explain for the Arabian Sea 'paradox' (Madhupratap et al., 1996). The mid-depth oxygen deficiency in the Arabian Sea is perhaps the most severely observed anywhere in oceans, as the concentration within ~ 150 – 1000 m are less than 0.1 ml/l within a large part of central and northeastern Arabian Sea (Naqvi and Jayakumar, 2000). This zone is characterised by intense denitrification, which is observed only in 3 regions among world oceans, the other two being observed in the Pacific. With such a delicate biogeochemical balance that exists in the oceanic oxygen-deficient zones, the Arabian Sea will perhaps be among the first to react to potential anthropogenic perturbations such as increased nutrient/organic loading (Naqvi et al., 2000). Any alterations in the rate of mid-depth water renewal or in sub surface oxygen demand may bring about large changes in chemical fluxes. Similarly, an expansion of the oxygen minimum zone, particularly towards the coastal zone, may also have deleterious effects on biological resources as evident from mass mortality of fish reported off Cochin during southwest monsoon, 1998 (Naqvi et al., 1998). It is still not clear as to how the suboxic ecosystem in the Arabian Sea will respond to changes induced by man.

There is an apprehension that environmental deterioration of coastal and estuarine waters will inevitably have consequences for the Arabia Sea's ecosystem. The symptoms are on as there is the impact of deterioration of estuarine waters on the coastal ecosystem (Nair et al., 1992; Naqvi et al., 2000; Jayakumar et al., 2001). The emerging big cities associated with industrial establishments and human settlements situated along the west coast of India, thus necessitates a critical evaluation of the nature and quantum of inputs to the Arabian Sea as well as their regional assimilative capacities. If there is a possible threat to the well being of the living resources of EEZ of India, then the coastal waters of southwest coast of India, and in particular, Cochin is one of the prime locations prone to trigger it. Being the second largest city along the West Coast, the coastal circulation of this region is critical because, as compared to the Mumbai coast where the mean tidal height is > 3 m, the southwest coast has only one meter. Because of the low tidal amplitudes, these coastal regions have small inter-tidal expanses, perhaps the smallest among the Indian coasts. This results in incomplete flushing, leaving behind parcels of perennially undulating water. Any substance released in such a waterbody will always have a fraction of it left behind, however small that might be whose residence time will continuously increase with increasing number of oscillations (Sen Gupta et al., 1989). Therefore, to estimate the carrying capacity or assimilative capacity of any coastal waters, it is imperative to critically examine the residual tidal effect of any eventual pollutant in their waters (Sen Gupta and Geetanjali Deshmukhe, 2000).

Cochin, the biggest city along the west coast of India after Mumbai, is one of the finest natural harbours of India and provides safe anchorage even during the roughest monsoon months. The booming city of Cochin has population of nearly 1.5 million (Anon, 1998) and 60 % of the chemical industries of Kerala are situated in this area (Table.1.1). Cochin backwaters are the largest of its kind on the west coast of India, occupying 256 km^2. The backwaters play a significant role in the socio-economic and cultural history of the State besides constituting an invaluable aesthetic resource (Anon, 1998). In recent years, great concern has been expressed with regard to deterioration of Cochin backwaters and consequent loss of supportive functions of this wetland system, especially due to urbanization, industrialization and agricultural activities in the downstream zones of the rivers. The 16 major and several minor industries situated in the upstream region of the backwaters discharge nearly 0.104 $Mm^3.d^{-1}$ of effluents (Anon, 1996), causing large-scale environmental pollution. Apart from this, the backwaters also receive organic wastes (~ 260 td^{-1}, Anon, 1998) from domestic sewage, coconut-husk retting yards, fish processing plants etc. The main factors affecting the coastal waters apart from sewage are fish processing, navigational dredging and dumping of dredge spoil and sand mining for filling and construction. In addition, the annual dredge spoil from the harbour area alone come to the tune of $10^7 m^3$, which are dumped in the coastal seas. To summarize all, as the system has been subjected to irrational economic exploitation during the past five decades, the environmental deterioration has ultimately resulted in ecological degradation. All these factors indicate that the coastal waters of Cochin are prone to receive a significant portion of the wastes arising from the increased developments finding their way to the backwaters.

1.1. Scope and Objectives

The basic requirement to characterise a coastal water body is to have systematic chemical oceanographic (environmental) data at close grids of the

Table.1.1 Potentialities of Cochin backwaters

Backwater area	256 km^2
Barmouth	450 m x 12 m
Population	1.5 million
Population density (Cochin Corpn.)	5500persons/km^2
Reclaimed backwaters (upto 1985)	700 ha
No. of major Industries (Cochin)	16 (Kerala 26)
Industrial effluents	0.104 Mm^3.d^{-1}
% of effluents from Kerala	69
Domestic sewage	~ 260 t.d^{-1}
Dredging	10 ^{7}m^3.y^{-1}
Fertilizer used (in Kuttanad)	20,000 t.y^{-1}
River discharge	~ 19,000 Mm^{3}y^{-1}

region covering seasonal signals and evaluate the results with the existing oceanographic processes along the coast. An integrated study of this dimension has not been carried out so far along these regions, which lead to take up this study. Eventhough information is available along the southwest coast of India, regional importance are missing and spatial intervals not less than one degree and regions of less than 30 meters are not studied intensively. With a view to delineate environmental changes of such a vulnerable region, detailed chemical oceanographic studies have been undertaken to monitor water quality and sediment characteristics of coastal waters of Cochin (Fig. 1.1). The survey provides important background information necessary for the study of the coastal processes.

The objective of this study is to evaluate the chemical oceanographic parameters of the coastal waters off Cochin during different seasons and also that of the adjoining backwaters and to make a comparative study of the water quality of these two different compartments to understand the probable changes that may arise in the coastal waters based on the behavior of some of the major environmental tracers like phosphate and nitrate.

1.2. Coastal waters

The Arabian Sea, which forms the western boundary of India, is under the influence of changing wind patterns associated with the summer and winter monsoons. Along the west coast of India, the surface currents are south to southeasterly from April to September and northwesterly from November to January. The Indian Ocean manifests the largest seasonal surface wind variation of the three major ocean basins. The southwest monsoon may persist from May to October and is characterized by a low-level jet (Findlater, 1977) directed from southwest to northeast over the Arabian Sea. During the northeast monsoon (variable between November and March) the winds reverse direction but do not approach the strength of the summer monsoon flow (David Young and John Kindle, 1994).

Fig . 1.1 Satellite imagery of Cochin region

(Source : IRS - IC /L - III of 18-01-2000, NRSA, Hyderabad)

According to Shankar (2000), coastal currents around India change direction with season. From November to January, the current off the Indian east coast, the East India Coastal Current (EICC), is equatorward all along the coast. It bends around Sri Lanka to flow along the Indian west coast as a poleward West India Coastal Current (WICC). The EICC reverses in February, and flows poleward during March-May, forming the western boundary current of a basin-wide anticyclonic gyre. The anticyclonic high off southwest India persists through March-April, weakening thereafter and giving way to a cyclonic low during the southwest monsoon (June-September); during this period, the WICC flows equatorward along much of the Indian west coast; it is poleward in the south, but is equatorward in the north.

The coastal zone of western India experiences upwelling from June to October (Banse, 1959; 1968; Ramasastry 1959; Ramasastry and Myrland, 1959; Naqvi et al., 2000). The studies by Shetye et al., (1990; 1994) led them to conclude that upwelling was largely forced by local winds. However, unlike the other two better-known centers located in the Arabian Sea of Somalia and Oman, upwelling off India is not entirely forced by local winds; instead a remote forcing from Bay of Bengal involving a coastally-trapped Kelvin wave appears to be equally, if not more, important causative mechanism (Shankar, 2000). The weaker wind forcing makes the vertical and cross-shelf advection somewhat sluggish. Moreover, the cold, saline upwelled water is usually capped by a 5 to 10 m thick warm, low-salinity layer formed due to a combination of large land runoff and local precipitation, causing strong stratification and poor ventilation of sub-pycnocline waters.

The upwelled water is derived from a poleward undercurrent, located just off the shelf break (Shetye et al., 1987), which has oxygen content of about 0.5 ml/l at 15°N. Over the shelf, the oxygen content is quickly depleted to near-zero levels owing to excessive consumption fuelled by high primary production mainly within the pycnocline (> 500 mg.C.m^{-3}d^{-1}, Jayakumar et al., 2001). As the season progress, severely hypoxic (dissolved oxygen < 0.5 ml/l) waters are found over almost the entire western shelf (Naqvi et al., 2000).

The sub-pycnocline oxygen depletion over the western Indian shelf, as in other similar environments off Namibia (Calvert and Price, 1971) and Peru (Codispoti and Packard, 1980), has been attributed primarily of natural origin because the nutrient enrichment occurs mainly through upwelling. These conditions start developing in June, reach peak intensity by September-October and dissipate by December. Thus, this shallow, seasonal suboxic zone is distinct from the deeper, perennial suboxic layer of the central Arabian Sea (Naqvi, 1987). The seasonal hypoxic zone on the Indian shelf is separated from the perennial suboxic zone of the central Arabian Sea by an undercurrent that transport waters with higher oxygen contents northward off the continental slope (Naqvi, 1987). The oxygen deficiency off western India was first noticed in 1950's (Banse, 1959; 1968; Carruthers, 1959) based on limited measurements in the inner shelf.

From May through September, during the southwest monsoon period, the mean flow continues southward in the upper layer. Upwelling of the Arabian Sea Water of salinity higher than 35 psu, is the dominant process during this period (Johannessen et al., 1987). This is evidenced by the lifting of the isotherms, with a shoaling and sharpening of the thermocline, and the penetration of the low oxygen water (< 0.5 ml/l) over the entire shelf. Another feature is the lowering of the surface salinity in the near shore region associated with the runoff due to south-west monsoon rains.

During the northeast monsoon period (November to February) the current reverses, advecting less saline Equatorial Surface Water from the equatorial region and Bay of Bengal northward, causing a sinking or retreat of the Arabian Sea Water (Johannessen et al., 1987; Pankajakshan Thadathil and Aravind Gosh, 1992; Muraleedharan et al., 1995; Hareesh Kumar and Basil

Mathew, 1997). Diminishing of the anticyclonic basin gyre and its slight contraction to the south and west evince the relaxation of southwest monsoon forcing. Associated with this westward propagation, the southward flow along the west coast of India propagates offshore (David Young and John Kindle, 1994).

The five-year study along the Kerala coast by Johannessen et al., (1987) showed a more repetitive pattern of the seasonal variation from year to year than could be demonstrated by the two-year studies by Darbyshire (1967), who concluded that the two-year study showed very different conditions and no conclusions was able to draw. They observed the upwelling to intensify in August-September, causing penetration of low-oxygen water over the entire shelf north of Quilon (~9°N), while south of Quilon it is less significant. The influence of land runoff was traced upto 60 nautical miles offshore. They have also observed changes in biological events: a peak in the plankton production associated with upwelling and pelagic fish concentrating in the surface layer due to the oxygen deficiency below the oxycline, and some species disappearing from the northern part of the shelf during the southwest monsoon months. Withdrawal of demersal fishes from bottom waters having oxygen saturation < 10 % have been reported by Banse (1959). Ramasastry (1959) observed that during southwest monsoon upwelling along Kerala Coast, the Arabian Sea surface water is displaced by the upper subsurface water, resulting a complete overturning in the entire water over the continental shelf.

International Indian Ocean Expedition (1962-65) recorded the nutrient data along with other parameters in the Arabian Sea and Bay of Bengal (Wooster et al., 1967; Rao and Jayaraman, 1968; Sankaranarayanan and Reddy, 1968; Varadachari et al., 1968). The earlier reports on the nutrient characteristics of Bay of Bengal were made by Jayaraman (1951); La Fond (1957); Ganapati and Sarma (1958); Sen Gupta et al., (1977); Rajendran et al., (1980); De souza et al., (1981) and Rao and Satyanarayana (1982).

Satyanarayana et al., (1987) reported the nutrient distribution of Bay of Bengal waters. Distribution of phosphates and silicates in the central western north Indian Ocean was reported by Reddy and Sankaranarayanan (1968). Sen Gupta et al., (1976a) studied the relationship between dissolved oxygen and nutrients in the north-western Indian Ocean. The nutrient fractionation and stoichiometric relationship in the northern and eastern basin were reported by Sen Gupta et al., (1976b). De Souza and Singbal (1986) presented the relationship of phosphorus and nitrogen compounds with the dissolved oxygen in the water masses of central Arabian Sea.

The chemical oceanographic features of Arabian Sea have been exhaustively studied by Banse (1959; 1968); Reddy and Sankaranarayanan (1968; Sankaranarayanan and Reddy (1970); Sen Gupta et al., (1979; 1980); Qasim (1982); Naqvi et al., (1982; 1993; 2000); Naqvi and Qasim (1983); Sen Gupta and Naqvi, (1984); Naqvi (1987; 1991; 1994); Naqvi and (1991) and Naqvi and Jayakumar, (2000).

During summer monsoon period, the nutrient values of the coastal waters shoot up, surface salinity and water temperature come down, detrital load increases and consequently light penetration diminishes. These rapid changes often lead to very high production at primary and secondary levels (Devassy, 1983; Madhupratap et al., 1990). Red tide caused by Noctiluca is a regular feature along the coastal waters and estuaries, especially during August, April and November, thus, exhibiting annual feature (Venugopal et al., 1979; Devassy and Nair, 1987). Even after the upwelling event tapers off, the effects are observed to last for a good part of the ensuing season (October-January) also. In Cochin backwater, the standing crops of phytoplankton reaches peak by the end of October (Devassy, 1983). Surface warming and increase in salinity are identified as preconditions for the onset of *Trichodesmium* blooms during Febrauary-April (Qasim, 1970; Ramamurthy et al., 1972; Devassy et al., 1978). *Trichodesmium* filaments are known to fix nitrogen and release it into the environment on its decay

(Devassy, 1983). Incidences of blooms of phytoplankton, discolouration of coastal and estuarine waters and swarms of zooplankton have been reported as regular features along the west coast of India (Nair et al., 1992). They have also found that this area is subjected to episodic introduction of nutrients during the summer monsoon through river run-off and coastal upwelling. Responses of phyto- and zooplankton to such inputs are often predictable and have been observed to form persistent patterns in numerous investigations. Spectacular bloom formations of *Trichodesmium* is a regular phenomenon during the later part of the NE monsoon season. At times, these blooms cover hundreds of kilometers.

Qasim et al., (1978) has exclusively studied the biological productivity of coastal waters of India. Compared to Cochin backwaters, the coastal waters are found to be less productive in zooplankton standing stock (Haridas et al., 1980). However, sudden increase of zooplankton swarms as a result of upwelling could occur in coastal waters (Madhupratap et al., 1977; 1980). Despite the high zooplankton productivity, the transfer coefficient from primary to secondary level was only 7 % in Cochin backwaters. This excess production in the backwaters might be contributing to the productivity of coastal waters, sustaining rich benthic biomass reported from this region. The species diversity progressively increased from 3.7 in the estuary to 5.9 in the coastal environment (Madhupratap, 1980). Benthic studies of Cochin coastal region by Harkantra and Parulekar (1987) revealed decrease in population density with depth and mainly constituted of polychaetes.

The studies by Hashmi et al., (1981) revealed deposition of clay-sized sediments in the nearshore regions by the process of flocculation, which resulted in trapping of coarse particles in the Cochin-Quilon coast. Higher degree of alteration is observed in the sediments of Central Kerala Coast suggesting its origin during Holocene period and the relict sands subsequently got mixed with the modern clay sediments supplied by coastal processes to form the present type of mixed sediments (Prithviraj, 1991). Compared to cross shelf transport, along shelf transport appear to be the more dominant mechanism for sediment transport on the western continental shelf of India (Ramaswamy, 1987). Ramaswamy and Nair (1989) have reported that the anthropogenically-derived pollutants, associated with clay particles discharged from the coast, would tend to remain within the narrow confines of the inner continental shelf.

The shoreline along Cochin has been classified under barrier beaches and the changes in morphology in response to different seasons are studied by Prasannakumar and Murthy (1987). They have observed differential wave activity together with static mud suspension at places in the nearshore region. Similar studies by Shenoi et al., (1987) have found an offshore mud bank that protects Narakkal region during southwest monsoon, as this region experienced the least shoreline variability. These observations are confirmed by wave refraction studies of Sajeev et al., (1997), in addition, they reported that Vypeen region experiences convergence of wave energy almost throughout the year.

1.3. Mudbanks of Kerala

The description mentioned above are the general oceanographic features observed in the Arabian Sea and along the southwest coast of India. This discussion, however, will not be complete unless a brief history about a unique feature appearing only along the southwest coast of India – the mudbanks- is given, which occupy the present study region. Mudbanks, locally called ***Chakara*** or zones of biorythm (Balchand et al., 1987) are those areas of sea adjoining the coast, which have a special property of dampening the waves resulting in clearly demarcated areas of calm turbid waters during the roughest monsoon period. Along the continental shelf between Mangalore and Quilon, the nature of bottom about 3.5 to 18 m depth is largely muddy. During monsoon, because of the wave actions and rip currents, the fine mud particles get churned up into a thick suspension (Udaya Varma and

Kurup, 1969) in which the wave energy gets consistently absorbed. This annually occurring feature has a semi-circular shape and is unique in many ways. There are several theories of formations of mud banks and their characteristics as put forward by Gopinathan and Qazim (1974); Jacob and Qasim (1974); Kurup and Varadachari (1975); Kurup (1977); Balchand et al., (1987); Nair (1990); Nair et al., (1992; 1993); Nambisan et al., (1987) etc. Mudbanks, as they appear and disappear in the sea, have been considered as unique formations experienced only along Kerala coast. Mudbanks are well known for their fishery during the monsoon months.

1.4. Estuarine studies

An estuary may be defined in several ways. One of the most suitable and widely adopted definitions is that offered by Cameroon and Pritchard (1963). "An estuary is a semi-enclosed coastal body of water which has free connection with the open ocean and within which seawater is measurably diluted with freshwater derived from land drainage". An alternative suggestion has been provided by Hedgpeth (1967), as "The estuarine system is a mixing region between sea and inland waters of such shape and depth that the net residence time of suspended matter exceeds the flushing time".

It is within the estuaries that seawater and land derived freshwaters are mixed, producing wide range of brackish waters of intermediate salinities. In this process, both fresh water and saline water interact physically and chemically. Secondly, the estuaries are aquatic environments within which there are interactions of the suspended matter, with the soluble constituents of a succession of fresh, brackish and marine waters. On global basis estuaries are quantitatively very important to the supply of dissolved and solid material to the oceans.

The chemical processes in estuaries are also influenced by fluctuations in estuarine conditions resulting from the variability of run off due to meteorological variations produce considerable changes in the amount of fresh water input from the catchments area and tidal conditions. These fluctuations often occur in an erratic manner in the supply of dissolved and suspended particulate matter thereby affecting the estuarine processes. The erratic fluctuations in river run off and rhythmic tidal cycle give rise to major difficulties in the sampling of the estuaries, modeling of estuarine processes and the comparison of individual estuaries with each other.

Although estuaries dominate the transport of natural weathering products to the oceans, they are also involved in the transport of pollutants. Pollution in estuaries occurs by the direct introduction of sewage and industrial wastes into them and also by the downstream transport of pollutants already present in rivers. Estuarine pollution is particularly relevant because of the fact that estuaries and their hinterlands are often sites of human settlement, commercial enterprise and recreation.

The Cochin backwaters from Cochin to Alleppey, the largest of its kind along the west coast of India form a bar built estuary with a channel forming the entrance to the Cochin harbour at Cochin and another opening further north at Azhikode. The backwater receives fresh water from six rivers namely Achen kovil, Pampa,Manimala, Meenachil and Muvattupuzha in the south and a branch of the Periyar in the north. Climatological mean of the rivers debouching into the Cochin estuary show that the river discharge varies drastically with the change in season. 33 % of the river discharge into the Cochin backwater is from Periyar. Percentage contribution from Muvattupuzha, Achenkovil, Pampa, Meenachil and Manimala were 24.2, 5.8, 19.70, 8.30 and 8.8 respectively (Srinivas, 2000). During the lean period January to May, Muvattupuzha river maintains a constant flow probably due to tailrace water from the Idukki hydroelectric power station.

The tides in the backwaters are of a mixed type, predominantly semi-diurnal with a maximum range of about 1 m and the tidal influence is felt approximately 25 km upstream. The backwaters, as the term implies, include a chain of brackish water lagoons, hundreds of miles long. These backwaters, in association with the adjoining low-lying lands, paddy fields and a network of canals form an extensive source of prawn and fish cultivation.

The backwaters adjacent to the Cochin harbour which form a part of investigation has a permanent connection to the Arabian Sea about 450 m wide, which forms the main entrance to Cochin harbour. This region is subjected to tidal influence and has all the characteristics of an estuary.

Cochin harbour, situated as it is on one of the islands (Willingdon Island) is surrounded on all sides by channels, which are being constantly dredged to permit the passage to shipping. Because of the influence of the harbour and land the entire area around Willingdon Island becomes polluted. The depth of the backwater varies considerably from place to place. Along the main channel it is maintained at about 10 to 12 m for navigational purposes while at other places it ranges from 2 to 6 m. The condition of the substrata is predominantly muddy.

The rainy season in the Cochin area extends from June to September, when there is a strong southwest monsoon and from November to January, which is the period of northeast monsoon. The annual rainfall at Cochin, based on the average of 10 years, is about 3200 mm of which nearly 75 % occurs from late May to September. The prevailing winds are southwesterly from June to September and northeasterly from October to January. For the rest of the year, the direction of the wind keeps changing. The mean wind velocity is approximately 10 to 12 km.

The industries situated at the upstream region of the backwaters are causing large-scale environmental pollution by way of industrial discharge (Table.1.1). The industrial typology includes fertilizer, pesticides, radioactive mineral processing, chemicals and allied industries, petroleum refining and heavy metal processing and fish processing. The fertilizer consumption in Kuttanad region (the main agricultural field draining to Cochin backwaters) alone is reported to be 20,239 ty^{-1} (Anon, 1998). The main factors affecting the coastal waters apart from sewage are fish processing, navigational dredging and dumping of dredge spoil and sand mining for filling and construction.

A number of multidisciplinary studies have been undertaken in the estuary during past five decades. The imbalance in the ecosystem by way of reduction in the carrying capacity of the backwaters, disruption in the life cycle of organisms, destruction of natural habitats, accumulation of pollutants, symptoms of eutrophication, tendency for over exploitation and dwindling of resources has stressed the need for the conservation of the ecosystem. Some of the important works worth mentioning in this context are Ramamritham and Jayaraman, 1963; Damodaran and Hridayanathan, 1966; Qasim and Reddy, 1967; Qasim and Gopinathan, 1969; Sankaranarayanan and Qasim, 1969; Murthy and Veerayya, 1972; Wyatt and Qasim, 1973; Manikoth and Salih, 1974; Joseph, 1974; Rajagopal, 1974; Anzari, 1974; Kurian et al., 1975; Unnithan et al., 1975; Vijayan et al., 1976; Qasim and Madhupratap; 1979, Saraladevi et al., 1979, 1991; Venugopal et al., 1980; Lakshmanan et al., 1982, 1987; Remani et al., 1983; Sankaranarayanan et al., 1984, 1986; Saraladevi, 1986; Baby and Menon, 1987; Lakshmanaperumalasamy, 1987; Gopalan et al., 1988; Nair et al., 1988; Joy et al., 1990; Nair et al., 1990; Kunjukrishna Pillai, 1991; Paul and Selvaraj, 1993; Mohandas and Ramamritham, 1993; Meenakumari and Nair, 1993; Revichandran et al., 1993; Balchand and Nair, 1994; Nair et al., 1994; Sunil Kumar and Antony, 1994; Mohan, 1995; Bijoy Nandan and Abdul Aziz, 1995b; Balachandran et al., 1996; Beenamma Jacob and Chandramonhanakumar, 1996; Rasheed, 1997; Dineshkumar, 1997; Maheswari et al., 1998; Thresiamma et al., 1998; Sheeba, 2000 and Srinivas, (2000). Partitioning of marine and estuarine sediments of this region has been carried out by Shibu et al., (1990); Nair, (1992) and Rajamani, 1994. The levels of trace metals in the water and particulate matter of Cochin estuary are reported by Nair et al., 1990, 1991.

Suraj et al., (1996) has studied clay mineralogy of Periyar river sediments and their role in the uptake of metals.

Environmental studies of similar nature have been reported from other regions also. Some of the latest references in this regard include the works of Prabhakara Murthy and Satyanarayana, (1999); Padmavathi and Satyanarayana, (1999); Deepak et al., (1999); Panigrahy et al., (1999); De Souza, (1999); Subramanian and Mahadevan, (1999); Bettina M. Loscher, (1999); Hydes et al., (1999); Palanichamy and Rajendran, (2000); Swamy et al., (2000); Corbett et al., (2000); Santchi et al., (2001) and Kieber et al., (2001).

CHAPTER 2

MATERIALS AND METHODS

2.1. Study area

While estuaries are important areas of chemical and biological processes, the intensity of chemical reactions in coastal zone far exceeds those of the open ocean. Thus, there is a need to identify the impact of estuary on the environmental changes of the coastal area. Accordingly, the strategic approach for the present study has been to divide the study area into two different environments, the coastal region (Fig.2.1 and 2.2) and the backwater system (Fig.2.3). The coastal region is studied for changing seasons and the backwaters on a synoptic scale and finally to derive the salient environmental changes in Cochin backwaters that have evolved through years to reach the present level and to monitor its impact on the coastal waters.

Coastal waters

The locations of stations are so selected that during October, as many as 56 stations from 7 transects are sampled from about 500 km^2 (between 9° 51'and 10° 09' N Lat., 76° and 76° 18' E Long.) area of coastal region (Fig.2.2). The southwest coast of India experiences intense upwelling during June to September, resulting in a complete overturning of the water column over the entire continental shelf (Ramasastry, 1959). October is thus selected for sampling because; it is during this short time that the coastal currents reverses its direction from south to north, with all possibility of developing a net resident and stratified water mass. The presence of upwelled waters combined with fresh water discharge from the backwaters may cause stratification. The stratification is not felt once the monsoon withdraws, and hence, study area has been extended to the southern region, stretching to about 100 x 23 km^2 area during February and November (between 9° 12' and 10° 12' N Lat., 76° and 76° 24' E Long.). The sampling stations are limited to 45 of 9 transects from Thottappally in the south to Azhikode in the north along the coast and approximately 25 km towards offshore. The details of the 9 transect samples during February and November is given in table 2.1.

Transects/Stations	Locations	Representation	Depth (m)
I / 1-5	Pallana	PALL	3.0 – 34
II / 6-10	Pazhayangadi	PAZH	3.1 – 34
III / 11-15	Alleppey	ALLA	2.7 – 33
IV / 16-20	Chethi	CHET	3.7 – 32
V / 21-25	Andhakaranazhi	ANDH	4.2 – 28
VI / 26-30	Kannamali	KANA	4.0 – 30
VI / 31-35	Fort Cochin	FORT	5.0 – 28
VIII / 36-40	Edavanakad	EDAV	5.5 – 28
IX / 41-45	Azhikode	AZHI	5.4 – 27

Cochin backwaters

The estuarine regions, including the harbour area are also sampled for similar oceanographic parameters to understand the possible impact of the backwaters on the coastal region. Four stations are occupied starting from the barmouth, the mid-harbour region, the Ernakulam channel, and an upstream station approximately 9 km from barmouth towards the northern limb where river Periyar is draining (Fig.2.3). Water quality monitoring has been carried out on two surveys covering simultaneous diurnal observations of a spring and corresponding neap tide during the month of November, 2000. Two hourly samples are collected from surface and bottom over a tidal cycle and analysed for various nutrients.

The observations carried out in the downstream sections of Cochin backwaters mainly targets to identify the sources and sinks of the nutrients and its variability during lean river discharge period. The quantity of nutrient salts introduced by the fresh water flow into the estuary is considerable. What happens to the large quantities of these nutrients accumulated in this estuary is not only of ecological interest, but also is relevant to water quality management. The influence of industries and sewage make the northern part of the backwaters moderately polluted, while towards the southern side, the industries are concentrated around Ambalamugal, upstream of the river

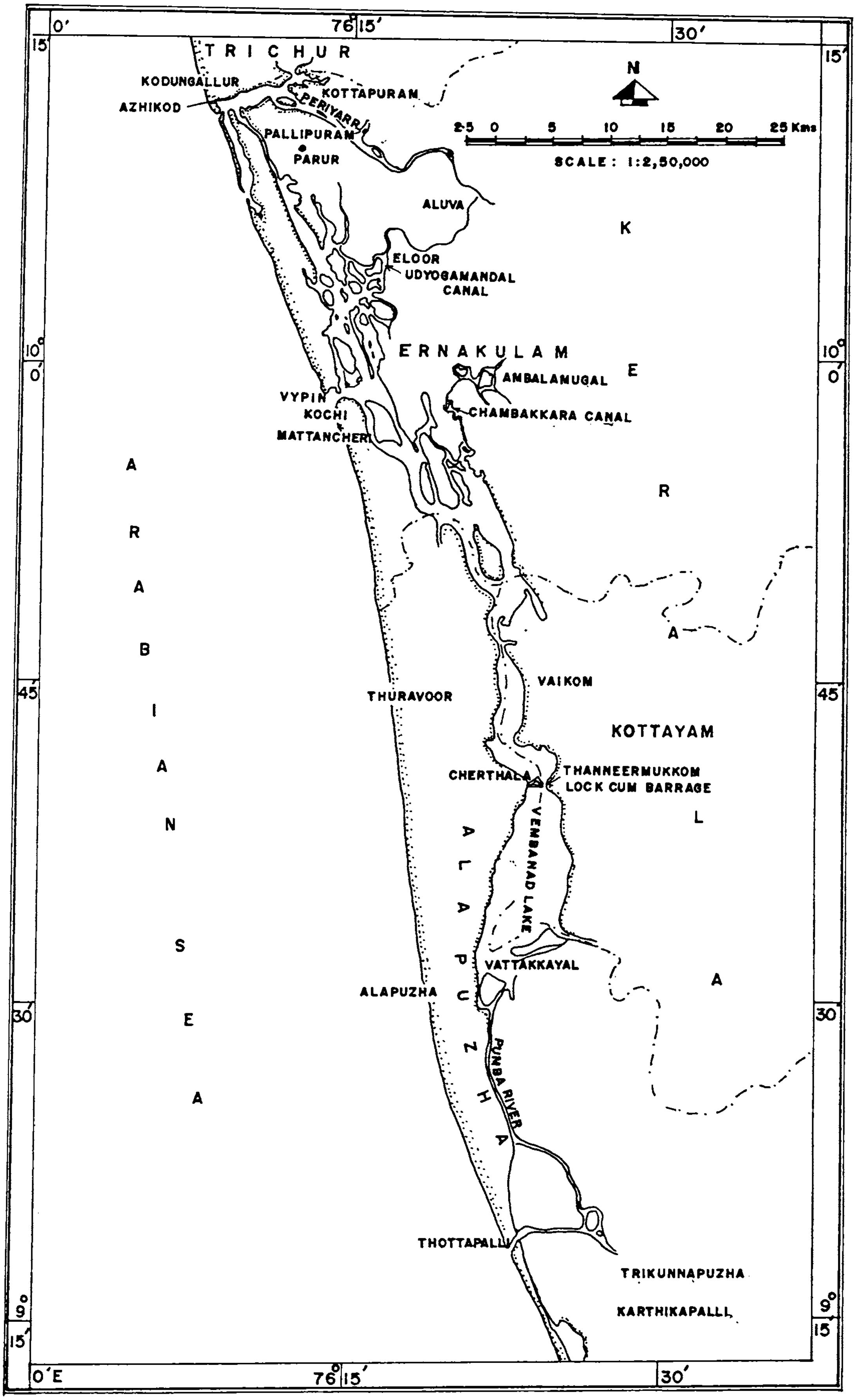
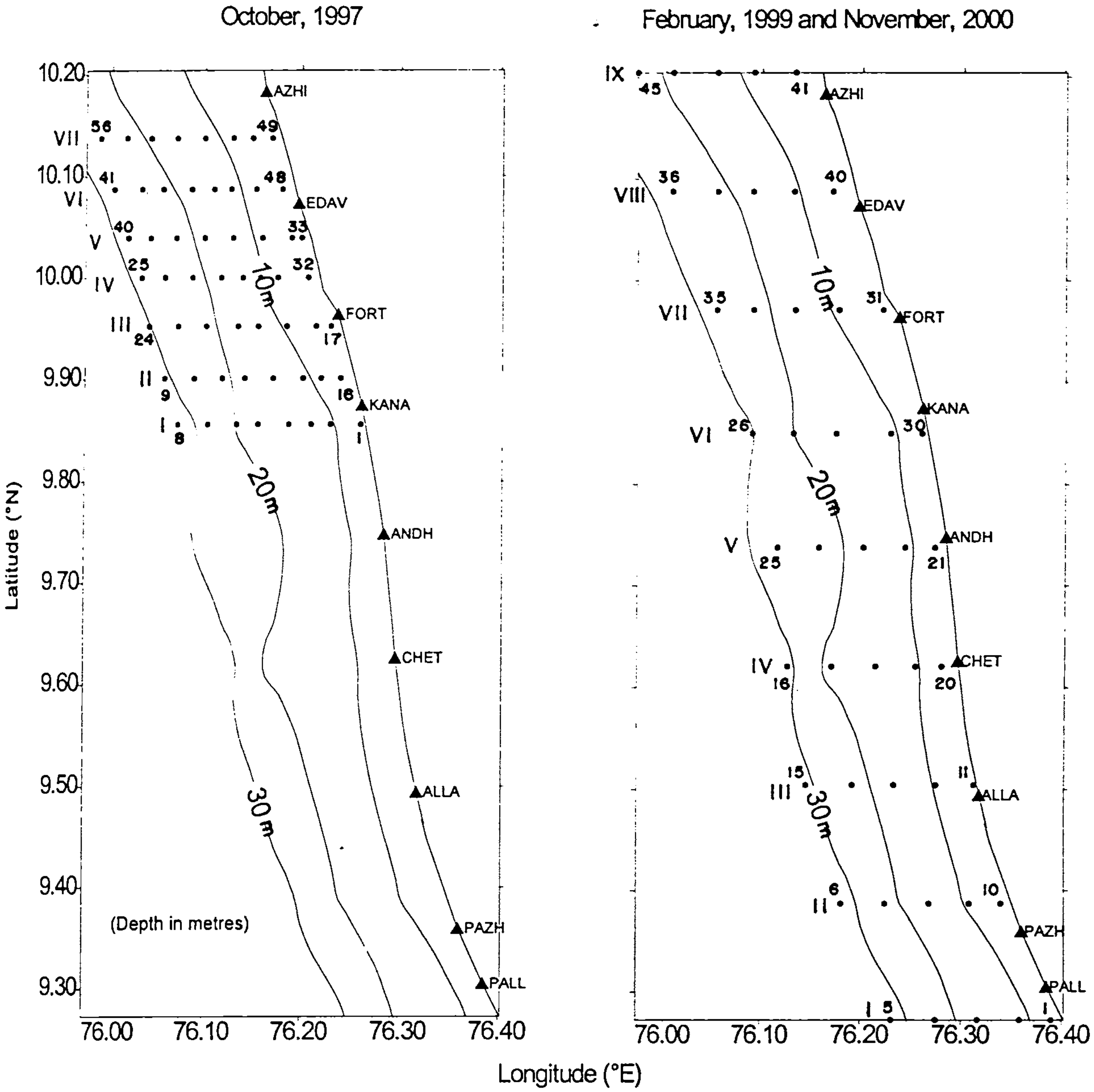


Fig. 2.1. Map showing the study area



Legend:
PALL : Pallana; PAZH : Pazhayangadi; ALLA : Alleppey
CHET : Chethi; ANDH : Andhakaranazhi; KANA : Kannamaly
FORT : Fort Cochin; EDAV : Edavanakkad; AZHI : Azhikode

Fig. 2.2. Study region with location of stations and bathymetry.

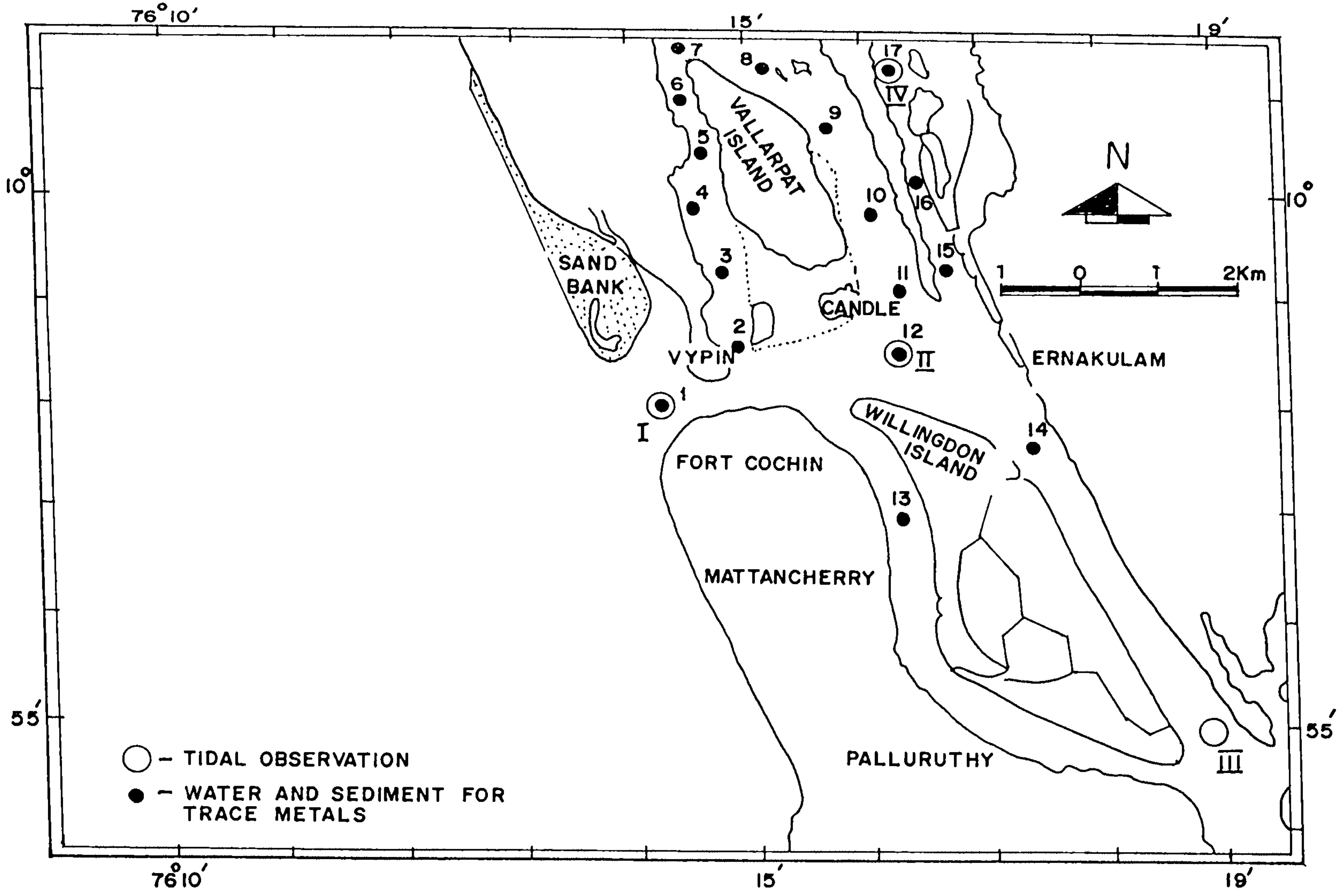


Fig. 2.3. Locations of sampling sites in Cochin backwaters.

Chitrapuzha. In order to get a brief account of the trace metal distribution in the backwater system, water and sediment samples for trace metal analysis are collected mainly from the harbour region and northern part of the estuary. Further, the survey is timed to sample the sediments of very recent origin succeeding the flushing of unconsolidated muds during the monsoon. For this purpose, water and sediment samples are collected from 17 stations during November, 2000 (Fig.2.3).

2.2. Sampling and analytical procedures

Water samples from 0.5m, mid-depth (at stations with depth > 5m) and 0.5m from the bottom are collected using all plastic 5 l Niskin samplers (Hydrobios-Kiel). Temperature and pH are recorded *in situ* and samples for dissolved oxygen are collected in 125 ml stoppered glass bottles without trapping air bubbles and fixed immediately with manganous chloride (Winkler A) followed by alkaline potassium iodide (Winkler B) solution. Water samples for the analysis of salinity and nutrients are collected in pre-cleaned polythene bottles and kept in iceboxes till analysis at the shore laboratory, within hours of collection. One litre each of water samples is collected in pre-cleaned, acid washed containers for dissolved trace metal analysis from surface and bottom at the shallow, middle and offshore stations of all transects. Similarly, one litre each of water samples are collected from surface and bottom to estimate the chlorophyll 'a' and particulate organic carbon from all the stations and kept in iceboxes till analysis. The nutrients (nitrite, nitrate, phosphate, ammonia and silicate) are analysed immediately after filtering through Whatman No.1 filter papers, following standard procedure (Grasshoff, 1983) and using a double beam Spectrophotometer (*Hitachi U-2000*), after proper calibration.

2.3. Analytical Methods

pH:

pH measurements are made using a portable pH meter (Perkin Elmer, accuracy ± 0.01) after calibrating with NBS standards.

Salinity:

Salinity is measured using an electrodeless induction type salinometer (*DIGI-AUTO model 3G*, Tsurumi Seiki, Japan, accuracy ± 0.001 psu) after calibration with standard seawater.

Dissolved Oxygen (D.O):

Dissolved oxygen is determined by the Winkler's method, in the form recommended by Strickland and Parsons (1972) with standard iodimetric titration. The principle of the determination and the possible sources of systematic errors are discussed by Grasshoff (1983).

Ammonia-Nitrogen (NH_3^+, NH_4^+) -N:

Ammonia-N is determined according to the indophenol blue method of Koroleff (1983). In a moderately alkaline medium, ammonia reacts with hypochlorite to form mochloramine, which in presence of phenol, catalytic amount of nitroprusside ions and excess of hypochlorite forms indophenol blue. The formation of monochloramine requires a pH between 8 and 11.5. At higher pH, ammonia is incompletely oxidized to nitrite. Both calcium and magnesium ions in seawater precipitate as hydroxide and carbonate at pH higher than 9.6, however their precipitation can be prevented by complexing them with citrate buffer. Great care is taken to ensure that samples, blanks and standards are not contaminated during the course of analysis. The samples are 'fixed' by the addition of reagents immediately after collection and the absorbance, after the colour development (about 6 hours) are measured at 630 nm. The measurement of ammonia included both free dissolved ammonia gas and the ammonium ions. This method estimates the sum of NH_4^+ and NH_3 and is denoted here as NH_4-N.

Nitrite-Nitrogen (NO_2-N):

Nitrite-N is measured by the method of Bendschneider and Robinson (1952). In this method, nitrite in the water sample when treated with sulphanilamide in acid solution results in a diazo compound, which reacts with N-1-naphthyl ethylene diamine dihydrochloride to form an azo dye. The absorbance of this colour complex is measured at 543 nm.

Nitrate-Nitrogen (NO_3-N):

Nitrate-N in the water sample is quantitatively reduced to nitrite by passing through a reduction column filled with copper coated cadmium granules and measured as nitrite. During the reduction stage, ammonium chloride buffer is added to the sample to maintain a stable pH (Grasshoff et al., 1983). The sample after reduction is analyzed for nitrite-N as described in the previous section.

Phosphate-Phosphorus (PO_4-P):

Phosphate-P is determined as inorganic phosphate by the formation of a reduced phosphomolybdenum blue complex in an acid solution containing molybdic acid, ascorbic acid and trivalent antimony. The most popular of the methods relying on this reaction, which was developed by Murphy and Riley (1962) is that given by Strickland and Parsons (1972). A variation of this method described by Grasshoff et al., (1983) is adopted in the present work. Instead of single solution reagent as in the Murphy and Riley procedure, two stable reagent solutions are used here. 0.5 ml of the mixed reagent containing molybdic acid and antimony tartrate followed by 0.5 ml of ascorbic acid reagent are added to 25 ml aliquots of the samples. The absorbance is measured in 5 cm cuvettes at 882 nm within 30 minutes to reduce any possible interference from arsenite.

Silicate-Silicon (SiO_4-Si):

The determination of dissolved silicate in seawater is based on the formation of a yellow silicomolybdic acid when an acid sample is treated with a molybdate solution (Grasshoff, 1983). This is further reduced by ascorbic acid in presence of oxalic acid (to prevent interference from phosphate) to a blue coloured complex (molybdenum blue). This blue color is measured at 810 nm.

Chlorophyll 'a':

Chlorophyll 'a' is estimated following the methods published by UNESCO (1966). A known volume of water sample is filtered through millipore filter paper (0.45 µm) with $MgCO_3$ suspension, the filters extracted with 90% acetone, centrifuged for 10 minutes at 3000-4000 rpm. The extinction of the supernatant solution is measured using spectrophotometer against a reference cell containing 90 % acetone at 665, 645 and 630 nm and the concentration is calculated using standard equations.

Particulate Organic Carbon (POC):

For particulate organic carbon analysis, 500ml of samples are filtered through GF/C filter papers (1.2 µm), and digested using chromic acid and back-titrated with standard ferrous ammonium sulphate (El Wakeel and Riley, 1957).

Suspended Particulate Matter (SPM):

A known volume of sample is filtered through pre-weighed Millipore filter paper (0.45 µm pore size) and the weight of the particles collected on the filter paper is gravimetrically determined to a constant weight.

Dissolved trace metals:

For trace metal analysis, extreme care has been taken in sampling and sub-sampling. Water samples are collected in acid-washed polythene jerry cans and kept in iceboxes till filtration. Known volumes of samples are filtered through pre-weighed millipore filter papers (0.45 µm) and the filtrate is acidified to pH > 2 using concentrated hydrochloric acid. The dissolved metals are extracted using Ammonium Pyrrollidine Dithocarbamate (APDC) and Methyl Isobutyl Ketone (MIBK) at pH 4.5 and brought back to aqueous layer by back-extraction with concentrated nitric acid and made upto 20 ml with mille-q water (Smith and Windom, 1972, Brook et al., 1967). The extracts are analysed in the flame AAS (*PE AAanalyst* 100)) for dissolved metals, viz: Cu, Cr, Co, Fe, Mn, Ni, Pb and Zn.

Sediment organic carbon and texture:

One portion of sediment is subjected to textural characteristics following pipette analysis (Krumbein and Petti John, 1938). The sand, silt and clay fractions are identified for all these samples. Organic carbon of the composite samples are analysed using wet digestion (Chromic acid) followed by back titration with standard ferrous ammonium sulphate (El Wakeel and Riley, 1957).

Sediment trace metals:

Sediment samples are collected at all stations by using a Van Veen grab. Sediments are scooped carefully from the middle portion without being disturbed, using a clean plastic spoon, to pre-cleaned plastic containers and are kept in iceboxes and then transferred to freezer until analysis is carried out. The samples, after drying are finely powdered and 1 gm. weighed accurately and digested with a mixture of $HF\text{-}HClO_4\text{-}HNO_3$, evaporating to dryness each time until the digestion is complete (Loring and Rantala, 1977, 1992), and brought into solution in 0.5 M HCl (25ml) and analysed using flame AAS (*PE AAanalyst 100*). The metals analysed by these three fractions are Cr, Co, Cu, Fe, Mn, Ni, Pb, and Zn after proper calibration with blanks and E-Merck metal standards.

Precision: The sensitivity and the reproducibility of the analytical procedures are checked by carrying out triplicate analysis of one set of samples on each occasion and was found comparable, and also comparable with similar studies elsewhere (Gupta and Chen, 1975). One set of certified marine sediments (BCSS) are analysed along with each analysis to evaluate the precision of analysis. The precision of the certified sediments are found to be within 10 %

except for Cd, which showed variation > 20 % and hence are not included in the present study.

Statistical analysis

Predictive models using multiple regression analysis

Chlorophyll ‘a’, particulate organic carbon and suspended particulate matter can be related to the environmental/water quality parameters by means of linear regressions. But this relation gives only the prediction efficiency of a single factor at a time. In the study of impact of environmental parameters on the ecosystem as a whole, a number of factors are jointly controlling the bioactivities at a point of time or space. Therefore, it is very essential that all the quantifiable parameters to be considered simultaneously to have the best predictive model. Pedersen et al., (1995) has given a method for choosing the minimal set of environmental variables that explain the variation in the affected parameter. Ter Braak (1990) has given a Monte Carlo permutation test that replaces the F test or the test in forward selection in univariate multiple regressions. Evonne et al., (1995) have used the interaction effect of cell mass M and taxonomic categories D_1 to D_5 in the multiple regression of representation on cell mass M and taxonomic categories D_1 to D_5. He had also stated that modeling the dependent variable only on the individual effects of the environmental parameters would become only an artifact on the production relation. Hence, an attempt is made to include the individual factors and their first order interaction effects of the environmental and water quality parameters such as temperature, salinity, dissolved oxygen, nitrite, nitrate, ammonia, phosphate, silicate and pH in the predictive model (Jayalakshmy, 1998).

Multiple regression model fitted is of the form

$$Y = a_0 + \sum_{i=1}^{k} a_k X_k + \sum_{i=1}^{k} \sum_{j=1}^{k} (X_i * X_j) b_{ij}$$

Where a_i and b_{ij}, $i, j = 1, 2, \ldots\ldots\ldots k$, $i < j$

are the regression coefficients. When independent variables are standardized using the transformation,

$Z_i = (X_i - \mu_i)/\sigma_i$ where μ_i = arithmetic mean

ie; mean of X_i and σ_i is the standard deviation of X_i , then the regression coefficients are called standard partial regression coefficients or the relative importance of the independent parameters. The model has been fitted by least square method considering the parameters and also their interaction effects of first order as the independent variables. The significance of the regression coefficients are tested using the Students' 't' statistic

$t_i = a_i / S_{ei}$ where a_i is the estimated value of the i^{th} regression coefficient and $S_{ei} = S\ (C_{ii})^{1/2}$ where S^2 is the deviation mean square and C_{ii} is the i^{th} diagonal element in the inverse of the matrix of sum of squares and products (Snedcor and Cochran, 1967).

When k parameters are considered there will be k (k-1)/2 interaction effects and total number of parameters for the model will be k + k (k-1)/2 , ie; k (k+1)/2 and total number of regression models fitted is $(2^k\text{-}1)$. The regression model of Y (dependent variable) on all the parameters (considering in each case) is also determined. Then among these 2^k prediction models, that model with highest value for the explained variability, V.E = [1 – MDSS/MTSS] * 100, where MDSS = Mean deviation sum of squares and MTSS = Mean total sum of squares, is considered. Further, the above analysis is repeated with different transformations for Y and X_i^s as

(1) Y on X_i^s (2) log Y on X_i^s (3) log Y on log X_i^s

(4) $\sqrt{Y}$ on X_i^s (5) $\sqrt{Y}$ on $\sqrt{X_i^s}$ (6) Y on $\sqrt{X_i^s}$.

Among these that model which explains the maximum variability is considered as the best predictive multiple regression model. In this model, the insignificant regression coefficients are deleted based on the t statistic, thereby reducing the number of parameters included in the model equation.

CHAPTER 3

COASTAL WATERS

Results and Discussion

The results of the survey on various physical, hydrochemical and biological parameters like temperature, salinity, pH, dissolved oxygen, ammonia-N, nitrite-N, nitrate-N, phosphate-P, silicate-Si, chlorophyll 'a', particulate organic carbon and suspended particulate matter of samples collected during the three periods of study viz. October, November and February are represented in figures. These figures are prepared as contour diagrams for the surface and bottom waters separately. Each figure depicts the distribution of one parameter over the entire study region of both surface and bottom during October (a, b), February (c, d) and November (e, f) respectively. To simplify the description, the October data is grouped into 7 transects of 8 stations each starting from south of Cochin. Similarly, the observations during February and November are grouped into 9 transects of 5 stations each. The range of various parameters measured for surface and bottom layers are furnished in tables (3.1 to 3.6). Ship drift data collected from an area bound by 8 to 11°N and 74 to 76.5° E by research and merchant ships during the years 1900 to 1993 are used in this study to delineate the coastal currents (INODC, 2000). After the necessary processing (Dr.K.V.Sanilkumar, Personal Communication), the available data are averaged for every 0.5° grids and plotted as current sticks.

3.1. Physical Characteristics

3.1.1. Currents:

The currents off the southwest coast of India vary from season to season. In general, the surface currents are southerly during pre and southwest monsoon periods (Murthy et al., 1982). These currents will weaken with the cessation of the southwest monsoon and become northerly during northeast monsoon season (Wyrtki, 1971; Johannessen et al., 1987; Shetye et al., 1994). In addition, a poleward undercurrent appears at

Table 3.1 Range in water quality parameters (October)

Transect		Temp		pH		Salinity (PSU)		D.O (ml/l)		NO2-N (μM)		NO3-N (μM)		NH4-N (μM)		PO4-P (μM)		SiO4-Si (μM)	
(St.No.)		S	B	S	B	S	B	S	B	S	B	S	B	S	B	S	B	S	B
I	Min.	29.0	26.5	7.99	7.98	31.04	32.74	3.09	2.17	0.00	0.04	0.00	0.41	0.00	0.00	0.00	0.03	0.00	1.21
(1-8)	Max.	30.8	29.5	8.23	8.27	33.82	34.46	5.09	4.80	0.63	1.30	0.82	5.19	2.36	0.39	0.88	2.31	6.97	7.23
II	Min.	28.5	26.3	7.98	8.05	30.08	32.94	3.51	1.15	0.00	0.08	0.00	0.00	0.00	0.00	0.33	0.17	4.08	4.54
(9-16)	Max.	31.2	30.1	8.24	8.32	33.18	34.49	5.09	3.74	0.69	1.19	1.62	4.19	4.48	2.43	1.23	2.36	8.61	14.94
III	Min.	29.0	26.0	7.91	8.01	30.65	34.22	2.01	2.01	0.04	0.00	0.00	0.04	0.00	0.00	0.15	0.10	3.80	4.75
(17-24)	Max.	30.0	29.0	8.27	8.27	33.82	34.51	4.13	4.51	1.22	1.33	1.12	7.81	2.53	2.55	1.35	2.55	14.10	8.87
IV	Min.	28.0	25.0	8.01	8.12	28.77	33.33	2.67	2.51	0.00	0.03	0.00	0.24	0.00	0.00	0.08	0.15	1.48	2.11
(25-32)	Max.	31.0	30.0	8.26	8.34	30.88	34.43	4.90	5.09	0.99	1.01	5.25	3.67	2.77	2.82	1.28	2.17	18.05	10.40
V	Min.	28.0	26.0	8.06	8.05	26.78	32.89	3.51	2.01	0.02	0.22	0.00	0.00	0.00	0.00	0.14	0.70	3.70	2.80
(33-40)	Max.	30.2	29.9	8.29	8.28	34.81	34.71	4.80	4.51	1.70	2.00	4.10	6.83	3.37	0.00	1.42	1.90	11.45	11.22
VI	Min.	29.0	26.5	7.92	7.94	24.90	32.07	3.51	1.50	0.06	0.12	0.30	0.56	0.00	0.00	0.06	0.05	3.70	4.65
(41-48)	Max.	30.7	30.0	8.29	8.20	31.07	34.50	4.51	4.50	1.52	1.46	3.81	6.08	0.01	0.00	1.44	2.17	13.67	10.35
VII	Min.	29.5	26.5	8.21	7.87	28.47	29.26	1.50	2.17	0.02	0.16	0.11	0.00	0.00	0.00	0.02	0.04	1.32	2.85
(49-56)	Max.	30.4	30.0	8.29	8.26	31.13	34.58	4.42	4.90	0.34	1.47	1.49	5.86	0.00	0.00	1.46	1.41	11.77	10.24
VIII	Min.	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
	Max.	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
IX	Min.	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
	Max.	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Overall	Min.	28.0	25.0	7.92	7.87	24.90	29.26	1.50	1.15	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.00	1.21
range	Max.	31.2	30.1	8.29	8.34	34.81	34.71	5.09	5.09	1.70	2.00	5.25	7.81	4.48	2.82	1.46	2.55	8.05	14.94

Table 3.2 Range in water quality parameters (February)

Transect (St.No.)		Temp		pH		Salinity (PSU)		D.O (ml/l)		NO2-N (μM)		NO3-N (μM)		NH4-N (μM)		PO4-P (μM)		SiO4-Si (μM)	
		S	B	S	B	S	B	S	B	S	B	S	B	S	B	S	B	S	B
I	Min.	29.8	29.2	7.52	7.93	31.40	31.45	4.06	4.52	0.14	0.14	1.50	2.10	0.35	0.00	0.52	0.30	3.78	2.85
(1-5)	Max.	30.3	29.8	8.11	8.15	31.53	31.55	6.55	6.77	0.32	0.48	3.07	2.75	5.61	2.46	1.10	0.79	10.76	7.62
II	Min.	29.2	28.8	8.05	8.10	31.24	31.38	4.29	3.61	0.06	0.11	2.69	1.90	0.00	0.00	0.26	0.33	1.57	1.98
(6-10)	Max.	29.8	29.3	8.15	8.15	31.38	31.63	5.65	5.19	0.62	0.65	6.09	6.27	1.79	4.59	0.78	0.92	4.07	4.89
III	Min.	30.0	29.4	8.11	8.12	31.26	31.49	3.39	2.94	0.20	0.17	6.47	6.24	0.00	0.00	0.15	0.20	7.21	6.63
(11-15)	Max.	32.5	32.4	8.15	8.17	31.64	32.02	5.19	5.19	0.70	0.56	8.35	8.37	0.48	2.04	0.39	0.99	12.91	9.95
IV	Min.	29.8	29.2	6.85	7.62	31.25	31.40	3.84	4.29	0.00	0.00	0.40	0.32	3.19	3.00	0.30	0.26	2.38	2.62
(16-20)	Max.	30.6	30.2	8.24	8.26	31.53	31.91	4.97	4.74	0.32	0.60	1.74	2.41	6.98	7.49	0.88	0.96	5.47	6.11
V	Min.	29.9	29.2	8.20	8.19	31.09	31.38	5.08	3.73	0.11	0.13	1.01	1.25	0.00	0.00	0.37	0.40	2.68	2.44
(21-25)	Max.	30.3	30.6	8.23	8.22	31.59	31.86	5.31	4.85	0.33	0.92	3.05	3.01	0.51	0.00	0.67	0.84	6.22	7.68
VI	Min.	29.9	29.2	8.05	7.93	31.12	31.47	4.52	4.52	0.05	0.22	0.73	0.75	0.00	0.00	0.31	0.49	2.97	3.26
(26-30)	Max.	30.3	29.9	8.12	8.12	31.70	32.03	6.21	5.76	0.25	0.62	2.26	4.04	0.48	0.10	0.70	0.79	7.04	7.04
VII	Min.	29.3	29.3	8.11	8.12	30.70	31.33	4.52	3.95	0.12	0.15	1.35	1.58	0.00	0.00	0.34	0.57	2.09	1.86
(31-35)	Max.	30.0	29.9	8.20	8.17	31.73	32.13	5.87	5.19	0.31	0.52	4.12	4.12	1.24	0.73	1.06	0.83	4.60	3.66
VIII	Min.	30.0	29.8	7.05	8.03	30.80	30.94	3.50	3.95	0.05	0.44	0.55	1.15	0.00	0.00	0.26	0.54	0.17	1.45
(36-40)	Max.	30.8	30.3	8.22	8.18	31.80	32.59	5.53	4.74	0.21	1.51	3.34	5.90	1.79	1.72	0.74	0.64	3.32	4.60
IX	Min.	30.8	30.0	7.86	7.92	31.11	31.16	3.39	4.85	0.03	0.07	1.52	2.45	0.16	0.00	0.43	0.46	1.57	0.93
(41-45)	Max.	31.3	31.0	8.17	9.18	31.92	32.39	5.98	5.98	0.14	2.02	3.11	7.48	5.74	0.70	0.85	0.71	3.43	6.34
Overall	Min.	29.2	28.8	6.85	7.62	30.70	30.94	3.39	2.94	0.00	0.00	0.40	0.32	0.00	0.00	0.26	0.20	0.17	0.93
Range	Max.	32.5	32.4	8.24	8.26	31.92	32.59	5.87	6.77	0.70	2.02	8.35	8.37	6.98	7.49	1.10	0.99	12.91	9.95

Table 3.3 Range in water quality parameters (November)

Transect		Temp		pH		Salinity (PSU)		D.O (ml/l)		NO2-N (μM)		NO3-N (μM)		NH4-N (μM)		PO4-P (μM)		SiO4-Si (μM)	
(St.No.)		S	B	S	B	S	B	S	B	S	B	S	B	S	B	S	B	S	B
I	Min.	29.8	29.6	7.84	7.90	34.11	34.40	3.79	3.56	0.06	0.25	0.30	0.56	0.00	0.08	0.43	0.80	4.65	5.34
(1-5)	Max.	30.3	30.3	8.06	8.02	34.92	35.58	4.86	4.62	0.46	2.03	1.64	2.65	2.04	1.04	1.70	1.37	10.57	11.04
II	Min.	29.2	29.2	7.77	7.83	31.29	32.00	3.79	3.32	0.14	0.84	0.95	1.70	0.23	0.00	0.55	0.80	5.47	7.78
(6-10)	Max.	29.3	29.8	8.11	8.08	34.88	35.30	4.50	3.79	0.77	1.44	3.28	3.05	2.90	1.88	0.83	1.78	14.63	14.07
III	Min.	29.2	29.3	7.92	7.96	32.00	34.08	3.79	3.44	0.14	0.47	0.70	1.04	1.10	0.00	0.29	0.90	1.49	2.39
(11-15)	Max.	29.9	30.0	8.17	8.14	34.86	35.12	4.27	4.38	0.60	0.82	1.88	2.30	2.36	7.07	0.94	1.37	8.01	9.00
IV	Min.	29.2	29.4	7.85	7.91	34.75	34.28	3.20	3.32	0.00	0.24	0.05	0.20	0.00	0.00	0.23	0.43	4.89	6.18
(16-20)	Max.	30.0	29.9	8.04	8.03	35.02	35.06	4.38	4.15	0.72	0.85	1.05	1.67	0.86	1.06	1.01	1.29	10.40	9.51
V	Min.	30.0	29.7	8.14	8..15	34.19	34.18	4.15	3.08	0.00	0.12	0.14	0.14	0.40	0.16	0.18	0.41	0.77	1.66
(21-25)	Max.	31.0	30.2	8.35	8.36	34.88	34.81	4.38	4.15	0.27	0.95	1.07	1.80	2.16	1.83	0.44	1.16	4.28	4.70
VI	Min.	30.0	30.0	8.03	7.95	33.70	34.43	3.67	2.84	0.09	1.04	0.31	0.87	0.00	0.66	0.28	1.43	2.38	4.52
(26-30)	Max.	30.2	31.0	8.07	8.00	35.26	35.55	4.74	3.64	0.73	1.29	4.97	5.30	4.16	2.04	0.90	2.21	5.62	9.28
VII	Min.	29.8	29.6	8.01	8.06	32.97	34.14	3.20	3.22	0.01	0.63	0.33	0.65	0.31	0.46	0.25	1.00	1.35	7.30
(31-35)	Max.	30.6	29.8	8.22	8.18	35.34	35.92	4.38	3.67	0.39	1.05	0.96	1.43	1.57	1.36	1.07	2.84	7.02	8.63
VIII	Min.	29.1	30.2	7.86	7.96	34.39	34.99	3.67	3.20	0.07	0.43	0.44	0.87	0.00	0.00	0.32	0.47	0.50	0.46
(36-40)	Max.	30.5	30.5	8.10	8.08	35.42	35.81	4.50	3.79	0.31	0.95	2.57	6.28	0.69	2.98	0.65	1.25	1.84	2.69
IX	Min.	30.0	30.0	7.84	7.94	34.60	34.94	3.56	2.96	0.34	0.46	0.56	0.46	0.00	0.00	0.53	1.00	4.89	4.79
(41-45)	Max.	31.0	30.4	8.12	8.12	35.65	35.83	4.27	3.91	0.55	1.29	1.41	2.82	2.59	2.79	1.16	2.79	8.88	9.05
Overall	Min.	29.1	29.2	7.77	7.83	31.29	32.00	3.20	2.84	0.00	0.12	0.05	0.14	0.00	0.00	0.23	0.41	0.50	0.46
range	Max.	31.0	30.5	8.35	8.36	35.65	35.92	4.86	4.62	0.77	2.03	4.97	6.28	4.16	7.07	1.70	2.84	14.63	14.07

Table 3.4 Chlorophyll a (mg/m)

		October			February			November		
TR.		Min.	Max.	Ave.	Min.	Max.	Ave.	Min.	Max.	Ave.
I	S	1.06	3.77	2.21	0.21	3.13	1.39	1.22	2.75	3.11
	B	1.29	8.79	3.64	0.38	4.70	2.06	1.63	4.28	3.30
II	S	1.56	4.92	3.27	0.99	6.57	3.31	1.23	2.17	1.63
	B	1.94	5.87	3.76	1.60	7.66	3.52	1.28	6.39	3.02
III	S	1.33	3.80	2.53	0.99	3.87	1.87	2.39	4.60	3.49
	B	1.53	5.37	3.20	2.11	7.44	4.71	0.76	3.83	2.52
IV	S	1.60	6.90	3.97	0.99	5.95	2.52	0.40	7.84	3.27
	B	1.80	3.30	2.61	1.43	5.63	2.76	1.28	2.79	1.77
V	S	0.67	5.09	3.95	1.43	8.60	5.10	1.22	7.86	4.66
	B	0.21	4.51	2.44	5.68	14.40	9.19	0.99	14.80	7.56
VI	S	1.43	13.36	4.87	0.44	2.69	1.75	0.20	4.28	2.09
	B	1.83	12.69	6.27	1.26	4.05	2.11	1.15	3.95	2.24
VII	S	1.33	8.05	3.90	1.23	4.60	3.01	1.69	6.13	3.45
	B	1.36	8..22	3.65	1.26	7.17	3.88	1.22	4.95	3.26
VIII	S	--	--	--	1.70	3.54	2.26	6.13	9.75	8.09
	B	--	--	--	2.11	6.50	3.31	1.12	5.52	2.55
IX	S	--	--	--	1.67	5.20	2.95	1.06	1.78	1.22
	B	--	--	--	1.02	7.79	3.87	1.17	1.48	1.27
Mean	S	--	--	3.52	--	--	2.68	--	--	3.44
	B	--	--	3.65	--	--	3.93	--	--	3.05

TR - Transect

Table 3.5 Particulate organic carbon (mg/l)

		October			February			November		
TR.		Min.	Max.	Ave.	Min.	Max.	Ave.	Min.	Max.	Ave.
I	S	0.13	4.03	1.15	0.00	0.63	0.35	1.69	2.94	2.23
	B	0.13	2.27	0.73	0.00	0.63	0.30	1.05	2.99	1.86
II	S	0.13	3.57	0.87	0.25	1.64	0.55	0.60	1.88	1.35
	B	0.13	0.76	0.41	0.13	2.14	0.81	1.30	1.80	1.52
III	S	0.13	1.64	0.77	0.13	0.63	0.28	1.50	2.30	1.84
	B	0.13	1.76	0.57	0.00	0.38	0.19	1.30	2.56	1.79
IV	S	0.13	3.28	0.96	0.38	1.89	0.98	1.10	2.60	1.53
	B	0.13	3.40	0.71	0.13	2.52	0.83	0.60	2.21	1.37
V	S	0.13	1.64	0.60	0.13	1.39	0.56	0.65	2.73	1.50
	B	0.13	4.41	1.06	0.13	1.39	0.63	1.04	2.99	1.87
VI	S	0.13	2.14	0.74	0.13	1.13	0.48	1.43	2.73	2.00
	B	0.13	5.04	1.29	0.25	1.01	0.73	1.56	2.34	2.05
VII	S	0.13	1.01	0.27	0.13	1.64	0.58	0.70	1.17	0.96
	B	0.13	1.39	0.52	0.13	1.51	0.56	1.04	1.30	1.14
VIII	S	--	--	--	0.38	2..02	1.01	0.52	2.21	1.35
	B	--	--	--	0.63	1.76	1.11	0.14	1.69	1.07
IX	S	--	--	--	0.25	1.39	0.61	0.78	1.95	1.38
	B	--	--	--	0.13	1.39	1.61	1.02	3.78	2.77
Mean	S	--	--	0.77	--	--	0.6	--	--	1.53
	B	--	--	0.76	--	--	0.64	--	--	1.71

TR - Transect

Table 3.6 Suspended particulate matter (mg/l)

		October			February			November		
TR.		Min.	Max.	Ave.	Min.	Max.	Ave.	Min.	Max.	Ave.
I	S	0.80	15.00	5.85	1.80	18.60	6.56	5.00	25.00	11.40
	B	4.80	140.00	41.50	0.80	25.20	10.40	7.00	53.00	19.80
II	S	0.60	53.20	10.54	2.00	32.80	14.88	5.00	20.00	12.40
	B	3.20	48.20	14.20	1.40	65.60	16.36	7.00	25.00	15.60
III	S	0.40	13.60	5.32	1.60	7.20	4.60	5.00	31.00	15.60
	B	5.20	74.20	37.30	2.60	40.60	21.40	5.00	41.00	19.20
IV	S	0.60	11.20	6.08	0.20	43.20	9.88	5.00	33.00	17.20
	B	6.20	122.00	36.30	0.80	79.00	25.00	5.00	33.00	16.60
V	S	4.00	19.80	9.05	2.60	36.60	10.56	9.00	19.00	13.60
	B	6.00	48.60	17.70	3.80	32.80	19.70	13.00	33.00	23.40
VI	S	0.60	12.80	6.20	0.60	10.60	3.12	4.00	29.00	12.40
	B	3.40	95.80	25.00	3.40	33.00	18.00	23.00	41.00	30.20
VII	S	1.00	30.40	10.07	0.40	14.40	5.36	17.00	19.00	18.30
	B	5.60	28.00	13.40	1.60	53.60	25.00	18.00	29.00	20.80
VIII	S	--	--	--	1.50	21.00	8.06	7.00	38.00	18.40
	B	--	--	--	7.10	39.00	23.40	7.00	30.00	18.80
IX	S	--	--	--	43.80	104.20	61.88	13.00	30.00	21.20
	B	--	--	--	83.60	156.20	110.50	15.00	43.00	26.60
Mean	S	--	--	7.59	--	--	13.00	--	--	15.00
	B	--	--	26.48	--	--	30.00	--	--	21.00

TR - Transect

subsurface depth during upwelling period (Antony, 1990). However, on closer examination, the currents are found to be variable for different areas and periods (Mathew et al., 1992; Muraleedharan et al., 1995). The present study (Fig.3.1) shows that during February, the direction and speed (0.2 to 0.5 knots) of currents vary for different grids. Nearer the coast, a divergence at 10 °N and a convergence at 8.5°N are observed. During October, currents become weak and more uniform with northerly direction in most of the grids, while they are non-uniform during November.

3.1.2. Temperature:

Temperature effects on water quality can be of physical, chemical and biological. Temperature affects the physical properties of water such as density, viscosity, vapour pressure, surface tension, gas solubility and gas diffusion. Temperature rise can cause stratification in ambient water; causing the overflow or underflow of the incoming water of different density. Chemically temperature affects not only the rate of reaction but also the extent to which the reactions takes place. Further, the water temperature – the easiest physical measurement – shows more significant variations seasonally than spatially and it is correlated with salinity and density.

Of the three observations, the surface water temperature (Fig.3.2) shows the lowest values during October (28.0 to 31.2 °C) followed by November (29.1 to 31.0°C) and February (29.2 to 32.5°C). October also registers the lowest bottom temperature (25 to 30.1°C) with higher values during November (29.2 to 30.5°C) and February (29.2 to 30.5°C).

The surface temperature during October along transects I to VII vary from 28.0 to 31.2°C. The entire region is however occupied by relatively cooler waters at the bottom with a vertical gradient of more than 4°C. The lowest values (25 to 27.5°C) are observed along the deeper layers of the offshore stations (stations 8, 9, 24, 25, 40, 41 and 56).

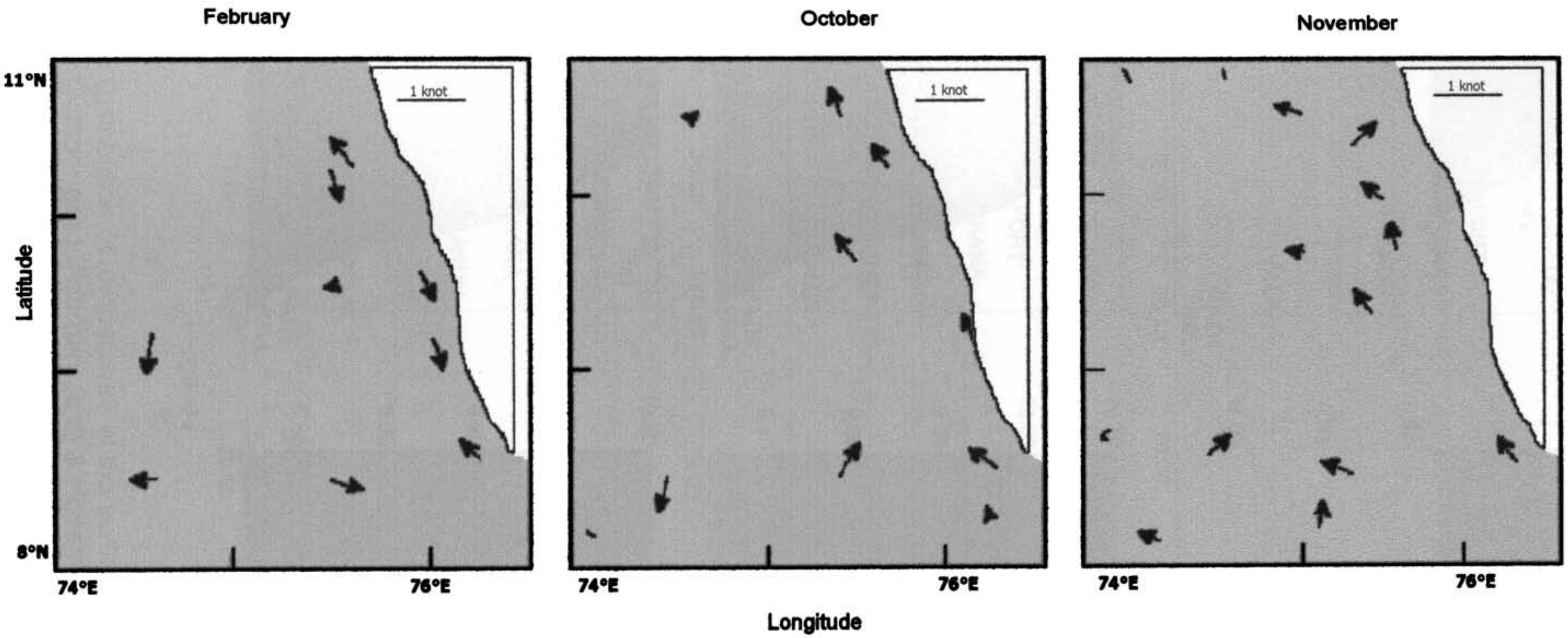


Fig.3.1 Surface currents along south-west coast of India (Data 1900-1993, Source INODC-2000)

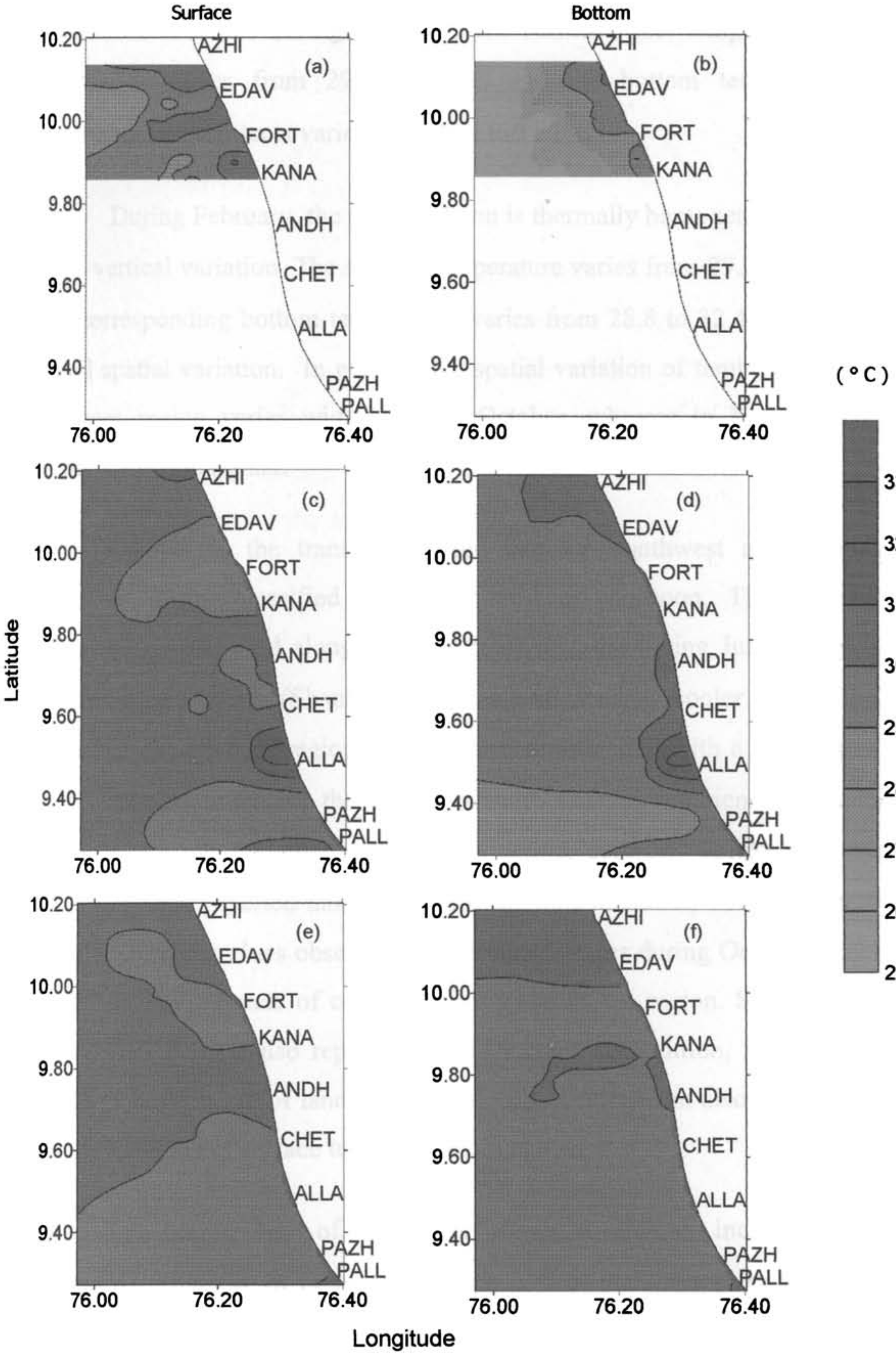


Fig. 3.2. Distribution of temperature at the surface and bottom during October (a,b), February (c,d) & November (e,f).

The water column temperature is higher during November, but lower than those observed during February. The surface water temperature during November varies from 29.2 to 31°C and the bottom temperature for corresponding transects varies from 29.2 to 31.1°C.

During February, the water column is thermally homogenous with very little vertical variation. The surface temperature varies from 29.2 to 32.5° and the corresponding bottom temperature varies from 28.8 to 32.4°C, with very small spatial variation. In general, the spatial variation of temperature in the offshore region varies widely during October, whereas in November and February it is marginal.

October is the transition period between southwest and northeast monsoon, better classified as the retrieval of monsoon. The upwelling phenomenon observed along the west coast of India during June-September persists upto October (Shankar, 2000), as evidenced by cooler (25 to 28°C) waters in the offshore region. Temperature stratification with a gradient of 2 to 4°C is also observed, the deeper offshore stations experiencing stronger gradient. During the intense upwelling period, seawater temperature upto 22°C has been reported along these coastal waters (Banse, 1959). Thus, the low temperature values observed in the bottom waters during October may be related to the presence of cold upwelled water in the region. Sastry and De Souza (1972) have also reported similar feature. In addition, the combined effect of large influx of land run-off and local precipitation also may account for the lowering of surface temperature during October.

The temperature of the water shows a definite increase during February. There is an increase of nearly 3°C at the surface for the period October to February, while at the sub surface levels the increase has been 4 to 5°C. Surface temperature between Pallana and Pazhayangadi and between Kannamali and Edavanakkad are lower (29.2 to 30.3°C). The bottom waters of Pallana and Pazhayangadi also show lower temperature and the variation is from 28.8 to 29.2°C. The maximum temperature for both the surface and bottom waters is observed along the transect III, off Alleppey, 32.5 and 32.4°C respectively. The temperature variation of the study region except transect III off Alleppey is low and is in the range of 29.2 to 31.3°C at the surface and 28.8 to 31.0°C at the bottom.

Darbyshire (1967) has classified the period between November and February as the period of sinking or downwelling. Temperature and salinity profiles during November indicate vertically mixed water column with a maximum of 1°C gradient in temperature and 1 psu salinity. As it is seen in Fig (3.1), the temperature distribution is uniform, indicating an isothermal layer throughout the study area during November.

Nair (1983, 1990), who studied the physico-chemical characteristics of the waters of mudbank region, situated south of Cochin, observed the lowest temperature (29°C) in June-July and highest in April-May (33°C). Rao et al., (1984) and Damodaran (1973) recorded such minimum temperature (< 27°C) in mudbank regions during June-July. The seasonally pooled average temperature reported for inshore surface waters of Cochin showed maximum of 30.5°C during pre-monsoon followed by 29.2°C during post-monsoon and 27.0°C during monsoon (Balachandran et al., 1989).

3.1.3. Salinity:

Salinity has been recognized as an important parameter in studying the physico-chemical characteristics of coastal waters and estuaries. The salinity distribution in coastal waters is mainly governed by factors such as coastal circulation, influx of fresh water through rivers, rainfall and evaporation. The salinity characteristics in coastal region depend to a great extent on forces such as pressure gradient, field acceleration, coriolis force, interfacial friction etc. acting on it. Thus, in understanding the different mixing processes taking place in estuaries and coastal waters, salinity distribution during different seasons of the year is a pre-requisite.

Fig.(3.3) depicts the variation of seawater salinity both at the surface and bottom during the three observations. In general, the bottom waters always remain more saline than the surface waters. The vertical gradient in salinity is maximum during October (24.91 to 34.81 psu) decreasing during November (31.29 to 35.92 psu) and is further reduced in February (30.70 to 32.59 psu).

The surface salinity during October along transect I to VII varies from 24.91 to 34.71 psu and the corresponding bottom salinity varies from 29.26 to 34.81 psu. The surface salinities of the study region during November along the 9 transects are in the range of 31.29 to 35.62 psu and the corresponding bottom salinities are in the range 32.00 to 35.92 psu. The salinity values of the waters during November are the highest of the three observations, though the vertical gradient remains low. The surface salinity varies from 31.29 to 35.65 psu and the bottom salinity from 32.0 to 35.92 psu.

During October, the surface salinity distribution shows a low saline lid of about 5 to 8 m thickness in the northern part of the section with salinity from 24.5 to 31.13 psu, while northwestern and southern region of the study area occupies comparatively higher saline water of 33.3 to 34.5 psu. This may be due to the influence of fresh water influx through the Cochin barmouth and the northerly coastal current resulting in low saline water in the surface layers. The bottom waters are high saline and it varies from 34.5 to 35.5 psu. Thus, a colder and high saline water mass, characteristic of upwelled water is present in the study region during October. The near-surface water circulation in the coastal region during this period is complex owing to the seasonal reversals forced by northeast and southwest monsoon winds. However, the tides are expected to result in significant cross-shelf oscillatory movement of surface water accounting for the offshore spreading of the low salinity surface water.

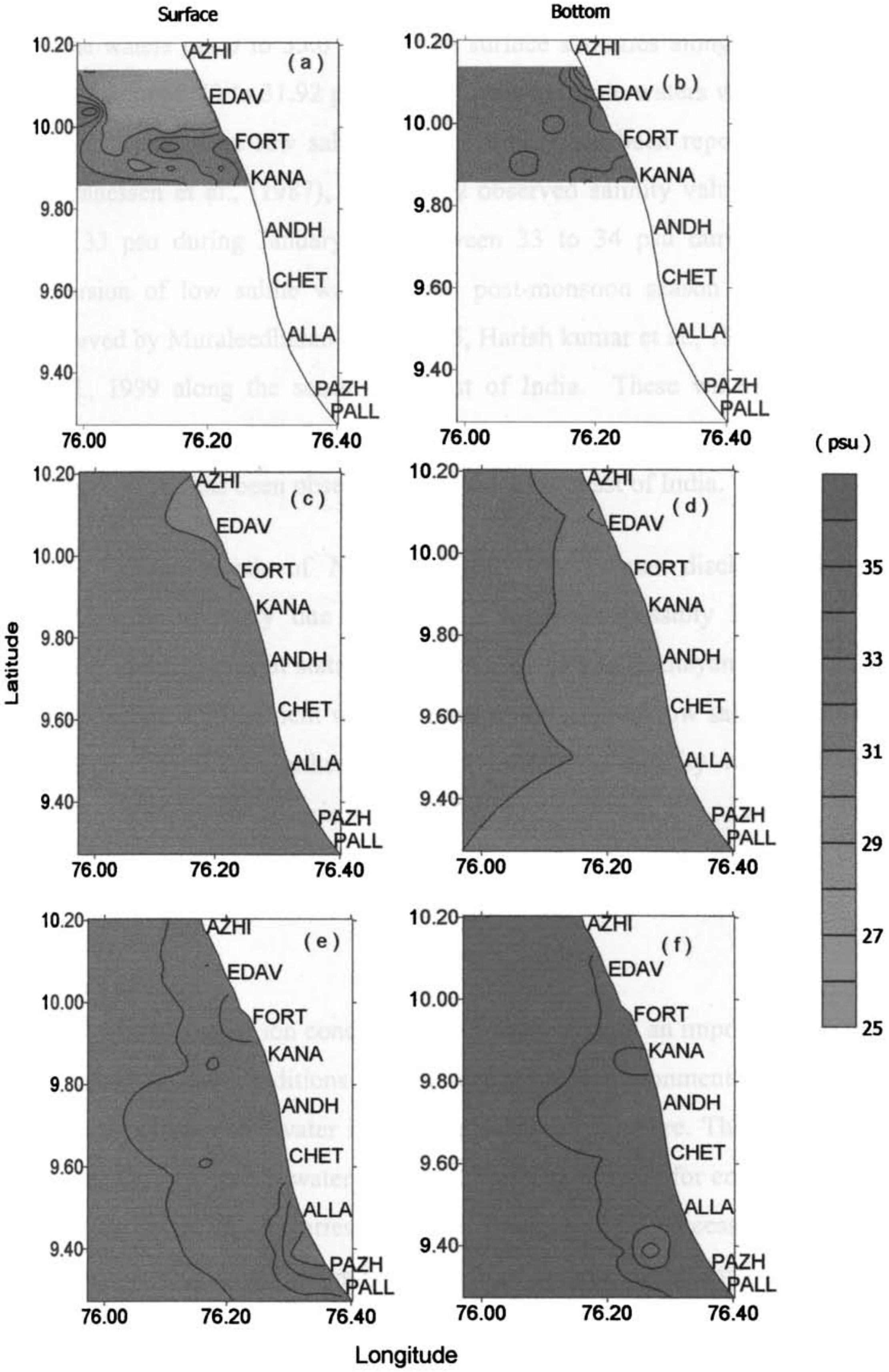


Fig. 3.3. Distribution of salinity at the surface and bottom during October (a,b), February (c,d) & November (e,f).

During the month of February, the entire region is occupied by low saline waters (31.0 to 33.0 psu). The surface salinities along the 9 transect varies from 30.70 to 31.92 psu and that of the bottom waters vary from 30.94 to 32.59 psu. The low salinity in this region has been reported earlier by Johannessen et al., (1987), where they observed salinity values between 32 and 33 psu during January and between 33 to 34 psu during December. Incursion of low saline water during post-monsoon season has also been observed by Muraleedharan et al., 1995, Harish kumar et al., 1997 and Shenoi et al., 1999 along the southwest coast of India. These waters have been identified as incoming flow of low saline water (> 33 psu) from Bay of Bengal, which has been observed along the west coast of India.

In the month of November, the fresh water discharge through Thottappally spillway due to northeast monsoon possibly influences the salinity and nutrients at stations between Pallana and Pazhayangadi, resulting in low saline high nutrient waters. Except this isolated low saline water in a small region of the southern coastal transects, the salinity values at other sections are high and it varies from 34.5 to 35.5 psu.

3.2. Chemical Characteristics

3.2.1. pH:

The hydrogen ion concentration (pH) of water is an important indicator of the chemical conditions of the depositing environment. It generally indicates whether the water is acidic or alkaline in nature. The range of pH expected for normal seawater is from 8.0 to 8.30 and that for coastal waters is from 7.90 to 8.20. It varies widely in estuaries. The processes of primary production, respiration and mineralization of organic matter may alter the pH of the system because they can cause significant changes in the oxygen and carbondioxide concentrations of aquatic environments. Gnaiger et al., (1978) suggested the involvement of photosynthesis in determining pH. Toxicity of ammonia as well as its oxidation to harmless compounds by bacteria is pH dependent.

The results of the three surveys on the pH at surface and bottom waters are given in Fig.(3.4). It may be noted from the figure that generally the surface pH is slightly lower than the bottom pH in all the three observations. The overall pH range during October, November and February vary from 6.89 to 8.34. During the month of February, the pH in the region of observation varies from 6.89 to 8.26 and shows a greater spatial variation.

During October, the surface pH variation along transects I to VII is in the range 7.91 to 8.29, while the bottom pH varies from 7.87 to 8.34 (Fig.3.4). During February, the variation in pH of the surface waters are in the range 6.85 to 8.24, with corresponding variation in bottom pH in the range 7.62 to 8.26. In November, the surface pH along transects I to IX varies from 7.77 to 8.35 and the bottom pH in the range 7.83 to 8.36. The lowest pH, 6.85 recorded is during February and the highest values are consistently observed in October bottom waters (7.87 to 8.34). The high value of pH observed during November represents the surface and bottom waters of Andhakaranazhi (transect V), where pH observed is 8.35 and 8.36 respectively.

pH is an important hydrochemical feature indicating the level of dissolved CO_2 in the water which may in turn, reflect the activity of phytoplankton and the level of dissolved oxygen in the sea (Skirrow, 1975). Qasim et al., (1978) have reported high phytoplankton production along the coastal waters of this region. The excess photosynthetic activity of algae will result in depletion of the amount of CO_2 and an increase in pH value. Similarly, the upwelled waters also influence the seawater pH to rise.

The moderate pH values observed during October may be due to the large influx of run-off associated with monsoon, which contain substantial amount of domestic and other industrial wastes. Factors like respiration,

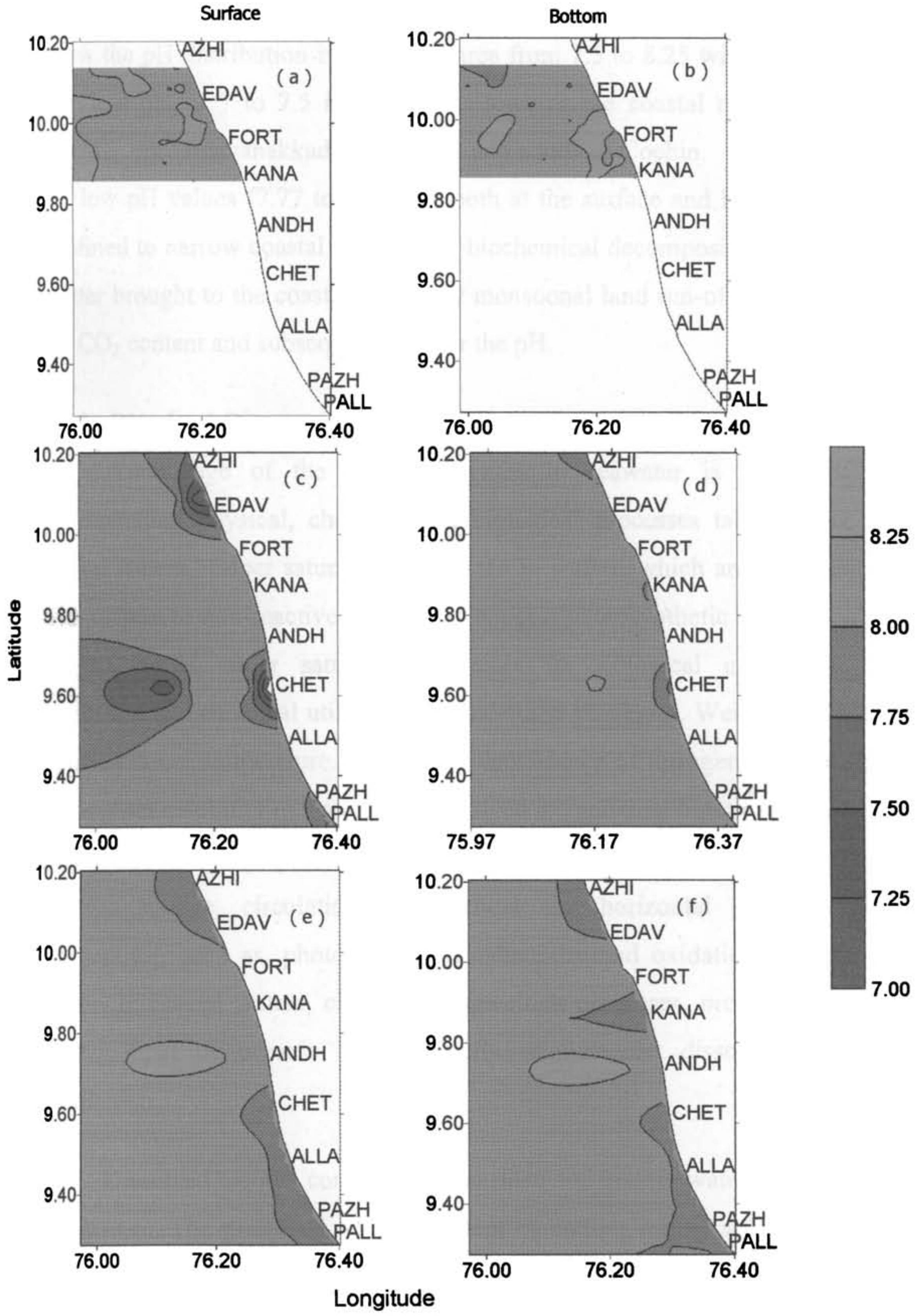


Fig. 3.4. Distribution of pH at the surface and bottom during October (a,b), February (c,d) & November (e,f).

mineralization etc. can also alter the pH of the coastal waters interlinked to the changes in oxygen and carbonate concentrations. February observations show the pH distribution in the study area from 7.5 to 8.25 with pockets of a few low pH of 7 to 7.5 in the waters towards the coastal region north of Cochin, near Edavanakkad and Chethi and south of Cochin. In Novermber, the low pH values (7.77 to 7.80) are both at the surface and bottom and are confined to narrow coastal region. The biochemical decomposition of organic matter brought to the coastal waters by monsoonal land run-off may increase the CO_2 content and subsequently lower the pH.

3.2.2. Dissolved Oxygen:

Knowledge of the dissolved gases in seawater is important in understanding physical, chemical and biological processes taking place in natural waters. Super saturation of oxygen in waters, which are equilibrated with respect to non-reactive gases, may suggest photosynthetic production of oxygen, while under saturation indicates its biological utilization for respiration and chemical utilization for oxidation processes. Weiss (1970) has formulated the temperature and salinity dependence of nitrogen, oxygen and argon gases solubility in water. The dissolved oxygen distribution in the sea is essentially regulated by two processes (i) physical, such as exchange across the sea surface, circulation and vertical and horizontal diffusion (ii) biochemical, such as, photosynthetic productivity and oxidation of organic matter. In coastal waters, circulation, upwelling processes, productivity and coastal input of organic matter chiefly regulate the dissolved oxygen distribution.

Dissolved oxygen content of the surface and bottom waters are plotted in Fig.(3.5). The dissolved oxygen content of bottom waters are in general, lower than that of the surface waters. The three observations outline distinct features in dissolved oxygen distribution characteristic of the coastal water. Overall distribution shows that during October, the dissolved oxygen levels exhibit maximum variation from 1.15 to 5.09 ml/l, followed by November,

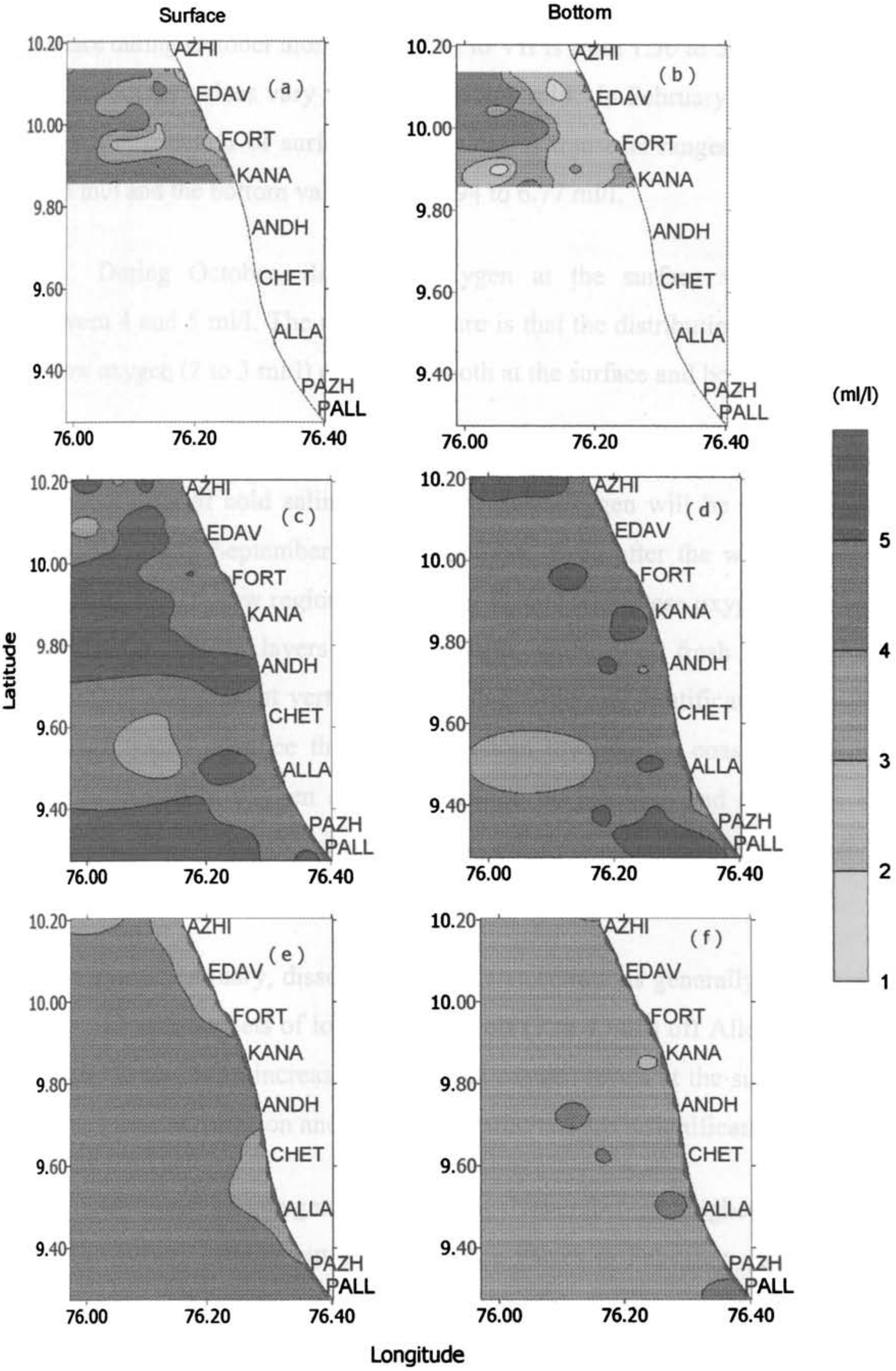


Fig. 3.5. Distribution of dissolved oxygen at the surface and bottom during October (a,b), February (c,d) & November (e,f).

2.84 to 4.86 ml/l and February, 2.94 to 6.77 ml/l. The spatial variation at the surface during October along transects I to VII is from 1.50 to 5.09 ml/l and at the bottom the values vary from 1.15 to 5.09 ml/l. In February, the dissolved oxygen distribution of surface waters along 9 transects ranges from 3.39 to 6.55 ml/l and the bottom values from 2.94 to 6.77 ml/l.

During October, dissolved Oxygen at the surface waters ranges between 4 and 5 ml/l. The notable feature is that the distribution shows a lob of low oxygen (2 to 3 ml/l) off Cochin both at the surface and bottom.

Naqvi et al., (2000) have observed that associated with the upwelling, the persistence of cold saline waters with low oxygen will be felt over the entire shelf until September or early October. Even after the withdrawal of upwelling, the shallow regions will be left behind with these oxygen deficient waters. The surface layers receiving large amount of fresh water from backwaters also prevent vertical mixing due to density stratification. As the upwelled waters advance through the bottom towards the coast, it will be further depleted in oxygen due to utilization by plankton and oxidation of organic matter. Thus, the sub-surface oxygen demand may be the causative factor of low oxygenated waters along the coastal region during this period.

During February, dissolved oxygen concentrations generally vary from 4 to 6 ml/l with pockets of low oxygen levels (3 to 4 ml/l) off Alleppey at 25 m depth. There is an increase in dissolved oxygen levels at the surface from shallow to offshore region and the spatial variations are insignificant.

The dissolved oxygen levels during November are higher than that observed during October but lower than the values in February. Generally, surface values are in the range 4 to 5 ml/l excluding the shallow regions between Cochin and Azhikode and between Chethi and Alleppey, where the values are 3 to 4 ml/l. However, bottom waters contain uniformly low dissolved oxygen of 3 to 4 ml/l. It can be presumed that these low levels of dissolved oxygen may be one of the factors leading to the comparatively higher nitrite concentrations along the bottom layers. The surface replenishment from atmospheric transfer, accompanied by photosynthetic activity result in dissolved oxygen content of surface waters to be slightly higher than sub-surface waters. More over, the process of oxidation of organic matter may also regulate the dissolved oxygen content of sub-surface layers (Naqvi et al., 2000). Particulate organic carbon shows high concentrations during this observation (upto 3.78 mg/l). Hence, it can be concluded that the high particulate carbon during November consumes the available dissolved oxygen for oxidation and subsequently reduce the ambient levels. The increased dissolved organic matter in the mudbank regions are reported to be high during post-monsoon periods (Nair and Balchand, 1992). Rao et al., (1984) have observed rapid reduction in dissolved oxygen levels during post-monsoon period and has attributed it to the heavy blooms of *Noctiluca*. Photosynthetic activity generally increases the dissolved oxygen in the sea (Chan, 1965), thus provide a general indication of primary productivity of that region (Mountford, 1969). The observed low dissolved oxygen concentrations during November may be due to the combined effect of primary production and oxidation of organic matter.

Nutrients

Nutrients are called biostimulants or fertilizers, usually represented by the dissolved inorganic forms of nitrogen, phosphorus and silicon, utilized by photosynthetic organisms in the formation of organic matter. Nitrogen and phosphorus are described as being biolimiting elements, because the concentrations of these elements limit biological growth. In recent years, there are signs of eutrophication of estuaries and coastal areas due to the release of nitrogen and phosphorus from excess fertilizers and sewage effluents (O' Neill, 1985). The great concern over this problem has stimulated much new research in the chemistry and biogeochemistry of nutrients in aquatic systems.

Distribution of phosphorus and other parameters like temperature, salinity etc. in the open ocean seems to be more uniform and regular than those in the coastal regions where proximity to land introduces complexity in the nature of distribution of these parameters. The content of nutrients in the surface layers is an important indicator of the productivity of a region. As mentioned already the nutrient levels in the surface layers are controlled by the utilization by phytoplankton. To delineate the potential productive and unproductive areas of the ocean, it is necessary to know the seasonal and spatial change in phosphorus in different regions of the ocean with particular reference to utilization by phytoplankton and regeneration.

Since nitrogen is a principal nutrient involved in the biological activity, its distribution in seawater is controlled by biological processes, resulting in the removal of this element from water in the upper euphotic layer. In some cases the nitrogen compounds are completely removed from the surface waters and this results in '**limiting**' the further growth of primary producers. Below the euphotic layer, the decomposition of sinking dead cells and faecal pellets of living organisms start, thereby liberating nitrogen compounds first as ammonia, which is oxidized to nitrate via nitrite as intermediate product. The decomposition of organic matter is accompanied by the utilization of dissolved oxygen present in water. The mineralisation of organic matter under oxidizing condition can be reported by the relation proposed by Richards (1965)

$$(CH_2O)_{106}(NH_3)_{16}\ H_3PO_4 + 138\ O_2 \Leftrightarrow 106CO_2 + 122\ H_2O + 16\ HNO_3 + H_3PO_4$$

According to the above relation, organic matter on mineralisation will liberate carbon, nitrogen and phosphorus in the atomic ratio

$$C : N : P = 106 : 16 : 1$$

Redfield et al., (1963) analyzed the rate of change of nutrients with respect to one another and, assuming that the change is entirely due to organism uptake and that there was a fixed organism composition. Thus, they have defined an organism stoichiometry of $C_{106}N_{16}PH_{263}O_{110}$ with 138 atoms O_2 for oceans.

Nitrogen compounds

Nitrogen is supplied through river mainly as dissolved nitrate, which is derived from rock weathering and drainage from agricultural lands. Nitrate (NO_3-N) is considered to be the most stable oxidation level of nitrogen in seawater (Grasshoff, 1983). It is an essential nutrient for the growth of many photosynthetic autotrophs and has been identified as the growth-limiting nutrient. Other important forms of nitrogen for biogeochemical process are nitrite, ammonia and dissolved and particulate organic nitrogen compounds. Nitrite is present generally in low concentrations, as an intermediate product of microbial reduction of nitrate or oxidation of ammonia and as an excretory product of plankton. In marine environment inorganic nitrogen compounds exist in their oxidizing or reducing forms. The general cycle is

$$NO_3^- \Leftrightarrow NO_2^- \Leftrightarrow NH_4^+$$

The occurrence and predominance of the different forms depend on the stage of process.

Nitrogen in living material is incorporated into a vast range of compounds ranging from simple amino acids to complex proteins. On death or decay, these compounds are released to the surrounding water and become part of the organically bound nitrogen fraction of natural waters. Thus, the productivity of a water body may depend on very effective regeneration of nitrogen from sediments (Aston, 1980). The important processes involved in the biogeochemical cycling of nitrogen species include the processes of rapid turnover in water column oxidation and remineralization, and in sediment they include burial, remineralization, biological uptake, oxidation, reduction and denitrification (Nixon and Pilson, 1983).

In most coastal environments, the majority of recycled nitrogen is released from sediments to water in the form of ammonium ion (Kemp et al., 1990). A portion of this ammonium ion regenerated by the decomposition and deamination of organic matter is oxidized to nitrate before it escapes from sediments. This nitrate may, in turn, be used as a terminal electron acceptor by denitrifying bacteria producing gaseous nitrogen and N_2O essentially unavailable to most coastal phytoplankton (Howarth et al., 1988). Thus the coupled process of nitrification-denitrification represents a sink that shunts nitrogen away from recycling pathways (Jenkins and Kemp, 1984). These processes are important in the nitrogen budget of estuaries and coastal environments where nitrogen losses via denitrification may account for half of the terrestrial inputs (Smith et al., 1985, Seitzinger, 1987).

The greatest influx of inorganic nitrogen into organisms results from ammonia and nitrate assimilation. These reactions predominate in the surface waters and are mediated primarily by phytoplankton. Nitrate tends to be the predominant inorganic nitrogen compound in surface waters but there is considerable evidence that ammonia is the preferred form for planktonic assimilation, since it is already at the reduction level (Conway, 1977). Thus, the concentration of nitrate in the open sea will generally be very low (~ 1 µM) in the euphotic zone, while below this layer of 40 to 50 m, it shows increasing trend reaching to 35 to 45 µM in deep oceans (Sen Gupta and Naqvi, 1984). Deficiency in oxygen levels in the environment will cause the nitrogen compounds to undergo reduction (denitrification).

3.2.3. Ammonia-Nitrogen:

Ammonia concentrations show peak values during February and lower values during October and November (Fig.3.6). The overall levels in ammonia during October, November and February range from 0 to 4.48 µM, 0 to 7.07 µM and 0 to 7.49 µM respectively. The surface water during October shows ammonia in the range 0 to 4.48 µM along transect I to V. Ammonia concentration is below detectable levels in the surface and bottom waters of transect VI and VII and in the bottom waters of transect V. Corresponding bottom concentrations in ammonia levels from transect I to V are in the range 0 to 2.82 µM.

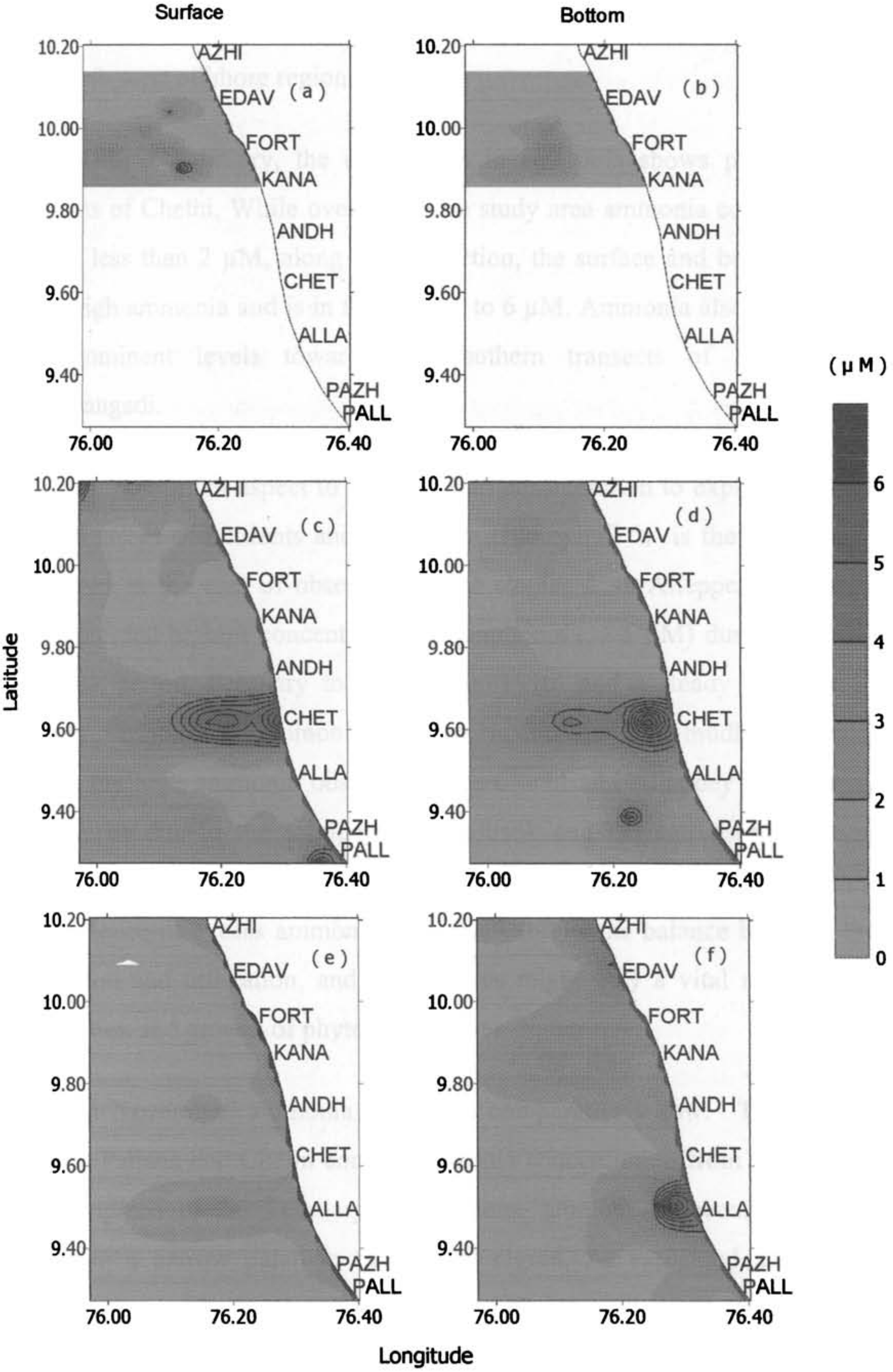


Fig. 3.6. Distribution of ammonia-N at the surface and bottom during October (a,b), February (c,d) & November (e,f).

It is evident from Fig.(3.6) that during the month of October, ammonia levels remain very low along the shallow regions as well as towards the north and north-west offshore regions.

During February, the distribution in ammonia shows peaks around transects of Chethi. While over the entire study area ammonia concentrations remain less than 2 µM, along Chethi section, the surface and bottom waters show high ammonia and is in the range 2 to 6 µM. Ammonia also shows less, but prominent levels towards the southern transects of Pallana and Pazhayangadi.

An important aspect to be taken into consideration to explain the high concentrations of nutrients and pockets of chlorophyll 'a' is the presence of mudbanks in the area of observation. The studies from Alleppey mudbanks have recorded highest concentrations of ammonia (32.5 µM) during the pre-mudbank period, February to May (Nair, 1990) and a steady decrease in periodic variability of ammonia from pre-mudbank to post-mudbank period. Hence, the high ammonia observed along Chethi and Alleppey region may possibly be due to the influence of mudbank and the active regeneration taking place in the sediments which are high in organic matter (Nair, 1990). The presence of excess ammonia in waters exhibits the balance between the production and utilization, and the reserves might play a vital role for the propagation and growth of phytoplankton at a higher rate.

In November, ammonia levels are comparatively low. The regions between Pallana and Chethi contain ammonia concentration from 2 to 5 µM. But compared to the February observations, ammonia concentrations are limited to a narrow patch in the coastal region. As explained above, the observed ammonia levels along these southern shallow regions can be attributed to the influence of the mudbank, existing in the region.

Among the various forms of nitrogen, ammonia is preferred by phytoplankton for assimilation (Conway, 1977). The high concentration of chlorophyll 'a' observed at places where the concentration of ammonia is high indicates their utilization. Higher rate of formation of ammonia may also be from high organic matter in the sediments by regeneration. The excess ammonia may be associated with the probability that the biological removal is not counter balanced by the ammonification processes.

3.2.4. Nitrite-Nitrogen

The nitrite concentrations in surface waters during the three observations (Fig.3.7) remained low except at stations near the coast and estuarine mouths of Cochin and Azhikode. The ranges in nitrite concentrations during October, November and February are 0 to 2.0 μM, 0 to 1.44 μM and 0 to 2.02 μM respectively. The ranges in nitrite levels at the surface during October are from 0 to 1.70 μM and at the bottom it is from 0 to 2.0 μM. February observations show the lowest nitrite concentrations with the surface values in the study region from 0 to 0.70 μM and the bottom values from 0 to 2.02 μM. It is observed that the bottom nitrite values are low at all shallow coastal stations except at stations in transects 8 and 9. During the month of November, the surface nitrite values from transect I to IX vary from 0 to 0.77 μM and the bottom values from 0.12 to 1.44 μM.

During October, nitrite concentrations ranging from 1 to 1.7μM are seen around Cochin barmouth and in the coastal waters extending to about 5 to 8 km offshore along the northwest direction. At the bottom, nitrite exhibits similar enrichment along the coastal region, and also shows higher concentration towards the offshore southwest region. Substantial amount of organic material and nutrients are brought into the coastal region through Cochin barmouth during this period, as evident from the high values of bottom particulate organic carbon (~ 5 mg/l) (Fig.3.12). The currents during October are in a transitory phase and their velocity either becomes zero or they run northward (Gopinathan and Qasim, 1974). The weak coastal

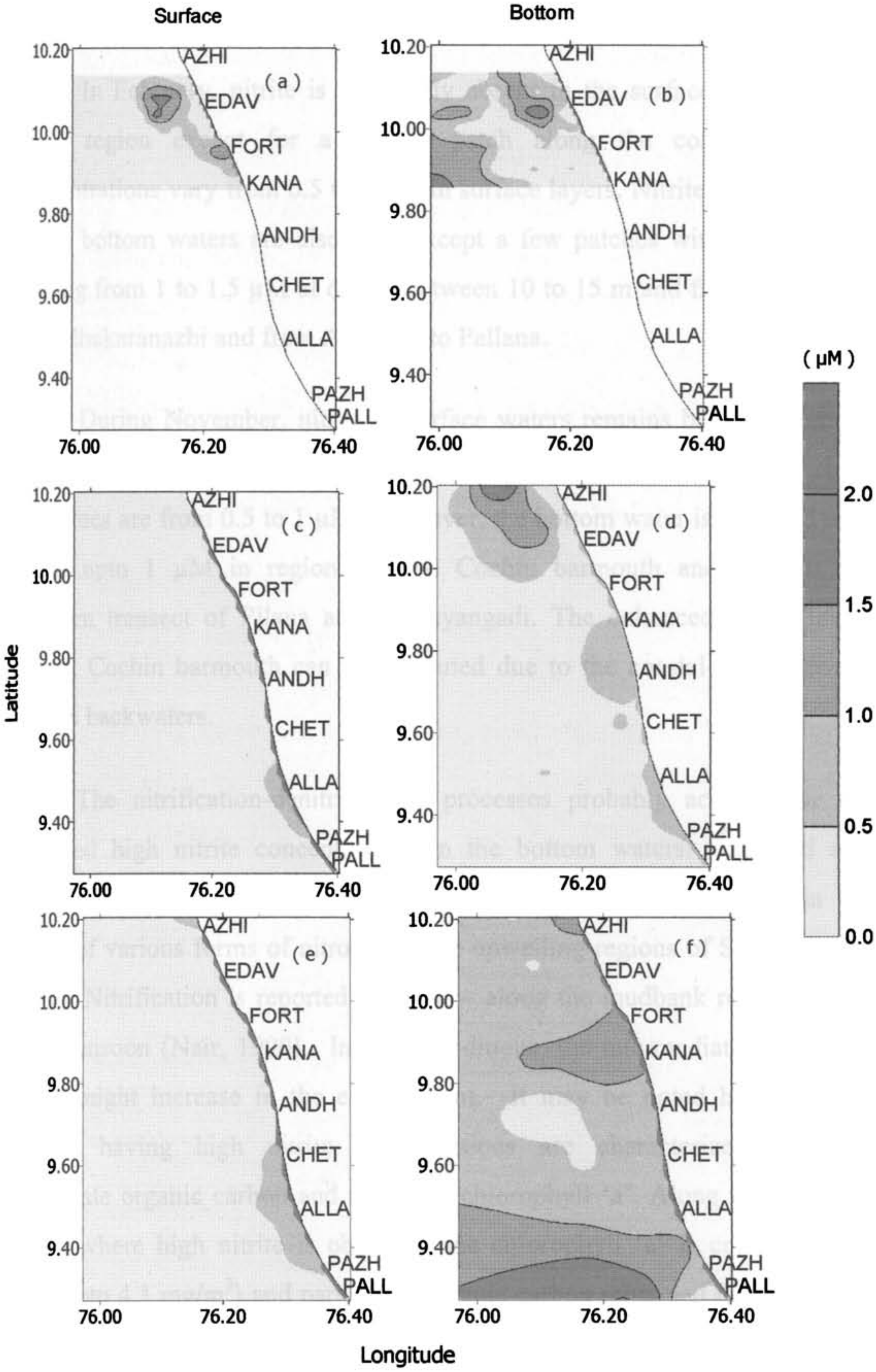


Fig. 3.7. Distribution of nitrite-N at the surface and bottom during October (a,b), February (c,d) & November (e,f).

currents may possibly lead to a build up of the materials due to inadequate dilution.

In February, nitrite is practically absent in the surface waters of the study region except for a narrow patch along the coast where the concentrations vary from 0.5 to 1 μM in surface layers. Nitrite concentrations in the bottom waters are also low, except a few patches with nitrite levels varying from 1 to 1.5 μM at depths between 10 to 15 m and from Kannamali to Andhakaranazhi and from Alleppey to Pallana.

During November, nitrite in surface waters remains below detectable levels except for the narrow coastal region between Pallana and Chethi where the values are from 0.5 to 1 μM. However, the bottom water is enriched with nitrite upto 1 μM in regions around Cochin barmouth and towards the southern transect of Pllana and Pazhayangadi. The enhanced nitrite levels around Cochin barmouth can be attributed due to the coastal input through Cochin backwaters.

The nitrification-denitrification processes probably account for the observed high nitrite concentrations in the bottom waters. Codispoti and Christensen (1985) have suggested this couple of reactions to explain the fluxes of various forms of nitrogen in the upwelling regions of South Pacific Ocean. Nitrification is reported to be slow along the mudbank region during post-monsoon (Nair, 1990). In such conditions, the intermediate forms like nitrite might increase in the environment. It may be noted here that the regions having high nitrite concentrations are characterized by high particulate organic carbon and also high chlorophyll 'a'. Along the southern region where high nitrite is observed, the chlorophyll 'a' is comparatively high (upto 4.3 mg/m^3) and particulate organic carbon remained the highest of the three observations (upto 3 mg/l).

It is to be noted that the high nitrite concentrations seen along the southern transects show excellent correlation with nitrate during November (Fig.3.8). Two processes are known to result in the build-up of nitrite in oxygenated near-surface waters: assimilatory reduction of nitrate during uptake by phytoplankton (Vaccaro and Ryther, 1960; Wada and Hattori, 1971) and differential photo-inhibition of ammonia and nitrite oxidation by nitrifying bacteria (Olson, 1981). The low levels of ammonia allow us to rule out nitrification as a significant process responsible for nitrite accumulation. Instead, the remarkable co-existence of nitrite with nitrate strongly suggests that the nitrite production is mostly due to assimilatory reduction. This is further substantiated by the high concentration of chlorophyll 'a' (4 to 6 mg/m^3) observed along these transects (Fig.3.11).

3.2.5. Nitrate-Nitrogen

The spatial distribution of nitrate levels during October, November and February are in the range 0 to 7.81 μM, 0.05 to 6.28 μM and 0 to 8.35 μM respectively (Fig.3.8). During October, the surface nitrate concentrations along transects I to VII are from 0 to 5.25 μM and the bottom nitrate from 0 to 7.81 μM. In November, the surface values of nitrate vary from 0.14 to 4.97μM and the bottom values vary from 0.14 to 6.28 μM. During February, nitrate concentration shows enrichment, with surface values ranging from 0.4 to 8.35 μM and the bottom values from 0.32 to 8.37 μM.

The nitrate levels show higher concentrations towards offshore at the bottom in the northwest region, where concentration upto 8 μM is observed. This may probably be due to the presence of upwelled water as evidenced from the distribution of temperature, salinity and dissolved oxygen. However, probably due to the rapid uptake of this nutrient salt by plankton, it is not as evident as in the shallow region, both at the surface and bottom. From the distribution, it is assumed that nitrate in this study region during October is mainly from the upwelled waters, since the fresh water contribution is not evident.

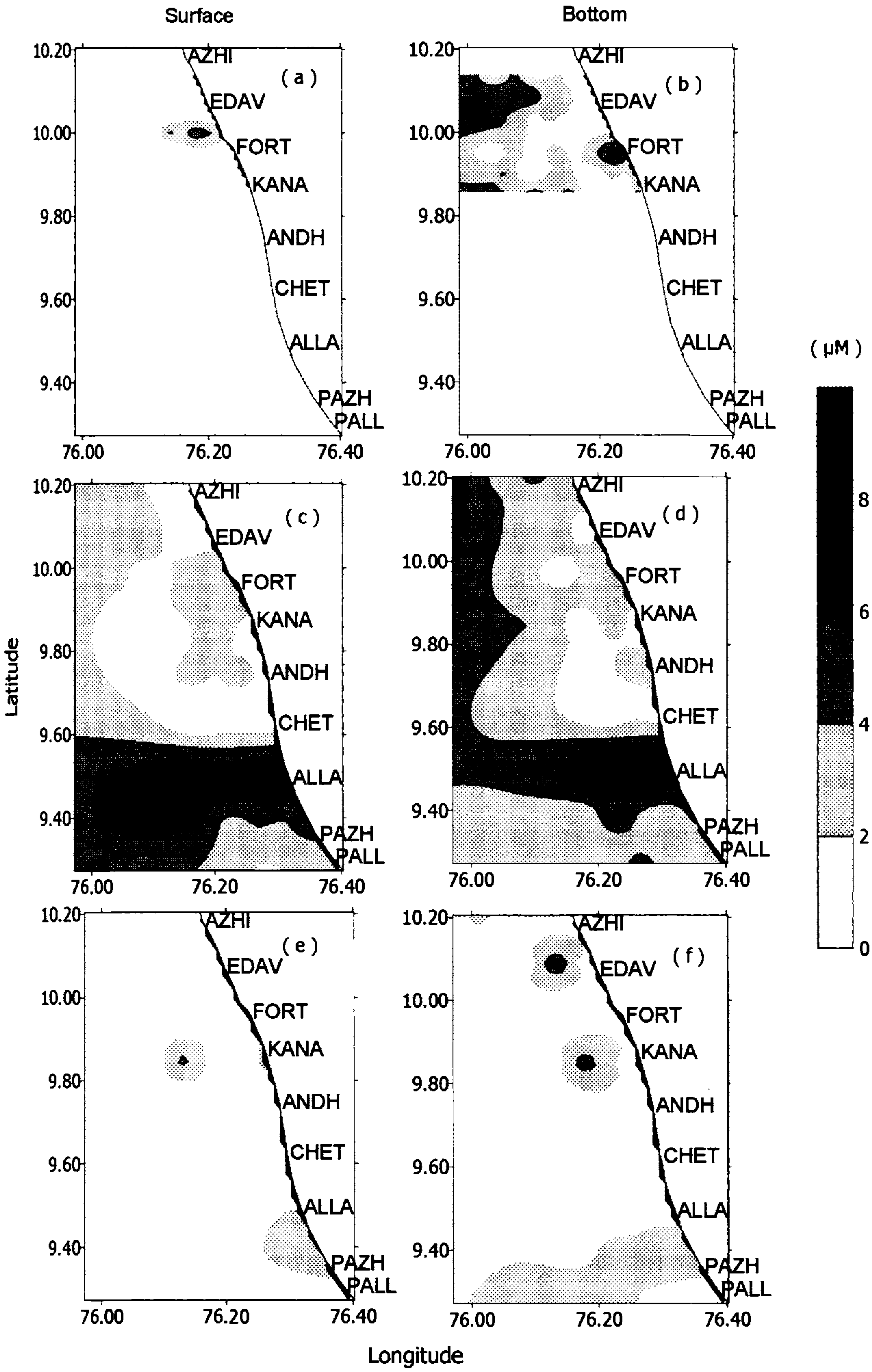


Fig. 3.8. Distribution of nitrate-N at the surface and bottom during October (a,b), February (c,d) & November (e,f).

In February, the distributions of nitrate show a general increase along transect III. Alleppey transects register comparatively high levels (8.35 and 8.37 μM) of nitrate both at surface and bottom. The bottom waters in the offshore region beyond 20 m depth also shows nitrate values, 4 to 5 μM and seems to extend from the shallow regions of the third transect.

During November, the entire study region is characterized by low nitrate concentrations both at the surface and bottom. The surface and bottom waters between Allappey and Pazhayangadi record nitrate concentrations upto 3.28 μM.

Phosphorus compounds

Ecological interest in phosphorus stems from its major role in biological metabolism in spite of its relatively small amounts in the hydrosphere. Weathering of earth's crust and surface water transport deliver phosphorus to coastal waters through rivers. During the period of active growth of phytoplankton, the concentration of phosphorus along with other nutrient salts is readily reduced in the aquatic environment. The utilization of these nutrients by plants is however, restricted to the euphotic zone. Due to metabolic activity of plants, animals and bacteria, phosphate is regenerated into the water column from the organic phase. Part of the regeneration occurs at the surface layers but there is a continuous transport of these elements away from the surface layers. Physical processes like vertical diffusion, convection and upwelling replenish the surface layers with these elements from the subsurface layers.

The species of inorganic phosphorus in seawater are orthophosphate ions, represented by phosphoric acid (H_3PO_4) and its dissociation products and ion complexes of these ions with the other constituents of seawater. In seawater of pH around 8.0, the predominant dissolved phosphate species are HPO_4^{2-} (87%), with PO_4^{3-} (12 %) and $H_2PO_4^-$ (1 %) making small contributions (Kester and Pytkowics, 1967). According to them, about 96% of

PO_4^{3-} and 44% of HPO_4^{2-} are present in association with calcium and magnesium as their ion pairs. Reactive phosphorus in solution exists mostly as ions of orthophosphoric acid (PO_4^{3-}). In river water, when pH is low (~ 7) phosphate is present mostly as $H_2PO_4^-$ with small fractions being present as HPO_4^{2-} and PO_4^{3-}. Though polyphosphates are not found in seawater, it may be present in estuarine and coastal waters as a result of pollution from detergents (Koroleff, 1983). The availability of phosphorus in natural systems significantly affects biological production (Jaworski, 1981; Schindler, 1985). In estuaries, the rate of phosphorus recycling has been found to vary considerably with turnover time of PO_4^{3-} ranging from minutes to days (Taft et al., 1975; Friebel et al, 1978; Berman, 1983).

In the coastal waters, the interaction between the water column and the sediment can have a large influence on phosphorus concentration and the overall productivity of the ecosystem (Jitts, 1959, Pomeroy et al., 1965, Nixon, 1981). In regions of high productivity, the sediments are often rich in biogenic debris, especially essential plant nutrients such as nitrogen and phosphorus compounds (Suess, 1981). Sediments can act either as a source or sink of phosphorus by adsorption-desorption reactions and buffer the phosphorus concentration in water (Carrit and Goodgal, 1954; Pomeroy et al., 1965; Buttler and Tibbits, 1972; Storm and Biggs, 1982). Nixon (1981) and Fisher et al., (1982) have reported that the rates of release of phosphate by a wide variety of marine sediments range from –15 to 50 μmoles/m^{-2} u 2^{-1}. They also observed that the regeneration could provide enough phosphate to support 28 to 50 % of primary production in the water column. Thus the phosphorus concentrations of coastal and estuarine waters are intimately linked to the fluxes of biogenic materials in the sediments. Biological activity by microbes and animals also controls the distribution of phosphorus and other elements in organic matter by altering the redox potential of sediments and hence, the chemical properties of phosphrus.

3.2.6. Phosphate-Phosphorus:

Of the three observations, phosphate concentrations remained moderately high during November, followed by October and the lowest during February (Fig.3.9). The general distribution during October, November and February shows the concentration levels from 0 to 2.55 μM, 0.18 to 2.84 μM and 0.15 to 0.92 μM respectively.

The presence of upwelled water in the study region characterized by low temperature, high salinity, low oxygen with high nutrients is observed in the coastal waters during October. Phosphate concentration upto 2.0 μM is observed around the Cochin barmouth and extending to about 5 to 8 km to the coast along the northwest direction. Bottom concentrations are more conspicuous and the plume spreads from the Cochin barmouth region towards the entire northern and northwest bottom waters.

Phosphate values are minimum during February, with surface concentrations ranging from 0.15 to 1.10 μM and the bottom values from 0.20 to 0.92 μM. The surface as well as bottom layers along the coast with concentrations upto 1 μM, and is found to spread offshore towards the northern region.

Both surface and bottom concentrations during November show the highest values among the three observations (1.7 and 2.84 μM). During October, the surface values of phosphate concentrations in transect I to VII vary from 0 to 1.46 μM and the corresponding variations at the bottom are from 0.1 to 2.55 μM. It may be noted that except at stations along transects V and I, all other stations in other transects consistently register higher phosphate levels during the three observations. In November, the concentration of phosphate decreased slightly with surface levels in the range 0.18 to 1.70 μM at stations in all transects and corresponding bottom values are from 0.41 to 2.84 μM. Higher values are registered in most of the shallow stations and in particular, around Cochin barmouth.

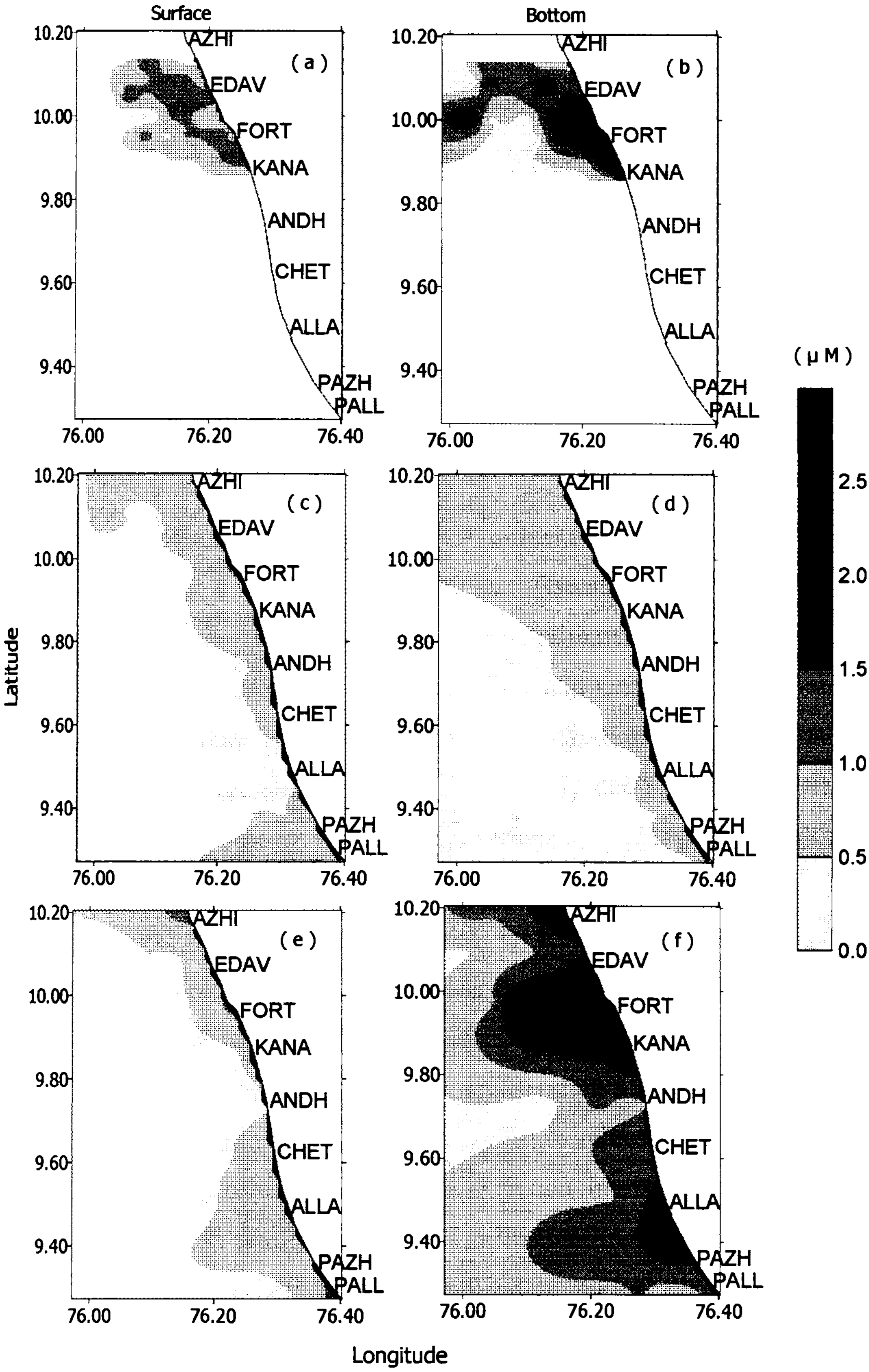


Fig.3.9. Distribution of phopsphate-P at the surface and bottom during October (a,b), February (c,d) & November (e,f)

Phosphate distribution during November shows peaks in phosphate (2 to 2.5μM) near Azhikode barmouth, Cochin barmouth and upto 2μM between Alleppey and Pazhayangadi, closer to the coast. High concentrations around Cochin and Azhikode river mouths give an indication of the coastal input through the backwaters. Regeneration from sediments during post-monsoon season has been widely reported for the enrichment of phosphate in the overlying waters (Seshappa, 1953; Seshappa and Jayaraman, 1956; Reddy and Sankaranarayanan, 1972; Jacob and Qasim, 1974; Nambisan et al., 1987). These areas, characterised by mudbanks consisting of clayey sediments, are proved to desorb significant amount of inorganic phosphate to overlying waters during post-monsoon (Nair et al.,1993).

The phosphate content in water is influenced by the dynamics of biological activity under natural conditions (Istvanovics et al., 1986). Phytoplankton blooms normally satisfy their requirement of phosphorus by direct assimilation of organic phosphorus (Riley and Chester, 1971). Nair et al., (1993) have observed interstitial phosphate to the tune of 5 times that of adsorbed phosphate from mudbank region, probably due to the sequestering nature of laterite bearing mudbanks (Seshappa, 1953; Seshappa and Jayaraman, 1956; Jacob and Qasim, 1974; Nambisan et al., 1987). Yet another feature that they have observed is the low dissolved organic phosphorus (sediment) during post-mudbank than pre-mudbank period due to desorption from sediment during post-mudbank. Thus, the $P_{sed}/P_{diss.}$influences the nutrient controlled biorythm, since the regeneration of phosphate is fast in mudbank areas. For inorganic $P_{diss.}$, post-mudbank values were only slightly higher than pre-mudbank values. This reduction in magnitude has been attributed to the high rate of diffusion of sedimental inorganic phosphate to counter balance the excess biological utilization during the pre-mudbank period (Nair et al., 1993).

3.2.7. Silicate-Silicon (SiO_4-Si)

The source of silica to the marine environment is mainly the river discharge (Livingstone, 1963), with sub-marine hydrothermal emanations and glacial weathering (Warnke, 1970; Wolery and Sleep, 1976) contributing substantially. Silicon is a biologically essential nutrient to marine organisms like diatoms, radiolarians and sponges for the growth and the formation of their skeletal materials. The uptake of silicon by the growing phytoplankton results in the depletion of silicon in the seawater. However, when these organisms die and disintegrate, silicon is rapidly liberated into the marine environment. Thus, as a consequence of its biological significance, silicon exhibits a strong seasonal dependence, reflecting the waxing and waning of the life processes. Silicon can also be used as an important chemical tool in oceanography since the wide variability of its concentration could be used for tracing water masses in the seas (Richards, 1958).

Diatoms are particularly characteristic of upwelling areas, where they produce intense blooms and provide the primary production base for short and trophically efficient food chains which are responsible for the most productive fisheries of the world's oceans (Ryther, 1969). The role of silicate in regulating the intensity, periodicity and duration of diatom blooms associated with monsoonally driven upwelling in the Arabian Sea is presently unknown.

David Young and John Kindle (1994) have opined that the highest silicate concentrations upto 10 µM in the surface waters of Arabian Sea are limited to the coastal margin, especially southwest coast of India, excluding the Somalia and Omani coastal waters. They have suggested that upwelled waters are not advected far offshore, but restricted to the southern coast of India. Hence, the unavailable silicate concentrations in surface waters of this region result from a combination of the uptake of silicate by diatoms and the limited westward advection of upwelled coastal waters. This explanation was consistent with the lack of diatomaceous remains in sediments of the southeastern Arabian basin and also the observation of Naidu et al., (1992) that biogenic siliceous sediments of the western continental margin of India are restricted to the shelf edge and upper slope. Further, increased amounts of terrigenous sedimentation may serve to "dilute" the contribution of diatom frustules to sediments (Calvert, 1983). Boyle et al., (1974) suggested that most estuaries and coastal environments however, do not remove a large percentage of the riverine silicate flux. There are reports both of conservative and non-conservative mixing of silicate in estuarine environments. The studies in Cochin backwaters indicated that silicon behaves non-conservatively in the salinity range 4 to 22 psu where substantial removal of this element is observed (Sankaranarayanan et al., 1984, Balachandran et al., 1996).

The concentrations of silicate vary widely (Fig.3.10) during October (0 to 18 µM) followed by a decrease in November (0.46 to 14.63 µM) and February (0.17 to 12.91 µM). During October, the surface silicate levels vary from 0 to 18.05 µM and the variation in bottom silicate concentration is from 1.21 to 14.94 µM. In February, the silicate levels generally remained low with surface values varying from 0.17 to 12.91 µM with corresponding bottom values varying from 0.93 to 9.95 µM. Surface silicate values during November are in the range 0.50 to 14.63 µM and the bottom values are in the range 0.46 to 14.07 µM.

During October, silicate is found to be high in surface waters throughout the study area, in conformity with the low saline waters. The low saline water mass seems to have originated from Cochin barmouth region and is enriched with silicate from 8 to 16 µM. This fresh water discharge extends to about 5 to 8 km from the coast along the northwest direction due to coastal currents. The bottom waters are low in silicate (< 8 µM) towards the coastal region, whereas higher levels (8 to 16 µM) are observed in the bottom waters of the offshore region indicating the presence of upwelled water.

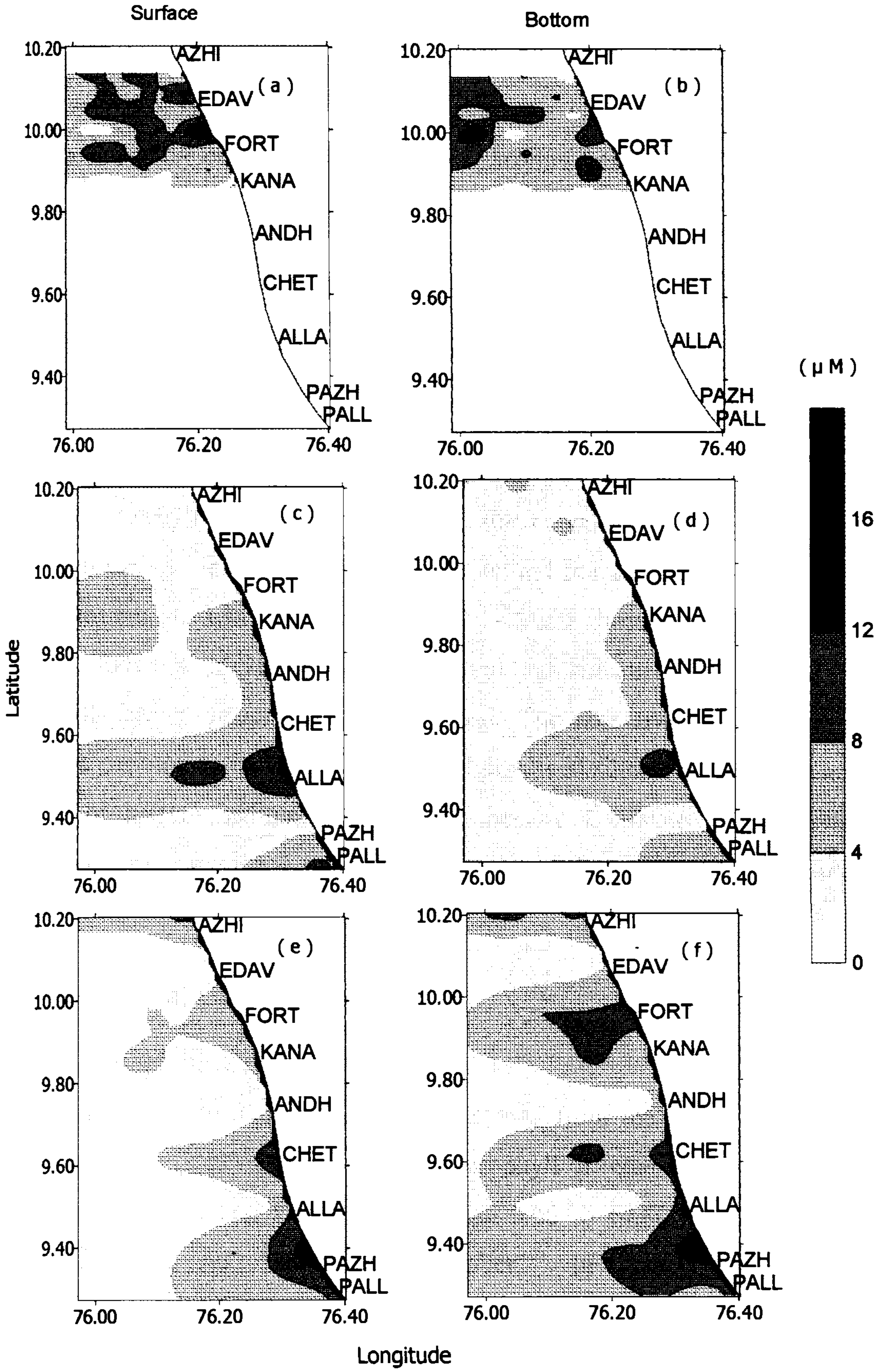


Fig. 3.10. Distribution of silicate-Si at the surface and bottom during October (a,b), February (c,d) & Novemebr (e,f).

Silicate distribution during February shows higher concentrations south of Cochin along the coastal region around Alleppey (4 to 12 μM). The bottom waters also show more or less the same trend in distribution. As the main source of silicate is the river discharge, the variation in its distribution may be due to the effect of littoral currents carrying fresh water.

Silicate values during November are in the range between 1 and 16 μM. The surface silicate concentrations are in the range 1 to 8 μM, whereas the bottom values are from 1.5 to 16 μM. The silicate distribution clearly shows the riverine influence and in general, the entire study region shows higher amount of silicate.

Nair (1990) has reported highest silicate value of 78.2 μM during monsoon period along the mudbank regions and the subsequent seasons of post-monsoon (42 μM) and the lowest of 17.5 μM during the pre-monsoon months. Rao et al., (1984) have also reported high silicate concentrations (35 to 50 μM) during the active mudbank period. The excessive turbidity during monsoon period may increase the supply of dissolved silicate by diffusion and mixing of bottom sediment enriched in dissolved silicate (Nair, 1990). Sediments in the mudbank regions are capable of desorbing nutrients under favorable conditions.

3.3. Biological Characteristics

3.3.1. Chlorophyll 'a':

The data collected during different period from the study region are presented in Fig.(3.11). In general, the chlorophyll 'a' concentrations during October, November and February vary from 0.20 to 14.80 mg/m^3 and the maximum values are observed in November. In October, the surface chlorophyll 'a' along the 7 transects vary from 0.21 to 13.36 mg/m^3 and bottom values from 0.21 to 12.69 mg/m^3. During February, the chlorophyll 'a' values are lower, more evidently in surface waters. During this period, the surface chlorophyll 'a' along the 9 transects vary from 0.21 to 8.60 mg/m^3 and

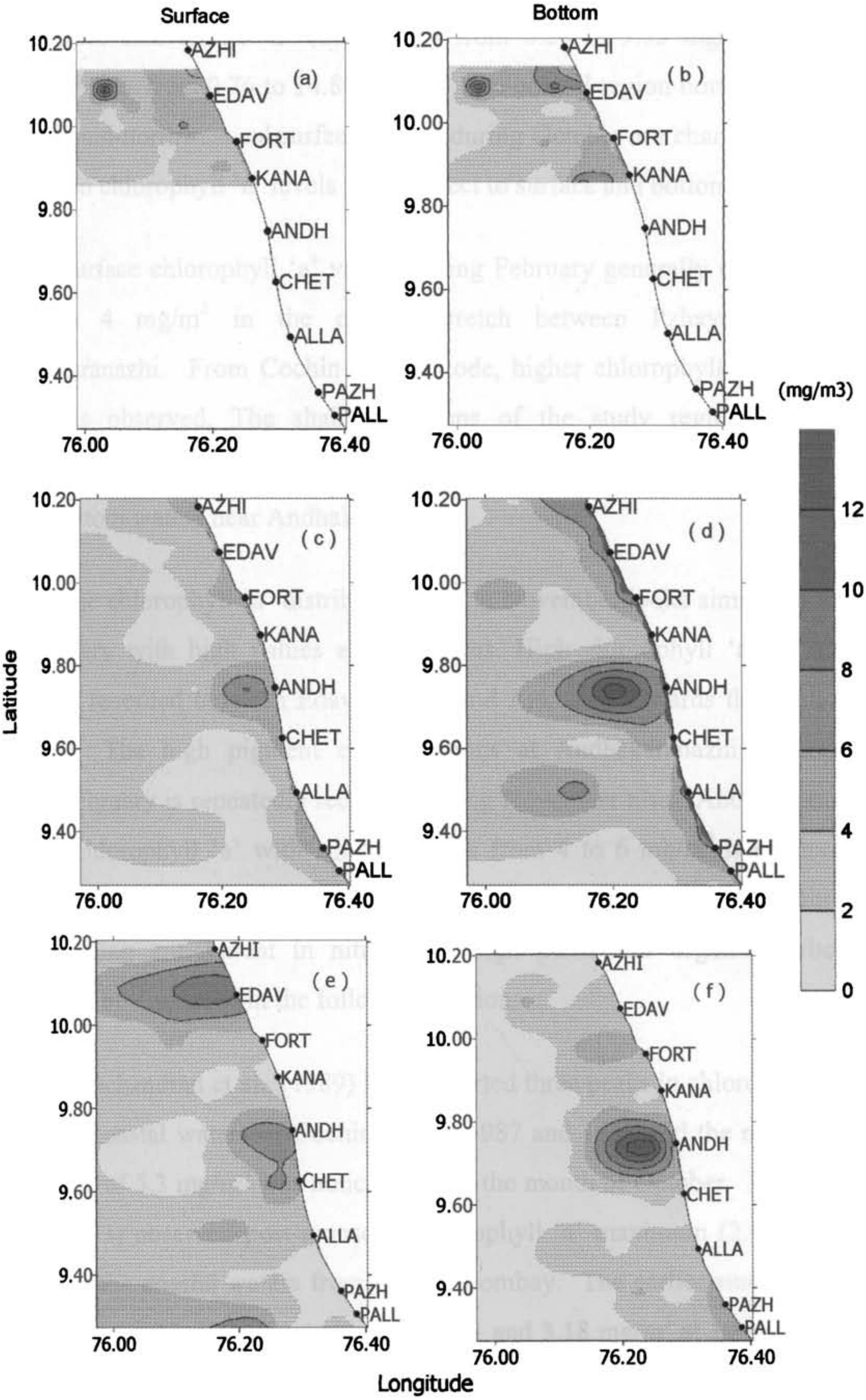


Fig. 3.11. Distribution of Chlorophyll 'a' at the surface and bottom during October (a,b), February (c,d) & November (e,f).

that of the bottom waters vary from 0.38 to 14.40 mg/m^3. During November, the surface chlorophyll 'a' values vary from 0.20 to 9.75 mg/m^3 and the bottom values from 0.76 to 14.80 mg/m^3. The coastal region north of Cochin and the mid-northwest subsurface waters during October are characterized by maximum chlorophyll 'a' levels with respect to surface and bottom layers.

Surface chlorophyll 'a' values during February generally ranged from < 1 to 4 mg/m^3 in the coastal stretch between Pzhayangadi and Andhakaranazhi. From Cochin to Azhikode, higher chlorophyll 'a', upto 6 mg/m^3 is observed. The shallow regions of the study region recorded chlorophyll 'a' values upto 10 mg/m^3, with highest concentration of 12 mg/m^3 in the bottom waters near Andhakaranazhi.

The chlorophyll 'a' distribution during November looks similar to that of February with high values at two places. High chlorophyll 'a' of 9.75 mg/m^3 is recorded between Edavanakkad and Azhikode towards the shallow stations. The high pigment concentrations at Andhakaranazhi observed during February is repeatedly recorded during November also. Another patch of high chlorophyll 'a' with concentrations from 4 to 6 mg/m^3 is observed along the southern transect, off Pallana. This region is also specific for a corresponding enrichment in nitrite and high particulate organic carbon, which will be discussed in the following section.

Balachandran et al., (1989) have reported three peaks in chlorophyll 'a' along the coastal waters of Cochin during 1987 and 1988 and the maximum production of 5.3 mg/m^3 was noticed during the month of October. Bhargava et al., (1973) observed post-monsoon chlorophyll 'a' maximum (2.4 to 18.8 mg/m^3) in the coastal waters from Goa to Bombay. The earlier studies have shown surface chlorophyll 'a' values of 1.93 and 3.18 mg/m^3 at 10 and 20 m stations reported by Nair et al., (1985) from this area during 1980, are comparable with the present values along the same depth zones. In the present study, large variations in the magnitude of chlorophyll 'a' values are experienced from station to station within a short time frame. The data collected by Qasim et al (1978) from Dabhol to Tuticorin during the month of March also reported wide fluctuations in the chlorophyll 'a' values (0.05 to 4.18 mg/m^3). Such variations in the inshore waters within a short time frame cannot be attributed to diurnal variability. It is likely that chlorophyll 'a' values have been proportionate with carbon production indicating a strong positive relationship binding it with nutrient related factors rather than seasonal or diurnal fluctuation.

3.3.2. Particulate organic carbon (POC):

A study of the life cycle in the pelagic realm indicates that a good amount of living matter occurs as nanoplankton, with which more resistant portion of decomposing organisms and detritus contribute what is termed as particulate organic matter. Most research on detritus food webs has focused on production of particulate organic matter. Particulate matter, whether derived from the standing biomass of water column or from autochthonous and allochthonous sources are of great value, as they form food for filter feeding pelagic animals and for benthos after decomposition. Organic carbon is associated with and is derived from all living systems. In its various forms, it may function as a nutrient, an energy source, growth stimulant and growth inhibitor. Thus, its role depends upon its chemical and biological state (Saraladevi, 1986).

Organic carbon and the energy contents of the water are closely related to the amount of particulate matter. An assessment of particulate organic matter and energy perhaps provides a more meaningful estimation of the pool of available energy to the next trophic level, particularly in shallow coastal and estuarine system dominated by detrital material.

It is important to stress the role of particulate organic matter as particle, carrying pollutants, which may be introduced into aquatic environment by surface run-off. Heavy metals and other pollutants carried by river transported particles may to an extent, be mobilized on estuarine mixing. Detrital feeders ingest these suspended particles thereby transferring the toxic metals to higher trophic levels.

During the present study, the average particulate organic carbon (POC) content along the coastal stretch is higher during October compared to the other two observations (Fig.3.12). The surface particulate organic carbon in general varies from 0.52 to 2.94 mg/l during November. The surface particulate organic carbon values in October vary from 0.13 to 4.03 mg/l along the 7 transects, with corresponding bottom values from 0.13 to 5.04 mg/l. During February, the surface and bottom particulate organic carbon concentrations along the 9 transects are in the range from 0.13 to 2.02 mg/l and 0 to 2.52 mg/l respectively. During November, both the surface and bottom particulate organic carbon exhibits higher concentrations. The surface values along the 9 transect vary from 0.52 to 2.94 mg/l and the bottom values from 0.14 to 3.78 mg/l.

The distribution of particulate organic carbon during October shows that the maximum values are observed around the coastal area between Cochin barmouth and Edavanakkad (3 to 5 mg/l).

The particulate organic carbon during February observation is very low (< 1 mg/l) for the central and southwest region. The coastal waters have higher particulate organic carbon levels (1 to 3 mg/l). It may be noted that the regions with higher chlorophyll 'a' show high organic carbon with high nutrient salts.

There is a substantial increase in the concentration of particulate organic carbon during November, when the entire study region represent markedly high values with mean surface and bottom concentrations of 1.54 and 1.71 mg/l respectively. Along the shallow regions, particularly south of Cochin to Pallana and around Azhikode, the particulate organic carbon shows

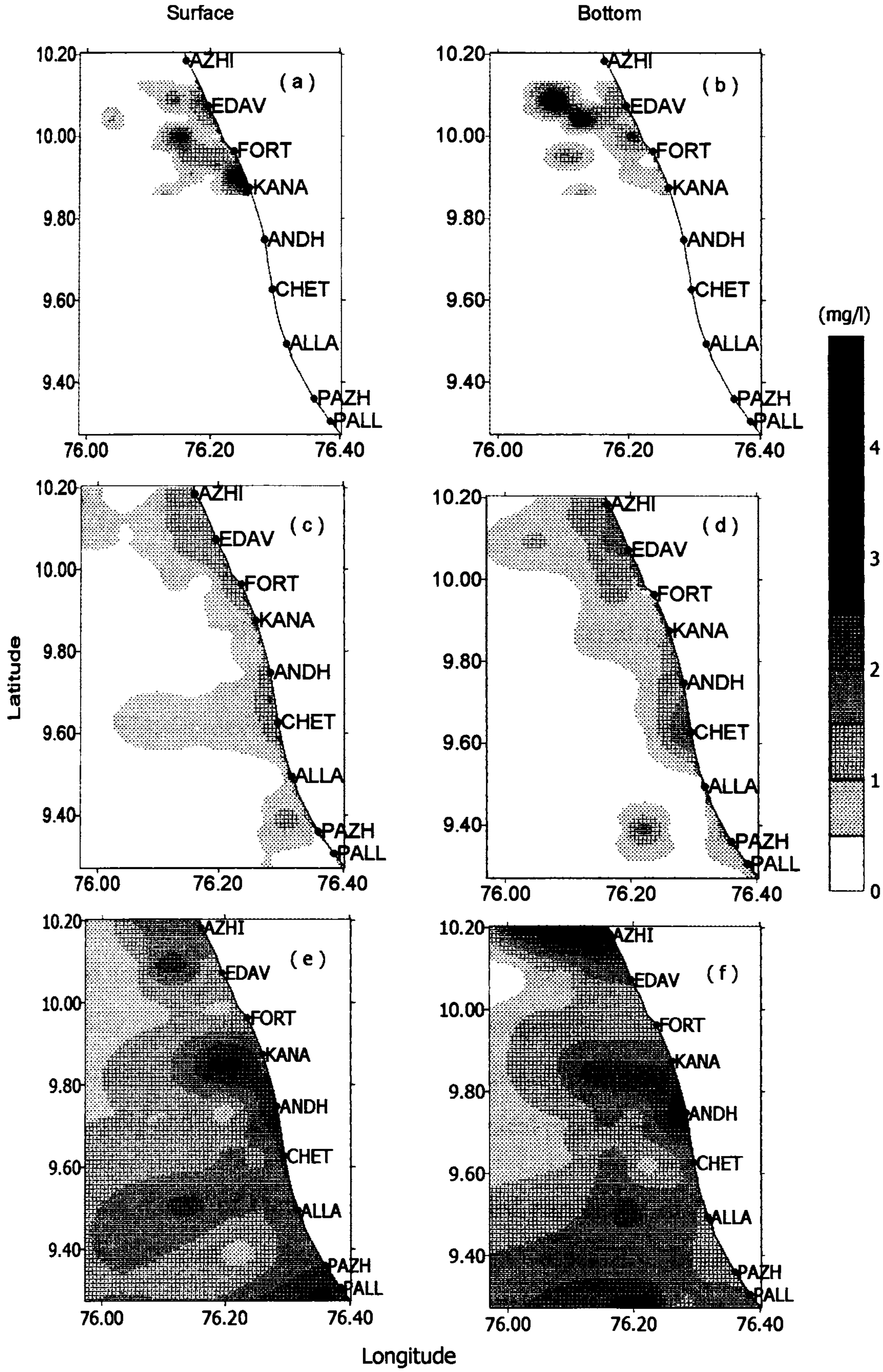


Fig. 3.12. Distribution of particulate organic carbon during October (a,b), February (a,b) & November (e,f).

values upto 3.78 mg/l. The surface and bottom contours show similar trend of uniformly increased values in offshore waters towards southern region.

The higher values of chlorophyll 'a' in the pre-mudbank period are associated with high primary production giving rise to phytoplankton bloom, more evidently noted in later months (Nair, et al., 1984; Nair and Balchand, 1992). The particulate organic carbon has a crucial role as it could potentially influence the biological production. Periodic variations in particulate organic carbon are associated with changes in chlorophyll 'a' content. Higher sediment organic carbon during November is also a characterisitic feature noted for this coastal region. It follows that finer clay has higher retaining capacity for organic carbon.

3.3.3. Suspended particulate matter (SPM):

The annual input of particulate suspended material to the world ocean, as estimated by different authors, varies from 12.7 x 10^9 to 51.1 x 10^9 tonnes (Lisitzin, 1974; Gordeyer, 1983). The organic matter contained in particulate materials consists of a) living planktonic algae and other green cells b) the remnants of various organisms and their faecal pellets c) organic matter in terrigenous and skeletal structure, and d) organic matter which has been co-precipitated, sorbed or aggregated. Thus, particulate material contains both living and non-living organic matter. Owing to their high activity, suspended solids play an important role in geochemical processes at the sedimentogenesis stage. It is, in effect, an indicator of basins productivity, its nutrient supply and of the intensity of biochemical processes.

In the month of October, the suspended particulate matter is low (< 30mg/l) at the surface, but at the bottom, especially in and around navigational channel of Cochin barmouth contain very high suspended load (75 to 138 mg/l). The surface concentrations vary from 0.4 to 53.2 mg/l and the bottom values from 3.2 to 140 mg/l. The higher concentrations observed at the bottom are between Cochin and Azhikode evidently showing the fluvial discharge through the backwaters and also the effect of dredge spoil which is discharged at about 12 m depth each on the south and north of the navigational channel (Fig.3.13). In February, the surface suspended load varies from 0.2 to 104 mg/l and the bottom values vary from 0.8 to 156 mg/l. Higher values are observed along transect 9, which is off Azhikode.

The suspended particulate matter distributions show a peculiar pattern during February, with an increasing trend towards the Azhikode transects. Surface waters along the northern transect (IX) is higher (30 to 60 mg/l) in suspended matter. The bottom waters show higher concentrations along the entire coastal area upto a depth of 10 m where the suspended particulate matter concentration is > 110 mg/l along Azhikode transect.

During November, though the shallow stations do not show much variation, the entire bottom suspended load is seen to increase. While surface suspended load during November range between 4 and 38 mg/l, the bottom values are also comparatively higher (5 to 53 mg/l).

Discussion

The percentage variability explained by the linear relation for all parameters with salinity is furnished in table (3.7). Linear correlation between various parameters for surface and bottom during October, February and November are given in tables 3.8 to 3.13. Salinity does not seem to have any significant relation with any of the nutrients during the study period. The maximum of 29.66 % (r = -0.56) variability explained for silicate for the surface waters during November indicates its riverine source. All other nutrients give very low variability indicating a rapid turn over rate of the coastal waters leading to a vertical homogeneity. Again, the low variability explained for nitrite during different seasons points out that its contribution to the coastal waters is through different sources. While during October and November, surface runoff brings in nitrite to the coastal waters; the bottom water during February is enriched through the regeneration of bottom

Table 3.7 Variability explained (%) by linear relation applied for different parameters with salinity

Parameters	October		February		November	
	S	B	S	B	S	B
D.O	N.S	N.S	N.S	N.S	0.87	15.68
NO2-N	10.29	3.1	N.S	13.93	19.1	N.S
NO3-N	8	14.81	N.S	N.S	9.76	N.S
NH4-N	N.S	N.S	N.S	1.59	9.07	4.17
PO4-P	9.07	N.S	8.38	N.S	7.1	N.S
SiO4-Si	6.31	2.1	N.S	5.01	29.66	2.39

N.S Not significant

Table 3.8

October (Surface) n = 54

	NO_2	NO_3	SiO_4
Sal	-0.36	-0.36	--
NO_3	--	--	0.56
PO_4	--	0.48	--

Table 3.9

October (bottom)

	T	Sal	NO_3	NH_4	PO_4
T		-0.42	-0.43	--	0.51
DO	-0.61	--	--	--	-0.38
pH	--	--	-0.35	--	--
PO_4	--	--	--	-0.38	--
Sal	--	--	0.42	--	--

Table 3.10

February (surface) n = 45

	NO_2	SiO_4
Sal	0.4	--
PO_4	0.4	--
T	--	0.39

Table 3.11

February (bottom)

	T	pH	NO_2	NO_3
NO_3		--	0.58	--
NH_4	--	-0.41	--	--
SiO_4	0.47	--	0.58	0.51

Table 3.12

November (surface) n = 45

	pH	NO_2	NO_3	NH_4	PO_4	SiO_4
Sal	0.42	-0.46	--	--	--	-0.56
DO	0.41	-0.67	--	-0.46	-0.62	-0.41
NO_2	-0.68		0.46	0.55	0.8	0.68
pH	--		--	--	-0.69	-0.69
PO_4				0.46	--	0.67

Table 3.13

November (bottom) n = 45

	T	pH	DO	NO_2	NO_3	NH_4	PO_4
Sal		--	-0.42	--	--	--	--
DO		--	--	-0.39	--	--	-0.43
NO_2	--	--		--	0.39	--	--
SiO_4	-0.43	-0.52		--		--	0.49

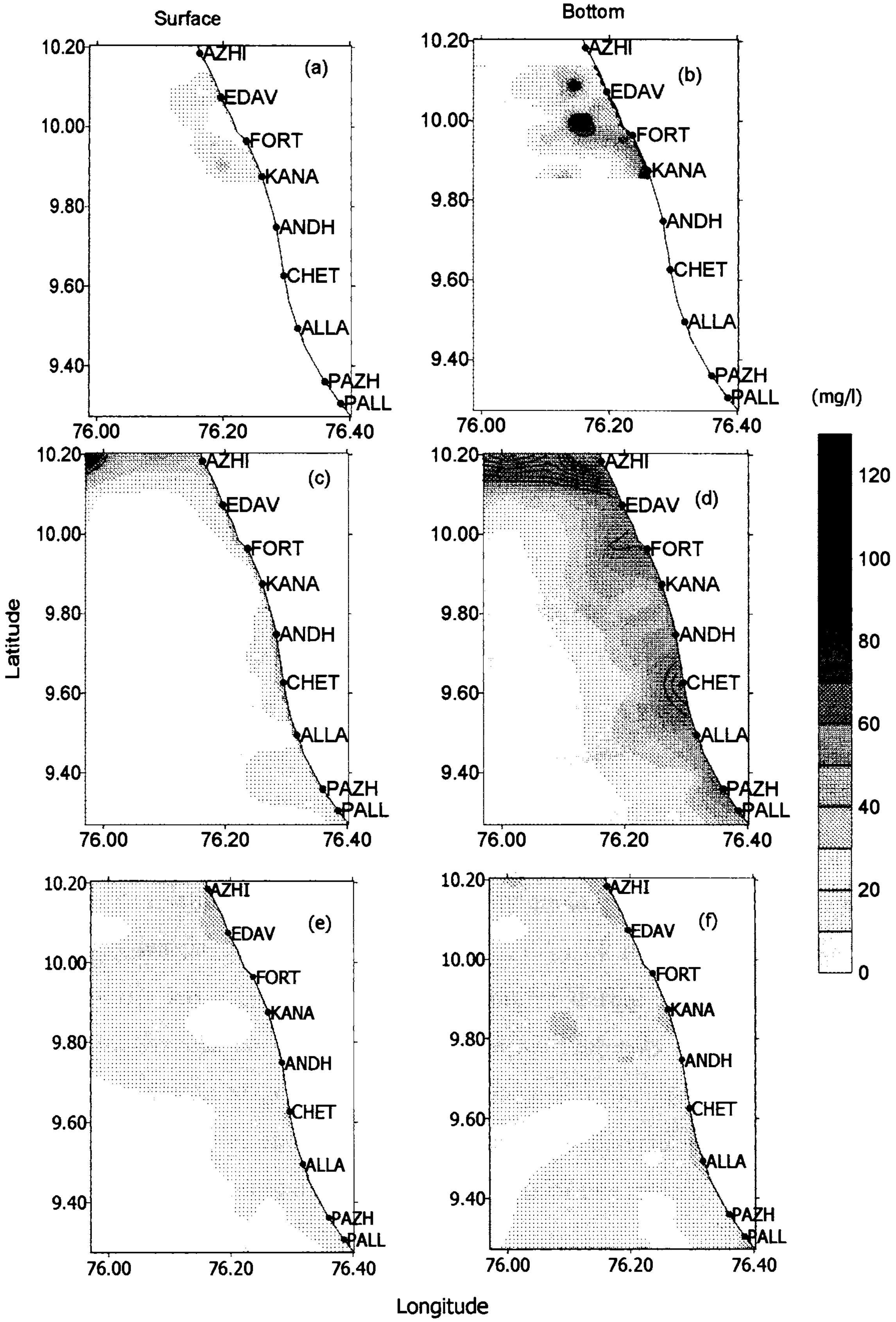


Fig. 3.13. Distribution of suspended particulate matter at the surface and bottom during October (a, b), February (c,d) & November (e, f).

sediments, especially from the mudbanks. The absence of variability with bottom nitrite during November suggests that assimilatory reduction of nitrate is independent of salinity variation. Similarly, 8 and 15 % variability for nitrate are explained by salinity during October in surface and bottom waters, indicating its influence from the surface runoff and upwelling waters respectively. However, the absence of any variability during February shows that nitrate is being introduced into the system by some other mechanism, may probably be the release from bottom mud. The overall variability of nutrients with salinity thus clearly shows that the concentrations of nutrients in the coastal waters of this region are consistent with respect to nutrient supply and seems to be independent of nutrients discharged into the system by anthropogenic sources.

The inter-relationship between various nutrient parameters also gives only very low correlation during these observations. The positive correlation of silicate and phosphate with nitrate for October surface waters indicate their common source through land drainage. During February, the positive correlation between nitrate, nitrite, silicate and temperature gives an indication of their common source within the system, the bottom sediment. The positive relation of nitrite with nitrate, ammonia, phosphate, and silicate for surface waters during November is indicative of surface runoff. The bottom nitrite has a positive relation with nitrate during November, which shows simultaneous occurrence of these two nutrient salts and its negative relation with dissolved oxygen shows enrichment of nitrite in low oxygenated waters. Saraladevi et al., (1997) have reported an inverse relationship for chlorophyll 'a' with nutrients in the coastal waters of this region.

3.4. Conclusion

The oceanographic studies carried out along the coastal waters of Cochin during three periods delineate changing hydrochemistry in response to each season. The October observations evince upwelling induced cold saline waters capping a lens of low saline waters through river runoff causing strong stratification, which prevents the upwelled water from reaching the sea surface. The sub surface water, which is deficient in dissolved oxygen, as it advances towards the shallow regions, are further depleted in dissolved oxygen levels by the increased demand for oxidation of organic matter and biological utilization. The fresh water containing high nutrients transported through Cochin barmouth extents upto about 10 km offshore, make a significant contribution.

In February the coastal waters are homogenous, vertically mixed and saturated with oxygen. The entire region is occupied with a salinity of 31 to 33 psu, which may probably be due to the northerly coastal current along the west coast of India, bringing in low saline waters from Bay of Bengal during this period. The nutrients remain low during this period except for a few parameters centered on Chethi and Alleppey. The phosphate concentrations do not show any spatial or vertical variation in the water column, but higher concentrations of ammonia, nitrate and silicate are observed at selected regions originating at the coastal nearshore regions and extending offshore. It is difficult to point out a definite source to these high nutrient values during this period, as the fresh water discharge is minimum. This could be only explained due to the active regeneration, which is taking place in the coastal sediments and thereby releasing nutrients to the overlying water.

November observations show homogenous mixed layer with higher salinity along the region of study. While the physical characteristics are more or less stable, there is considerable variability with respect to nutrient distribution and chlorophyll 'a' concentration. A marked decrease in sub surface dissolved oxygen is the characteristic feature of this period, which is concomitant with a corresponding enrichment in nitrite, phosphate and silicate concentrations. Ammonia and nitrate also seem to be elevated at some regions along southern transects. An increased particulate carbon level also is a noticeable feature during November. The decrease in dissolved oxygen is attributed to the increased rate of oxidation of particulate organic matter during the period. The elevated nitrite levels around Cochin may be due to the coastal input through the backwaters, which receive substantial quantity of nutrients through various anthropogenic sources. Higher values of nitrite observed towards the southern offshore waters of Pallana can be explained as follows. Two processes are known to result in a build-up of nitrite in oxygenated near-surface waters: assimilatory reduction of nitrate during uptake by phytoplankton (Vaccaro and Ryther, 1960; Wada and Hattori, 1971) and differential photo-inhibition of ammonia and nitrite oxidation by nitrifying bacteria (Olson, 1981). The regions occupying high nitrite are also found to contain nitrate levels upto 3 μM and the low levels of ammonia rule out nitrification as a significant process responsible for nitrite accumulation. Instead, the remarkable co-existence of nitrite with nitrate strongly suggests that the nitrite production should mostly be due to assimilatory reduction. This is further substantiated by the high concentration of chlorophyll 'a' (4 to 6 mg/m^3) observed along these transects (Fig.3.11). Similarly, the uniform enrichment of the coastal waters with phosphate has been related to the regenerative activity of sediments and its contribution from mudbank area. It is to be noted here that even when the discharges from the Cochin backwaters bring in substantial amount of phosphorus to the coastal waters, the sediments of the shallow coastal region including the mudbank sediments are mainly regulating the adsorption-desorption of phosphate to the overlying waters. Earlier reports also support November as the period when phosphate regeneration from sediment is maximum along this region.

Chlorophyll 'a' values during this study are by far the highest reported from this region, the maximum chlorophyll 'a' concentration recorded being 14 mg/m^3 during each observation. The wide variations in the nearshore-offshore chlorophyll 'a' and particulate organic carbon concentrations are probably related to the intensity of freshwater discharge, coastal currents, stability of the coastal waters and other coastal processes like upwelling, sinking etc. (Bhattathiri and Devassy, 1977). It is likely that chlorophyll values are proportionate to carbon production indicating a strong positive relationship binding it with nutrient related factors rather than seasonal or diurnal fluctuation.

Nutrients are regenerated in the bottom mud, which by turbulence and tidally induced advection fertilize the surface layers. Qasim et al., (1969) have stated that while there is a close relationship between cycles of phosphorus and organic production in the backwaters, nitrogen was completely independent of productivity rhythm. The present study also shows low values of nitrate as well as nitrite compared to silicate and phosphate, except during February. It can be observed from the Fig.(3.14) that N/P ratio of this coastal waters is below 10 along the entire water column during November, probably due to the disproportionate release of phosphate into the water column. In October, a rise in the N/P is observed in the offshore waters between Kannamali and Azhikode, which is mainly due to the presence of nitrate in the upwelled waters. During February also, this ratio remain > 10 only in the region between Chethi and north of Pazhayangadi. The low N/P in these waters are indicative of nitrogen as a limiting nutrient, which may not be due to the high amount of phosphate alone. The general negative relationship shown by nitrate and nitrite with productivity could be indicative of a rapid uptake of these salts leading to depletion or lowering of concentration at the peak production period. N: P ratios of 1.85 to 6.89 are reported for the Bay of Bengal waters, north of Visakhapatanam (Satyanarayana et al., 1987), which is considerably lower than the general oceanic ratio of 15:1 (Redfield et al., 1963). These low N/P values have been attributed to various factors like low rate of regeneration of nitrate compared to phosphate, dilution of surface waters by runoff and precipitation and denitrification prevailing in the deeper layers (Satyanarayana et al., 1987). Sankaranarayanan (1978) has stated that because of differing marine conditions, the stoichiometric relationships may not hold good for coastal regions due to the proximity of land, river runoff and also the influence of local flora and fauna. The present study shows that the regions with high chrolophyll 'a' (Fig.3.11) always co-vary with the regions having low N/P ratio. The role of denitrifying bacteria in lowering

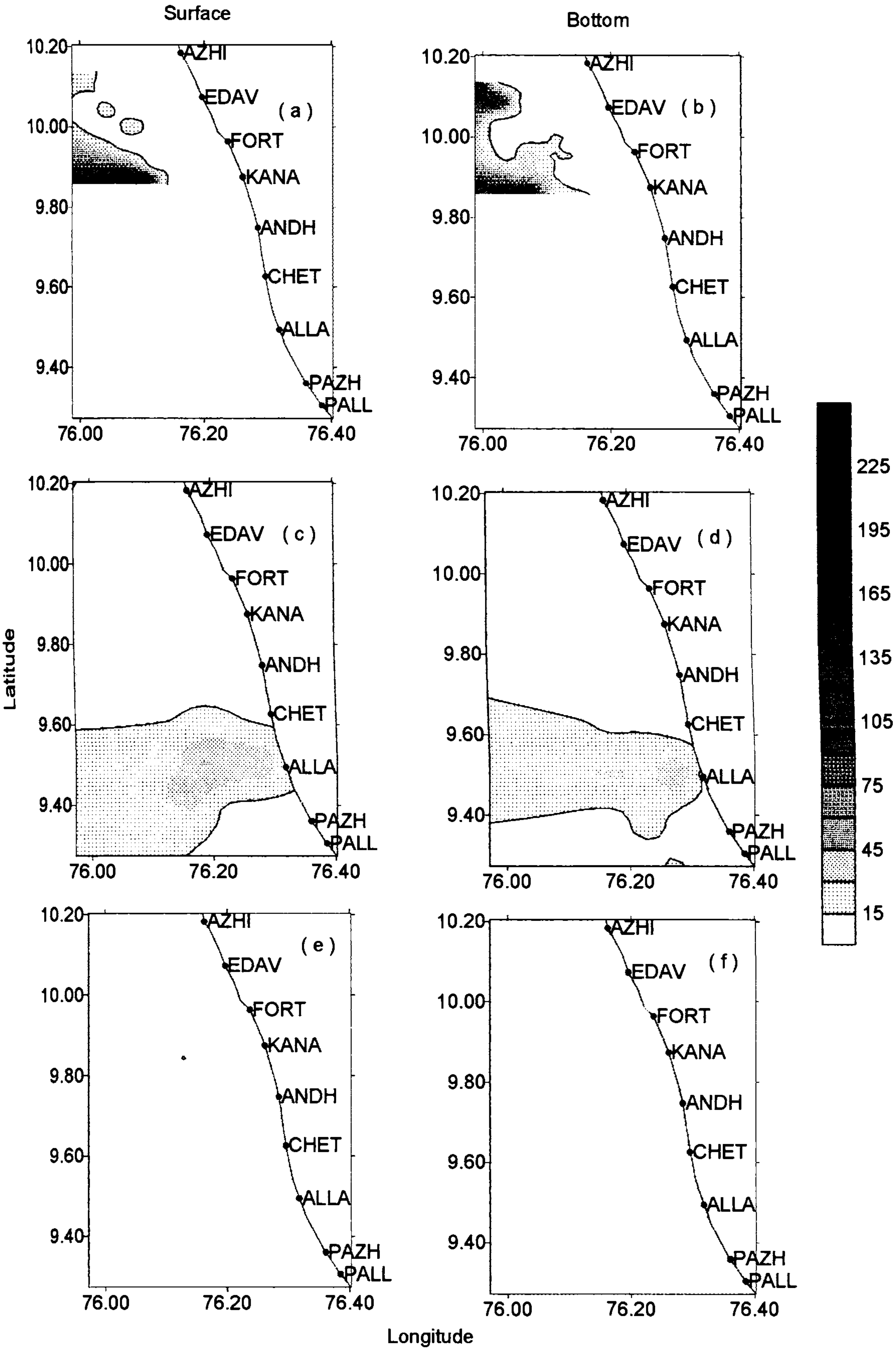


Fig. 3.14. Distribution of N/P ratio at the surface and bottom during October (a,b), February (c,d) & November (e,f).

nitrate concentrations and the release of nitrogen species by *Trichodesmium* filaments are also to be looked in. The studies by Nair and Balchand (1993) and Damodaran and Hridayanathan (1966) from these regions showed that phosphate in water and sediments was the highest during mudbank period, and the organic phosphorus in sediments was more than 100 times than that in non-mudbank region. High amounts of phosphate found in the present study, especially along the shallow regions compared to other regions are quite remarkable. It is well known that when the mudbank is active, there is an increase in turbidity and release of dissolved phosphate to overlying waters. Presence of large surface area of clay can retain a very high load of phosphate. The fluvial and sedimentary phases of the mudbanks with high organic matter content seem to have significant contribution towards the nutrient dynamics of these shallow coastal waters.

Predictive regression model

Particulate organic carbon (October, surface): The best model is that of log POC on log values of parameters, viz. temperature(X1), pH(X2), salinity(X3), NO3(X4), NH4(X5), PO4(X6), SiO4(X7) and the equation is

$$\log POC = -0.2993 + 0.2469\,X1 + 0.2332\,X2 + 0.6149\,X3 - 0.1076\,X4 - 0.2888\,X5 + 0.3193\,X6 + 0.3835\,X7 + 0.08665\,X1X2 - 0.6981\,X1X3 + 0.03232\,X1X4 - 0.1948\,X1X5 - 0.3282\,X1X6 + 0.0957\,X1X7 + 0.2584\,X2X3 - 0.2741\,X2X4 + 0.4172\,X2X5 - 0.3504\,X2X6 + 0.03951\,X2X7 - 1.0315\,X3X4 + 0.1062\,X3X5 + 0.1228\,X3X6 + 0.3796\,X3X7 - 0.5994\,X4X5 - 0.3813\,X4X6 + 0.0224\,X4X7 - 0.2420\,X5X6 - 0.2552\,X5X7 + 0.4735\,X6X7.$$

This model explains 50.9599 % of the spatial variation in the POC distribution, $F(28, 27) = 3.0412$, $P \le 0.05$.

The relative importance of the parameters could be given as

Sal*NO3 > T*Sal > Sal > NO3*NH4 > PO4*SiO4 > pH*NH4 > SiO4 > NO3*PO4 > Sal*SiO4 > pH*PO4

Particulate organic carbon (October, bottom): The best model is that of square root of POC on square root of the parameters, viz. pH(X1), salinity(X2), NO2(X3), NO3(X4), NH4(X5), PO4(X6) and SiO4(X7). The equation is

$$\sqrt{POC} = -0.1351 - 0.2831\,X1 + 0.8649\,X2 - 0.1041\,X3 + 0.2662\,X4 - 0.1087\,X5 + 0.3819\,X6 + 0.0551\,X7 - 0.6199\,X1X2 - 0.4449\,X1X3 + 0.1087\,X1X4 - 0.2433\,X1X5 - 0.5572\,X1X6 - 0.0419\,X1X7 + 0.4769\,X2X3 - 0.00669\,X2X4 + 0.1192X2X5 + 2.2659\,X2X6 - 0.2014\,X2X7 - 0.5994\,X3X4 - 0.0403\,X3X5 - 0.2988\,X3X6 - 0.0936\,X3X7 + 0.7485\,X4X5 - 0.2541\,X4X6 + 0.3199\,X4X7 + 0.1089\,X5X6 + 1.01798\,X5X7 + 0.3198\,X6X7.$$

This model explains 21.86% of spatial variation in the POC distribution, $F\,(28, 27) = 1.5895$, $P \le 0.10$. The parameters can be graded as

Sal*PO4 > NH4*SiO4 > Sal > NO3*NH4 > pH*Sal > NO2*NO3 > pH*PO4 > Sal*NO2 > pH*NO2 > PO4

Particulate organic carbon (February, surface): The best model is that of POC on parameters, viz. temperature(X1), salinity(X2), NO2(X3), NO3(X4), NH4(X5), PO4(X6), SiO4(X7). The model equation is

$$POC = 0.6803 + 0.0769\,X1 - 0.2149\,X2 + 0.6333\,X3 - 0.9595\,X4 - 0.0141X5 - 0.2613\,X6 + 0.009114\,X7 + 0.3549\,X1X2 + 0.3342\,X1X3 - 0.4271\,X1X4 - 0.06198\,X1X5 + 0.4593\,X1X6 + 0.1612\,X1X7 + 0.1773\,X2X3 - 0.05608\,X2X4 + 0.1237\,X2X5 - 0.1638\,X2X6 - 0.5092\,X2X7 - 0.2051\,X3X4 + 0.3108\,X3X5 + 0.2476\,X3X6 + 0.0922\,X3X7 + 0.6370\,X4X5 - 0.4565\,X4X6 - 0.8052\,X4X7 - 0.5694\,X5X6 - 0.1304\,X5X7 - 10.01662\,X6X7$$

This model explains about 60.82 % of the spatial variation in the POC distribution in the surface waters during February, $F\,(28, 18) = 3.5505$, $P \le 0.05$.

The most important parameters are

NO3 > NO3*SiO4 > NO3*NH4 > NO2 > NH4*PO4 . Sal*SiO4 > T*PO4 > NO3*PO4 > T*NO3 > T*Sal

Particulate organic carbon (February, bottom): The best model is that of original values of POC on original values of the 9 parameters. The equation is

$$POC = 0.1239 - 1.8167\ X1 - 2.6929\ X2 - 0.9225\ X3 - 1.3946\ X4 + 1.8455\ X5 + 0.5793\ X6 - 1.8652\ X7 + 0.2908\ X8 - 1.0038\ X9 - 161.4384\ X1X2 - 1.0669\ X1X3 - 2.7672\ X1X4 + 1.5474\ X1X5 - 0.4829\ X1X6 + 1.4886\ X1X7 - 4.3929\ X1X8 - 1.1699\ X1X9 - 0.7945\ X2X3 + 158.3823\ X2X4 + 0.2954\ X2X5 - 3.9151\ X2X6 + 0.5067\ X2X7 - 1.6497\ X2X8 + 0.5435\ X2X9 + 0.6914\ X3X4 - 1.3373\ X3X5 + 0.8191\ X3X6 + 0.6610\ X3X7 + 0.7968\ X3X8 + 1.1402\ X3X9 - 0.5854\ X4X5 - 1.8055\ X4X6 - 0.2872\ X4X7 - 3.4230\ X4X8 - 0.6972\ X4X9 - 0.7489\ X5X6 - 0.66666X5X7 + 1.1396\ X5X8 - 0.5593\ X5X9 + 1.0044\ X6X7 - 0.8212\ X6X8 + 0.2335\ X6X9 + 0.1576\ X7X8 + 0.0251\ X7X9 + 0.1539\ X8X9$$

This model explains 94.46 % of the spatial variation in the bottom distribution of POC, F (45, 1) = 18.4306. The relative importance of the parameters is

T*pH > pH*DO > T*PO4 > pH*NO3 > DO*PO4 > T*DO > pH > NH4 > NO2 > T > DO*NO3

Particulate organic carbon (November, surface): The best model is that of POC on values of all the 9 parameters. The equation is

$$POC = 0.1201 + 2.4065\ X1 + 1.0212\ X2 - 0.3276\ X3 - 1.6623\ X4 + 0.9305\ X5 + 1.7166\ X6 - 2.3803\ X7 + 0.4452\ X8 - 0.6252\ X9 + 0.6458X1X2 + 0.9893\ X1X3 - 4.7401\ X1X4 + 0.1603\ X1X5 + 3.1602X1X6 - 0.2694\ X1X7 - 0.7513\ X1X8 - 2.4583\ X1X9 + 0.5349\ X2X3 + 0.6458\ X2X4 - 0.1012\ X2X5 + 2.4599\ X2X6 + 0.4571\ X2X7 + 0.6288\ X2X8 - 0.09138\ X2X9 - 2.8403\ X3X4 - 2.0366\ X3X5 - 5.3511\ X3X6 - 2.7306\ X3X7 + 2.1060\ X3X8 + 1.7998\ X3X9 - 0.6378\ X4X5 + 1.0021\ X4X6 - 0.1551\ X4X7 - 2.5407\ X4X8 - 4.6546\ X4X9 + 3.0366\ X5X6 - 1.0607\ X5X7 + 0.6505\ X5X8 -$$

$$1.9457\,X5X9 + 0.7145\,X6X7 - 0.5903\,X6X8 + 2.5991\,X6X9 - 2.7693\,X7X8 - 2.7651\,X7X9 + 0.2005\,X8X9$$

This model explains about 82.52 % of the spatial variation in the surface distribution of POC during November. F (45, 1) = 5.8253, $P \leq 0.05$

The relative importance of the parameters is

Sal*NO3 > T*DO > DO*SiO4 > T*NO3 > NO2*NO3 > Sal*NO3
> PO4*NH4 > NH4*SiO4 > Sal*NH4 > NO3*SiO4

Particulate organic carbon (November, bottom): The best model is that of POC on square root of all the 9 parameters. The model equation could be given as

$$\sqrt{POC} = -0.7800 + 0.7657\,X1 + 2.2180\,X2 + 2.6661\,X3 + 1.6986\,X4 - 0.1017\,X5 - 0.2751\,X6 + 1.5902\,X7 + 0.0972\,X8 + 2.1592\,X9 + 9.7149\,X1X2 + 0.8448\,X1X3 + 1.3452\,X1X4 + 0.3165\,X1X5 - 1.1848\,X1X6 + 0.5769\,X1X7 + 2.3502\,X1X8 + 0.05759\,X1X9 + 0.4709\,X2X3 - 9.4881\,X2X4 + 3.3608\,X2X5 + 2.8856\,X2X6 + 0.8172\,X2X7 - 0.7758\,X2X8 - 0.4952\,X2X9 - 0.8183\,X3X4 + 0.7032\,X3X5 - 0.0582\,X3X6 - 1.1426\,X3X7 + 0.7205\,X3X8 - 2.0017\,X3X9 + 0.08249\,X4X5 - 0.9293\,X4X6 - 1.7709\,X4X7 + 3.5325\,X4X8 - 2.4312\,X4X9 + 1.9499\,X5X6 + 0.5498\,X5X7 + 4.1468\,X5X8 - 3.6339\,X5X9 - 0.03788\,X6X7 - 1.1874\,X6X8 - 1.1960\,X6X9 + 1.1030\,X7X8 - 0.2380\,X7X9 + 0.6300\,X8X9$$

This model explains about 81.32 % of the spatial distribution of POC in the bottom waters. F (45, 1) = 5.4503, $P \leq 0.05$.

The relatively most important parameters could be given as

T*pH > pH*DO > NO2*PO4 > NO2*SiO4 > DO*PO4 > pH*NO2 > pH*NO2 > Sal > T*PO4 > DO*SiO4

Suspended particulate matter (October, surface): The best model is that of log suspended matter on log [parameters], where the parameters are temperature, pH, salinity, dissolved oxygen, NO2, NO3, NH4, PO4 and SiO4. The model equation is

$$\log \text{suspended solid} = 28.0256 - 19.05\,X2X4 + 18.76\,X1X2 + 2.8272\,X1X5 - 2.1649\,X6X8 - 2.0683\,X3X8 + 1.5628\,X4X7 - 1.5007\,X2X7 - 1.4332\,X1X8 + 1.2236\,X3X5 - 1.0656\,X4X8 - 1.0595\,X2 - 0.8893\,X1X4 - 0.8311\,X6X7 + 0.8279\,X2X6 - 0.7110\,X3 - 0.71104\,X4 + 0.6429\,X1X6 - 0.6157\,X5X6 - 0.6135\,X5 + 0.5984\,X1X9 - 0.5949\,X1X3 - 0.5254\,X2X3 + 0.4938\,X5X9 + 0.4843\,X4X6 - 0.4282\,X5X8 - 0.4118\,X7X9 + 0.3725\,X4X5 + 0.3563\,X3X4 + 0.3269\,X2X9 - 0.3244\,X7 + 0.3181\,X3X6 - 0.2745\,X3X9 - 0.2668\,X1 + 0.2656\,X1X7 - 0.2373\,X2X5 + 0.2106\,X6 + 0.2062\,X4X9 + 0.1945\,X3X7 - 0.1720\,X8X9 - 0.1594\,X7X8 - 0.1430\,X9 - 0.0608\,X2X8 + 0.0244\,X5X7 + 0.1184\,X6X9 - 0.000238\,X8$$

This model explains about 48.04 % of the spatial variations. $F(9, 46) = 5.2918$,

$P \leq 0.05$.

The parameters are arranged according to the relative importance as

pH*DO > T*Sal > T*NO2 > NO3*PO4 > Sal*PO4 > DO*NH4 > pH*NH4 > T*PO4 > Sal*NO2 >DO*PO4

Suspended particulate matter (October, bottom): The best model is that of log suspended solids on log [parameters]. The parameters considered are temperature, salinity, DO, NO2 and NO3. The equation is

$$\log [\text{suspended particulate matter}] = -0.0205 + 0.8630\,X1 - 0.10444\,X2 + 0.1768\,X3 + 0.0218\,X4 + 0.2695\,X5 - 0.1288\,X1X2 + 0.0351\,X1X3 - 0.1869\,X1X4 + 0.1281\,X1X5 - 0.4232\,X2X3 - 0.6696\,X2X4 + 0.1910\,X2X5 - 0.3738\,X3X4 + 0.3499\,X3X5 - 0.4129\,X4X5$$

This explains 53.93 % of the spatial variation. $F(15, 40) = 5.2918$, $P \leq 0.05$.

The parameters are graded as

T > Sal*NO2 > Sal*DO > NO2*NO3 > DO*NO2 > DO*NO3 > NO3 > Sal*NO3 > T*NO2 > DO

Suspended particulate matter (February, surface): The best model is that of suspended particulate matter on pH, salinity, DO, NO2, NO3, NH4, PO4 and Si04. The prediction equation is

Suspended particulate matter = 0.03618 – 8.5639 X1X3 + 6.0458 X6X7 – 5.057 X2X9 – 3.709 X1X9 – 3.5193 X4X8 – 3.2268 X3X4 + 3.1145 X4X9 + 2.4151 X7 – 2.0832 X2 + 2.0202 X2X8 + 1.8604 X6X7 + 1.7055 X5X6 – 1.6592 X8X9 – 1.5461 X2X3 – 1.5039 X6X9 – 1.4320 X1X7 + 1.4073 X6 + 1.3654 X2X5 + 1.3319 X1X4 + 1.2765 X1X5 – 1.2333 X2X7 + 1.2162 X3X7 – 1.2124 X3X8 – 1.1555 X4 + 1.0554 X3X6 + 0.8957 X1X8 + 0.8815 X5 + 0.6803 X1 –

0.6526 X4X5 – 0.6091 X2X6 + 0.5834 X4X7 – 0.5128 X5X8 + 0.4916 X9

- 0.4529 X8 + 0.4388 X3 – 0.4071 X3X5 – 0.3565 X7X9 + 0.3110 X1X6 –

- 0.3102 X2X4 – 0.3102 X1X2 – 0.2823 X4X6 – 0.2736 X5X9 + 0.2403 X5X7

– 0.0786 X7X8- 0.0306 X3X9

This model explains about 91.91 % of the spatial variation in the suspended particulate matter distribution. F (45, 1) = 12.6204

The parameters, which are relatively more important, are

T*Sal > NO3*PO4 > pH*SiO4 > T*SiO4 > DO*PO4 > Sal*DO

> DO*SiO4 > NH4 > pH > pH*PO4

Suspended particulate matter (February, bottom): Original values of suspended particulate matter on the original values of the 8 parameters except silicate as given earlier is

Suspended particulate matter = - 0.01959 + 0.6549 X1 – 0.6583 X2 + 0.4956 X3 – 0.7962 X4 – 0.05749 X5 + 0.4998 X6 – 0.9423 X7 + 1.0150 X8 – 0.4349 X1X2 + 0.3815 X1X3 + 1.6146 X1X4 + 0.3193 X1X5 + 1.1546 X1X6 + 0.2977 X1X7 – 0.9532 X1X8 + 1.5919 X2X3 – 0.2761 X2X4 – 0.8083 X2X5 + 0.3606 X2X6 – 0.7524 X2X7 + 1.0902 X2X8 – 0.1045 X3X4 – 0.2177 X3X5 – 0.2702 X3X6 – 0.3477 X3X7 – 0.3742 X3X8 – 0.5499 X4X5 – 0.7829 X4X6 – 0.8937 X4X7 + 0.8509 X4X8 + 0.1583 X5X6 +

$0.3660\ X5X7 + 0.05236\ X5X8 - 0.1321\ X6X7 - 1.5019\ X6X8 + 0.2432\ X7X8$

This model explains 83.44 % of the spatial variation in the bottom distribution of suspended particulate matter during February. F (36, 10) = 7.4414, $P \leq 0.05$.

The relatively most important parameters are graded as

T*DO > NO3*PO4 > T*NO3 > pH*PO4 > PO4 >T*PO4 > NH4 > DO*NH4 > DO*PO4 > pH*NO2

Suspended particulate matter (November, surface): The best model is that of suspended particulate matter on the 9 parameters as discussed earlier. The model equation is

$$\text{Suspended particulate matter} = -0.3322 - 4.0719\ X1 - 3.2486\ X2 + 0.8736\ X3 + 0.9811\ X4 - 0.7321\ X5 - 1.7102\ X6 + 1.9423\ X7 + 0.5711\ X8 - 1.3734\ X9 - 1.4538\ X1X2 + 0.5522\ X1X3 + 6.4911\ X1X4 + 1.6883\ X1X5 - 3.4048\ X1X6 - 0.1729\ X1X7 + 0.6102\ X1X8 + 6.0173\ X1X9 - 1.3411\ X2X3 - 1.4538\ X2X4 + 0.7257\ X2X5 - 1.5934\ X2X6 - 4.1423\ X2X7 - 0.7272\ X2X8 + 0.9661\ X2X9 + 1.7378\ X3X4 + 0.6635\ X3X5 + 3.4004\ X3X6 + 1.4395\ X3X7 - 2.5309\ X3X8 - 5.1632\ X3X9 + 0.7212\ X4X5 - 1.7452\ X4X6 - 0.6221\ X4X7 + 1.7429\ X4X8 + 3.2130\ X4X9 - 1.6923\ X5X6 + 2.8884\ X5X7 - 1.2591\ X5X8 + 0.1231\ X5X9 + 1.1394\ X6X7 - 0.5963\ X6X8 - 1.5516\ X6X9 + 0.9461\ X7X8 + 0.4590\ X7X9 + 1.0309\ X8X9$$

This model explains about 87.45 % of the spatial variation in the distribution of suspended particulate matter in the bottom waters, F (45, 1) = 8.1217, $P \leq 0.05$

The relatively most important parameters are

DO*NO2 > T*DO > T*SiO4 > Sal*SiO4 > pH*NH4 > T > T*NO3 > Sal*NO3 > Sal > DO*SiO4

Suspended particulate matter (November, bottom): The best predictive model is that of square root of suspended particulate matter on square root of 9 parameters as given earlier. The model equation is square root of suspended particulate matter $= -0.1083 + 0.3229\ X1 + 0.4276\ X2 + 0.9551\ X3 - 0.1012\ X4 - 0.4031\ X5 + 0.04787\ X6 + 0.6087\ X7 + 0.4884\ X8 + 0.2958\ X9 - 1.6394\ X1X2 + 0.1568\ X1X3 - 0.5950\ X1X4 - 0.06877\ X1X5 - 0.2688\ X1X6 + 0.04307\ X1X7 - 0.02596\ X1X8 + 1.0913\ X1X9 - 0.1945\ X2X3 + 0.8752\ X2X4 + 0.006571\ X2X5 + 0.3762\ X2X6 + 0.7188\ X2X7 - 0.51196\ X2X8 - 0.47199\ X2X9 - 0.4476\ X3X4 - 0.2918\ X3X5 - 0.3861\ X3X6 + 0.1817\ X3X7 + 1.7321\ X3X8 + 0.3709\ X3X9 - 2.4444\ X4X5 + 1.2578\ X4X6 - 0.8119\ X4X7 + 1.3060\ X4X8 + 0.0598\ X4X9 - 1.0614\ X5X6 + 0.7343\ X5X7 + 0.2117\ X5X8 - 0.3175\ X5X9 - 0.1918\ X6X7 + 0.5847\ X6X8 - 0.7833\ X6X9 + 0.02272\ X7X8 + 0.4211\ X7X9 - 0.7899\ X8X9$

This model explains about 99.775 % of the spatial variation of the bottom distribution of suspended particulate matter, $F(45, 1) = 453.6371$, $P \leq 0.05$

Since almost all the variables are explained by these parameters, it is not necessary to include any more additional factors for the prediction of suspended particulate matter during November. The relative importance of the model parameters could be given as

DO*NO2 > Sal*PO4 > T*pH > DO*PO4 > T* SiO4 > NO2*NO3 > Sal > pH*DO > DO*NH4 > PO4*SiO4

Chlorophyll 'a' (October, surface): The model is log chlorophyll 'a' on original values of the parameters viz. pH(X1), salinity(X2), DO(X3), NO_3(X4), PO_4 (X5) and SiO_4(X6). The equation is

log Chl.a $= 0.3636 - 0.2903\ X1 - 0.5884\ X2 + 0.1551\ X3 + 0.0780\ X4 + 0.3843\ X5 - 0.1710\ X6 - 0.1648\ X1X2 = 0.3526\ X1X3 + 0.5198\ X1X4 - 0.4817\ X1X5 + 0.3180\ X1X6 + 0.3536\ X2X3 + 0.2256\ X2X4 + 0.05344\ X2X5 + 0.3827\ X2X6 + 0.4208\ X3X4 + 0.2222\ X3X5 + 0.1583\ X3X6 + 0.0223\ X4X5 + 0.514\ X4X6 - 0.04989\ X5X6.$

This model explains 48.69 % of the spatial variation, $F(21, 34) = 3.4854$ $P < 0.05$. The relative importance of the model parameters could be given as

Sal > pH*NO3 > NO3*SiO4 > DO*NO3 > PO4 > Sal*SiO4 > Sal*DO> pH*DO > pH*SiO4 > pH.

Chlorophyll 'a' (October, bottom): The best predictive model is that of log chlorophyll 'a' on original values of the parameters. The model equation is

$\log \text{chl. a} = 0.006640 - 0.3473\ X1 - 0.3824\ X2 + 0.0583\ X1X2$ where $X1 = DO$, $X2 = NO2$. This model could explain only 20.015 % of the spatial variations, $F(3, 52) = 5.5877$, $P < 0.05$. The relative importance is

NO2 > DO > NO2*DO

Chlorophyll 'a' (February, surface): The most efficient predictive model is that of chlorophyll 'a' on parameters; pH (X1), Sal (X2), DO (X3), NO2(X4), NH4(X5). The relation is

$$\text{Chlorophyll 'a'} = -0.4157 + 1.2242X1 - 0.2010\ X2 - 0.1342\ X3 - 0.0504\ X4 + 0.8075\ X5 + 0.1404\ X1X2 - 0.0333\ X1X3 + 1.099\ X1X4 + 0.7508\ X1X5 - 0.8147\ X2X3 - 0.3403\ X2X4 - 0.0726\ X2X5 + 0.2038\ X3X4 - 0.2897\ X3X5 - 0.4651\ X4X5$$

This model explains about 37.11 % of the variability $F(15, 31) = 2.8098$, $P < 0.05$ The order of importance of parameters is

pH > pH*NO2 > Sal*DO > NH4 > pH*NH4 > NO2*NH4 > Sal*NO2 > DO*NH4 > DO*NO2 > Sal.

Chlorophyll 'a' (February, bottom): Best model is that of square root of chlorophyll 'a' on square root of the 9 parameters given earlier. The model equation is

$$\sqrt{\text{Chl.a}} = -0.3828 + 2.3212\ X1 + 6.6292\ X2 + 1.7109X3 + 0.8105\ X4 - 3.6216\ X5 - 0.8005\ X6 + 1.5984\ X7 + 3.0092\ X8 + 0.8031\ X9 + 13.4478\ X1X2 + 3.9031\ X1X3 + 2.8590\ X1X4 + 0.5456\ X1X5 - 0.6848\ X1X6 - 4.1846\ X1X7 + 5.2124\ X1X8 + 2.3449\ X1X9 + 2.1065\ X2X3 - 9.9409\ X2X4 - 3.3192\ X2X5 + 5.8553\ X2X6 + 1.0773\ X2X7 + 0.5698\ X2X8 - 5.2351\ X2X9 - 1.7696\ X3X4 + 0.02712\ X3X5 - 1.1031\ X3X6 - 1.3483\ X3X7 - 0.6599\ X3X8 + 1.7001\ X3X9 + 0.8929\ X4X5 + 4.5061\ X4X6 - 0.9515\ X4X7 + 2.6338\ X4X8 - 2.3441\ X4X9 + 0.9274\ X5X6 + 3.8425\ X5X7 - 3.0929\ X5X8 - 1.2590\ X5X9 - 3.6846\ X6X7 + 2.2959\ X6X8 - 1.3214\ X6X9 - 0.3043\ X7X8 + 2.1595\ X7X9 - 2.3031\ X8X9.$$

This model explains about 69.21 % of the spatial variation in the bottom distribution of chlorophyll 'a', $F (45, 1) = 3.298$, $P < 0.05$. The relatively important parameters are

T*pH > pH*DO > pH > pH*NO3 > pH*SiO4 > T*PO4 > DO*NO3 > T*NH4 > T*DO > NO2*NH4

Chlorophyll 'a' (November, surface): The best predictive model is that of log chlorophyll 'a' on log values of the 9 parameters. The model equation is

$$\log \mathrm{chl.a} = 0.6120 - 7.4330\,X1 - 5.8609\,X2 + 1.4632\,X3 - 0.7133\,X4 - 9.6135\,X5 + 5.0905\,X6 - 0.9956\,X7 + 3.8983\,X8 - 3.6969\,X9 - 17.2511\,X1X2 + 9.2291\,X1X3 + 5.9416\,X1X4 + 4.5114\,X1X5 + 1.3546\,X1X6 - 1.8461\,X1X7 - 2.1871\,X1X8 + 7.6911\,X1X9 + 1.1444\,X2X3 + 10.6338\,X2X4 - 1.4324\,X2X5 - 4.5618\,X2X6 + 6.0322\,X2X7 - 1.5401\,X2X8 - 8.5672\,X2X9 + 8.2181\,X3X4 + 6.6513\,X3X5 + 11.5450\,X3X6 - 6.0193\,X3X7 + 0.5138\,X3X8 - 8.8638\,X3X9 + 6.1475\,X4X5 - 1.9786\,X4X6 - 3.2485\,X4X7 + 6.8465\,X4X8 - 1.3091\,X4X9 + 0.2833\,X5X6 + 8.8471\,X5X7 + 5.0991\,X5X8 - 7.2562\,X5X9 + 4.7485\,X6X7 - 3.1375\,X6X8 - 4.3571\,X6X9 + 1.2421\,X7X8 - 3.0793\,X7X9 - 0.5873\,X8X9$$

This 45 parameter model explains 76.9999 % of the spatial variation in the distribution of chlorophyll 'a', $F (45, 1) = 4.4221$, $P \leq 0.05$. The relative importance of the parameters can be given as

T*pH > Sal*NO3 > pH*DO > NO2 > T*Sal > Sal*SiO4 > NO3*NH4 > pH*SiO4 > Sal*DO > T*SiO4

Chlorophyll 'a' (November, bottom): The best model is that of square root of chlorophyll 'a' on square root values of the 8 parameters other than silicate. The model equation is

$$\sqrt{\mathrm{Chl.\ a}} = -4.7574 + 0.10604\,X1 + 0.7539\,X2 + 0.2781\,X3 - 0.04115\,X4 - 0.2721\,X5 + 0.7233\,X6 + 0.04865\,X7 + 0.3023\,X8 + 0.31190\,X1X2 - 0.3677\,X1X3 - 0.3650\,X1X4 - 0.06258\,X1X5 - 0.1186\,X1X6 + 0.7034\,Z1Z7 - 1.3286\,X1X8 + 0.8164\,X2X3 + 0.5079\,X2X4 - 0.3971\,X2X5 - 0.04451X2X6 + 0.5984\,X2X7 - 0.7240\,X2X8 + 0.7146\,X3X4 - 0.6526$$

X3X5 + 0.8261 X3X6 + 0.3261 X3X7 + 0.3430 X3X8 + 0.7372 X4X5 + 0.5781 X4X6 + 0.9617 X4X7 – 0.8482 X4X8 – 0.8774 X5X6 – 0.4455 X5X7 – 0.3059 X5X8 + 0.0129 X6X7 + 0.6222 X6X8 + 0.3815 X7X8.

This model could explain about 77.42 % of the spatial variation in the bottom distribution of chlorophyll 'a' during November, F (36, 10) = 5.3807, $P \leq 0.05$.

The relatively most important parameters could be graded as

T*PO4 > DO*NH4 > NO2*NO3 > DO*PO4 > pH*Sal > pH > DO*NO2
pH*PO4 > NO3 > Sal*DO

			Relative importance of the model parameters
Oct.	Chl.a	S	Sal > pH*NO_3 > NO_3*SiO_4 > DO*NO_3 > PO_4 > Sal*SiO_4 > Sal*DO>pH*DO > pH*SiO_4 > pH.
	Chl.a	B	pH > pH*NO_2 > Sal*DO > NH_4 > pH*NH_4 > NO_2*NH_4 > Sal*NO_2 > DO*NH_4 > DO*NO_2 > Sal.
Feb.	Chl.a	S	pH > pH*NO_2 > Sal*DO > NH_4 > pH*NH_4 > NO_2*NH_4 > Sal*NO_2 > DO*NH4 > DO*NO2 > Sal.
	Chl.a	B	T*pH > pH*DO > pH > pH*NO3 > pH*SiO4 > T*PO4 > DO*NO3 > T*NH4 > T*DO > NO2*NH4
Nov.	Chl.a	S	T*pH > Sal*NO3 > pH*DO > NO2 > T*Sal > Sal*SiO4 > NO3*NH4 > pH*SiO4 > Sal*DO > T*SiO4
	Chl.a	B	T*PO4 > DO*NH4 > NO2*NO3 > DO*PO4 > pH*Sal > pH > DO*NO2 > pH*PO4 > NO3 > Sal*DO

Regarding the chlorophyll 'a' distribution in the coastal waters, the 9 environmental factors plays selective roles, either as controlling or limiting factors and their interaction (*) effects are quite decisive in pigment production. The interaction effect of PO4 with NO3 determines the outcome of interspecific competition at different nutrient concentrations as stated by Kautsky (1981), because the intakes of these parameters are species specific to a great extent. As the present studies do not reflect this interaction effect, it could be assumed that the pigment productions in these coastal waters are not controlled by this interaction: ie; availability of both these nutrients are not restricted. Temperature is obtained as an important factor for this model during February and November, suggesting that temperature sets the condition for optimal metabolic activity with increase in the abundance of flagellates and succession of diatom species (Fisher and Gray, 1983). Platt (1986) has also stated that primary productivity has been found to be a function of surface irradiance. In some cases, limiting factors are found to be more important than controlling factors. Since (NO2*NO3) interaction is obtained as one of the controlling factors during November, it follows that the growth of phytoplankton is often controlled to a certain extent, by the supply of ammonium excreted by zooplankton and members of other trophic levels (Kiefer and Atkinson, 1984).

Since nitrogen compounds and DO are obtained as important factors, it means that they are also brought into the medium by decomposition of particulate organic carbon (Robinson et al., 1982). The controlling effects of pH and the interaction effects of pH and ammonia with NO2, DO, T and NO3 is also a controlling factor in primary production. Similarly, pH and salinity are found to be a dominant and interactive factor in the present study region, which was not been observed for a similar study in the Arabian Sea (Jayalakshmy, 1998). This may probably be associated with the greater land-sea interaction and also due to the fact that the biological production induced by chemical changes in coastal zones far exceed that of the oceanic region. It is worth mentioning here that while this predictive model for the Arabian Sea could explain only less than half the variability in primary production (for 21 parameters), the same analysis in the present study (especially during November and February) could explain more than 70 % of the variability. Higher variability explained implies a more stable environment. This shows that the predictive model is more significant when applied for this coastal waters than in oceanic region. This also consolidates the view that, inspite of seasonal fluctuations associated with monsoon, these coastal waters are pre-conditioned for the primary production during most of the time. This is because, the high variability explained for the predictive model for chlorophyll 'a' is suggestive of a more stable coastal waters.

The unexplained variability for the model may be due to other factors like transparency, turbidity, upwelling, stratification etc. and inclusion of these factors will improve the efficiency of this predictive model. Janse and Aldenberg (1990) have stated that the greater amount of uncertainity in the model can be due to the limited knowledge of the selective grazing rates and mineralisation processes. Hence, by incorporating these two variables the uncertainty in the predictive model can be further minimized.

3.5. Dissolved trace metals in the coastal waters

Knowledge of trace element composition of estuarine and coastal waters is essential to understand the marine geochemical budget, as the rivers supply dissolved and particulate matter to the oceans (Riley and Chester, 1971). The concentrations of dissolved metals in water are often close to the background due to their efficient removal from the water column through hydrolysis and adsorption by suspended particulate matter. There is an upper limit to the concentration that any metal ion can attain in seawater depending upon the solubility of its compounds (Krauskopf, 1956). Hence sediments serve as the ultimate sink for several trace metals and their analysis can serve as a useful indicator of metal pollution. However, it must be emphasized that the levels of metals in the aquatic environment depend on several natural factors such as particle size, the rock from which they have been derived, pH, redox potential and texture. Hence, detailed investigations involving several parameters are required for interpretation of sediment contamination. However, gross estimates are possible through adequate comparison with baseline information.

Dissolved trace metals, copper, zinc and iron are determined in the surface and bottom seawater samples. Sampling has been restricted to surface and bottom of three stations (shallow, middle and offshore) in each transect.

The observed data show large variability in the distribution of metals in the dissolved phase.

3.5.1. Copper

Highest concentration of dissolved copper is observed in the month of October. The surface concentrations range from 3.0 to 11.9 µg/l and the bottom concentrations from 4.1 to 7.8 µg/l (Fig.3.15). The mean surface and bottom dissolved copper values are 6.99 and 5.22 µg/l respectively. The highest concentration of 11.8 µg/l is observed along the third transect (Table.3.14). During February, the concentration of dissolved copper in the surface and bottom waters along the 9 transects range from below detectable limit to 3.2 µg/l. Higher concentrations are observed along transects I, IV, V and VI in the coastal stations close to the river mouth. The mean concentrations of dissolved copper in surface and bottom waters during February are 1.2 and 1.53 µg/l respectively. Surface concentration of dissolved copper increases in November, while bottom waters contain very low levels. The surface value varies from below detectable limit to 7 µg/l and bottom values vary from below detectable limit to 2 µg/l and the mean concentrations of surface and bottom are 1.91 and 0.67 µg/l respectively. High values of 7 µg/l observed are along transects 7 and 9, which are at the river mouths of Cochin and Azhikode.

3.5.2. Zinc

Dissolved zinc levels in the water vary widely during October with the surface values from 10.4 to 33.6 µg/l and bottom values from 11.5 to 42.3 µg/l (Fig.3.16). In general, bottom waters show higher zinc levels. However, along transects III to V surface values are high (Table.3.15). The mean concentrations during this period for surface and bottom waters are 18.2 and 18.9 µg/l respectively. Surface and bottom samples of station 1 record the highest concentration of dissolved zinc. While dissolved copper distribution show higher levels during November, the distribution of dissolved zinc in the study area shows maximum value during February. During February, the

Table 3.14 Range in the concentration of dissolved copper (µg/l)

		October			February			November		
TR.		Min.	Max.	Ave.	Min.	Max.	Ave.	Min.	Max.	Ave.
I	S	2.9	4.59	3.7	0	3.2	1.6	0.8	2	1.6
	B	4.5	8.1	6.3	0.80	1.60	1.30	0.80	2.00	1.20
II	S	--	--	--	0.00	1.60	1.00	0.80	2.00	1.20
	B	--	--	--	0.80	1.60	1.20	0.00	0.00	0.00
III	S	9.3	11.9	10.6	0.00	1.60	1.00	0.80	2.00	1.20
	B	5.2	5.9	5.5	0.00	1.60	0.50	0.00	0.80	0.30
IV	S	--	--	--	1.60	1.60	1.60	0.00	0.00	0.00
	B	--	--	--	0.80	3.20	2.10	0.00	0.80	0.30
V	S	6.3	7.8	7	0.80	2.40	1.60	0.00	2.00	0.70
	B	4.4	7.8	6.1	2.40	3.60	3.10	0.00	0.80	0.50
VI	S	--	--	--	1.60	3.20	2.10	0.80	3.00	2.30
	B	--	--	--	2.40	2.40	2.40	0.00	0.80	0.30
VII	S	4.5	6.2	5.3	0.80	1.60	1.00	3.00	7.00	5.00
	B	4.1	4.5	4.3	0.80	2.40	1.60	0.80	2.00	1.60
VIII	S	--	--	--	0.00	0.00	0.00	0.80	2.00	1.60
	B	--	--	--	0.00	1.60	0.50	0.00	2.00	0.90
IX	S	--	--	--	0.80	1.60	1.00	0.80	7.00	3.30
	B	--	--	--	0.80	1.60	1.10	0.80	0.80	0.80
Mean	S	--	--	6.7	--	--	1.20	--	--	1.90
	B	--	--	5.6	--	--	1.53	--	--	0.70

TR - Transect

Table 3.15 Range in the concentrations of zinc (µg/l)

		October			February			November		
TR.		Min.	Max.	Ave.	Min.	Max.	Ave.	Min.	Max.	Ave.
I	S	15	33	24	35.00	48.00	41.00	0.00	9.00	3.00
	B	14	42	28	60.00	86.00	73.00	0.00	4.00	1.30
II	S	--	--	--	55.00	61.00	58.00	0.00	3.00	1.70
	B	--	--	--	51.00	55.00	53.00	1.00	9.00	5.70
III	S	19	20	20	14.00	41.00	28.00	1.00	6.00	3.00
	B	21	31	26	20.00	45.00	31.00	2.00	6.00	3.30
IV	S	--	--	--	10.00	17.00	14.00	0.00	3.00	1.70
	B	--	--	--	14.00	26.00	19.00	0.00	5.00	1.70
V	S	10	23	17	6.00	28.00	19.00	3.00	7.00	4.70
	B	26	32	29	10.00	23.00	18.00	3.00	4.00	3.70
VI	S	--	--	--	12.00	14.00	13.00	2.00	9.00	6.00
	B	--	--	--	8.00	35.00	21.00	0.00	7.00	3.00
VII	S	11	12	12	10.00	21.00	14.00	8.00	14.00	11.00
	B	11	20	16	8.00	15.00	12.00	6.00	8.00	6.70
VIII	S	--	--	--	9.00	15.00	13.00	0.00	12.00	7.00
	B	--	--	--	11.00	18.00	14.00	4.00	9.00	6.00
IX	S	--	--	--	9.00	19.00	14.00	2.00	17.00	9.70
	B	--	--	--	11.00	22.00	14.00	5.00	8.00	6.00
Mean	S	--	--	18	--	--	23.8	--	--	5.30
	B	--	--	25	--	--	28.3	--	--	4.2

TR - Transect

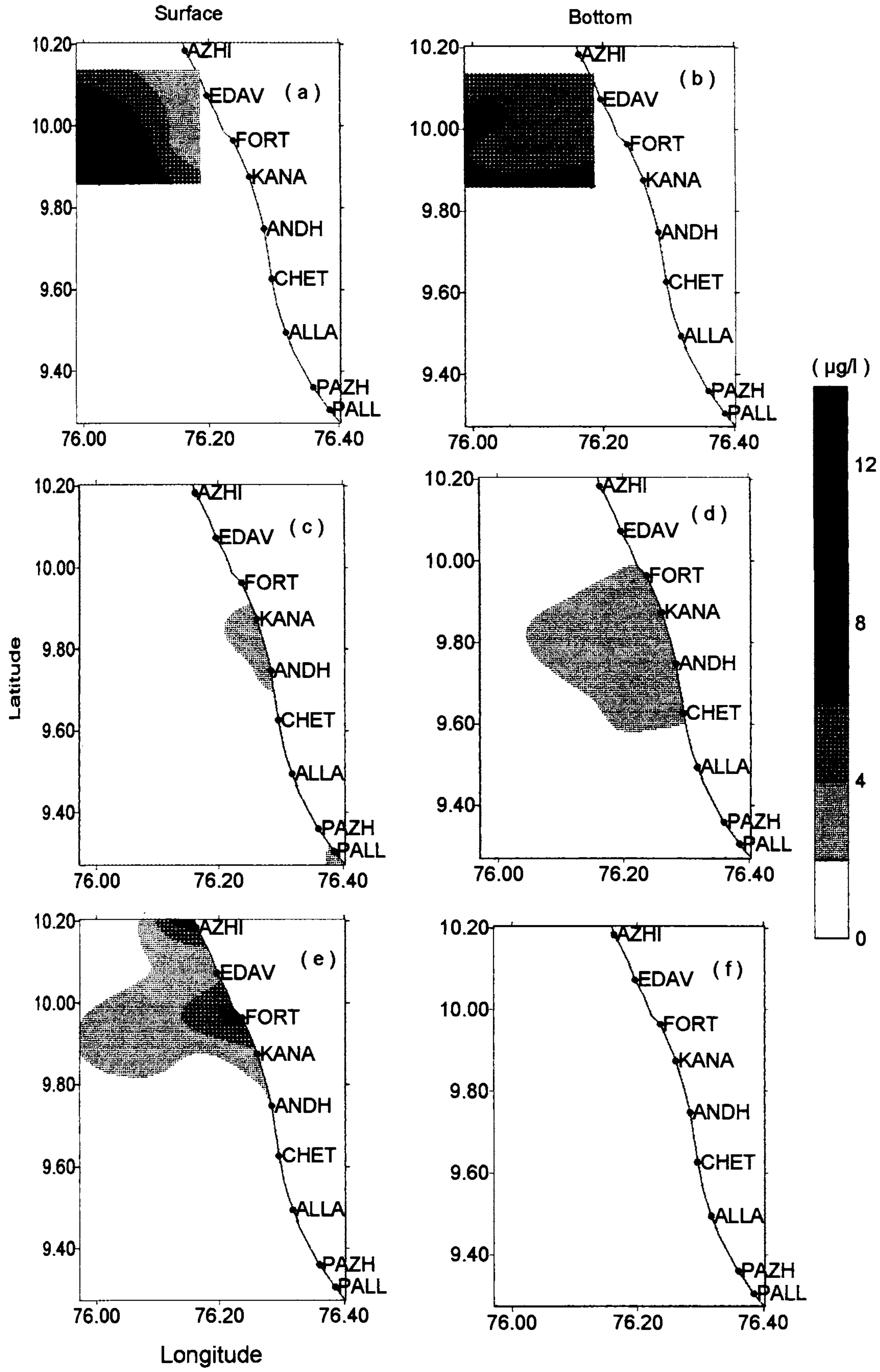


Fig. 3.15. Distribution of dissolved Copper at the surface and bottom during October (a,b), February (c,d) & November (e,f).

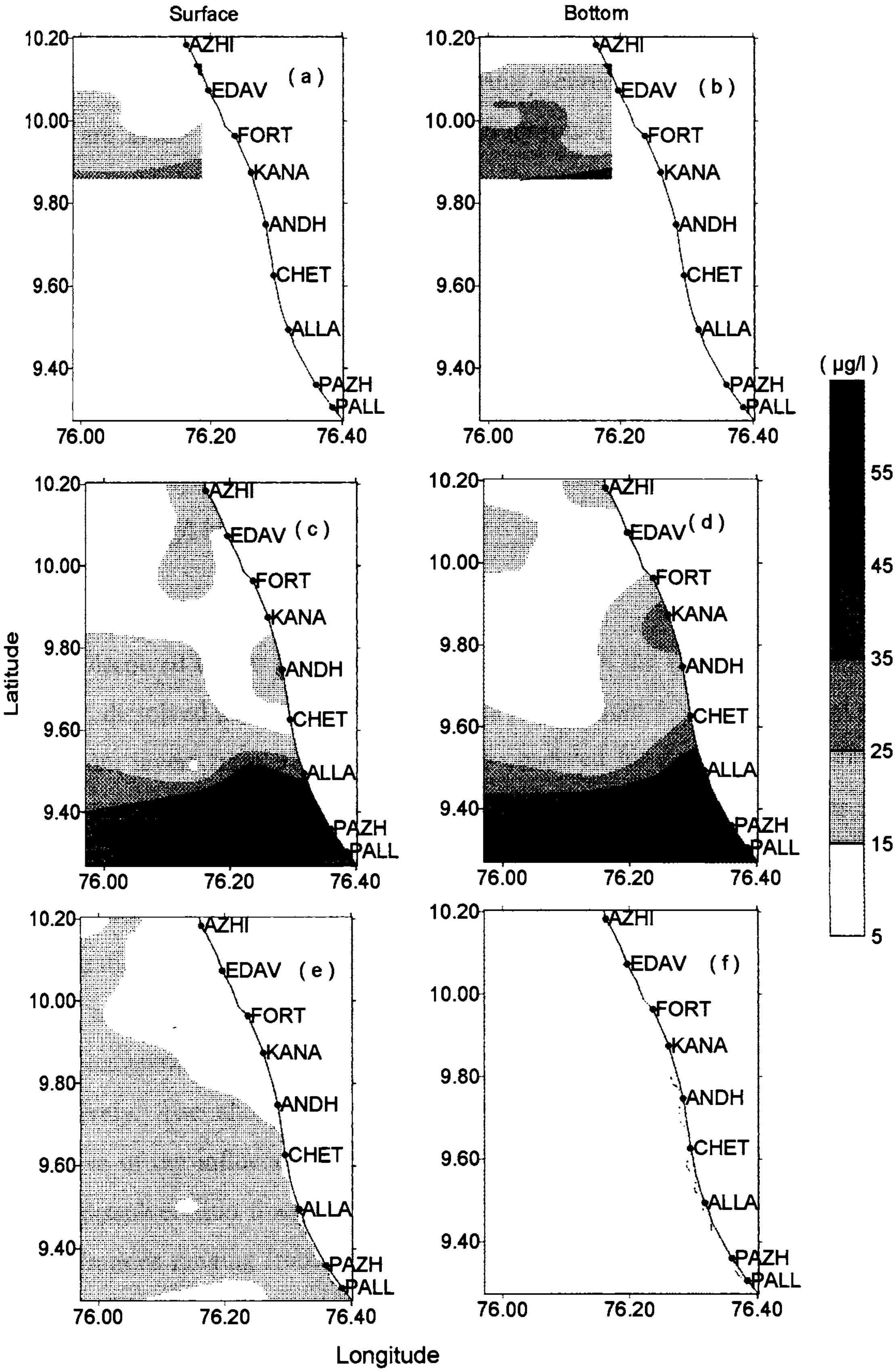


Fig. 3.16. Distribution of dissolved zinc at the surface and bottom during October (a,b), February (c,d) & November (e,f).

variation in dissolved zinc in the surface waters is from 6 to 55 µg/l, while for the bottom waters, it ranges from 8 to 86 µg/l. The bottom waters are always found to be enriched in this element during February, and the maximum values are along the shallow stations of transects I, II and III. The mean concentrations of surface and bottom values are 23.8 and 28.3 µg/l respectively. During November, the dissolved zinc is considerably stripped off from the water column, with surface concentrations varying from below detectable limit to 14 µg/l and the bottom concentrations from below detectable limit to 9 µg/l. The mean concentrations during November for surface and bottom waters remain low, 5.31 and 4.16 µg/l respectively. Rajamani (1994) has reported dissolved Zn in coastal waters to vary from 0.26 to 34.64 µg/l in this region.

3.5.3. Iron

Dissolved iron is the most abundant element in the study area. During October, dissolved iron in the surface waters ranges from 4 to 270 µg/l and in the bottom layers from 32 to 380 µg/l. As observed for Zn, this metal also shows higher concentrations at the bottom (Fig.3.17). Mean concentrations of dissolved iron during October for surface and bottom layers are 73 and 137 µg/l respectively (Table.3.16). During February, the surface and bottom concentrations show variation from below detectable limit to 303 µg/l for the surface and below detectable limit to 526 µg/l for the bottom waters. The mean concentrations for surface and bottom waters are 54.4 and 97 µg/l respectively. The shoreward enrichments of dissolved iron are probably indicative of the influence of the land runoff. November observations show higher dissolved iron fractions along the entire study region, with the surface concentrations ranging from 8 to 355 µg/l and bottom concentrations from 58 to 489 µg/l. Shoreward increase in concentration is clearly depicted in the Fig.3. . The mean concentrations for surface and bottom waters are 108 and 230 µg/l respectively. Concentration of dissolved Fe observed in this region from earlier reports varied from 0.1 to 306 µg/l (Rajamani, 1994). Higher values observed along the shallow stations have been explained due to the

Table 3.16 Range in the concentration of dissolved Iron (μg/l)

		October			February			November		
TR.		Min.	Max.	Ave.	Min.	Max.	Ave.	Min.	Max.	Ave.
I	S	15	266	140	40	45	43	26	221	91
	B	144	213	178	4	80	30	58	404	238
II	S	--	--	--	0	303	110	15	256	102
	B	--	--	--	2	526	265	103	321	226
III	S	24	62	43	0	5	2	35	260	128
	B	119	381	250	15	109	60	132	300	231
IV	S	--	--	--	29	61	45	8	217	89
	B	--	--	--	18	135	63	163	340	236
V	S	20	32	26	27	77	55	32	103	56
	B	89	209	149	7	139	68	59	288	165
VI	S	--	--	--	2	295	118	15	355	131
	B	--	--	--	5	461	233	104	430	284
VII	S	4	162	83	6	55	25	45	329	185
	B	32	51	41	12	148	61	196	489	338
VIII	S	--	--	--	0	59	27	16	173	82
	B	--	--	--	0	19	6	44	318	189
IX	S	--	--	--	0	137	65	44	224	112
	B	--	--	--	0	259	89	114	227	164
Mean	S	--	--	73	--	--	54	--	--	165
	B	--	--	154	--	--	97	--	--	411

TR - Transect

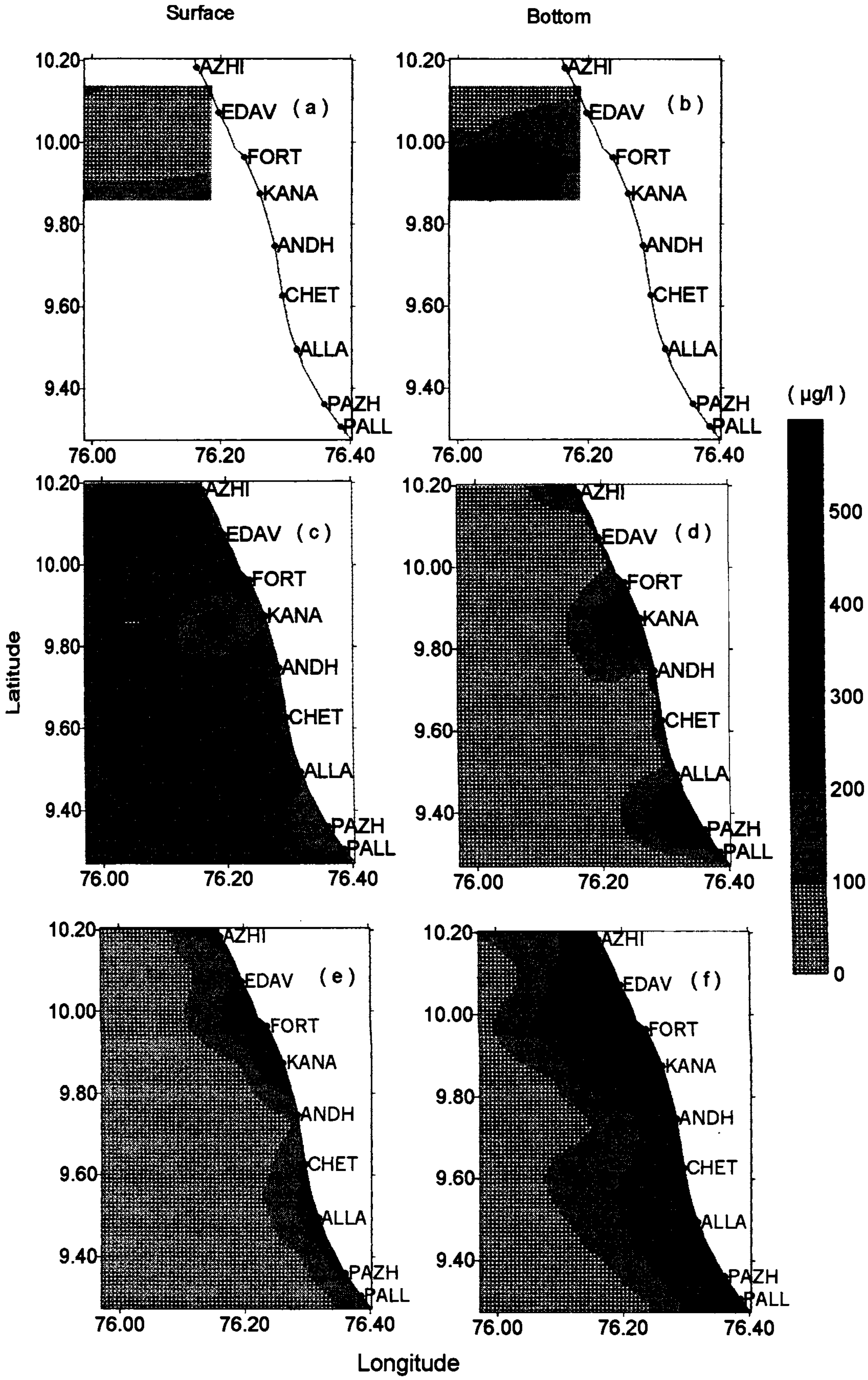


Fig. 3.17. Distribution of dissolved Fe at the surface and bottom during *October (a,b), February (c,d) & November (e,f).*

resuspension of bottom sediments and activities of mudbank, whereby iron is desorbed from the surface sediments to the overlying water.

3.6. Sediment characteristics of the coastal region

The sediment composition and texture are related to geology, bathymetry and physical factors of the aquatic environment. The major rock types of the study area belong to crystalline rocks of Archaen age, sediments of tertiary age, and laterite cappings on crystallines and sediments of sub-recent to recent age (Mallik et al., 1987). The crystallines include charnokite and Khondalite and granites traversed by basic rocks. Charnokite is widespread in the hill ranges of the Western Ghats, from where the rivers of Kerala originate. The heavy-mineral suit of the coastal and river sediments of Kerala consists of opaques, horn-blende, hypersthene, tremolite/actinolite, pyroxene, epidote, zieron, silimite, Kyanite, staurolite, andalusite, monazite, rutile, spene, apatite and toumaline (Reddy and Rao, 1992). The light minerals consist of quartz, feldspar and some mica. The opaque heavy minerals include ilmenite, a little magnetite, rutile, spinel and leucoxene.

Two main factors controlling the distribution of trace elements among the various phases in the aquatic system are the textural characteristics and organic matter content. The textural characteristics and the organic carbon content of the sediments of the study region for the three observations are discussed here. For better representation of the data, the variations of trace metals in sediments are discussed by grouping the stations into four depth intervals. Accordingly, the stations in the entire study area is grouped into four depth zones; viz. upto 10 m, 10 to 20 m, 20 to 30 m and greater than 30 m zones (Table.3.17).

The average values for the organic carbon content and the grain size distribution of the sediment samples during October, February and November are given Table.(3.18). The highest organic carbon and clay fractions are

Table. 3.17 Grouping of stations in to depth zones

Depth zone	Month	Station Nos.	Month	Station Nos.	Month	Station Nos.
Upto 10	Oct.	1,15,16,17,18,19,31,32,33 34,35,47,48,49,50,51	Feb.	1,9,10,11,12,20,21,30,31 32,40,4142	Nov.	1,9,10,11,12, 20,21,30,31, 32,40,41,42
10-20	Oct.	2,3,4,5,12,13,14,20,21,28, 29,30,36,37,44,45,46,52,53,54	Feb.	2,3,8,13,17,18,19,22,23,28 29,33,38,39,43,44	Nov.	2,3,8,13,17,18, 19,22,23,28,29. 33,38,39,43,44
20-30	Oct.	6,7,10,11,22,23,25,26,27 38,39,40,41,42,43,55,56	Feb.	4,7,14,24, 25,26,27,34,35,36,37, 45	Nov.	4,7,14,24,25, 26,27,34,35, 36,37,45
> 30 m	Oct.	8,9,24	Feb.	5,6,15,16	Nov.	5,6,15,16

Table.3.18 Textural Characteristics

	October			February			November		
Depth (m)	Min.	Max	Mean	Min.	Max.	Mean	Min.	Max.	Mean
Sand (%)									
< 10	0.1	85.0	16.5	0.6	91.6	31.5	0.1	42.0	9.0
< 20	0.0	8.4	1.4	0.1	84.9	20.4	0.3	46.5	6.7
< 30	0.0	75.8	28.9	0.4	95.0	38.1	0.1	88.8	26.2
> 30	22.0	70.1	43.2	29.9	80.4	52.6	15.0	47.0	32.6
Clay(%)									
< 10	2.6	98.7	54.0	4.0	77.0	38.3	40.8	80.0	63.6
< 20	38.0	85.0	66.6	18.6	87.7	55.8	26.4	95.0	63.0
< 30	24.1	83.1	54.6	0.8	86.9	44.5	10.2	90.6	49.0
> 30	28.0	49.8	41.2	17.0	46.0	32.4	25.0	46.0	31.6
Silt(%)									
< 10	0.2	49.0	29.1	0.2	85.8	30.4	9.0	53.0	27.3
< 20	15.0	53.0	32.0	1.8	68.6	24.9	3.6	54.6	30.4
< 30	0.0	56.0	15.9	0.7	82.8	16.8	1.0	61.0	24.6
> 30	1.6	28.4	15.5	0.2	30.0	15.0	23.0	50.5	35.8
Org.C(mg/g)									
< 10	0.4	29.0	19.7	2.1	32.4	19.0	10.8	40.7	27.5
< 20	4.1	29.7	22.3	7.9	33.8	23.6	11.4	40.4	30.0
< 30	0.4	28.3	13.3	1.7	30.0	17.3	0.4	28.2	16.4
> 30	10.0	24.5	19.6	9.7	19.0	14.3	5.9	25.7	15.6

during November along the entire near-shore sediments, while variation in silt and sand fractions are marginal over the three observations.

3.6.1. Sand

The percentage of sand fluctuated widely during the study with maximum sand fraction during February (53 %). The ranges in sand fraction (Fig.3.18) across the four depth zones of 10, 20, 30 and > 30 m are < 1 to 92 %, < 1 to 89.4 %, < 1 to 94.9 % and 29.9 to 80.3 % during October; < 1 to 85.4 %, < 1 to 8.4 %, < 1 to 75.7 % and 22.1 to 70 % during February; and < 1 to 42.2 %, < 1 to 46.8 %, < 1 to 89.2 % and 15.4 to 47.3 % during November respectively. Mean values in sand fraction along 10, 20, 30 and >30 m zones are 17, 1, 29, 43 % for October; 32, 20, 38, 53 % for February and 9, 7, 26, 33 % for November (Table.3.18).

3.6.2. Silt

Silt content in the study region exhibits different pattern of distribution during the three observations. While at the 10 m zone, there is no significant change over the three periods, a definite increase in silt content during November at 20, 30 and >30 m zones is observed (Fig.3.18). The variations of silt fraction during October across the 10, 20, 30 and >30 m depth zones are < 1 to 49 %, 15.4 to 52.7 %, < 1 to 56.3 % and 1.8 to 27.7 % respectively. In February, the variations in silt fractions are in the range < 1 to 85.7 % at 10 m, 2.2 to 68.8 % at 20 m, < 1 to 83.1 % at 30 m and < 1 to 30.4 % at >30 m. During November the variation in silt fractions at 10, 20, 30 and >30 m zones are in the range 8.7 to 53.2 %, 4.3 to 54.8 %, 1.2 to 60.8 % and 22.8 to 51.3 %. Thus, even when wide fluctuations are observed along 10, 20 & 30 m zones during February, as these high values represent only some of the 'pockets', the average is still lower than the corresponding silt fractions during November. In November, the silt fraction at >30 m zone is the highest (36 %). The overall mean silt fractions across the 10, 20, 30 and >30 m zones are 29, 32, 16, 16% (October); 30, 25, 17, 15 % (February); and 27, 30, 25, 36 % (November) respectively.

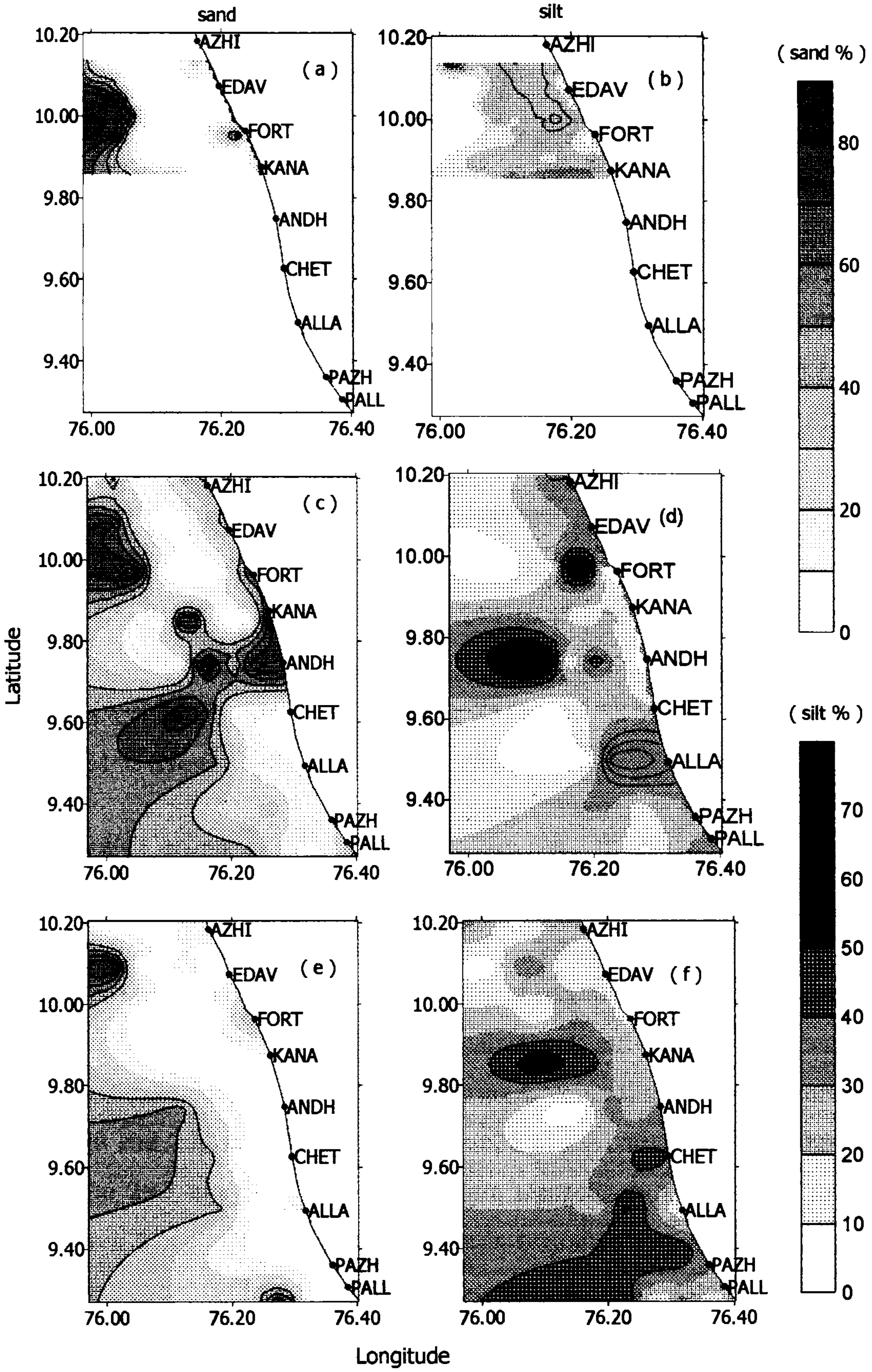


Fig. 3.18. Distribution of Sand (a,c,e) & Silt(b,d,f) in the sediment during October, February & November.

3.6.3. Clay

Percentage of clay fractions in the sediment is one of the important factors in regulating the trace metal geochemistry of marine sediments. The distribution of clay fraction in the study region clearly shows that during October and November the percentage distribution is more or less same and there is considerable reduction in the levels during February along the first three zones. The clay fraction during October at 10, 20, 30 and >30 m depth zones varies from 2.6 to 98.7 %, 38.1 to 85.4 %, 24.3 to 83.2 % and 28.4 to 49.8 % respectively (Fig.3.19). In February, the corresponding variation in the 10 m zone is from 3.8 to 77.2 %, at 20 m zone is from 18.6 to 87.7 %, at 30 m zone is from < 1 to 86.9 % and at >30 m zone is from 17.4 to 46.3 %. During November, the values at 10, 20, 30 and >30 m depth zones range from 41.3 to 79.7 %, 26.4 to 94.6 %, 10.2 to 90.6 % and 24.8 to 45.7 % respectively. The overall mean clay fraction along the four depth zones during the different observations are: 54, 67, 55, 41 % (October); 38, 55, 45, 32 % (February) and 64, 63, 49, 31 % (November).

3.6.4. Organic Carbon

The behavior of organic carbon in the sediment shows close similarity to the distribution of iron and clay fractions of sediment, with no significant enrichment or impoverishment during any of the observations. In all the three observations, the middle zones (20 m) are always found to contain more organic carbon compared to other zones. During October the organic carbon at 10, 20, 30 and >30 m zones varies from 0.35 to 29.1 mg/g, 4.1 to 29.8 mg/g, 0.35 to 28.3 mg/g and 10 to 24.5 mg/g respectively (Fig.3.19). In February, even though there is wide variation in organic carbon content, the average values decrease (Table.3.18). The ranges during this period at 10, 20, 30 and >30 m depth zones are 2.1 to 32.4 mg/g, 7.9 to 33.8 mg/g, 1.7 to 29.9 mg/g and 9.7 to 19.1 mg/g respectively. Organic carbon records its highest concentrations in November, when 10 and 20 m zones show values upto 40.4 and 40.7 mg/g respectively. The general variation in organic carbon during November is from 10.8 to 40.7 mg/g at 10 m, 11.4 to 40.4 mg/g at 20 m, 0.35

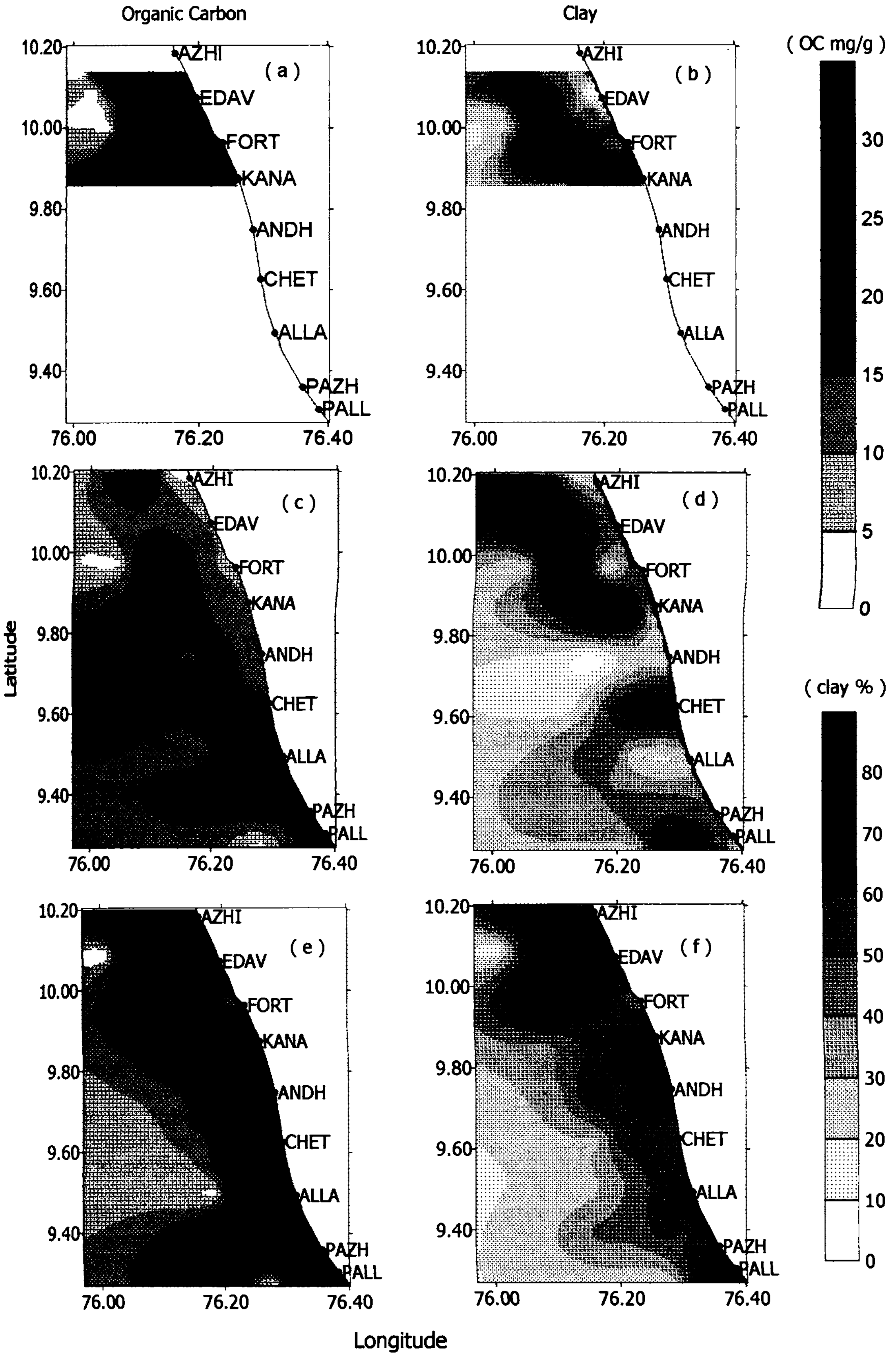


Fig. 3.19. Distribution of organic carbon (a,c,e) and Clay (b,d,f) in the sediment during October, February & November.

to 28.2 mg/g at 30 m and 5.9 to 25.7 mg/g at >30 m. The mean concentrations of organic carbon across the four zones are: 20, 22, 13, 20 mg/g during October; 19, 24, 17, 14 mg/g during February and 28, 30, 16, 16 mg/g during November.

3.7. Trace elements

A steadily growing interest in the research on trace elements has been evinced recently, partly due to the concern over the protection of the environment and their influence on biological systems. Most of the biologically active as well as potentially toxic trace metals are highly reactive and are, therefore, accumulated in authegenic material and organisms. Some of them like Cu and Zn are also recognised as effective catalysts in biological systems (Mandelli, 1978). The role of rivers in transporting material from continents to oceans is paramount, being 10 times that of glaciers and 100 times that of wind (Goldberg, 1976). They carry metal in solution, adsorbed in inorganic solids as metallic coatings in organic solids and in detrital crystalline materials (Gibbs, 1973). Due to their easy accessibility and consequent high human influence, rivers, estuaries and coastal waters are found to be more susceptible to pollution effects (Venugopal, 1982).

Trace metals have acquired a well-known reputation as toxins. They are natural constituents of the environment, over 1/3rd of the 100-plus elements that make up the fabric of the planet fall into this category. The anthropogenic inputs must therefore be seen in the context of natural geochemical cycles. The human impact on the geochemical cycles of most trace metals is predominantly a localized one, involving the redistribution of the element from its mineral deposits. Eventhough they undergo some perturbation during these processes, metals are rapidly returned to the lithosphere by sedimentary deposition. As they are persistent and non-biodegradable, they cannot be eliminated but can only be relocated or converted into forms of reduced accessibility or bioavailability (Barbour, 1988). Various factors that may be responsible for the differential behaviour of the elements are productivity, exchange of elements between solid and liquid, formation of colloids and flocculation, diagenesis and mixing with marine sediments.

Aquatic organisms are well known for their ability to take up trace elements from solution and particulate (Bowen, 1966; Riley and Chester, 1971). Correspondingly, the underlying sediments are rich in organic matter. It is therefore possible that the elements are incorporated into the sediments in association with organic matter to a certain extent (Murthy and Veerayya, 1972).

The ability of pre-existing solids to adsorb trace elements from solution under both fresh water and marine conditions has been well established *(Krauskopf, 1956; Aston and Duursma, 1973).* The estuaries and coastal waters represent a situation in which solid-solution exchange of trace elements lead to the enrichment or depletion of trace element content of suspended matter and, in turn, of the bottom sediments. Clay minerals of a river suspended matter are capable of adsorbing certain trace metals in fresh water and partially desorbing them upon contact with seawater (Kharkar et al., 1968; Borole et al., 1977; Graham et al., 1976, Evans et al., 1977).

The precipitation of hydrated oxides of Fe and Mn from seawater has important consequences for trace element solid-solution exchange. These hydroxides act as effective scavengers in the removal of other trace elements from solution by adsorption or lattice substitution processes. The studies of Sankaranarayanan and Qasim (1969) suggest that the estuarine regions are favorable for the formation of colloids of Fe and Mn oxides and their flocculation. Hence incorporation of these elements into the sediments is also possible through adsorption by hydroxides of Fe and Mn. The coastal and estuarine regions are highly productive and the underlying sediments are correspondingly rich in organic matter. The process of diagenesis and the consequent enrichment of elements like Mn, Cu through the creation of anaerobic conditions in the estuarine sediments at sub-surface levels (Aston and Chester, 1976) modify the concentrations of these elements in these regions.

It is well known that Kerala is a zone of intense weathering. Studies conducted by Nagernder Nath et al., (2000) on major-element, trace element and rare-earth systematics of the clay-size sediments from this region have reported an identical pattern of distribution from fluvial, brackish and marine environment. Geochemical data also suggest that the sediments have undergone extreme chemical weathering at the sources.

The textural composition of the present study area in general, goes well with the observed clay mineralogy of this coast reported earlier (Nair and Murthy, 1968; Nair, 1976; Rao et al., 1984). Nair and Murthy, (1968) have also observed low percentage in the outer shelf and high percentage (20 to 50 %) in the inner shelf. These variations have been attributed to the differences in the energy of various environments and due to size segregation of minerals.

Concentrations of the 8 trace metals in the sediments collected from the samples during October, February and November are discussed here. As mentioned earlier in the section of textural characteristics, the distributions of metals are grouped into 4 zones to which they represent viz. upto 10 m, upto 20 m, upto 30 m and greater than 30 m zones.

Variations of different metals along the 4 depth zones during the three observations are given in (Table.3.19). In general, it can be seen that zonal variations are found to be less significant as compared to the variations within the zone for most of the metals.

3.7.1. Lead

Lead is a cumulative poison to human beings. The large affinity of Pb^{2+} for thiol and phosphate containing ligands inhibits the biosynthesis of haeme and thereby affects membrane permeability of kidney, liver and brain cells. This results either in reduced functioning or complete breakdown of these tissues. Metabolism of lead and calcium are similar both in their deposition and in mobilization from bone. Since lead can remain immobilized for years, metabolic disturbances can also remain undetected. Under normal conditions more than 90 % of the lead retained in the body is in the skeleton. Although lead is a non-essential element, it is present in all tissues and organs of mammals. The main sources of input of lead are atmospheric fall out, smelting operations and automobiles.

In the month of October, lead concentrations in the sediments are found to be higher throughout the study region followed by a decrease in November and February. During October, the concentrations of lead across the 10, 20, 30 and > 30 m depth zones vary from 36.1 to 50.3 μg/g, 18.4 to 59.8 μg/g, 17.75 to 60 μg/g and 37.2 to 46.4 μg/g (dry weight) respectively. During February, there is only a slight decrease observed along the first two zones, while along 30 m and > 30 m zones, the concentrations decrease (Fig.3.20). The variations at these four depth zones during the period are from 7.1 to 70.8 μg/g dry weight. The decrease in the concentration towards offshore can be attributed to the higher sand percentage (29 to 53 %) in the clayey-sediments. In November, the observations show the lowest concentration of lead along 10 and 20 m zones and increase over the November levels along 30 and > 30 m zones. This can be explained by the significant increase in the organic carbon content of the first two zones where the highest concentration registered is 28 and 30 mg/g for organic carbon. The overall mean concentrations of Pb during October, February and November along these 4 zones are: 47, 33 and 24 μg/g (10 m), 43, 34, 29 μg/g (20 m), 3S, 12, 28 μg/g (30 m) and 41, 15, 20 μg/g (> 30 m) respectively (Table.3.19).

Lead in the coastal sediments reported earlier varied from 18 to 81 μg/g along Kerala coast and 33 to 117 μg/g (Table. 4.4) in Cochin estuary and

Table 3.19 Range in the concentration of trace metals in sediments (µg/g-dry wt.)

		Pb			Ni			Co			Cr		
October	Depth(m)	Min.	Max.	Mean	Min.	Max.	Mean	Min.	Max.	Mean	Min.	Max.	Mean
	< 10	36.5	60.0	47.0	49.2	174.6	126.0	28.2	37.4	33.0	98.9	186.0	160.0
	< 20	18.0	60.0	43.0	23.0	213.0	130.0	11.0	40.0	31.0	41.0	199.0	149.0
	< 30	18.0	60.0	38.0	16.0	175.0	102.0	5.0	40.0	25.0	31.0	195.0	120.0
	> 30	37.0	46.0	41.0	80.0	134.0	111.0	26.0	34.0	30.0	127.0	190.0	155.0
February	< 10	6.6	71.3	32.7	0.0	39.8	13.5	4.2	15.6	11.6	22.0	133.0	80.0
	< 20	13.0	57.0	34.0	0.0	39.0	16.0	11.0	19.0	15.0	0.0	146.0	51.0
	< 30	0.0	32.0	12.0	0.0	36.0	14.0	0.0	14.0	6.0	10.0	123.0	48.0
	> 30	0.0	26.0	15.0	7.0	25.0	15.0	3.0	13.0	8.0	29.0	85.0	56.0
November													
	< 10	0.0	38.0	24.0	0.1	83.0	56.0	0.0	26.0	16.0	0.1	205.0	147.0
	< 20	13.0	53.0	29.0	0.0	74.0	51.0	7.8	24.9	19.0	33.0	195.0	128.0
	< 30	13.0	53.0	28.0	1.6	73.1	46.0	0.0	21.5	14.5	11.4	188.0	124.0
	> 30	6.5	26.6	20.0	1.7	54.0	28.5	0.0	29.6	13.4	13.0	131.0	73.0

		*Fe			Cu			Zn			Mn		
October	Depth (m)	Min.	Max.	Mean	Min.	Max.	Mean	Min.	Max.	Mean	Min.	Max.	Mean
	< 10	23.0	43.0	37.0	6.9	30.0	23.0	52.0	128.0	83.0	124	773	293
	< 20	18.0	42.0	38.0	4.0	34.0	25.0	41.0	155.0	92.0	147	344	241
	< 30	6.0	42.0	25.0	1.4	33.0	19.0	23.0	139.0	74.0	124	322	219
	> 30	26.0	41.0	33.0	15.0	31.0	22.0	29.0	122.0	70.0	147	271	189
February	< 10	11.2	55.6	35.0	3.0	40.0	20.8	21.2	106.2	63.1	148	255	188
	< 20	35.0	48.0	43.0	16.0	42.0	27.0	8.0	82.0	52.0	150	260	183
	< 30	0.2	49.0	19.0	1.5	26.0	10.0	8.7	80.0	30.0	38	178	113
	> 30	6.0	36.0	22.0	1.5	16.0	9.0	10.0	50.0	30.0	56	185	126
November													
	< 10	0.0	34.0	24.0	0.0	36.0	23.0	0.1	132.0	17.0	0.2	279	163
	< 20	8.0	36.8	28.7	3.0	32.6	21.8	10.5	121.7	70.0	70.5	238	164
	< 30	2.5	31.0	19.0	1.0	31.4	19.0	0.1	89.7	49.0	34.8	210	138
	> 30	2.4	37.0	18.4	2.0	27.0	13.0	5.2	153.0	62.7	13.5	277	143

* Fe-(mg/g)

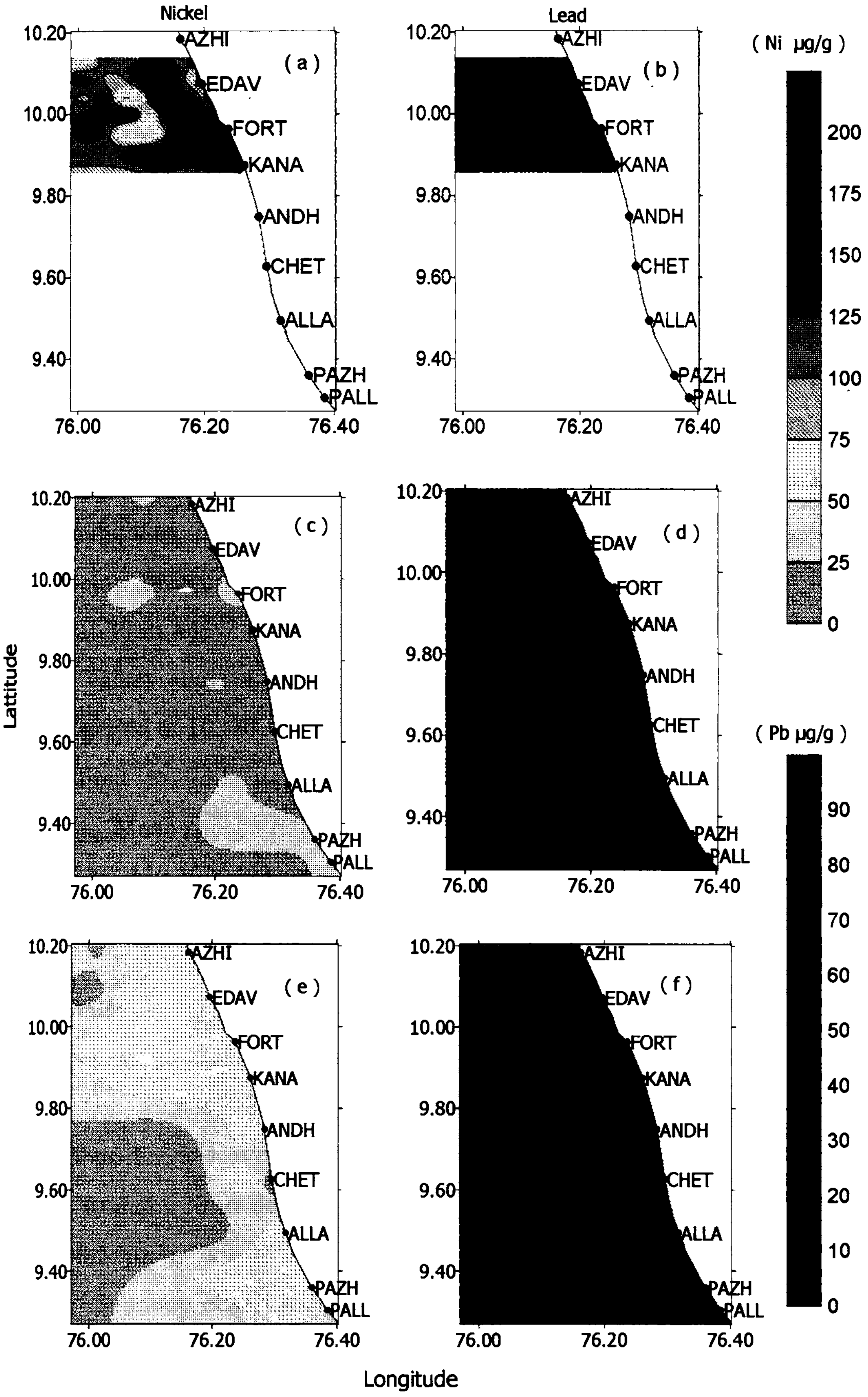


Fig. 3.20. Distribution of Ni (a.c.e) & Pb (b,d,f) in the sediment during October, February and November.

20 to 88 µg/g in Chaliyar estuary (Rajamani, 1994). Though lead is very toxic to biota, studies showed that the "bioavailability" of lead in the estuarine and marine environment is much reduced through the geochemical 'immobilization' of this metal in these environments.

3.7.2. Nickel

The concentrations of nickel in sediments are the highest during October and decrease during November and further to the lowest during February. The ranges in concentration at 10, 20, 30 and >30 m zones in October are: 49.4 to 174.1 µg/g, 23.3 to 213 µg/g, 15.7 to 175.3 µg/g and 79.9 to 133.7 µg/g respectively (Fig.3.20). In February, when the concentrations are at the minimum, and the variations are: below detection limit to 39.9 µg/g at 10 m, below detection limit to 40 µg/g at 20 m, below detection limit to 35.8 µg/g at 30 m and 7 to 24.8 µg/g at >30 m (Table.3.19). In November, the nickel values show a gradual decrease towards offshore. The ranges during the period at 10, 20, 30 and >30 m zones are: < 1 to 83.3 µg/g, below detection limit to 73.8 µg/g, 1.8 to 72.7 µg/g and 2.2 to 53.9 µg/g respectively. Mean concentration of nickel across 10, 20, 30 and >30m depth zones are 126, 130,102, 111 µg/g during October; 14, 16, 14, 15 µg/g during February and 56, 51, 46 and 29 µg/g during November.

3.7.3. Cobalt

The concentrations of cobalt in the study region remain quite normal, with October values remaining comparatively higher and decreasing concentrations during November and February. The ranges in concentrations at 10, 20, 30 and >30 m depth zones during October are 27.9 to 37.1 µg/g, 11.4 to 40.2 µg/g, 4.9 to 40 µg/g and 26.2 to 34.1 µg/g respectively (Fig.3.21). February observations record the lowest values in all these depth zones with a variation from 4.4 to 15.9 µg/g at 10 m, 11.1 to 19.3 µg/g at 20 m, below detection limit to 14.2 µg/g at 30 m and 3.3 to 13 µg/g at >30 m respectively (Table.3.19). Redistribution in sediments are seen during November resulting an increase in the cobalt concentrations along these zones

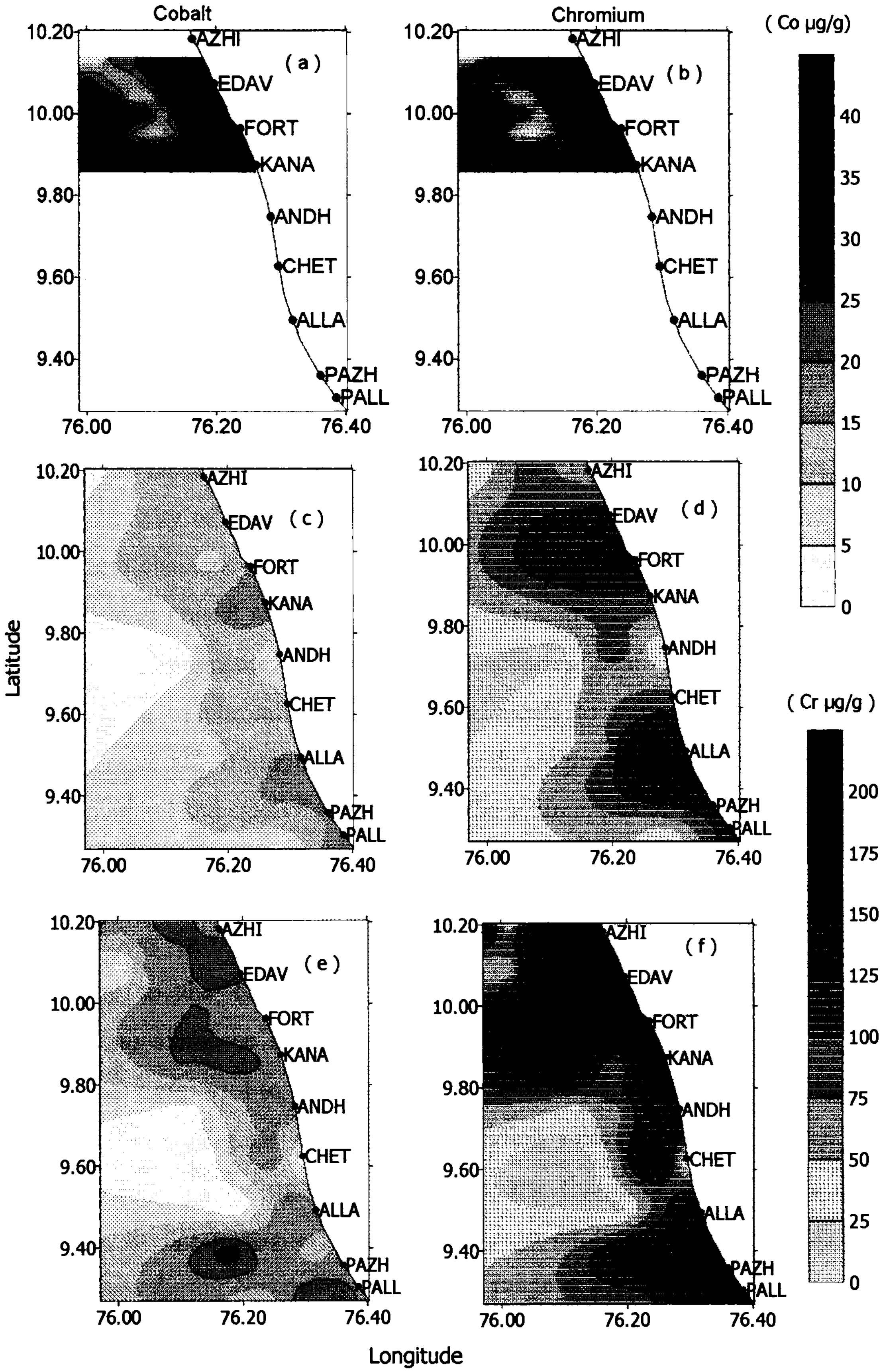


Fig. 3.21. Distribution of Co (a,c,e) & Cr (b,d,f) in the sediment during October, February and November.

varying from < 1 to 26.2 µg/g at 10 m, 8.4 to 24.9 µg/g at 20 m, below detection limit to 22.3 µg/g at 30 m and below detection limit to 30 µg/g at >30 m respectively. Mean concentration observed in the different depth zones during the three observations are: 33, 31, 25, 30 µg/g during October, 12, 15, 6, 8 µg/g during February and 16, 19, 15, 13 µg/g during November respectively.

3.7.4. Chromium

Chromium is not a significant contaminant of plant tissues although concentrations in marine plants are usually higher than those in fresh water plants (Claus Dieter and Diether Schmidt, 1992). Compared to other trace elements, toxicity of chromium for aquatic organism is generally low due to the hard acid character of chromium ions. Typical chromium concentrations in sediments of crustal rocks are 100 µg/g. Elevated levels of chromium are detectable in sediments of rivers and estuaries near industrial areas. Remobilization of chromium from the sediments to the water column is frequently reported. Bottom water enrichments are possible by dissolution of biogenic material and catalytic oxidation at the sediment-water interface.

The distribution of chromium in sediments also show high values during October and low values during February with November values intermediate to the other two observations. In general, the ranges in concentrations along the 10, 20, 30 and > 30 m depth zones in October are: 98.8 to 186.3 µg/g, 41.4 to 198.7 µg/g, 31.1 to 195.2 µg/g and 127.4 to 190.3 µg/g respectively (Fig.3.21). The corresponding variation during February range from 22.1 to 133.4 µg/g at 10 m, below detection limit to 145.9 µg/g at 20 m, 10.2 to 123.2 µg/g at 30 m and 29.3 to 84.7 µg/g at >30 m. The concentrations during November vary in the range < 1 to 205 µg/g at 10 m, 33.2 to 194.9 µg/g at 20 m, 10.9 to 188.3 µg/g at 30 m and 13.4 to 131.1 µg/g at >30 m depth zone respectively (Table.3.19). Mean concentration of chromium at various depth zones of the study region are: 160, 149, 120, 155 μg/g during October; 80, 51, 48, 56 μg/g during February and 147, 128, 124, 73 μg/g during November respectively.

3.7.5. Iron

Iron and manganese are the most abundant and mobile heavy metals in the aquatic environment, while the others posses a high index of relative pollution potential which are enriched by man's activities by a factor of ten or more in the sediments (Lowe, 1970; Prater, 1975).

Of the 8 metals studied, iron is found to be the most abundant element present in the sediment in the study region. As mentioned earlier, dissolved iron is also found to be abundant in the overlying waters during the same period of observation. However, unlike the distribution of many other elements, the concentration of iron in sediments does not show wide variation during the three observations. In general, the zonal values in iron show comparatively higher values during October, except along the 20 m zones where the iron concentration is more during February (43 mg/g). The concentrations of iron during October along the depth zones 10, 20, 30 & > 30 m vary from 23.1 to 43.2 mg/g, 17.7 to 42.4 mg/g, 5.9 to 41.8 mg/g and 26.2 to 40.8 mg/g respectively (Fig.3.22). The corresponding ranges in values during February are: 11.3 to 56.2 mg/g at 10 m, 34.7 to 48.4 mg/g at 20 m, < 1 to 49.3 mg/g at 30 m and 6.4 to 35.8 mg/g at >30 m depth zone. During November the concentration of iron at 10, 20, 30 and >30 m depth zones vary in the range < 1 to 34.2 mg/g, 7.8 to 36.7 mg/g, 3.2 to 31.4 mg/g and 1.9 to 37.2 mg/g respectively (Table.3.19). Mean iron contents of the sediment at 10, 20, 30 and >30 m depths zones during the different observations are: 37, 38, 25, 33 mg/g in October; 35, 43, 19, 22 mg/g in February and 24, 29, 19, 18 mg/g in November, respectively.

It is evident from the above uniform distribution for iron, that the sediments form the major repositories for iron in coastal environment. Perhaps iron may be the most sensitive element in aquatic system to pH

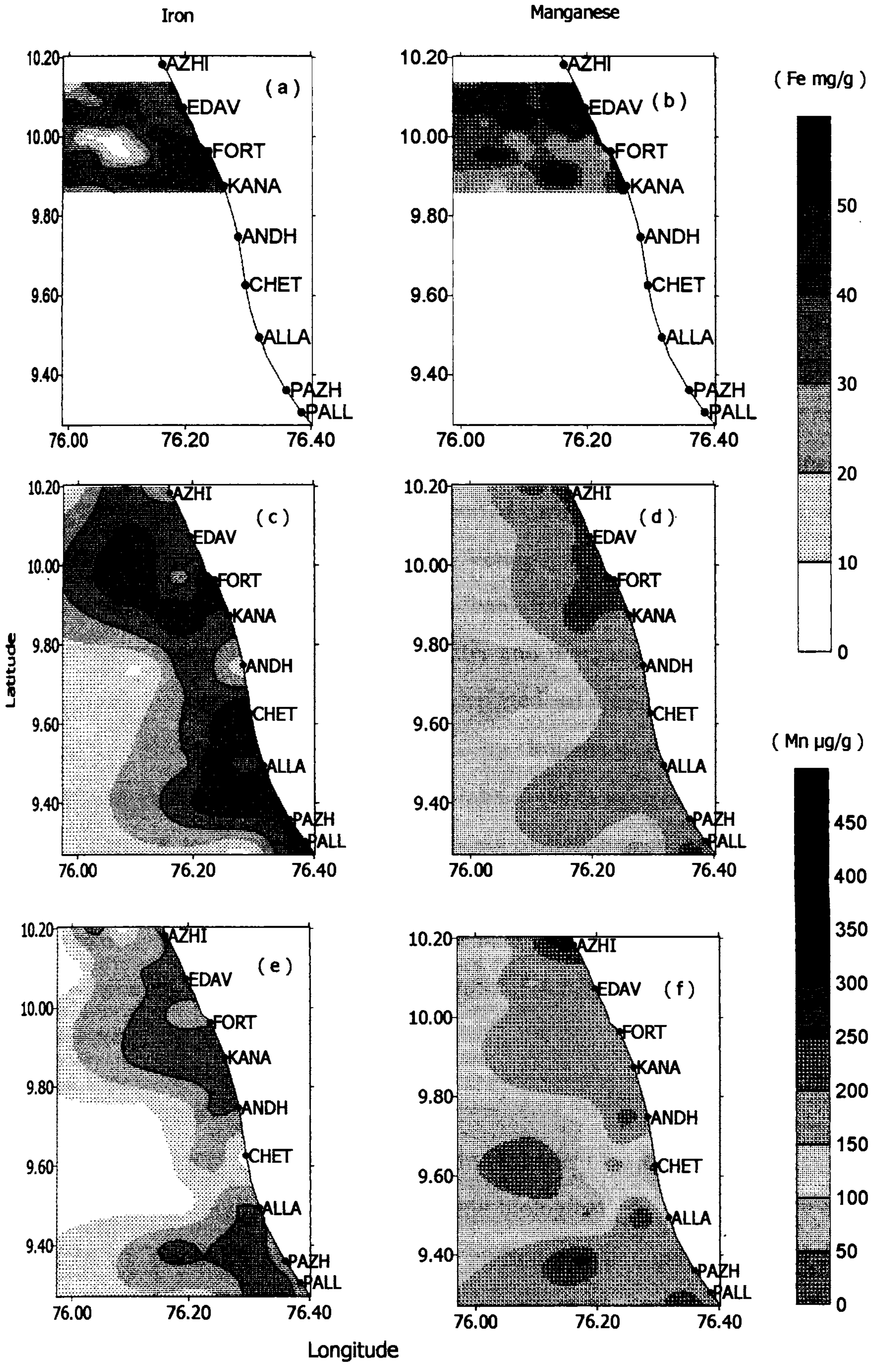


Fig.3.22. Distribution of Fe(a,c,e) & Mn (b,d,f) in the sediment during October, February & November.

changes, forming new solid phases capable of scavenging other trace elements from solution with a rise in pH (Boyle et al., 1977; Mayer, 1982). The redox sensitive iron and manganese hydroxides under oxidizing conditions constitute significant sinks of heavy metals in aquatic systems. These hydroxides readily adsorb or co-precipitate cations and anions. In presence of higher concentrations of dissolved organic matter, these adsorbed heavy metals are readily mobilized, thus acting as a major source of dissolved metals in natural waters (Jenne, 1976). Studies have also suggested iron as a limiting element in phytoplankton growth (Martin and Fitzwater, 1988). Iron concentration in sediments along Kerala coast is in the range 5 to 55 mg/g and in the Cochin backwaters (Table. 4.4), the levels vary from 15 to 55 mg/g, which are comparable with the values reported earlier from this area (Murthy et al., 1973; Murthy and Veerayya, 1981; Venugopal et al., 1982; Mallik and Suchindan, 1984 and Nair, 1992). The mudbank forming clayey silt sediments off Alleppey containing high organic matter and inorganic phosphate (Jacob and Qasim, 1974) was found to be depleted of residual iron fraction (Rajamani, 1994). Studies carried out by Rajamani (1994) showed a progressive increase in residual iron fractions towards upstream, which have been attributed to the settling of suspended particulates in early phase of saline intrusion by way of, enhanced ionic concentrations. She has also reported that the mineral held iron fraction brought to the estuary by the sewage effluent is retained around the site of discharge itself without being flushed out of the area.

3.7.6. Manganese

Manganese is an essential element in biological system. Manganese is not normally limiting in supply for estuarine biological processes, its interest lying in its reactivity and response to environmental conditions, and its speciation. The reactivity of manganese in aquatic system exhibits a complex behavior with conservative and non-conservative nature depending upon a number of factors such as the concentration in sediment, water and suspended particles, ionic strength, pH, Eh etc. (Burton and Liss, 1976; Duinker et al., 1979).

Manganese is found to be the second most abundant metal to be present in the study region. Similar to iron, manganese is also enriched in sediments, with peak values during October, concentrated in the shallow regions during February and in the deeper regions during November. In October, the manganese concentrations in the 10, 20, 30, >30 m zones vary from 124.4 to 773 µg/g, 147.4 to 344 µg/g, 123.7 to 321.8 µg/g and 146.8 to 270.9 µg/g respectively (Fig.3.22). In February, there is a reduction with respect to the concentrations of manganese in sediments and the general ranges at 10, 20, 30 and >30 m depth zones are 147.6 to 254.8 µg/g, 149.7 to 260.3 µg/g, 37.9 to 178.1 µg/g and 55.7 to 185.3µg/g respectively (Table.3.19). During November the ranges in manganese concentrations are < 1 to 278.7 µg/g at 10 m, 71.8 to 238 µg/g at 20 m, 34.6 to 209.7 µg/g at 30 m and 14.1 to 276.8 µg/g at >30 m respectively. Mean concentrations along these different zones are 83, 92, 74, 70 µg/g during October; 63, 52, 30, 30 µg/g during February and 70, 70, 49, 63 µg/g during November.

Rajamani (1994) has reported manganese concentration to vary from 44.1 to 318 µg/g in Kerala coast and 123 to 280 in Cochin estuary. More than 50 % of manganese in sediments was found to be in non-lithogenous fraction indicating the high chemical reactivity of manganese in marine environments.

3.7.7. Copper

The presence of copper in plant and animal tissues was recognized more than 150 years ago. Long before it was recognized as an essential element in the diets of birds and animals, it was detected as a component of blood proteins of snails. Copper is an essential metal in a number of enzymes, necessary in the biosynthesis of chlorophyll, thus functions as an essential trace element in the nutrition of plants and animals including man. Copper in aquatic systems received attention mostly because of its toxic effects on biota at higher levels. Algae and molluscs are particularly sensitive to copper. Studies showed that copper toxicity was apparently related to the soluble form of copper ion occurring in presence of carbonate ion (Gray and Ventilla, 1973). In aquatic environment, the behaviour of copper differs from that of iron and manganese. The major portion of copper in tropical seawater has been found to be associated with organic matter (Lee and Hoadley, 1967; Slowey et al., 1967).

The distribution of copper in the sediment responds closely to the variation of iron over the entire study area. Seasonal variation of copper is found to be insignificant and generally the concentrations remained normal. In October, the zonal levels of copper ranged from 7.1 to 30.4 µg/g, at 10 m, 4.2 to 34.7 µg/g at 20 m, 1.1 to 33.4 µg/g at 30 m and 14.6 to 30.9 µg/g at >30 m respectively with a mean concentrations of 23, 25, 19 and 22 µg/g at these zones (Fig.3.23). During February, when most of the metals showed a decrease, the copper content does not show any reduction and it varies from 2.8 to 39.7 µg/g at 10 m, 16.3 to 42.3 µg/g at 20 m, 1.8 to 25.7 µg/g at 30 m and 2.1 to 15.9 µg/g at >30 m with a mean concentration along these zones being 21, 27, 10 & 9 µg/g respectively (Table.3.19). The November observations also showed a similar trend with the concentration range across the 10, 20, 30, > 30m zones being < 1 to 35.9 µg/g, 2.9 to 33.4 µg/g, 0.9 to 30.6 µg/g and 2.3 to 27.4 µg/g with a mean concentration of 23, 22, 19 & 13 µg/g respectively.

Rao et al., (1974) have studied the partition patterns of copper in the sediments of Western Continental shelf of India. Sankaranarayanan and Reddy (1973) have observed copper content in the inshore and estuarine waters along the central west coast of India. Nair et al., (1990) have reported a wide variability in the spatial and seasonal distribution of copper in the surface sediments of Cochin estuary. The copper concentration in the sediments of Kerala coast varies from 5.1 to 48.1 µg/g and in Cochin estuary (Table. 4.4), from 5.52 to 51.3 µg/g (Rajamani, 1994). Comparatively higher

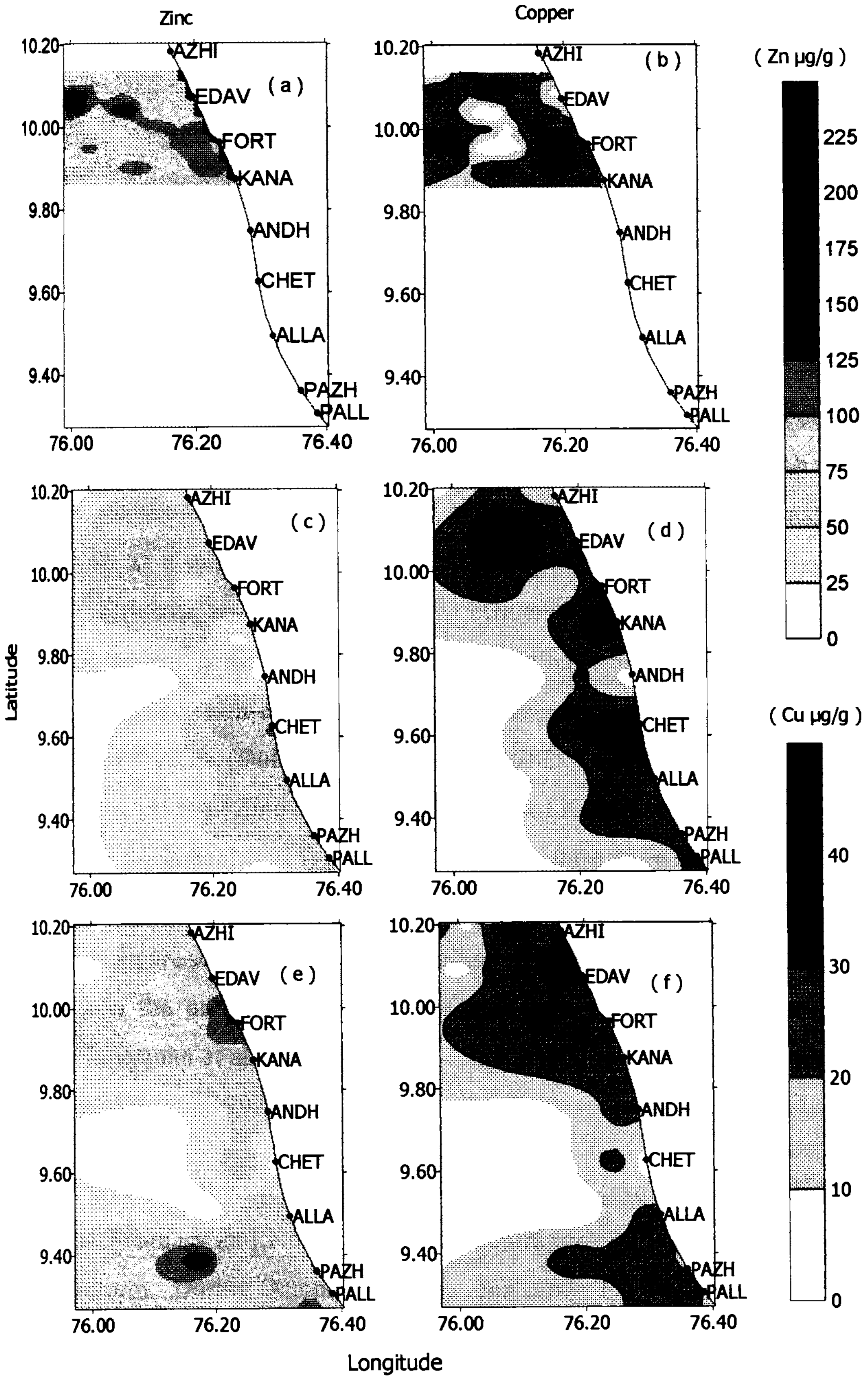


Fig. 3.23. Distribution of Zn (a,c,e) & Cu (b,d,f) in the sediment during October, February and November.

values for exchangeable fraction of copper in the sediments of Alleppey is due to the silty-clay texture of sediments having very high organic matter content providing ample sites for adsorption. The low values of easily reducible fraction of copper observed along the Kerala coast are attributed to the greater association of copper with iron oxides than with manganese oxides. Very high levels of copper found in the moderately reducible fraction have corroborated the above observation.

3.7.8. Zinc

Zinc is a required and beneficial element in human metabolism. Deficiency of zinc leads to growth retardation in children. Eventhough zinc minerals are abundant, due to the lack of solubility it is present in natural waters only as a minor constituent. The main pollutant sources of zinc are industrial effluents, sewage sludge, mining effluents, agricultural sources such as animal wastes, fertilizers etc. Several studies have been reported on both conservative and non-conservative behaviour of zinc in polluted and unpolluted estuaries (Duinker and Nolting, 1982; Danielsson et al., 1983; Paulson et al., 1989). Zinc content of sediments of Kerala coast varied from 7 to 149 µg/g (Rajamani, 1994) and found to be the third abundant heavy metal in the sediments of Chaliyar estuary and Kerala coast while enriched levels of zinc and manganese are present in the sediments of Cochin estuary. This is attributed to the anthropogenic input of zinc into the Cochin backwaters (Sankaranarayanan et al., 1978; Paul and Pillai, 1983; Nair et al., 1990; Shibu et al., 1990; Ouseph 1992,).

The zinc content in sediment register elevated levels during October, but during February and November the concentrations remain low and more or less uniform. During October, the variations across the 10, 20, 30 and >30 m depth zones are 52.2 to 128.3 µg/g, 40.8 to 154.8 µg/g, 23.4 to 139.2 µg/g and 29 to 121.7 µg/g respectively to give a mean concentration along each zone as 83, 92, 74 and 70 µg/g (Fig.3.23). During February, the zinc content is found to reduce to about 20 % in the first two zones and more than 50 % in the last two zones and the concentrations vary from 21.8 to 106.2 µg/g at 10 m, 7.9 to 81.6 µg/g at 20 m, 8.8 to 80.1 µg/g at 30 m and 9.8 to 50.4 µg/g at >30 m to give a mean concentration of 63, 52, 30, 30 µg/g respectively (Table. 3.19). The November observations give zinc concentration a range intermediate to that during October and February. The ranges in concentrations during November at 10, 20, 30 and >30 m zones are < 1 to 132.2 µg/g, 10.8 to 121.7 µg/g, < 1 to 90.3 µg/g and 5.4 to 153 µg/g, with mean values of 70, 70, 49 and 63 µg/g respectively.

3.7.9. Elemental distributions in October

The textural characteristics of the sediments show that clay and silt fractions dominate the coastal sediments; clay being particularly concentrated towards 10 to 20 m zone, extending to southeast coastal region (Kannamali). The silt fraction is also high (30 to 40 %) along the same region. During this observation, all the metals studied are at elevated levels in the study region. When the trace metal concentrations are plotted on a map, two distinct patterns are found to emerge. First, there is no definite gradation in the metal distribution from the shallow to the deeper regions. Second, the sediments lying at 10 to 20 m are relatively impoverished in certain metals. The distribution pattern appears to be in accordance with the low saline front observed during this period. The samples collected near the Cochin barmouth show lower concentrations than those farther from the barmouth, suggesting that the active discharge through the barmouth is sweeping away the fine-grained sediments into the coastal environment. Iron is found to be the most abundant element with its enrichment around the barmouth as well as towards the deeper regions of southwest and northwest areas. Mn is the next most abundant element, followed by Cr > Zn > Ni > Cu > Pb > Co. Manganese shows higher concentrations towards the northern coastal region and does not show any definite distribution pattern in the remaining region. The offshore regions of the navigational channel along 10°N are impoverished of any metal accumulation as particulate matter tends to bypass, leaving this area impoverished in metals. Their elevated levels and irregularity in distributions are attributed to the strong estuarine discharges showing their source from land drainage.

3.7.10.Elemental distributions during February

During February, the metal concentrations decrease from the shallow to deeper portions systematically. Sediments with > 70% clay occupy the stretch extending from northwestern part of the study region, which extend down upto the coast of Kannamali. The sand dominates the coastal and middle regions of Andhakaranazhi to the central and southwest deeper offshore regions. Around the central area of Andhakaranazhi, silt (> 70 %) is found to be high. South of this region and extending offshore, silt fraction upto 50 % is observed. The metal concentrations are the lowest during February. High organic carbon levels are observed around the middle section of the region between Kannamali and Edavanakkad and the mid-shelf of Azhikode transect (25 to 30 mg/g). However, the western regions of Cochin and Alleppey to Pallana are low in carbon content.

3.7.11.Elemental distributions during November

After the retrieval of monsoon, the coastal environment is slowly getting stabilized during Novermber, and the salient feature of these unstable and stable seasons is reflected on the textural characteristics. The metal levels are elevated, though not upto the level observed in October. However, there is always a gradient from the coast to the offshore region for all the elements concerned. Two regions of accumulation of metals are clearly observed in the contours; first around the region between Kannamali and Edavanakkad and the other, between Chethi and Alleppey. These two environments represent entirely different sedimentary sources, which are ultimately remobilized and settled within the 30 m depth zones.

3.7.12.Correlation between different elements

Fe, Mn, Ni, Co, Cr and Cu in sediments show a close relationship with the texture of the sediment (Table.3.20 to 3.22). Elemental concentrations

Table3.20 Correlation Matrix for Metals in sediments (October)

	Pb	Ni	Co	Cr	Fe	Cu	Zn	Mn	Sand	Clay
Pb										
Ni	0.73									
Co	0.85	0.78								
Cr	0.72	0.85	0.86							
Fe	0.39	0.53	0.47	0.58						
Cu	0.63	0.87	0.71	0.91	0.56					
Zn					0.65	0.36				
Mn		-0.4								
Sand										
Clay								-0.5	-0.74	
Silt									-0.64	
O.C		0.43			0.41				-0.73	0.59

Table3.21 Correlation Matrix for Metals in sediments (February)

	Pb	Ni	Co	Cr	Fe	Cu	Zn	Mn	Sand	Clay
Pb										
Ni										
Co		0.5								
Cr	-0.84	0.65								
Fe	0.50	0.51	0.89							
Cu	0.59		0.81		0.87					
Zn	0.53		0.72		0.88	0.84				
Mn			0.72		0.66	0.49	0.59	0.47		
Sand	-0.5									
Clay										
Silt										
O.C	0.6			-0.5	0.54	0.54				

Table3.22 Correlation Matrix for Metals in sediments (November)

	Pb	Ni	Co	Cr	Fe	Cu	Zn	Mn	Sand	Clay
Pb										
Ni	0.56									
Co	0.59	0.81								
Cr	0.41	0.92	0.75							
Fe	0.53	0.64	0.7	0.59						
Cu	0.46	0.96	0.85	0.92	0.62					
Zn	0.53	0.76	0.83	0.7	0.69	0.79				
Mn	0.48	0.73	0.86	0.68	0.68	0.77	0.83			
Sand		-0.5	-0.5	-0.5	-0.51	-0.5	-0.41	-0.47		
Clay		0.48	0.5	0.52	0.44	0.53				
Silt										
O.C		0.48	0.51	0.45	0.47	0.47				

increase with decrease in grain size. Fine-grained sediments are enriched in their metal content. In October, Fe and Ni bear a moderate relationship with organic carbon of the sediments ($r = 0.41, 0.43$). During this period, Ni, Co and Cr are the principally more concentrated metals, closely associated with Pb, Cu and Zn. The association of Fe with all the elements is more apparent as the linkage of different elements with organic carbon seems to be regulated by this metal alone. The correlation matrix shows that each of the metal Co-Ni-Cr is strongly related followed by their significant relationship with Cu and Pb ($r > 0.7$). Iron exhibited moderate correlation ($r < 0.7$) with all the metals and also with organic carbon. It may be noted that the dominant forces resulting in the enrichment of Co, Ni, Cr and Pb during October are not due to their organic interaction through Fe precipitation, but through their common source and interaction between elements. Another feature observed is that Mn being the second most abundant element does not show any correlation with other elements. Mn also shows a negative relationship with clay ($r = 0.5$) and Ni ($r = -0.38$). The enrichment of Ni, Co and Cr may probably due to the fluvial transport in the coastal region by detritus of inorganic nature. However, large-scale enrichment in the case of Pb, Ni, Co and Zn along the 10 and 20 m zones is conspicuous and biogenic influence or association through Fe-adsorption onto clay particles cannot be ruled out.

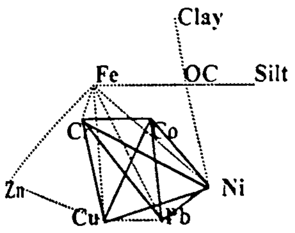
During February, the inter-relationship between Fe-Co-Zn-Cu- (Mn) gives significant correlation ($r > 0.7$), while moderate correlation between Fe, Pb & Cu with organic carbon ($r > 0.5$) and Ni with Fe and Co ($r > 0.5$). Cr is correlated only with Ni ($r = 0.65$). There has been a substantial reduction in concentration of almost all elements during this period. This can be related to a progressive increase in the percentage of sand coupled with a decrease in the percentage of clay, while the percentage of silt remained more or less unaltered.

During November, though the concentrations are not as high as in October, correlations between different elements record the maximum.

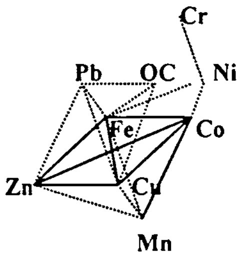
Significant correlations exist between Co, Cu, Ni, Fe, Zn, Mn and Cr ($r > 0.7$), while moderate correlation is obtained for organic carbon and percentage of clay with Cu, Co, Ni, Fe and Cr ($r > 0.45$). All the metals are moderately correlated to Pb ($r > 0.41$). Absence of any relation between Zn and Mn with organic carbon is striking during this period. Generally, the metal concentrations show an increase with increase in clay fraction. In addition, silt fraction seems to contribute to the enrichment of metals along the offshore transects.

The processes by which trace elements are preferentially segregated can be easily explained by sketching the matrix obtained through linear correlation analysis. The principal crystal lattice is constructed clubbing all elements having significant positive correlations ($r > 0.7$). Similarly, the secondary layer is formed for those elements in decreasing value of moderate correlation ($0.7 < r > 0.5$) and the elemental distributions during the three observations are simplified into the following schematic representation. This representation clearly shows that the elemental concentrations in the study region are chiefly regulated by its interaction with other elements as well as the textural characteristics, mainly the clay and organic carbon.

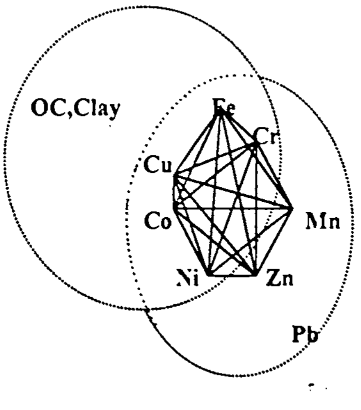
The impoverishment of Ni, Cr, Co and Zn during February is mainly due to its lack of association with organic carbon and clay. Both October and November observations show moderate relationship for Zn, Co and Ni with organic carbon and clay indirectly.



(October)



(February)



(November)

Hence, the comparative enrichment of these 3 elements during October may be due to its contribution through the silt fraction, which has a moderate correlation with organic carbon throughout the study. Further, desorption of Zn from sediment may be another factor for its low concentration in sediment during February. Probably, biogenic zinc deposition is taking place during February as evidenced by relative enrichment of zinc in water during this period.

The higher concentration of Cu in February when compared to other two surveys could be explained due to its moderate positive correlation with organic carbon. The high dissolved Cu in bottom waters during February also possibly implies its greater accumulation in sediments during the period.

Being most abundant, Fe is the binding element controlling the redistribution of other elements, and show maximum interaction, especially with organic carbon and clay. The distribution of Fe in sediment and overlying waters in general behave complementing each other in that, when there is an enrichment of dissolved Fe, correspondingly the sediments are impoverished in Fe content. This is clearly observed in November, when dissolved Fe is high and the corresponding sediment concentrations are low.

The organic association as well as its binding efficiency of lead with other elements controls the geochemistry of lead in the sediments. During October, the significant correlation with Cr, Ni, Co and Cu ($r > 0.6$) and moderate association with organic carbon and silt through iron make Pb concentration the highest among the three surveys. The distribution slightly changes in February since Pb is no longer in the principal lattice, which is occupied by Fe-Zn-Cu-Co. The association of organic carbon is moderate during this period and compensates its association in sediments during February. In November, eventhough all the elements maintain moderate correlation ($r < 0.6$) with Pb, it is not as high as that during October. The lack of correlation of Pb with organic carbon and clay substantially alters it distribution. Either or a combination of these two mechanisms seem to explain the distribution of Pb during November.

Mn exhibits a different geochemistry along this region. During October, though Mn show the highest concentration along with all other elements, it fails to establish any correlation with other metals, organic carbon, sand, silt and clay. It is highly enriched in sediments of the shallow stations of Edavanakkad, which is known for the existences of unconsolidated loose mud (Prasannakumar and Murthy, 1987). It is likely that the elevated Mn during October is through river runoff which brings in large amount of particulate matter The absence of correlation with organic carbon and clay make the distribution of Mn more even during the other two seasons. Manganese, along with iron constitutes the most enriched metals in sediment. Eventhough iron differs from toxic metals in that it is mobilized in reducing conditions; it is still effective as a trace metal adsorbent. Manganese responds and acts essentially the same as iron. Hence this is a very important second line of defense against mobilization of toxicants on the sea floor (Pequegnat, 1988).

3.7.13. Conclusion

In general, the sediment distribution of trace metals show that the anomalies are associated with the coastal sediments. Higher metal concentrations are located along the coast and mid-shelf region around Cochin and there is a decreasing gradient towards the inner and outer shelf. This gradient takes place across sediment of similar texture and composition. Thus, this type of distribution can be attributed to the regional influence as a result of coastal input. This trend is interrupted towards the southern region, between Chethi and Pallana during February, where metals tend to accumulate towards the inner shelf as evidenced by higher concentration of some of the elements. In the coastal region around Cochin, sediment accumulation is mostly towards the north at depths between 10 and 20 m and towards the coastline in the south. This may probably be due to the prevailing currents in this region leading to two distinct regional accumulation of sediment. The annual current speeds along this area ranges from 8 to 40 cm/s (Gopinathan and Qasim, 1974; Annon, 1999), which are northerly during November-February and southerly during April-September. Under such conditions, the principally low-energy longshore currents distribute fine sediment particles and associated metals may partly get deposited on the inner shelf towards the southern region. However, due to the strong barrier effect of the Cochin barmouth, the coastal currents may get modified, ultimately favoring the sedimentation towards the mid-shelf regions of 10 to 20 m depth, north of the barmouth.

Another strong but much smaller effect is produced by some of the metals, which are present in low levels at stations situated near the Cochin barmouth, and the coastal sediments between Chetti and Pallana, indicating that the enrichment of these metals in the coastal sediments are not through the land drainage. This invokes the possibility of some other mechanism, which is pertinent and influencing in this coastal environment. It is to be mentioned here that, over the past several years, the navigational channels of Cochin harbour region are dredged regularly for maintenance as well as deepening the channels. The two dumping sites of the dredge-spoil are situated at about 10 to 12 m depth, each on the southern and northern side of the entrance channel (Annon, 1993). Hence, the dispersion of these sediments from the dumping sites may be the reason for the substantial metal levels found in the inner-shelf of the north and in the sediments towards the coast of southern region. This distribution reveals that the dumped sediments instead of getting diluted by the offshore currents, tend to spread along the mid-shelf north of Cochin and southeast regions near Kannamali. A comparison of the earlier data from this region as well as the present study show that the metal distribution in these regions are exhibiting wide variations (Table. 3.23). The shallow regions from Azhikode in the north to Pallana in the south are known for the occurrence of mudbanks during monsoon season. The exchange of

Table 3.23 Comparision of present data with earlier data from the study region

	Year	Fe	Ni	Co	Mn	Zn	Cu	Pb
		(mg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)
ppey 5m *	1992	41	-	-	193	77	22	65
ppey 15m*	1992	33	-	-	128	67	20	21
ppy 5m Ó	2000	31	63	16	122	61	23	33
ppy 15mÓ	2000	30	48	21	263	83	21	33
b.puzha**	1980	49	44	64	250	-	64	-
dbank**	1980	53	115	20	188	-	175	-
dbank***	1987	2	39	5	21	120	21	12
hin 5m*	1992	46	-	-	184	140	29	76
hin15 m*	1992	38	-	-	146	111	31	26
hin 5 m Ó	2000	29	57	16	172	110	24	26
hin 15 m Ó	2000	33	72	22	171	99	32	26

Murthy et al ., (1981)

Nair (1990)

Rajamani (1994)

lv(2000)

nutrients and trace elements from the mudbank sediments have been estimated to be immense (Nair, 1990) and as they persist for three to four months, the fluxes of materials they occluded might be quite significant.

In the outer shelf, heavy metal concentrations are very close to those determined for unpolluted sediment. The accumulation rate of modern contaminated sediment in this area must be insignificant because outer shelf surface deposits are rich in relict sand. These components produce a sharp increase in their carbonate content and also large grain size and hence, heavy metals are impoverished in these sediments.

CHAPTER 4

COCHIN BACKWATERS

Introduction

Estuarine chemical variability is complex and highly variable compared to other marine environments. The dominant feature controlling the distribution, speciation and reactivity of chemical components within estuaries is the mixing of fresh and saline waters. Differences in the nature of *the fresh and saline mixing components produce gradients and transitions of* physico-chemical properties within an estuary in response to the circulation and mixing pattern. Estuaries are characterized by complex gradients of salinity, tidal action, current velocity, bottom erosion and sediment accumulation. They are subject to major and often unpredictable variations in response to river flow as well as wind and storm patterns.

In an estuary, mixing occurs between natural waters of very different chemical composition and physico-chemical properties. Although the salinity of seawater is high as compared with the total salt content of the river waters, the plant nutrient elements nitrogen, phosphorus and silicon are higher in fresh water than in seawater. Ionic strength and physico-chemical parameters such as pH and redox potential may change during estuarine mixing. Estuarine waters also contain suspended solids derived from the inflowing river or seawater or by resuspension of bedload sediment as a result of tidal stirring.

Characterization of estuarine samples with respect to salinity is a standard procedure for chemical investigations in estuaries (Morris, 1985). Correlation of the concentration of a dissolved chemical species with salinity for samples collected over a salinity range allows an assessment of source or sink or conservation of the constituent and an indication of the relative contributions of the species from the separate marine and freshwater sources. One can also deduce the salinity related location of reactivity and the extent to which it has progressed.

The distribution and variation of nutrients in estuarine systems are controlled by a variety of physical, chemical and biological processes (Pritchard and Schubel, 1981). Understanding the behavior of nutrients in estuaries has important implications for global nutrient budgets and for controlling eutrophication of these systems. The study of hydrographical features and the effect of nutrient enrichment are essential in understanding the water a useful resource. A discussion of the sources and sinks of nutrients and their distribution with the estuarine system is of great importance. Perhaps one of the most pivotal questions concerning nutrients in estuaries is the degree to which estuaries behave as traps, retaining and recycling nutrients within the system and the relative contributions of external nutrient supply. The potentially largest term in most estuarine nutrient budgets is the exchange of nutrients with offshore waters, which is usually determined by difference or ignored due to difficulties involved in measuring (Kjerfve et al., 1982). In addition, nutrient accumulation rates in estuarine sediments are difficult to measure against the large background of C, N or P already present, and are complicated by resuspension, bioturbation and deposition rates that vary widely over time and location (Nowicki and Oviatt, 1990).

4.1. Physical Parameters

Currents and Tides

Tidal characteristics studied at Cochin by several authors, have shown that the tides in the area are of mixed with predominantly semi diurnal in character having a maximum height of one meter. The difference in height between the observed and predicted tide was upto 25 cm (Jomon Joseph and Kurup, 1987). In the Cochin tidal inlet, as the cross sectional area is larger than the critical area, an increase in channel cross section will reduce the channel velocity, which will expedite the sedimentation processes (Ajith Joseph, 1996). However, a decrease in inlet cross sectional upto the critical cross sectional area results in increase of velocity maximum and the capacity to transport sediments, helping to establish near equilibrium condition. Range and duration of the spring flood are greater than that of spring ebb tide in all months during the period of the study.

The subsurface waters of Cochin backwaters (2-6 m) are moderately turbid due to many factors such as turbulence, estuarine flocculation, river inputs, re-suspension from bottom etc. This is more significant during post-monsoon and pre-monsoon seasons, when intense maintenance dredging is carried out in the navigational channel. During this period, vertical and longitudinal extent of turbidity zones will be decided by turbulent factors, the circulation features brought about by currents and to some extent by salinity stratification.

Suspended particulate matter (SPM)

In shallow estuaries like Cochin backwaters, ebb and flood currents accompany the vertical tide. Generally the horizontal tides are sinusoidal, symmetrical in shape and the amount of water carried through a certain point over the ebb equals the amount of carried over the flood. The ideal situation of symmetrical tide is often not realized. In the Cochin backwater system near the barmouth, a residual component is present which causes the amount of water carried over the flood exceeds that of ebb, resulting in a net sediment transport in the up-stream direction.

The fine-grained suspended sediment matter reacts with certain inertia to changes of current velocity. Usually there is a time lag between turn of the tide, when the current velocity is zero and the moment at which the lowest suspended silts are found. During the period of decreasing current velocity, some time is required for the material to set and when the current speed increases, it takes time before the material is resuspended. Because of this lag effect, fine-grained suspended matter is often considerably higher than in the adjoining open sea. Tidal variations of suspended sediment at four stations in the harbour area are furnished in Fig.4.1.

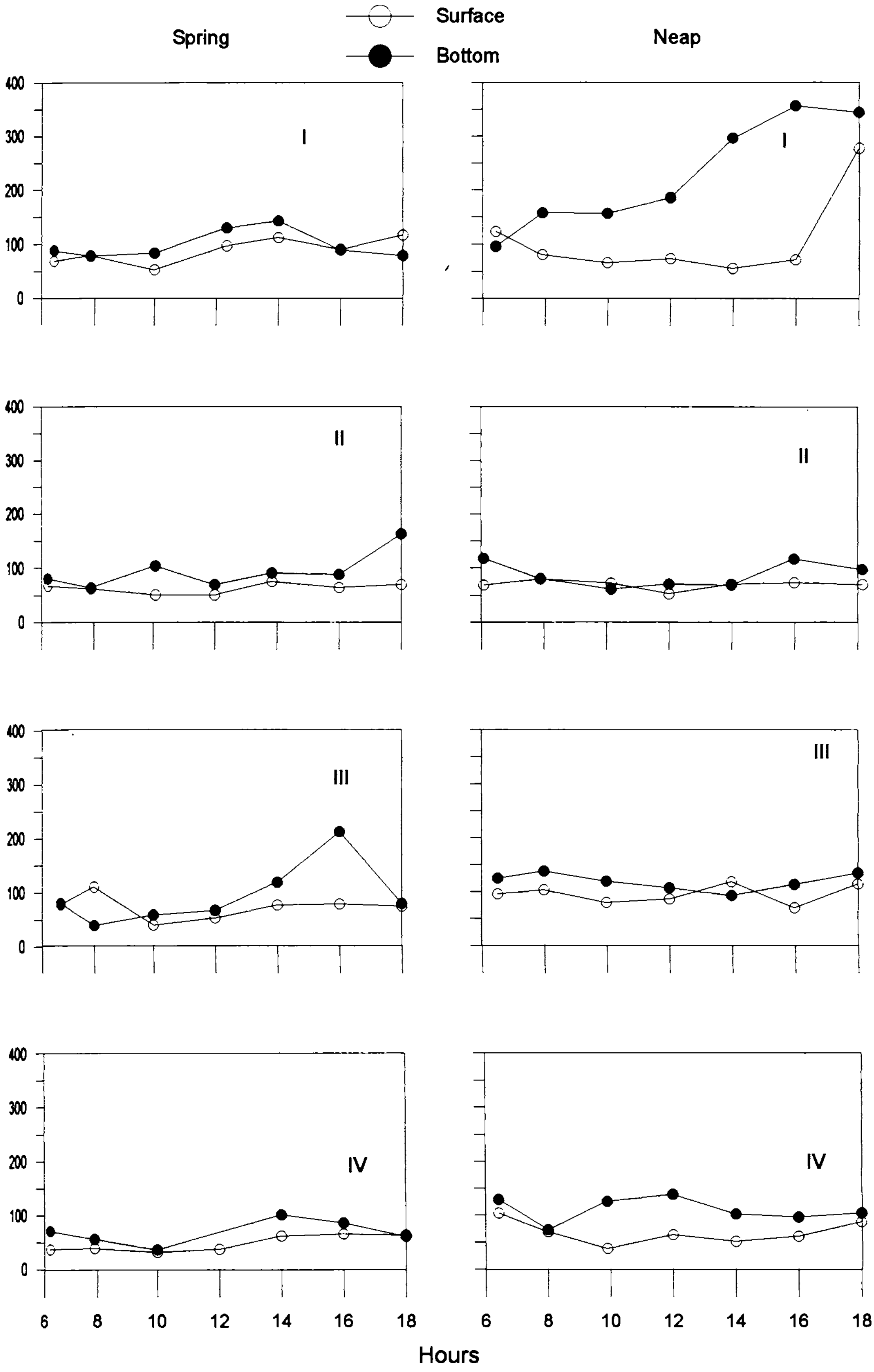


Fig. 4.1. Variation in suspended particulate matter over a tidal cycle during Spring and Neap tide.

During spring tide, surface suspended sediment concentration at station I varies from 30 mg/l to 120 mg/l and the bottom concentration between 90 and 140 mg/l. Highest concentration observed is towards flood tide. During neap tide, sediment concentration is relatively higher both at the surface and bottom. Surface pattern follows the same pattern of the tide. The suspended sediment concentration and tides do not seem to have any direct relationship at station II. Surface concentration is between 60 and 90mg/l, whereas the bottom is in the range 8 to 170 mg/l. More or less same trend is observed during neap tide also. At station III, there is a relationship observed between the suspended sediment concentration and tide both at surface and bottom during spring tide. Highest concentration is observed at the high tide. Bottom suspended sediment concentration varies between 30 and 210 mg/l and the surface concentration varies between 30 and 105 mg/l. Trend is same during the neap tide but the concentrations are lower. The distribution of suspended particulate matter at station IV also follows the trend of the tide, with maximum concentration towards the high tide. Surface sediment concentration varies between 40 and 60 mg/l and the bottom variations are in the range 30 to 105 mg/l. Neap tide variation is similar to that of spring tide.

Temperature

During spring tide, temperature distribution of the water column generally exhibits slight increase with tide and surface temperature is showing more variability when compared to the bottom temperature. There is an increase in both surface and bottom temperature from stations I to IV. The tidal mean surface and bottom temperatures of stations I to IV are 31.4 and 30.8, 32.0 and 31.6, 31.1 and 31.0, 32.5 and 32.2°C respectively (Table.4.1). During the neap tide, the trend in variation is the same, but the vertical gradient of > 1°C is observed. There is also an increase in temperature both at the surface water at station III and bottom waters at stations I and IV. The tidal mean temperatures of surface waters are 31.0, 31.9, 31.9, 32.6°C and

Table 4.1 Tidal mean values for various parameters in Cochin backwaters

Spring		T	pH	DO	SAL	NO2-N	NH4-N	NO3-N	PO4-P	SiO4-Si
		°C		ml/l	PSU	µM	µM	µM	µM	µM
Stn.1	S	31.39	7.87	4.88	26.62	0.72	4.27	3.06	2.63	18
	B	30.8	7.93	4.81	30.38	0.85	3.3	4.6	2.28	16.15
Stn.2	S	32.06	7.89	3.89	21.74	0.87	9.93	11.67	3.37	30.73
	B	31.63	7.88	3.46	24.6	1.06	12.23	11.67	4.36	29.91
Stn.3	S	31.1	8.15	4.75	22.27	0.9	7.85	9.44	6.41	41.45
	B	30.96	8.21	4.27	24.76	1.11	9.48	9.42	7.02	38.72
Stn.4	S	32.46	7.78	4.42	15.53	0.95	12.89	15.56	6.36	51.69
	B	32.2	7.79	4.3	17.25	0.97	12.95	16.48	7.16	49.1
Neap										
Stn.1	S	31.03	7.97	4.5	21.69	1.11	1.79	8.98	2.98	31.67
	B	30.21	8.09	3.91	32.29	1.52	2.57	7.38	4.49	12.95
Stn.2	S	31.88	8.06	4.7	20.28	0.88	7.54	13.62	3.31	14.32
	B	31.43	8.19	4.19	22.23	0.99	7.7	19.37	3.57	13.08
Stn.3	S	31.94	8.17	5.12	13.86	0.83	2.88	14.11	2	23.58
	B	31.06	8.05	3.55	23.36	0.77	6.69	17.44	2.53	15.4
Stn.4	S	32.6	7.3	4.09	10.17	0.88	10.46	30.25	2	19.84
	B	31.77	7.7	5.12	22.62	0.77	8.95	28.97	3.43	11.36

Mean and C.V. in the estuary

	T	pH	DO	SAL	NO2-N	NH4-N	NO3-N	PO4-P	SiO4-Si
	°C		ml/l	PSU	µM	µM	µM	µM	µM
Spring Mean	31.53	7.9	23.83	4.12	0.93	9.9	8.5	4.48	32.42
C.V (%)	2.38	2.9	26.35	21.12	25.81	62.93	60	60.27	54.9
Neap Mean	31.42	8.02	21.86	4.2	0.94	16.48	5.52	2.96	16.1
C.V (%)	3.15	4.36	30.74	30	47.87	61.41	69.02	48.65	59.69

C.V. – Coefficient of Variation

that of bottom waters are 30.2, 31.4, 31.0, 31.8°C. It can be seen that temperature variation is minimum at station III except for neap surface values.

As it is clear from the Fig.(4.2), there is an increase in the surface and bottom temperatures upstream, especially during the neap tide which may be due to the riverine influence and shallow nature. Compared to temperate estuaries, the annual variation in temperature is found to be less in tropical estuaries. Qasim and Gopinathan (1969) observed lack of vertical thermal stratification for Cochin backwaters due to its shallow nature. Higher ranges in temperature at the upstream sections of this estuary have been attributed to their shallow nature and weak tidal forcings, which facilitates water exchange and nullifies localized thermal excursions (Saraladevi et al., 1979). The influx of fresh water and intrusion of seawater with tide have profound influence on the distribution of temperature in Cochin backwaters (Sankaranarayanan and Qasim, 1969). Ramamritham and Rao (1973) also observed similar feature in Cochin backwaters and along the west coast of India. The temperature distribution during January to May is reported to be uniform throughout the estuary recording maximum in April (Sankaranarayanan and Qasim, 1969).

Salinity

The spring tide observations generally represent a homogenous water body of more or less isohaline conditions at upstream stations. The surface and bottom salinities increase progressively with tide indicating a weak stratification at stations II and III towards the high tide (Fig.4.3). While at station IV stratification is absent, station I shows slight stratification during low tide. The tidal mean values of surface and bottom salinities at stations I to IV are 26.62 and 30.38, 21.74 and 24.60, 22.27 and 24.76, 15.53 and 17.25 psu respectively (Table.4.1).

During the neap tide, except at station II, the entire region exhibit stratification and the gradient in salinity upto 17 psu are recorded at stations I

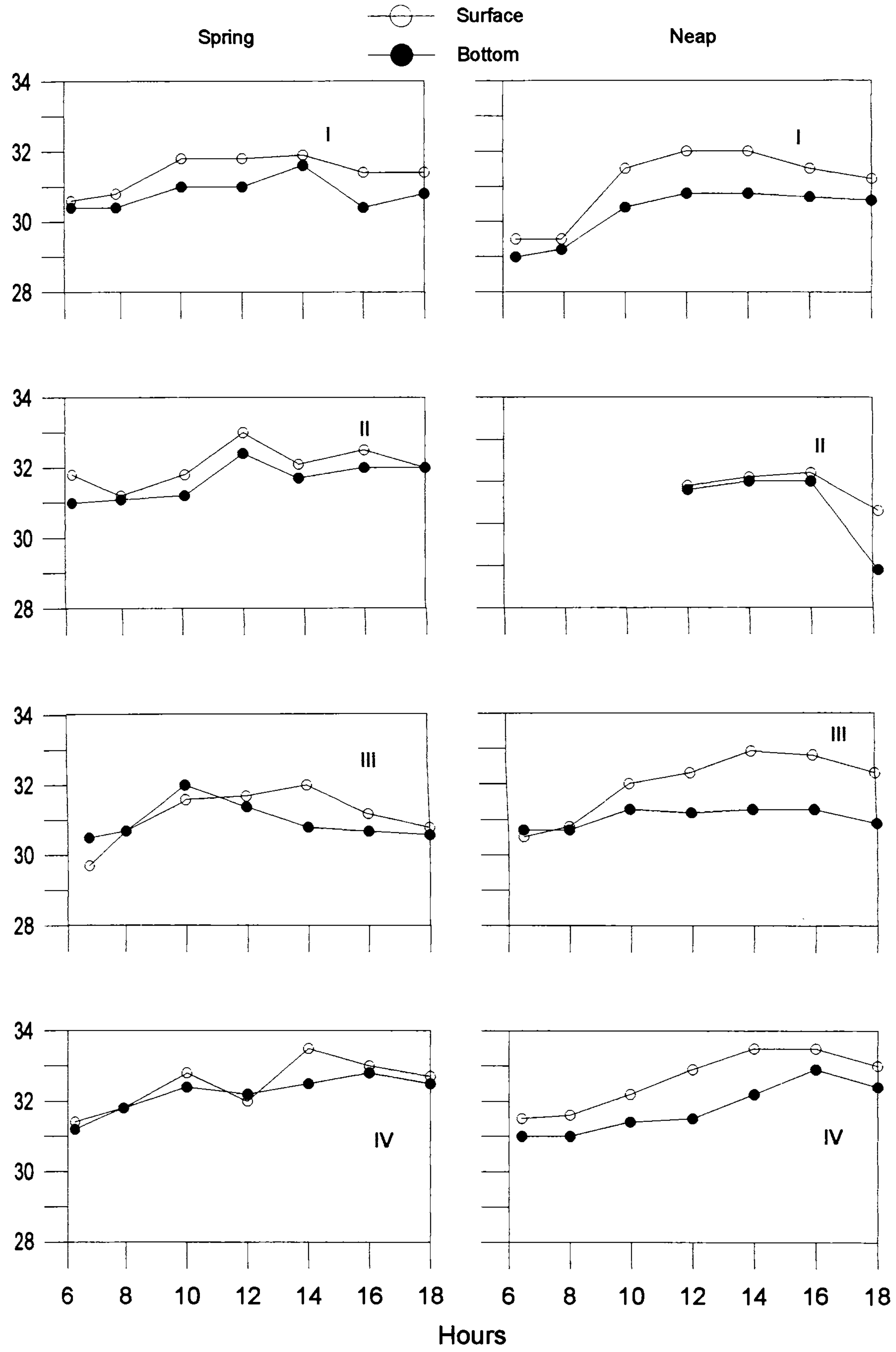


Fig. 4.2. Variation in temperature over a tidal cycle during Spring and Neap tide.

and IV. The tidal mean salinity of surface and bottom waters from station I to IV are 21.69 and 32.39, 20.28 and 22.23, 13.86 and 23.86 and 10.17 and 22.62 psu respectively.

In general, the variation in salinity follows the tidal rhythm. During the flood tide, salinity increases and during the ebb tide it decreases. The spring tide observation shows a nearly marine condition with high and vertically uniform salinity at station I and the spatial variations in upstream sections exactly follow the tidal amplitude. When the tidal forcing is reduced during neap tide, the bottom become more saline and the surface waters are still dominated by upstream discharge.

The results of the present study are comparable with the observations made by several workers in this estuary and other estuaries along the south west coast of India. Wide variability in salinity of Cochin backwaters is known due to the extreme conditions of drought and monsoon modifying its flushing characteristics (Haridas et al., 1973, Balakrishnan and Shynamma, 1976). Saraladevi (1986) and Nair et al (1988) observed wide range of variation (0.24 to 31 psu) in this estuary and attributed the feature to the shallow nature, monsoonal flow and the tidal forcing.

Sankaranarayanan et al., (1986) have observed salinity intrusion beyond 21 km in the Periyar river estuary during pre-monsoon and upto 5 km during the monsoon. They have also noticed a vertical gradient of less than 3 psu during pre-monsoon and post-monsoon periods and > 10 psu during the monsoon period. A salinity wedge extending upto 10 km was observed in the Mandovi and Zuari estuaries during monsoon (Qasim and Sen Gupta, 1981). Nair et al., (1983c) observed a distinct seasonal pattern of salinity in the Ashtamudy estuary with highest values during pre-monsoon. Jose (1993) observed well-mixed (26 psu salinity) estuarine conditions upto 15 km upstream in Chaliyar river estuary.

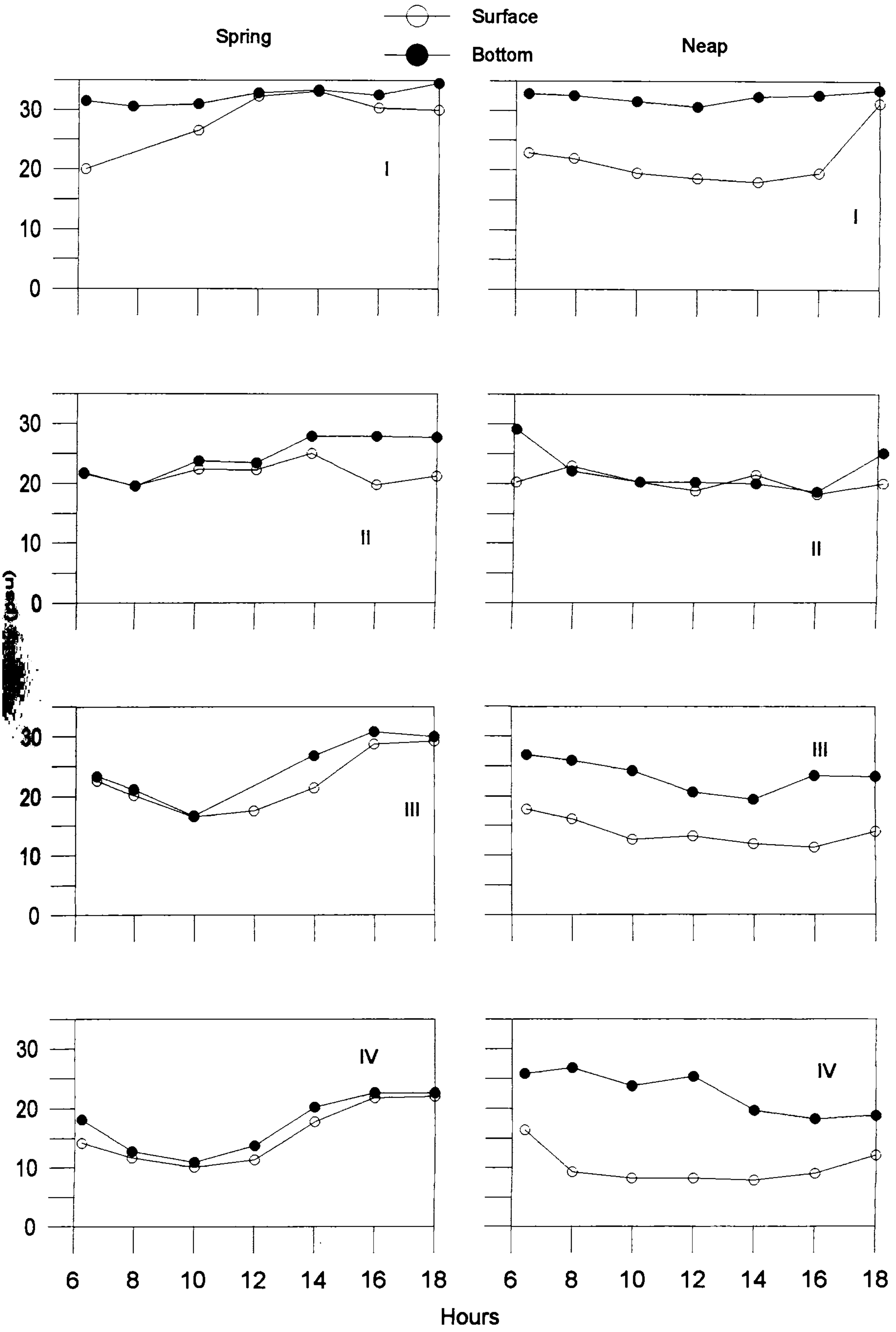


Fig. 4.3. Variation in salinity over a tidal cycle during Spring and Neap tide.

In general, the distribution pattern of salinity observed in the present study in the lower reaches of Cochin backwaters shows a similar trend as reported earlier for the same season. The present study reveals a higher salinity gradient during neap tide at stations I, III and IV, with lower salinity (8.2 psu) at the surface during neap-low and highest salinity (34.95 psu) at the bottom during spring-high. This observation is in agreement with Jomon Joseph and Kurup (1987) who also observed the lowest salinity at the surface and highest at the bottom during neap-low and spring-high. They have also observed that the duration of flooding and ebbing on spring tide is longer than those on neap tide. The diurnal variations are found to be in phase with the tides, increasing towards the estuarine mouth and with flood tide. The absence of vertical salinity gradient during spring tide shows the prevalence of well-mixed condition, probably enhanced by strong tidal currents as stated by Bowden, (1980). Thus, the estuary varies from a well-mixed type to partially mixed type even during the lean discharge period.

4.2. Chemical Parameters

pH

Fig.(4.4) illustrates the diurnal variation of pH in the four stations during spring and neap tide. The tidal mean pH for surface and bottom waters during spring is 7.87, 7.89, 8.15 & 7.78 and 7.93, 7.88, 8.21 & 7.79 respectively. Surface waters are generally having a low pH and so also the upstream waters. During the neap tide, the upstream pH shows marked variation. The tidal mean pH for surface and bottom waters during neap tide is 7.97, 8.06, 8.17 & 7.3 and 8.09, 8.19, 8.05 & 7.70 respectively (Table.4.1). The drop in pH is associated with the upstream discharge, as evident from the corresponding low saline waters.

The pH distributions in the two observations are not showing much fluctuation. The increase in pH observed at station III during spring and at station II during neap tide is due to some alkaline discharge, which are commonly experienced along the southern limbs of the backwaters (Sheeba,

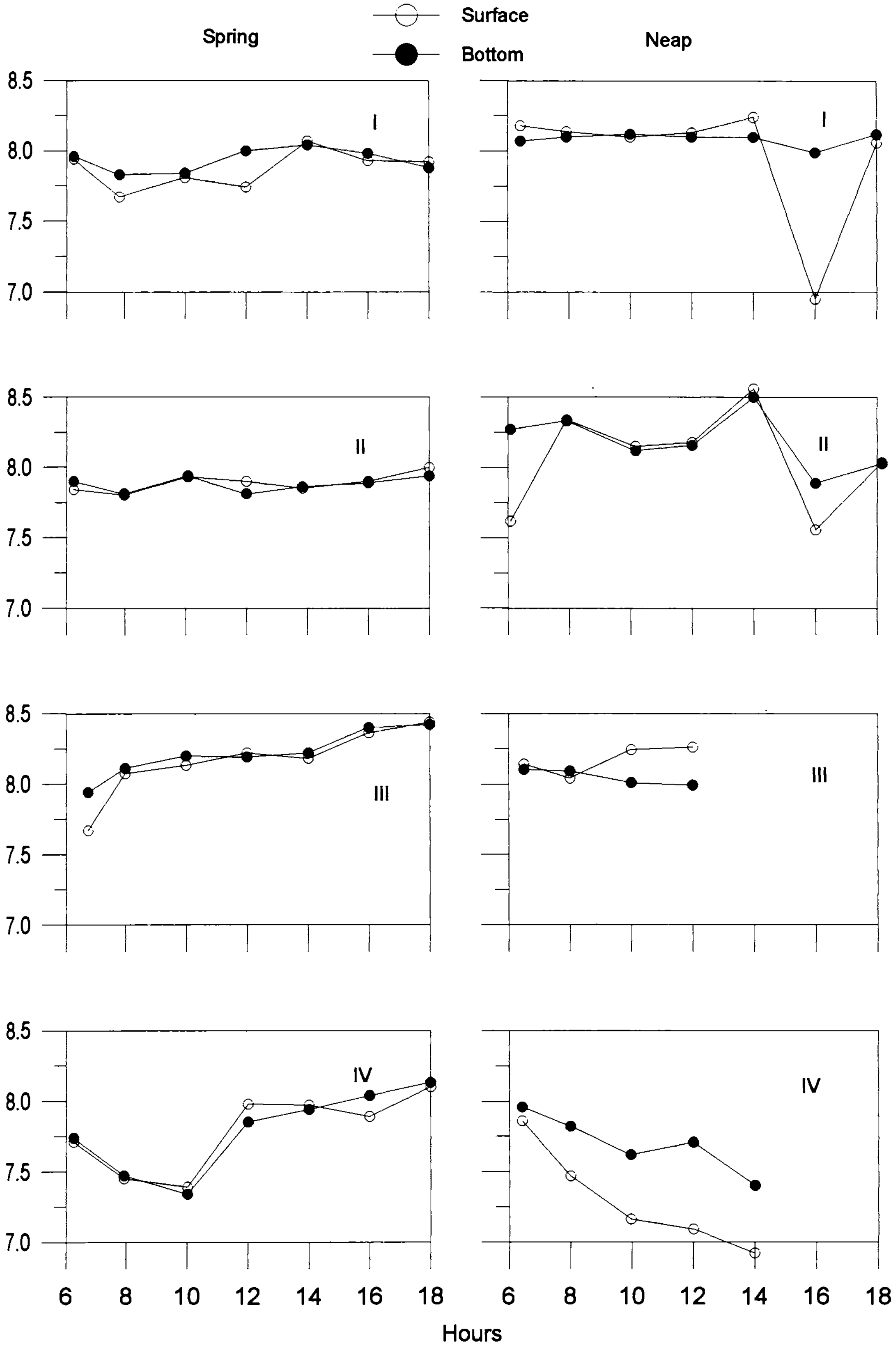


Fig. 4.4. Variation in pH over a tidal cycle during Spring and Neap tide.

2000). Nair et al., (1988) have recorded low pH in Cochin backwaters during monsoon period. Drastic changes in pH in Periyar river estuary due to the intermittent release of effluents were observed by Saraladevi et al., (1991). Sankaranarayanan and Qasim (1969) have reported absence of any stratification in pH distribution in Cochin backwaters during pre-monsoon period.

Dissolved Oxygen

Diurnal variations in the dissolved oxygen profiles generally show insignificant variation except at station III during the neap tide. Upstream station station IV shows a marginal decrease in the dissolved oxygen in surface waters during both spring and neap tides (Fig.4.5). The tidal mean values of dissolved oxygen at the surface and bottom waters during spring tide are 4.88, 3.89, 4.75 & 4.42 and 4.81, 3.46, 4.27 & 4.3 ml/l respectively. Corresponding tidal mean value for neap observation at the surface and bottom are 4.50, 4.70, 5.12 & 4.09 and 3.91, 4.19, 3.55 & 5.12 ml/l respectively (Table.4.1). The dissolved oxygen distribution generally shows a good oxidizing environment and at any stage of the tide, no depletion in dissolved oxygen concentrations is encountered at these stations. Earlier reports also underline this feature (Sankaranarayanan and Qasim, 1969; Saraladevi, 1983; Anirudhan, 1988; Nair et al., 1988; Kunjikrishna Pillai, 1991 and Sheeba, 2000).

An inverse relationship between dissolved oxygen and salinity is reported for Cochin backwaters with high dissolved oxygen during flood tide and low during ebb tide (Qasim and Gopinathan, 1969, Vijayalakshmi and Venugopalan, 1973). However, the absence of any direct relationship between these two parameters in the present study indicates that neither the flood nor the ebb flow influences the oxygen saturation of estuarine waters. The saturation with respect to dissolved oxygen may also be due to increased primary production. According to Burton (1976), photosynthetic production of oxygen in estuarine waters alone averages at a rate of 1000 $g.m^2.y^{-1}$, a

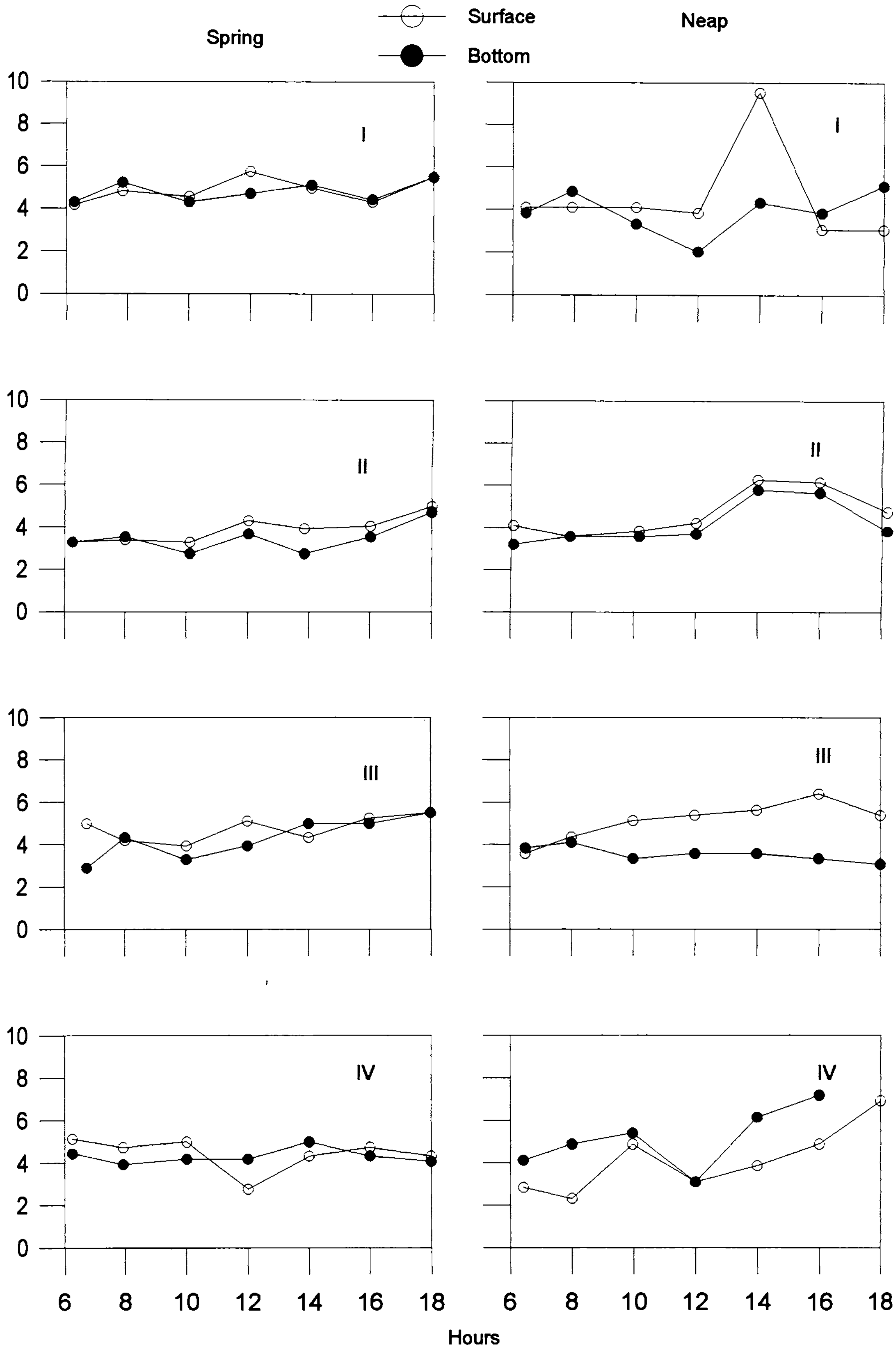


Fig. 4.5. Variation in dissolved oxygen over a tidal cycle during Spring and Neap tide.

value about 4 times its globally averaged river input of oxygen in estuaries. De Souza and Sen Gupta (1986) have noticed saturation with respect to oxygen in the upper reaches of Mandovi estuary due to photosynthetic activity.

Ammonia-Nitrogen

The spring and neap observations generally show uniform concentrations of ammonia with marginal variations with tide only at station II and IV. Upstream stations normally contain higher ammonia values perhaps due to the proximity to the industrial discharges. The tidal mean concentrations of ammonia at the surface and bottom waters of station I to IV during spring observations are 4.27, 9.93, 7.85 & 12.89 and 3.30, 12.23, 9.48 & 12.95 µM respectively (Fig.4.6). The corresponding neap tide values for stations I to IV at the surface and bottom are 1.79, 7.54, 2.88 & 10.46 and 2.57, 7.70, 6.69 & 8.95 µM respectively (Table.4.1). In both the observations, station IV records the maximum concentration of ammonia.

Earlier studies in Cochin backwaters show very high variability in the levels of ammonia due to various anthropogenic activities. Saraladevi (1991) has reported ammonia levels to vary from 2 to as high as 500 µM towards the northern limb of the estuary, especially north of Eloor, about 16 km from barmouth and 7 km from station IV of the present study, where the industries are situated. Very high levels of ammonia are regularly observed in the upstream region of this estuary (NIO data). Recently Sheeba (2000) has reported Cochin backwaters to receive substantial amount (> 150 µM) through industrial discharges from the fertilizer factory at Ambalamugal.

While all these reports point out extensive discharge of ammoniacal wastes into the backwaters, the concentrations observed in the present study do not seem to have substantially elevated ammonia levels in the environment. The ammonia variation from 10 to 23 µM as observed at station IV during spring-high is in agreement with the values reported in these

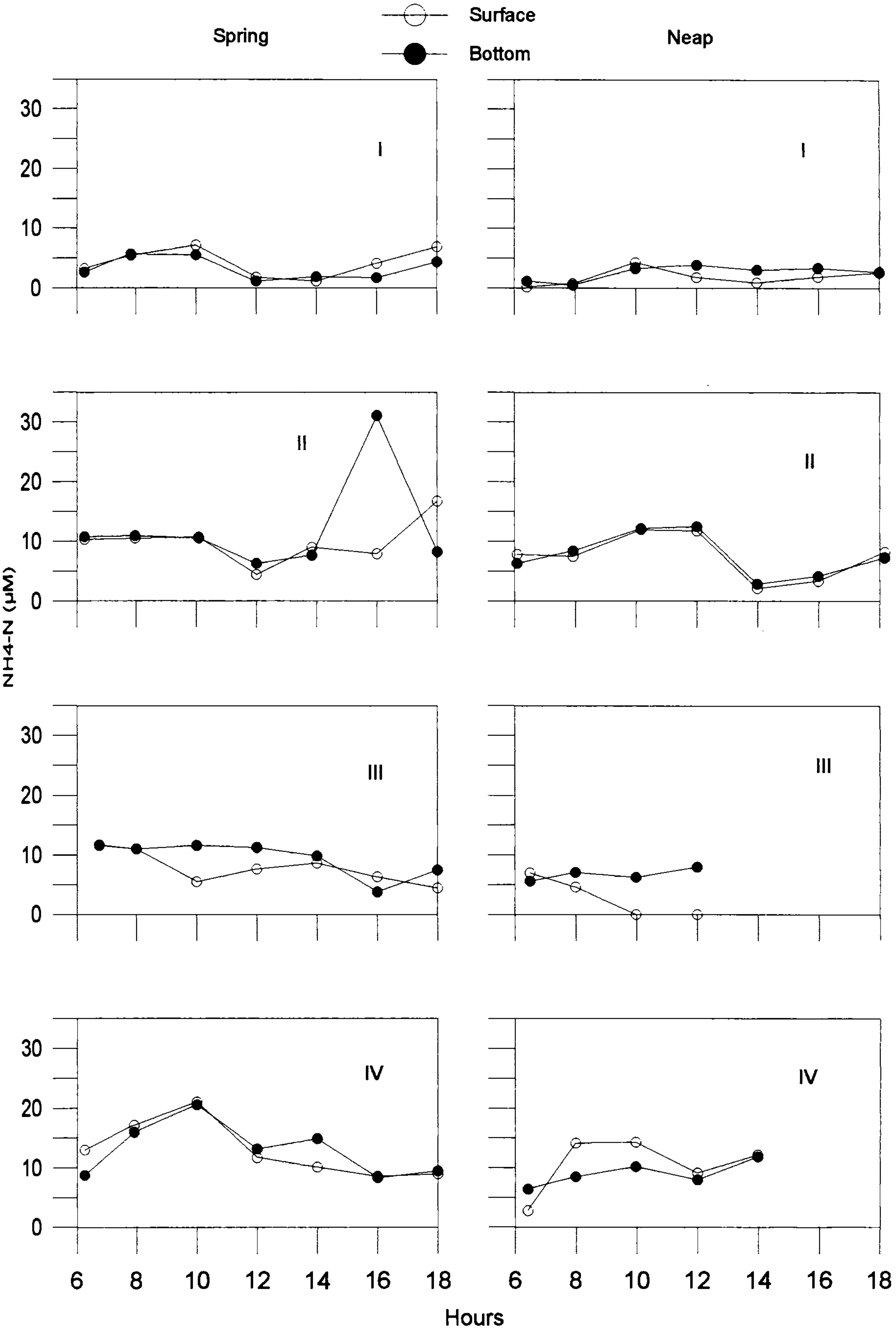


Fig. 4.6. Variation in ammonia-N over a tidal cycle during Spring and Neap tide.

estuarine sections during 1985-86 (Anirudhan, 1988). These levels are not in any way, the levels found in unpolluted estuaries, and could also be due to biodegradation of urea and other organic matter apart from terrigenous and effluent influence (Segar and Hariharan, 1989).

Nitrite-Nitrogen

Nitrite seems to exhibit very low variability at all stations during both the spring and neap tide observations. While the surface nitrite remain < 1 µM throughout the study period, bottom nitrite indicates almost similar pattern during spring, but during neap-low, both the surface and bottom waters at station I show an increase in nitrite levels to 3.8 µM (Fig.4.7). Except this high value, nitrite exhibits quite normal values throughout the estuary. The tidal mean nitrite concentration for the surface and bottom waters during spring observations are 0.72, 0.87, 0.90 & 0.95 and 0.85, 1.06, 1.11 & 0.97 µM respectively. During neap tide, the corresponding tidal mean concentrations for the surface and bottom waters are 1.11, 0.88, 0.83 & 0.88 and 1.52, 0.99, 0.77 & 0.77 µM respectively (Table.4.1).

Nitrite concentration upto 6.68 µM is reported for barmouth region of Cochin backwaters during post-monsoon (Anirudhan, 1988). The values reported by Sankaranarayanan and Qasim (1969) show low nitrite levels in the Cochin backwaters with vertical homogeneity during pre-monsoon season. The present study is found to be in agreement with this observation. The nitrite concentrations have been varying over the years, with maximum of 2.5 µM (Sankaranarayanan and Qasim, 1969) to 27.8 µM towards the upstream of Periyar (Saraladevi at al., 1991) and upto 42 µM at Ambalamugal (Sheeba, 2000). However, the present studies do not reflect enrichment with respect to nitrite at any of the stations observed.

Being thermodynamically unstable, nitrite concentrations in the sea is small as compared to that of nitrate and ammonia, although in temperate waters it shows a slight increase during winter (Riley and Chester, 1971). In

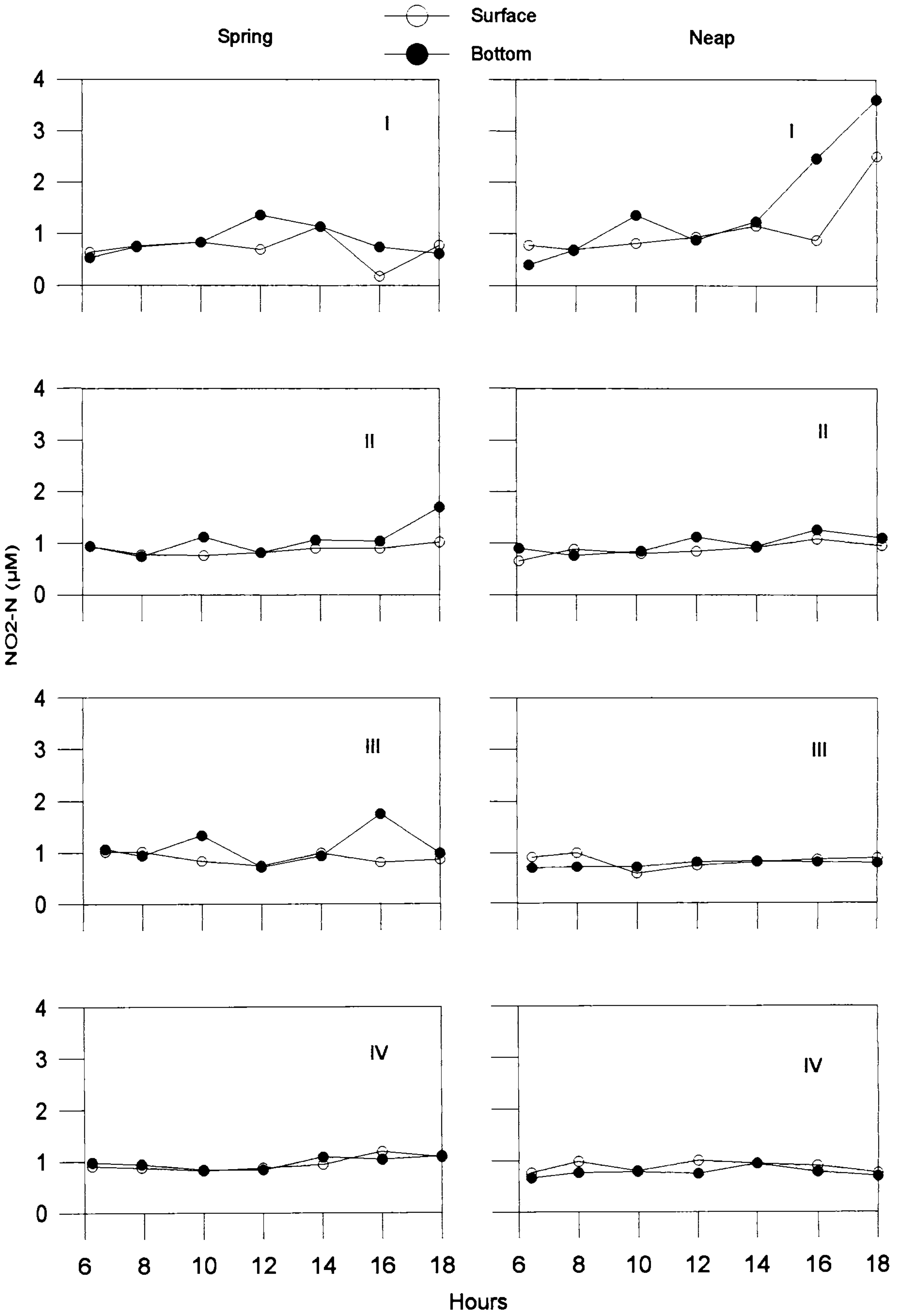


Fig. 4.7. Variation in nitrite-N over a tidal cycle during Spring and Neap tide.

Cochin backwaters, both forms of nitrogen appear at the bottom, probably as a result of decomposition of organic nitrogen within the sediment. Regarding the general trend, this may be true, but observing the levels of ammonia, it is assumed that some additional source such as sewage and industrial effluents also may be contributing to the input of ammonia towards the lower reaches of Cochin backwaters.

Nitrate-Nitrogen

The distributions of nitrate concentration during spring and neap tides are presented in Fig.(4.8). It is evident that nitrate exhibits wide variation in the estuary with higher concentrations being observed during neap tide, especially at the lower reaches of the estuary. Nitrate concentration is high in the bottom waters along the downstream sections, probably due to vertical mixing. The tidal mean concentrations of nitrate at the surface and bottom of station I to IV during spring observations are 3.06, 11.67, 9.44 & 15.56 μM and 4.6, 11.67, 9.42 & 12.95 μM respectively (Table.4.1). The corresponding neap tide values for the surface and bottom waters are 8.98, 13.62, 14.11 & 30.25 μM and 7.38, 19.37, 17.44 & 28.97 μM respectively. The trend generally shows increasing levels during neap tide.

Various physical, chemical and biological processes affect diurnal variation of various nitrogenous nutrients. The contribution of different nitrogen fractions to the total nitrogen pool of the estuary is observed to vary spatially and temporally. The major source of inorganic nitrogen is mainly the river discharge associated with sewage and industrial wastes discharged into the system. Compared to spring observations, neap observation is found to reflect maximum variability in the levels of nitrate in the estuary.

Phosphate-Phosphorus

Unlike the distribution of nitrate, the diurnal variations of phosphate in the backwaters feature some variation during spring tide. Upstream stations show higher amount of phosphate during spring tide and also the bottom

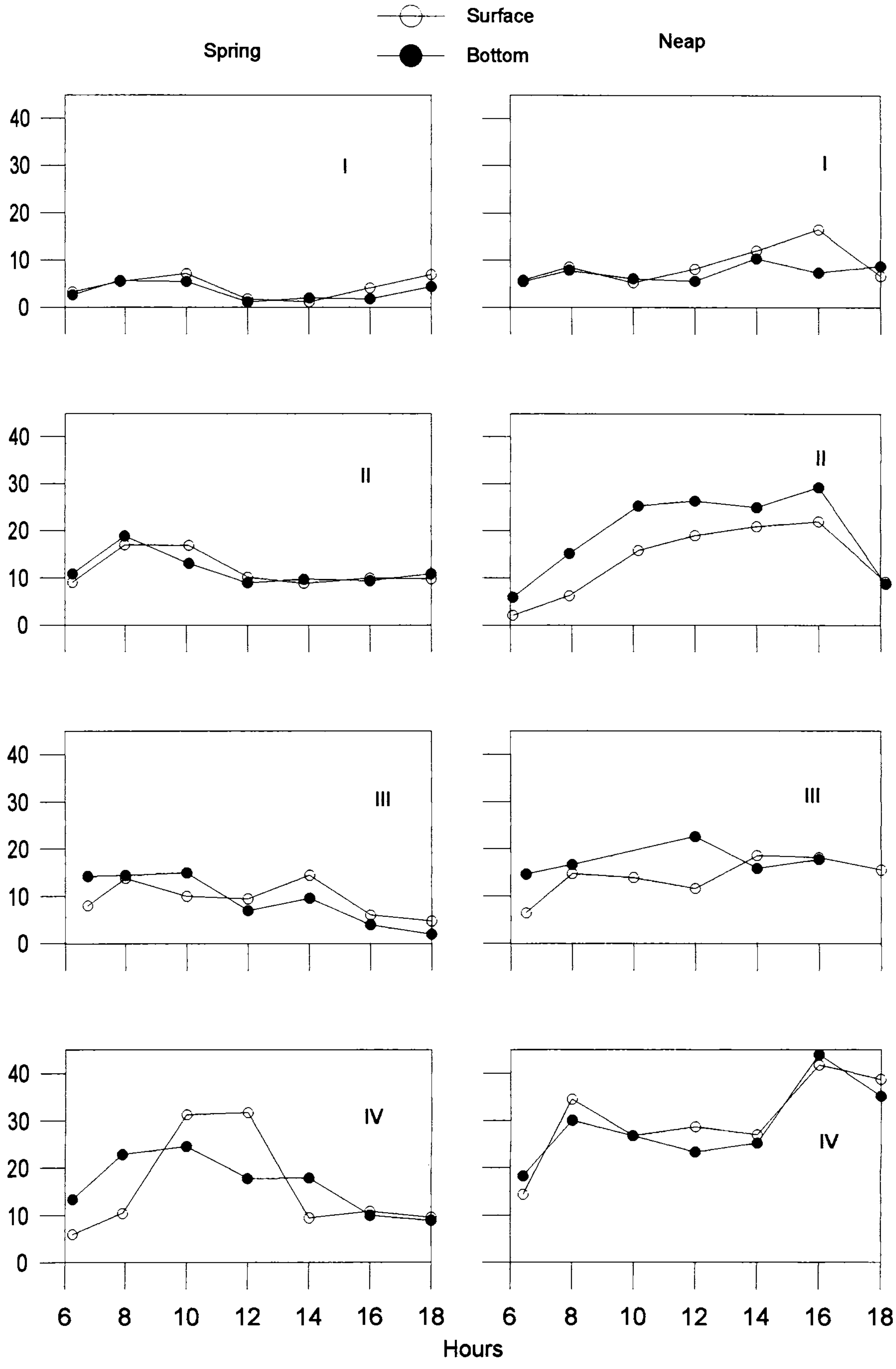


Fig. 4.8. Variation in nitrate-N over a tidal cycle during Spring and Neap tide.

waters always contain more phosphate than the surface waters (Fig.4.9). The tidal mean concentrations of phosphate at surface and bottom at stations I to IV during spring observations are 2.63, 3.37, 6.41 & 6.36 μM and 2.28, 4.36, 7.02 & 7.16 μM respectively (Table.4.1). The tidal mean neap tide concentrations at the surface and bottom are 2.98, 3.31, 2.0 & 2.0 μM and 4.49, 3.57, 2.53 & 3.43 μM respectively.

The temporal and spatial variations of inorganic phosphate differ from that of nitrogen fractions. However, high concentrations at station III and IV indicate its transport from upstream. While nitrate and salinity during both spring and neap tide in the entire study region exhibit a negative linear relationship, phosphate salinity relationship shows a deviation from it (Table.4.2). The relationship is negative and significant during spring observation, but during the neap tide, it is not significant. This suggests the presence of some alternate source of phosphate in the high saline waters during neap tide. Buffering of phosphate from sediment to overlying waters is one mechanism that can contribute phosphate enrichment in estuaries having organic rich clayey sediments (Nair et al., 1993). As there is no substantial increase in phosphate levels either at station III or IV, it can be presumed that these waters are the water parcels of previous tidal cycles where nutrient-rich waters have been pushed through. The approximate residence time of Periyar estuary is 39 days (Hema Naik, 2000), which means that the system is capable of flushing only < 5 % of estuarine waters in a day during lean discharge period. Hence a substantial percentage of the upstream input will be retained after each tidal cycle, which may result in oscillation of such enriched water masses towards the barmouth. Thus, during the neap observation, phosphate levels at the barmouth (station I) actually rise in high saline waters as the flood tide peak, and the concentrations at the surface and bottom levels reach 10 and 8 μM respectively. It must also be noted here that the phosphate concentrations at Cochin barmouth is around 2 μM at any stages of the observation, inferring that in spite of the dilution of estuarine inputs, the barmouth region is also susceptible to enriched nutrient levels quite often.

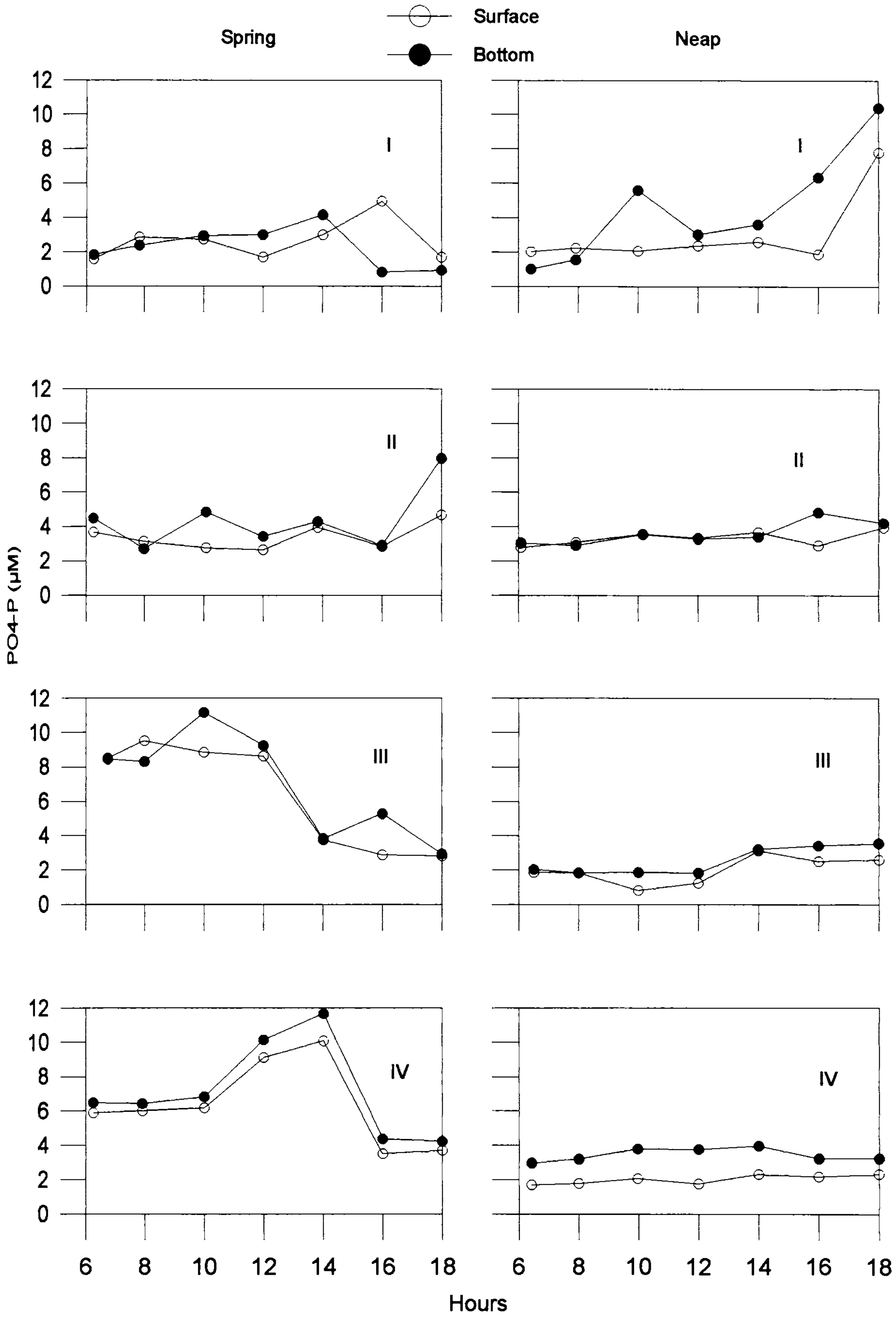


Fig. 4.9. Variation in phosphate-P over a tidal cycle during Spring and Neap tide.

The variation in nitrogen and phosphorus compounds in the estuarine region is also evident from the corresponding variability in their N/P fractions during spring and neap tides (Fig.4.10). The N/P ratio remain below 10 for most of the occasion during spring tide, indicating higher contribution of phosphorus compounds in the estuary. During the neap tide however, as there is an increase in the concentrations of nitrogenous compounds, the N/P ratio shows wide fluctuation, reaching a maximum of 28 towards the upstream station IV. The low ratio, in general, gives an indication that eventhough nitrogen and phosphorus compounds are always present in significant levels, their rate of input into the estuary vary widely.

The presence of phosphorus in seawater, though in traces, is to be dealt with extreme care, as phosphorus is suggested as an ultimate limiting nutrient (Toby, 1999; Toggweller, 1999). Toby's model (Toby, 1999) predicts that the balance between nitrogen fixation and denitrification is ultimately set by the river input of phosphate; more phosphate input leads to more denitrification, which in turn leads to more nitrogen fixation. The nitrogen cycle, being more adaptable than the phosphorus cycle, adjusts to the input and loss of the more limiting nutrient. Toby's findings can be taken as a temporary resolution to the long-standing debate over the relative importance of nitrate and phosphate for ocean productivity. These have possible implications for management of nutrient fluxes to coastal waters and semi-enclosed seas, especially where mixing between surface and deep waters is more rapid than for the global ocean as a whole. If the model is correct, then it is phosphates, not nitrates, which should be removed from waste water in order to reduce eutrophication. Phosphorus is predicted to be the ultimate limiting nutrient, whose rate of supply simultaneously regulates total ocean productivity.

Silicate-Silicon

Silicate levels in the Cochin backwaters always keep phase with tidal forcing and salinity variation. Silicate is found to vary widely during spring

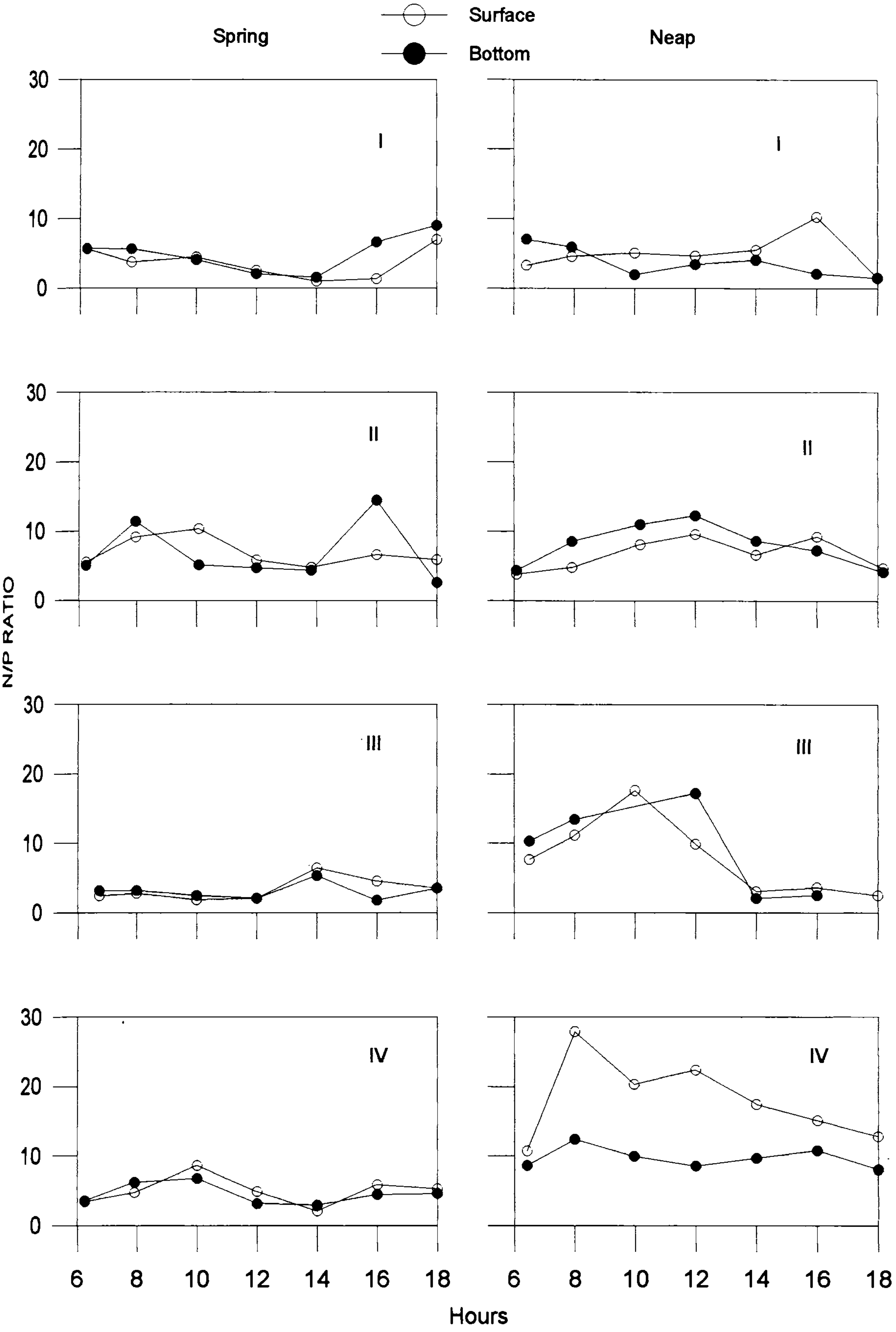


Fig. 4.10. Variation in N/P ratio over a tidal cycle during Spring and Neap tide.

tide from station I to IV, but the variations are observed only at station I and IV during the neap observation (Table.4.1). During the spring observation, silicate levels decrease with flood tide and increase with ebb tide. At station II for silicate also, gradient is not observed. While at station I and II, silicate concentration increases upto 45 µM, the upstream station record upto 70 µM during the ebb flow (Fig. 4.11). The decrease in silicate levels is in accordance with increase in salinity and flood tide. The correlation between silicate and salinity (r = -0.76) during this period clearly indicates the riverine source of silicate (Table.4.2).

During the neap observation, there is a considerable reduction in silicate levels, probably associated with a reduction in the fresh water fraction and the variations are also not as broad as that during the spring observations. The poor correlation (r = -0.32) also suggests that instead of receiving silicate from upstream, the estuary acts as a sink for silicate during the neap tide. Estuarine removal of silicate due to biological uptake has been reported from Cochin backwaters, especially during pre-monsoon (Sankaranarayanan et al., 1984; Balachandran et al., 1996). Increased residence time and enhanced nitrogen and phosphorus fractions are attributed to favor primary production, which in turn, strip off the available silicate from the estuary at a greater rate than it is being supplied.

Physical, chemical and biological processes affect distribution of nutrients in the estuary. The major source of inorganic nutrients, as evident from the figures is upstream discharge. Correlation between the different parameters studied separately for each observation for the estuarine waters are given in table 4.2. To obtain higher statistical reliability, the concentration values from all the sampling depths are included in the regression analysis. During the spring tide, salinity exhibits a good negative correlation with silicate (r = -0.76), nitrate (r = -0.71), phosphate (r = -0.59) and ammonia (r = -0.57). Neap tide observations show lower, still significant correlation with silicate (r = -0.32), nitrate (r = -0.55), phosphate (r = -0.37) and ammonia (r =

Table 4.2 Linear Correlation between various parameters (Cochin Back Waters)

Spring tide / Stations 1-4 / S & B / n = 70

	T	Sal	% variance*	DO	NO_2	NO_3	NH_4	PO_4
T		-0.37	14					
NO_3	0.4	-0.71	51	-0.31				
NH_4	0.3	-0.57	32			0.63		
PO_4		-0.59	34			0.48	0.43	
SiO_4		-0.76	58			0.71	0.49	0.72

Neap tide / Stations 1-4 / S & B / n = 70

	T	Sal	% variance*	pH	DO	NO_2	NO_3
T		-0.76	58	-0.39			
pH		0.48	23				
DO	0.4	-0.32	10				
NO_3	0.7	-0.55	30	-0.4	0.37		
NH_4	0.4	-0.4	16	-0.43			0.51
PO_4		0.37	13			0.87	
SiO_4		-0.32	10				

* % variance – each parameter with salinity

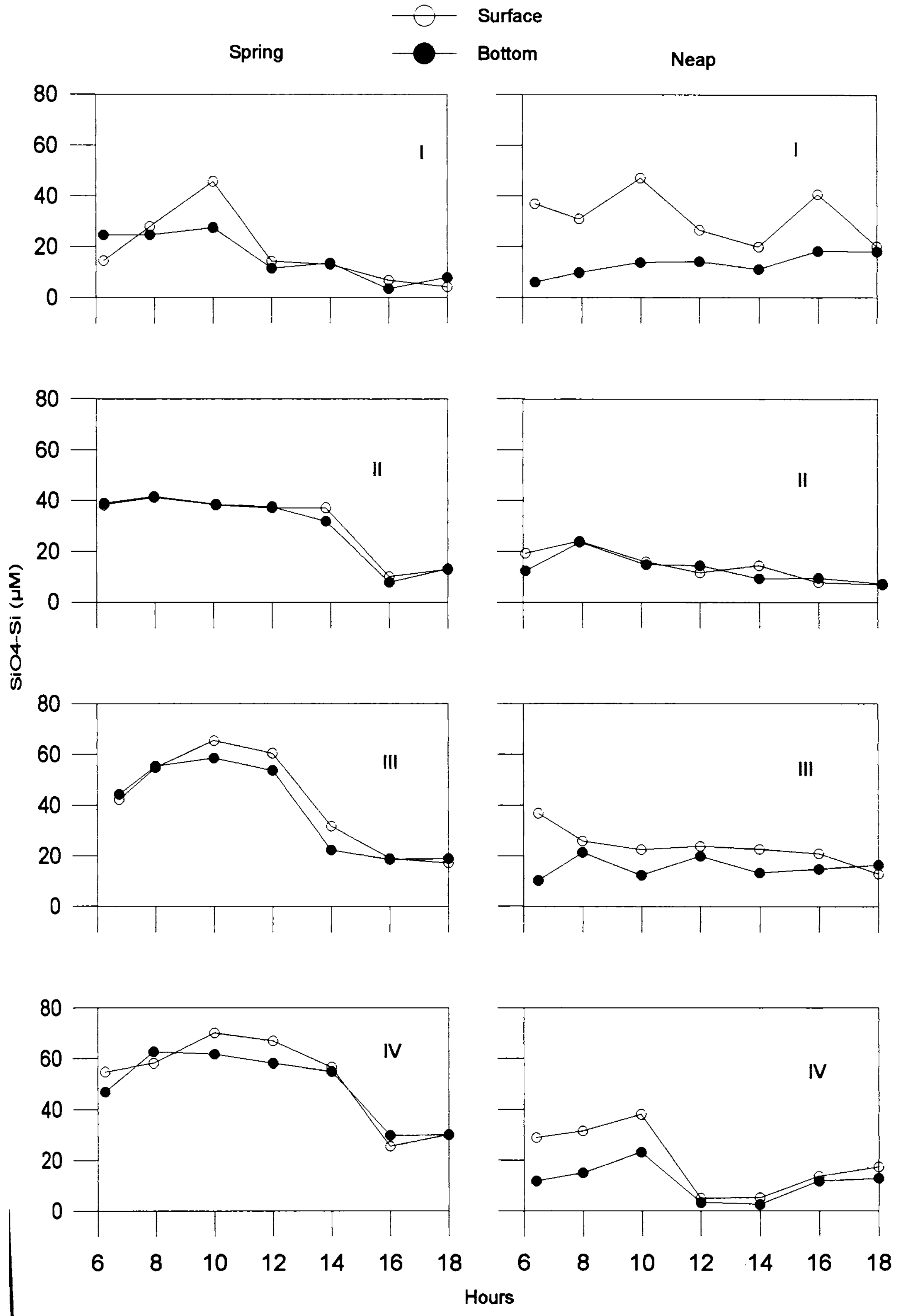


Fig. 4.11. Variation in silicate-Si over a tidal cycle during Spring and Neap tide.

-0.40). The lowering in correlation coefficients during neap tide can be attributed to the decrease in fresh water fraction present in the study region at a given time. It can be seen that there is a very strong negative correlation between salinity and nutrients within the estuary indicating that the nutrient levels within the estuary is controlled by the upstream discharges. The nitrogen fractions seem to have greater fluctuation than other nutrients. A reason for this may be that nitrogen input can increase disproportionately when there is greater fresh water flow (Korner, 1987). In the coastal waters, it is seen that salinity do not show any correlation with these nutrients, confirming that coastal waters behave independently and once the nutrients enter the coastal water, it is governed by the natural processes occurring in the coastal region from time to time. This kind of analysis is being used widely to alleviate the sources and sinks of non-conservative parameters in an environment using salinity as a conservative tracer (Korner and Weichart, 1992; Rajagopal, 1997). The correlation analysis also indicates that the nutrients are transported into the estuary through upstream discharges.

Nutrients are called fertilizers or biostimulants, usually represented by the dissolved inorganic forms of nitrogen, phosphorus and silicon utilized by photosynthetic organisms in the formation of organic matter. Nitrogen and phosphorus are described as being biolimiting elements, because the concentrations of these elements limit biological growth. The processes that govern the fate of these elements in estuaries differ and consequently the ratios of inorganic nitrogen to phosphorus in estuaries may vary widely with time and space. Estuaries function as important sinks and transformations of nutrients transported from land to the sea (Jordan et al., 1991). Most of the estuaries receive some of the highest inputs of nutrients through leaching from agricultural land and other anthropogenic activities. The resulting N and P inputs lead to elevated phytoplankton blooms (Ryther and Drunston, 1971, Nixon and Pilson, 1983, Keller, 1988) and can lead to hypoxia and eutrophication. There has been an increase in recent years in the rates of eutrophication of lakes, rivers and estuaries due to the release of N and P from excess fertilizers and sewage effluents (O'Neill, 1985). The great concern over this problem has stimulated much new research in the chemistry and biogeochemistry of nutrients in aquatic systems.

4.3. Trace elements in Cochin backwaters

The fluvial dynamics of Cochin backwaters are influenced by the interaction of discharges through the perennial rivers, Periyar and Muvattupuzha and the tides acting through the barmouth. During monsoon, the region is characterized by enhancement in the estuarine transport of alluvium. Sedimentary charts denote the post-monsoon season as a period of new-fledged sediment restitution, while silting environments prevails during the pre-monsoon (Mallik and Suchindan, 1984).

As mentioned earlier, the effluent discharges from the factories as well as from the city sewage works are identifiable sources of water pollution in the backwaters (Remani et al., 1979, 1980; Nair et al., 1990). The influence of industries and sewage make the northern part of the backwaters moderately polluted, while towards the southern side, the industries are concentrated around Ambalamugal, upstream of Chitrapuzha. In order to understand the environmental conditions of the backwater system, water and sediment samples for trace metal analysis are collected mainly from the harbour region and northern estuary.

The results of the chemical analysis of the samples are presented in Fig. 4.14 and 4.15. The textural characteristics and the sediment organic carbon are provided in Fig. 4.12. The distribution of dissolved metals at 17 stations is presented in Fig. 4.13. A comparison in range and mean concentrations of various trace metals from different geographical locations are given in Table.(4.3, 4.4). Also a comparison is made for the trace metal levels at the Cochin barmouth region over the years (Table.4.5).

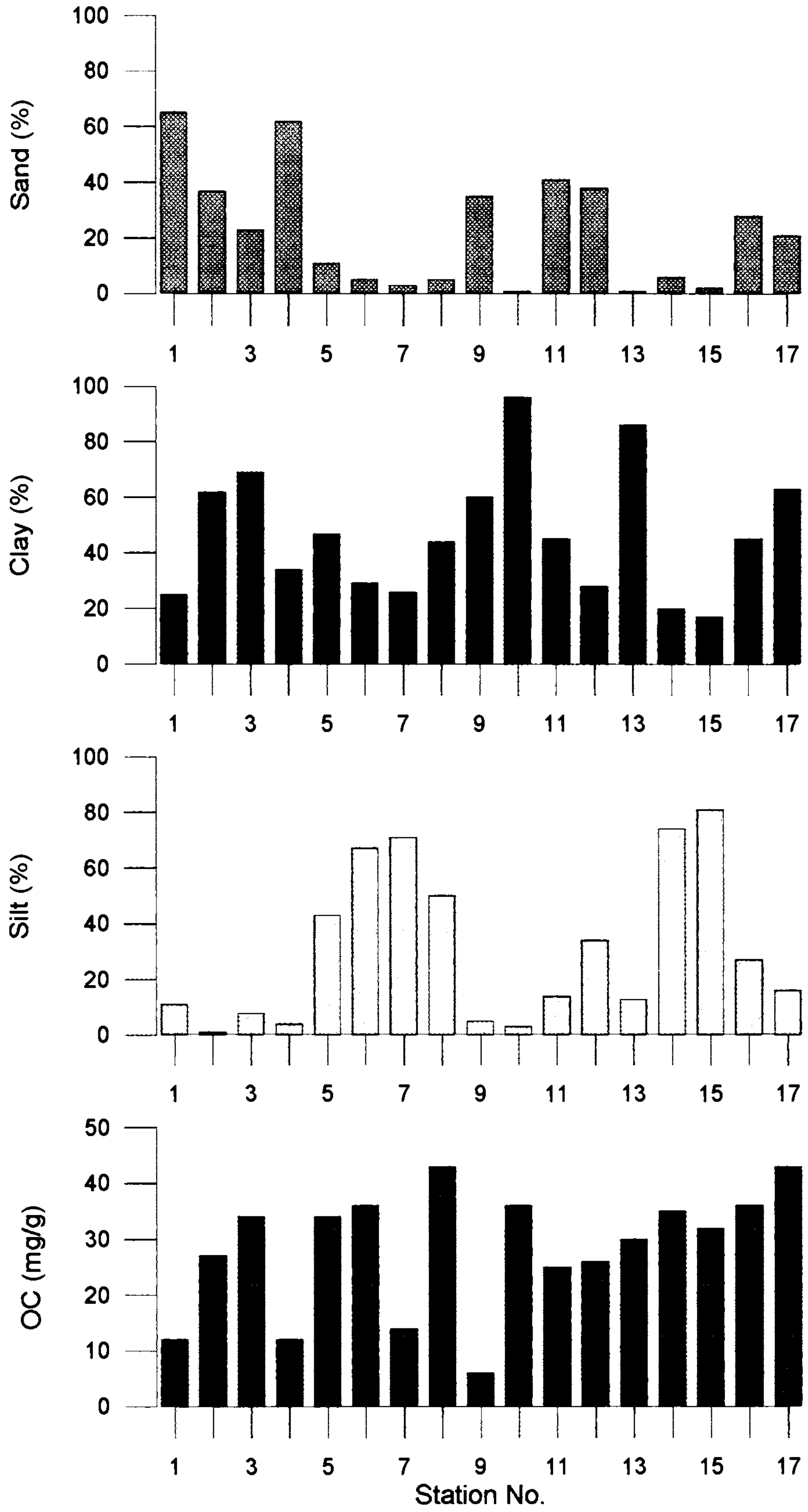


Fig. 4.12. Textural characteristics of sediments in Cochin backwaters.

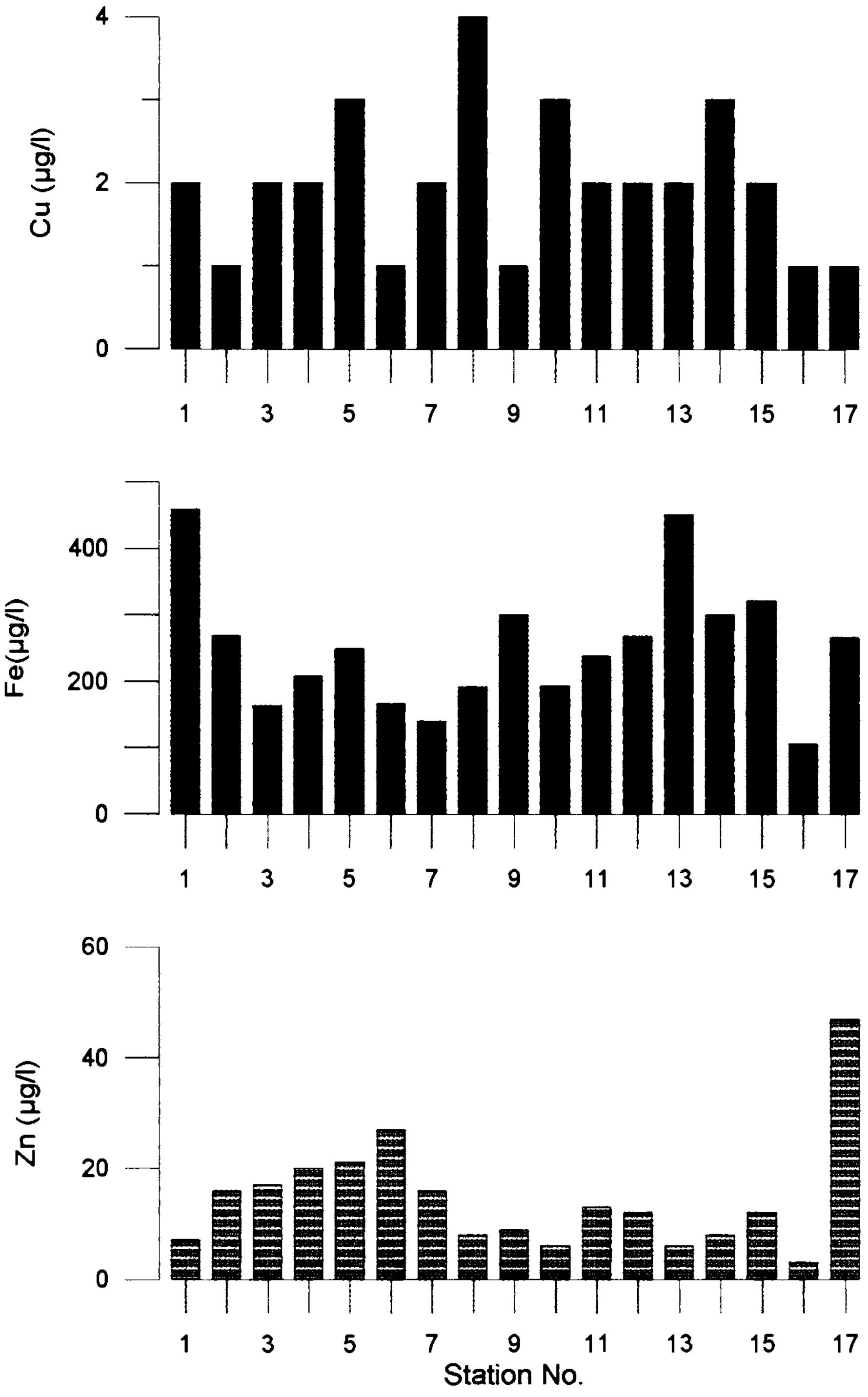


Fig. 4.13. Dissolved metals in Cochin backwaters (surface).

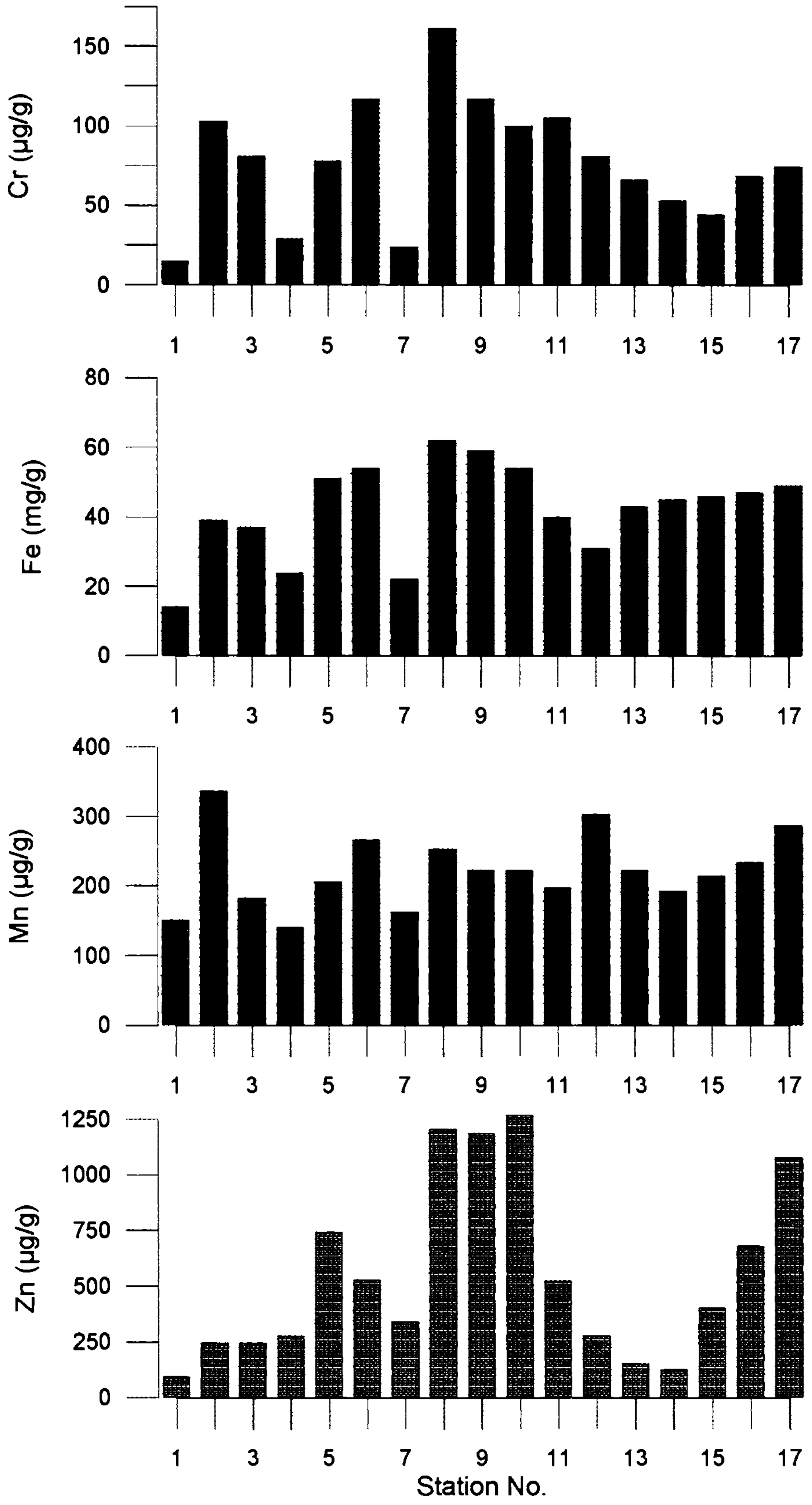


Fig. 4.14. Metal concentrations in recently deposited sediments in Cochin backwaters.

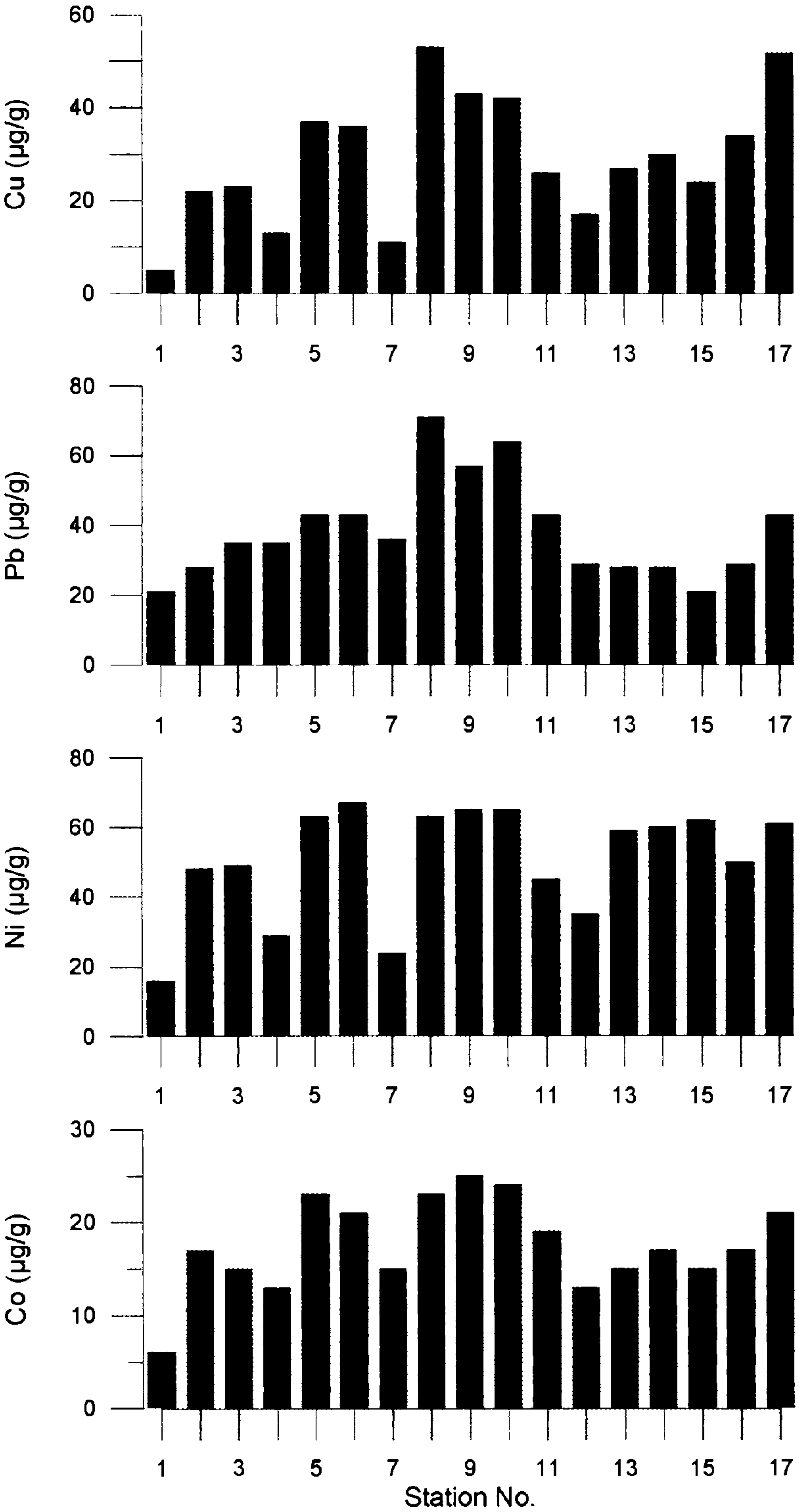


Fig. 4.15. Metal concentrations in recently deposited sediments in Cochin backwaters.

Textural characteristics and sediment organic carbon

The textural analysis of the sediments shows higher sand percentage at the barmouth (65 %) and at station 4 (62 %). The substratum generally represents a combination of clay, sand and silts; the colour being grayish black. The study region is mainly dominated by clay (> 40%). Silt is comparatively lower, showing >70 % at station Nos.6, 7, 14 and 15 (Fig.4.12). The concentration of organic carbon is also high and irregular in its distribution with comparatively lower concentrations at station Nos.1, 4, 7 & 9. Organic carbon is greatly influenced by salinity of overlying waters as the increased ionic strength may lead to flocculation. The barmouth region is always low in organic carbon, with low percentage of clay, silt and high percentage of sand. This may be the reason for the corresponding low levels of all the metals at the barmouth. The irregularity in the behavior of organic carbon may be due to biological utilization of carbonaceous detrital matter.

Iron

The distribution of iron in sediments shows concentrations > 40 mg/g towards the northern and southern limbs of the estuary, indicating a post-monsoonal metal enrichment in the middle estuary. Except for the low levels at the barmouth (14 mg/g), the concentrations are high in the middle estuary (Fig.4.14). The higher metal concentrations are also observed to be associated with organic carbon (r = 0.58). However, correlation between iron and clay is found to be insignificant (r = 0.37). In view of the non-conservative behavior of this element, the precipitation of iron during estuarine mixing is evident, which is well established (Stumm and Morgan, 1970). The dissolved iron in the estuary is showing a trend opposite to the trend given by iron in sediment (Fig.4.13). The concentration of dissolved iron at the barmouth shows the maximum value of 459 µg/l and at station 13 it is 451 µg/l. These stations are correspondingly impoverished in sediments. The same trend has been observed throughout, with enriched iron in dissolved phase overlying a decrease in its levels in sediment. The observations carried out for the coastal waters of Cochin during November also delineate this feature, inferring that sedimentary transfer of this element is the cause for its elevated concentrations in water column.

Earlier studies from this region have shown association of iron with clay and absence of correlation with organic carbon (Nair et al., 1990), whereas very strong correlation between iron, organic carbon and clay is reported by Nair et al., (1993). Speciation studies of the sediments of the same region have revealed a tendency for iron to lock up in the residual fraction (Nair and Balchand, 1993). They have also observed that surficial sediments of 0 to 5 cm of this system is quite sensitive to the periodic addition of detritus, mainly composed of inorganic matter (fine silt and clay) to which organic matter adhered and formed aggregates. The varying responses of iron towards sediment texture and organic carbon suggest that increasing salinities promote coagulation and settling of organic matter and fine clay.

Chromium

The distribution indicates a general increase towards the northern region. Low levels of chromium (< 30 µg/g) are found at barmouth and at station Nos. 4 and 7 with majority of stations showing enrichment with respect to chromium (Fig.4.14). The correlation of chromium with iron, copper and zinc are significant (r > 0.6, Table.4.6). It can be concluded that the strong influence of salt water modifies sediments to leach out chromium, as inferred from the low values at the barmouth.

Manganese

The concentrations of manganese do not give any pattern and is evenly enriched in the whole study region. Here also, barmouth sediments show lesser values and in general, the concentration range from 141 to 337 µg/g (Fig.4.14).

Zinc

The present observations show exceptionally high values for zinc in the Cochin backwaters. While zinc concentration at barmouth remain at 92 µg/g, towards the northern study region and in the middle estuary, the concentrations are found to increase (Fig. 4.14). The highest values > 1000 µg/g are observed at station Nos. 8, 9, 10 and 17 which are in the middle parts of the estuary. These high values are evidently due to external sources released from upstream. Earlier studies have also reported high concentrations of zinc (Paul and Pillai 1983; Nair et al., 1990). Zinc concentrations are the second highest values after iron in the mid-estuarine region. However, the poor correlation with clay (r = 0.41) and organic carbon (r = 0.28) goes well with the earlier observations of low levels of zinc in organic and sulphidic fraction (Nair et al., 1991). Anthropogenic inputs of zinc into the northern parts of this estuary have been identified earlier (Paul and Pillai, 1983; Shibu et al., 1990). The same distribution is reflected in the distribution of dissolved zinc also. The concentrations are low near the barmouth and increases sharply towards stations 6 & 17 where concentrations upto 47 µg/l is observed (Fig.4.13). The highest dissolved zinc value reported from this region during 1986 is 116 µg/l (Nair et al., 1990) and 89 µg/l during 1991 (Rajamani, 1994). Shibu et al., (1995) have identified mid-estuarine maxima in labile zinc. He has also computed that approximately 80 tonnes of zinc is being accumulated in this part of the estuary annually. The present observation show the higher concentration of zinc in Cochin backwaters as compared with earlier studies, it can be inferred that the anthropogenic source is regulating the enrichment in the sediment.

Copper

Sediment copper levels in the study region ranges from 5 to 53 µg/g (Fig.4.15). The lowest concentrations are observed at the barmouth with an increase towards the northern region. This region is reported to contain high amount of particulate Cu (Rajamani, 1994). Organic and sulphide-bound sediments characterize this region, which has a strong tendency to associate with copper (Ranjamani, 1994; Nair et al., 1991). Hence organic association of copper seems to regulate the geochemistry of copper in this estuary. The inputs give rise to non-uniform behavior, irrespective of sediment texture. The concentrations in the overlying water do not exhibit any relative variability to explain the non-uniformity (Fig. 4.13). Dissolved copper in the entire region is low and it varies from 1 to 3 µg/l. Concentrations of dissolved copper upto 6 µg/l have been reported earlier from this region (Shibu et al., 1990; Rajamani, 1994). Apart from geochemical control, biological uptake of this element is quite remarkable from the significant correlation obtained with organic carbon ($r = 0.62$). Shibu et al., (1990) have opined that distribution of copper in water is greatly influenced by biological and geochemical processes. Significant enrichment of copper in the sediments of this region has been observed earlier also (Nair et al., 1990).

Lead

There is considerable variation in the concentration of lead in the estuarine sediments as the maximum concentration > 50 µg/g is observed towards the northern region of study (Fig.4.15). The lowest values are recorded at the barmouth, where saline conditions prevail during most of the year. However, anthropogenic input of lead into this estuary seems to be insignificant, as very high concentrations are not encountered at any station. The mid-estuarine enrichment can be attributed to the sedimentation of metal-associated suspended solids and to flocculation due to increasing salinity. The residual fractions of lead in this middle region are found to be an order of magnitude higher than those at less saline regions; eventhough the carbonate-bound lead is uniformly present (Nair et al., 1991). Thus the above-mentioned sedimentary processes probably control lead accumulation in Cochin backwaters.

Nickel

The distribution of nickel is similar to that of cobalt with lower levels at the barmouth and an increasing towards upstream (Fig.4.15). Nair et al.,

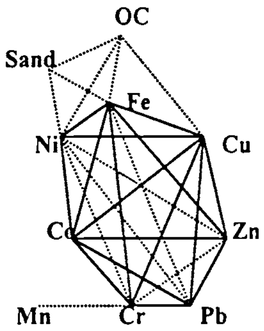
(1990) have reported post-monsoon deposition of this metal. Most of the stations contain nickel concentrations greater than 60 µg/g, and comparable with the earlier data, showing the absence of pollution with respect to nickel. Suraj et al., (1996) have observed selectivity in adsorption of this metal to clays in Periyar river sediments. They have suggested that the river sediments play an important role in the cleaning up of domestic as well as industrial contaminants, as the kaolinite is capable of adsorbing most of the metal ions onto it within a short time.

Cobalt

Cobalt exhibits strong incorporation into the sediments during the observation. As for other metals, cobalt is also comparatively enriched in the sediments of northern region with a maximum concentration of 25 µg/g at station 9 (Fig.4.15). These values are in agreement with reported levels from this region (Nair et al., 1990) and hence indicate absence of additional source for this element.

The correlations studies indicate that none of the metals have significant correlation with organic carbon and clay fraction. The correlation coefficient for Ni, Cu and Fe with organic carbon are r = 0.62, 0.62 and 0.58 respectively (Table.4.6). This indicates that metal association in the Cochin backwaters is probably not taking place according to the textural characteristics. However, significant correlation obtained for iron with all other metals except for manganese gives an indication that the elemental accumulation in sediments may be controlled by the precipitation of iron onto organic matrix. The significant correlation between the metals except for manganese shows the common source of metal. The absence of any significant correlation for manganese may be due to its sedimentary origin, identical to the observation for the coastal sediments. Hence it is presumed that natural processes control the distribution of most of the metals studied in the estuary, while the zinc is influenced more by anthropogenic input.

The model developed to predict the metal enrichment in the sediments of Cochin backwaters follows a pattern similar to that obtained for the coastal environment during November. Here also Fe form the principal lattice bound strongly with Ni, Cu, Co, Zn, Cr and Pb exhibiting significant correlation within their association. Mn is having only a moderate correlation with Cr and no correlation with other metals. Organic carbon, through its moderate correlation with Fe, Ni and Cu, form the secondary layer is indicative of metal association through the scavenging nature of Fe. The absence of correlation between organic carbon and Zn, and to a certain extent, Pb suggests the abiological processes by which these elements are deposited in this region. The interaction of organic carbon and clay with other elements seems to be a main factor differentiating the trace metal distributions in the coastal and estuarine sediments.



Thus, the trace metal concentrations in recently deposited sediments show varying and differential behavior influenced by natural as well as anthropogenic factors. Basically, most of the metals considered in this study are significantly enriched in lower reaches of the northern parts of the estuary. The high values may be due to anthropogenic inputs from industries situated on the banks of the river Periyar. Compared to the metal levels of other regions (Table.4.3, 4.4) and the earlier reported values for the same region (Table.4.5), it can be seen that Cochin barmouth and harbour region are not enriched in metals to greater levels, but the northern parts of the estuary, where the influence of river discharge is predominant, an enrichment of metals, especially zinc is evident. Nair et al., (1990) have also reported post-

Table.4.3 Metal concentration (range with mean in paranthesis) of suficial sediments of various geographical locations (µg/g-dry wt. except for Fe-(mg/g)

	Location	Co	Cr	Cu	Ni	Pb	Zn	Mn	Fe
1	Narragansett	<1-8	13-81	26-98	6-34	17-81	53-168		
	Bay*	(5)	(46)	(53)	(18)	(44)	(110)		
2	Raritan Bay*		(428)	(1015)	(54)	(279)	(490)		
3	Bombay harbour	(50)		(105)	(111)	(48)	(155)	(1140)	
4	Bombay	(51)		(105)	(89)	(25)	(138)	(1059)	
5	Thana Creek	(50)		(132)	(132)	(28)	(206)	(980)	
6	New York Bight*		(102)	(142)	(23)	(173)	(252)		
7	Firth of Clyde,*Scotland		48-303		34-70	76-322	139-825		
8	Gulf of Mexico	3.8	36-66		10-23				
	Shelf*	(5)	(49)	(10)	(29)	(24)			
	California, baseline*		(22)	(8.3)	(9.7)	(6.1)	(43)		
10	Los Angeles County		109-148	14-937	16-134	19-578	54-2880		
	Outfall zone*		(260)	(164)	(52)	(102)	(332)		
11	Southern California*		34-62	13-21	9-17	6-12	54-75		
12	Astamudi estuary			20-145	10-15	33-41	52-110		1-3
13	Chaliyar estuary			6-40		20-88	25-71	197-545	18-60
14	Cochin estuary (1988)*	3-22	3-118	1-42	11-123	8-40	23-245		
15	Cochin estuary(1991)			5-51		33-117	29-291	123-280	15-55
16	Cochin estuary (2000)	6-25	15-161	5-53	16-67	21-53	92-1266	141-337	14-69

Reference 12_Nair et al.,(1987) 3,4&5 _ Zingde et al.,(1987)

* _Nair et al.,(1990) 13,14 _Rajamani(1994)

15 _Present study

Table.4.4 Concentrations of metals in sediments from the region (µg/g) except for Fe (mg/g)

Location	Metal	Concentration	Reference
Cochin Estuary	Fe	8.32	Nair (1992)
Cochin Estuary	Fe	15 – 55	Rajamani (1994)
Cochin Estuary	Fe	14 _ 62	Present study (2000)
Kerala coast	Fe	5 – 55	Rajamani (1994)
Cochin Estuary	Mn	66	Nair (1992)
Cochin Estuary	Mn	123 - 280	Rajamani (1994)
Cochin Estuary	Mn	151- 337	Present study (2000)
Kerala Coast	Mn	44 - 318	Rajamani (1994)
Cochin Estuary	Cu	12	Nair (1992)
Cochin Estuary	Cu	5.5 - 51.3	Rajamani (1994)
Cochin Estuary	Cu	5-53	Present study (2000)
Kerala Coast	Cu	5.1-48.1	Rajamani (1994)
Cochin Estuary	Zn	70	Nair (1992)
Cochin Estuary	Zn	29.3-290.5	Rajamani (1994)
Cochin Estuary	Zn	92-1266	Present study (2000)
Kerala Coast	Zn	7.42-148.75	Rajamani (1994)
Cochin Estuary	Pb	15	Nair (1992)
Cochin Estuary	Pb	33.2-117.1	Rajamani (1994)
Cochin Estuary	Pb	21 - 71	Present study (2000)
Kerala Coast	Pb	17.9 - 80.9	Rajamani (1994)

Table.4.5 Long-term changes in metal concentrations in Cochin backwaters (µg/g except for Fe mg/g)

	Pb	Ni	Co	Cr	Fe	Cu	Zn	Mn	Reference
Barmouth									
1979	--	67	26	--	--	29	210	190	Venugopal et al., (1982)
1989	7	15	4	2	0.4	4	40	23	Nair et al., 1990)
1991	52	--	--	--	35	24	88	190	Rajamani (1994)
2000	21	16	6	15	14	5	92	151	Present study
Station.12									
1991	63	--	--	--	45	30	125	210	Rajamani (1994)
2000	43	45	19	105	40	26	525	197	Present study
Station.15									
1989	8	40	7	18	2	20	110	23	Nair et al., (1990)
1991	65	--	--	--	58	53	290	210	Rajamani (1994)
2000	21	62	15	44	46	24	402	215	Present study

monsoonal mid-estuarine build up of metals in sediments. The absence of such a kind of accumulation in the sediments of harbour and barmouth regions may be attributed to the fact that these regions are subjected to periodic dredging whereby removing recent depositions on a long-term.

The variability in the metal content of present study is compared with the reported values for the same region and also from other parts. The ranges of concentrations of these studies are comparable with the present study. For the Cochin backwaters, seasonal hydrographic changes play an impotant role in regulating the metals in the sediments. Generally, the post-monsoon periods are associated with the build-up of materials, which become enriched in the accumulative phases of the sedimentary material. Terrestrial transport appears to occur mostly during the monsoon season, which is associated with high river discharge and bed-load movements (Nair et al., 1993). The absence of significant correlation of metals with organic carbon and clay is indicative of metal enrichment through inorganic processes. High concentration of zinc in the mid-estuarine region is identified to be due to industrial discharge through the river Periyar.

Table. 4.6 Correlation Matrix for trace metals in sediments (Cochin backwaters)

	Pb	Ni	Co	Cr	Fe	Cu	Zn	Mn	Sand	Clay	Silt
Pb											
Ni	0.48										
Co	0.81	0.81									
Cr	0.74	0.64	0.75								
Fe	0.65	0.95	0.89	0.78							
Cu	0.73	0.84	0.88	0.73	0.92						
Zn	0.87	0.57	0.83	0.62	0.73	0.85					
Mn	--	0.41	0.35	0.58	0.45	0.44	0.26				
Sand	0.28	0.66	0.5	0.26	0.58	0.49	0.28	0.17			
Clay	0.42	0.39	0.42	0.37	0.37	0.42	0.41	0.22	0.2		
Silt	0.14	0.17	--	0.1	0.14	--	0.14	--	0.59	0.68	
O.C	0.2	0.62	0.39	0.42	0.58	0.62	0.28	0.46	0.61	0.22	0.26

CHAPTER 5

ENVIRONMENTAL QUALITY OVER THE YEARS

5.1. Cochin backwaters

In the previous chapter, general environmental conditions of Cochin backwaters are discussed and the estuarine waters are found to be well-oxygenated and rich in nutrients. A comparative study of the various environmental parameters collected presently as well as the earlier data collected will indicate how this system has behaved over the years. The data collected from the estuarine mouth, near Cochin harbour has been chosen for the comparison as several workers has repeatedly sampled this region since 1965. The reason for taking the barmouth as an index for estimation of these pollution load is because this is the point where the pollutants are brought down to the minimum by dilution before being exported to the coastal waters. These values can also give an approximation of how much of these nutrients are being transported out into the sea during different years. Studies conducted by several workers on the nutrient levels of Cochin backwaters since the sixties reveal interesting variations over the period of time. The mean surface concentrations of phosphate and nitrate recorded at the barmouth of the non-monsoon months (October to May) from 1965 to 2000 are plotted in Fig.5.1. It can be seen from the table 5.1 that both nitrate and phosphate were present in very low levels upto mid 70s' from where, due to the combined effect of increased industrial as well as agricultural activities, the levels increased during 80s' and 90s'. During 1965, the surface phosphate and nitrate concentrations were 0.75 and 2.0 µM, which has increased to 2.9 and 6 µM respectively by 2000 eventhough, between the years it show still higher levels. The trend also shows a build up of nitrogen and phosphorus fractions after 1975 and from 1980 onwards, the concentrations remained high. Enrichment of phosphorus with respect to nitrogen is more leading to mesotrophic waters. However, this enhanced nutrient levels have not lead to any oxygen depletion in the environment, possibly because the river discharge

Table. 5.1 Long term concentrations of nutrients at Cochin barmouth (surface)

Year of study	Salinity (PSU)	NO3-N (μM)	PO4-P (μM)	Reference
1965	19.00	2.00	0.75	Sankaranarayan and Qasim (1969)
1966	18.00	2.50	0.85	Qasim and Gopinathan (1969)
1968	--	--	0.90	Reddy and Sankaranarayanan (1972)
1972	--	--	0.30	Joseph, 1974
1973	7.00	2.50	1.30	Manikoth and Salih (1974)
1976	--	4.50	2.90	Lakshmanan et al., 1987
1980	21.00	11.50	4.10	Nair et al., (1988)
1981	25.60	13.50	3.90	Saraladevi (1986)
1982	--	--	3.00	Sankaranarayanan et al., (1986)
1984	22.90	--	3.30	NIO Data, 1985
1986	25.50	13.90	5.10	Anirudhan, 1988
1989	18.60	16.00	2.90	NIO Data, 1990
1992	1.30	29.50	3.20	NIO Data (1993)
1993	26.10	14.50	5.00	NIO Data (1993)
1995	24.40	8.00	3.43	NIO Data (1996)
1996	15.80	11.00	4.15	NIO Data (1997)
1997	25.60	42.30	5.25	Sheeba, 2000
2000	24.10	6.00	2.81	Present study

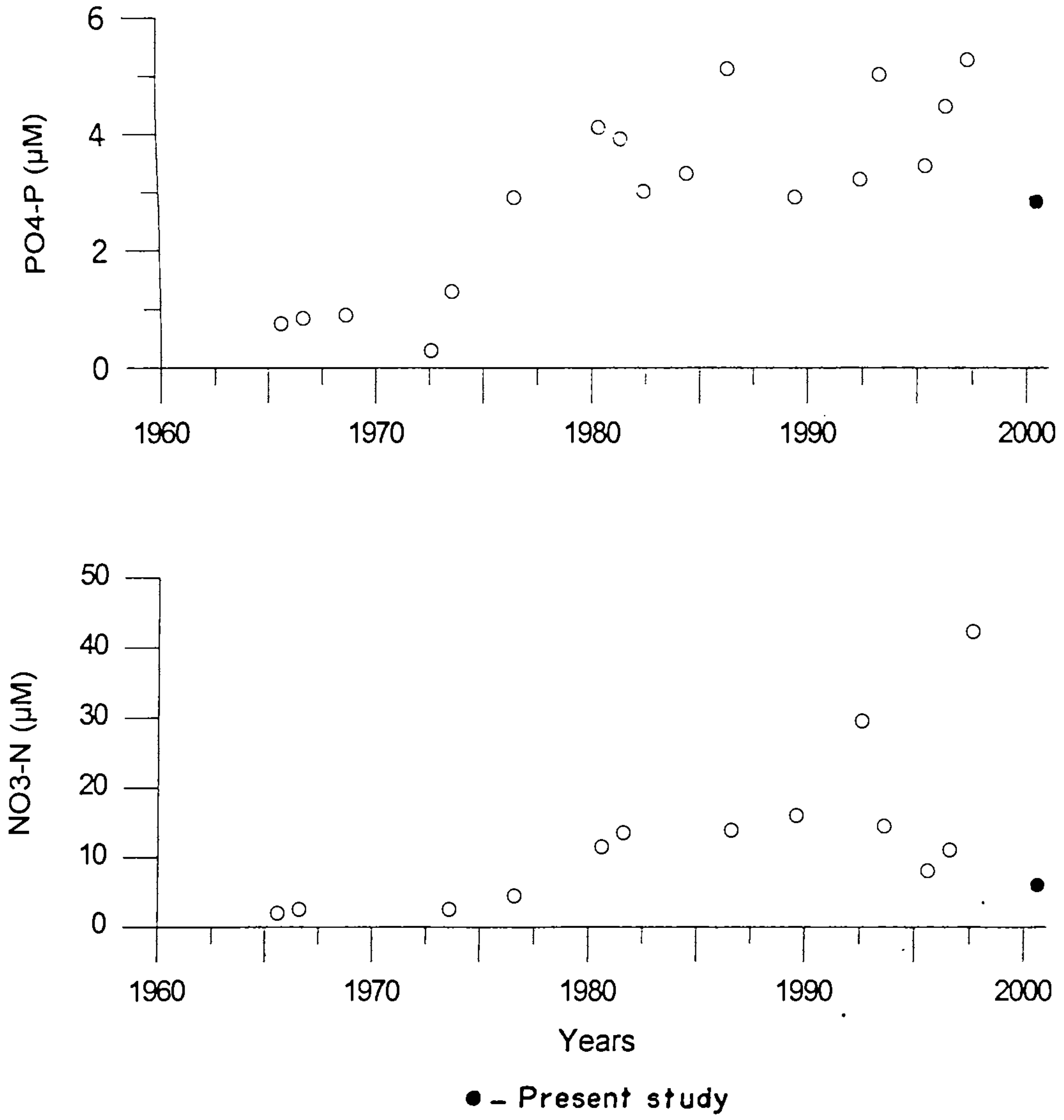


Fig. 5.1. Long-term trends in nutrient levels at the Cochin barmouth.

and tidal exchange may be sufficient enough to renew the estuarine waters and prevent deoxygenation even during lean discharge period.

The nutrient concentrations reported in the table are only the minimum as it represents the barmouth, but the maximum levels observed by the same workers towards the upstream reaches are quite alarming. For example, in the case of inorganic phosphate, the build up has started after 1973, and subsequent increase in waste discharges have ultimately resulted in extreme levels of ammonia, phosphate and nitrate in the estuarine region. During 1980-81, the backwaters of present study region recorded nitrate and phosphate concentrations upto 40 and 12 μM -upstream peaks are 108 μM for nitrate and 186 μM for phosphate- respectively (Saraladevi, 1986). Sankaranarayanan et al., (1986) have recorded phosphate concentrations upto 88 μM during 1982-83, in the northern upstream stations of Cochin backwaters while during the same period, the present study region was found to contain phosphate from 5 to 40 μM. During 1985-86 Anirudhan (1988) has observed an annual variation of nitrate from 7 to 39 μM and phosphate from 1.63 to 9.69 μM at the barmouth. During 1990, the nutrient maximum reported from this estuarine region was 98.48 μM for nitrate and 15.11 μM for phosphate (Kunjikrishna Pillai, 1991). Recent studies by Sheeba (2000) also underline the nutrient enrichment in the Cochin backwaters, as she recorded nitrate upto 451 μM and phosphate upto 33 μM at the barmouth alone.

The analysis of environmental data in previous section signals a general conclusion that over the years, Cochin backwaters has shown deterioration in environmental quality owing to several factors, all related to human interventions. One of the recent estimates show that in spite of receiving 42.4×10^3 mol.d^{-1} of inorganic phosphate and 37.6×10^3 mol.d^{-1} of inorganic nitrate from Periyar estuary, the export to the coastal waters is only 28.2×10^3 mol.d^{-1} of inorganic phosphate and 24×10^3 mol.d^{-1} of inorganic nitrate (Hema Naik, 2000). Thus, the estuary acts as a sink for the nutrients, flushing out only a portion of the pollutant load that it receives. The enhancement with respect to these nutrients in Cochin backwaters shows the signs of eutrophication.

One of the noticeable changes that has happened to this estuary is that there has been a considerable reduction in the exchange volume of water with coastal waters. The tidal transports during 1950 to 1970 were about 90, 126 and 65 Mm^3/tidal cycles (Gopinathan and Qasim, 1971; Wyatt and Qasim, 1973; Rama Raju et al., 1975) respectively. This has been reduced to about 35 Mm^3/tidal cycles during 80's (Jomon Joseph, 1989). The reduction in export volume in turn, is the reduction in the flushing characteristics of the backwaters. In the present study also, during the neap tide, considerable build up of nutrients is observed at the barmouth (StationI) and at station II. The residual currents are found to be towards the estuary at barmouth and non-directional at station II. Flood currents always dominate the ebb currents, as observed earlier (Udaya Varma et al., 1981; Jomon Joseph and Kurup, 1987). All these observations invoke a possible direct relationship between the diminished flushing rate and estuarine build-up of materials. Developments of 'null zones' in estuaries of natural flushing are observed towards the upstream sections where early salinity is experienced (Pattersen et al., 1975). But considerable shrinkage of the Cochin backwaters as a result of human interference (Gopalan et al., 1988) has reduced the tidal expanse of this system and it is probable that the null zones are shifted more towards downstream. The response of such events is complex, as the suspended sediment in the estuarine waters, instead of flushing out into the sea, is pushed upstream and ultimately is retained within the lower estuary itself. The upstream stations of the present study seems to occupy null zones as it is evident that the sediments of this regions are enriched with organic matter and clayey sediments, which may also favor metal accumulation.

Eventhough these are only approximations; the trend gives a warning by the backwaters in reducing its flushing qualities. This has ultimately resulted in consequent loss of supportive functions of this wetland system, especially due to increased reclamation, deforestation in catchments, inadequate waste treatment and similar other poor management plans. The response of the backwaters was slow initially, but it is now recognized that the deterioration with respect to environmental quality has already taken place and there has been considerable reduction in estuarine fishery.

5.2. Coastal waters of Cochin

The long-term changes in the Cochin backwaters give an indication as how anthropogenic influences have dominated the natural process in the estuary. The same analysis is extrapolated for the coastal waters to understand the dominant forces that are controlling the coastal water ecosystem.

An attempt has been made to evaluate linear trends on some of the water quality parameters in the study region, viz: coastal waters of Cochin between lat. 9° to 10° 30'N and long. 75°30' to 76°40'E, upto depth less than 50m covering approximately 41-year period from 1958 to 1999. Non-availability of long-term monitoring station off Cochin and inadequacy of yearly continuous data have created reservations for critical analysis of data and predictions. Albeit, this being first approximation in this kind along the coastal waters of India, the trend can be used as baseline information which, after fine tuning and refining, can be applied to any coastal environments for better management and conservation.

The data used in the present analysis has been pooled from INODC (2000) data. Except for dissolved oxygen, majority of cruise data during 1958-1990 are sparse in other environmental parameters. The information used here is entirely based on the data sorted out to represent those fall only in the present study region. Sorting of the data has been done subjected to condition that the bottom values are not considered, to avoid their interference (resuspension and sediment-water exchange) in the trend analysis. The data collected during the monsoon season has not been included as the present study covers only the period October to February. Thus, only the data falling under the non-monsoon months (October–May) are pooled. Further, as the depth of the study region is shallow (5 to 30m), the analysis has been done combining all the data from surface and 10 m depths, treating the coastal waters as homogenous.

The linear trend for dissolved oxygen and nutrients like phosphate, silicate and nitrate for the period 1958 – 2000 are presented in Fig.5.2 (solid circles). In order to visualize the impact of Cochin backwaters on the coastal waters, the corresponding surface values of phosphate and nitrate for the barmouth region during the same period are also overlaid in the same figure (open circle). The results show that the influence of the anthropogenic inputs through the Cochin backwaters has not significantly affected the coastal waters, as their behavior is more or less consistent when compared to the trends observed at the barmouth. The dissolved oxygen concentrations indicate that over the 41 years, there has been only a very slight reduction in oxygen levels (< 10 %). The trends for the nutrients are however found to be varying. While silicate shows periodic enrichment in the coastal waters after 1990, phosphate and nitrate seem to deviate slightly from being consistent.

Phosphate and silicate show a slight build up over the decades. According to the linear regression, surface values of phosphate increased from 0.29 μM to 0.59 μM in 42 years: ie; 2 fold (Table.5.2). Corresponding increase at 10m levels is 1.6 fold (0.32 to 0.51 μM). While the surface nitrate decreased from 2.78 μM to 1.67 μM, the levels at 10 m showed an increase from below detectable limit to 1.67 μM. Similar analysis for silicate shows that the surface silicate has almost doubled over the period (4.14 to 8.27 μM) while at 10 m, the increase was 1.8 fold (3.42 to 6.21 μM). The rate of change of these four parameters per year is estimated at surface and 10 m as

Table.5.2 Comparison of long term concentrations in the dissolved oxygen and nutrients (off Cochin) with present study

Depth	Year	D.O (μM)	D.O (ml/l)	PO_4-P (μM)	SiO_4-Si (μM)	NO_3-N (μM)
Surface	1955	211	4.58	0.29	4.14	2.78
Surface	1999	189	4.23	0.59	8.27	1.67
Surface*	97-00	192	4.29	0.57	5.41	1.64
10m	1955	198	4.44	0.32	3.45	bdl
10m	1999	190	4.23	0.51	6.21	1.67
Bottom*	97-00	173	3.87	0.95	5.79	2.58

* Present study (Mean of Oct.,Feb. and Nov.)

bdl – below detectable limit

Dissolved Oxygen 1 ml/l =44.64(μM)

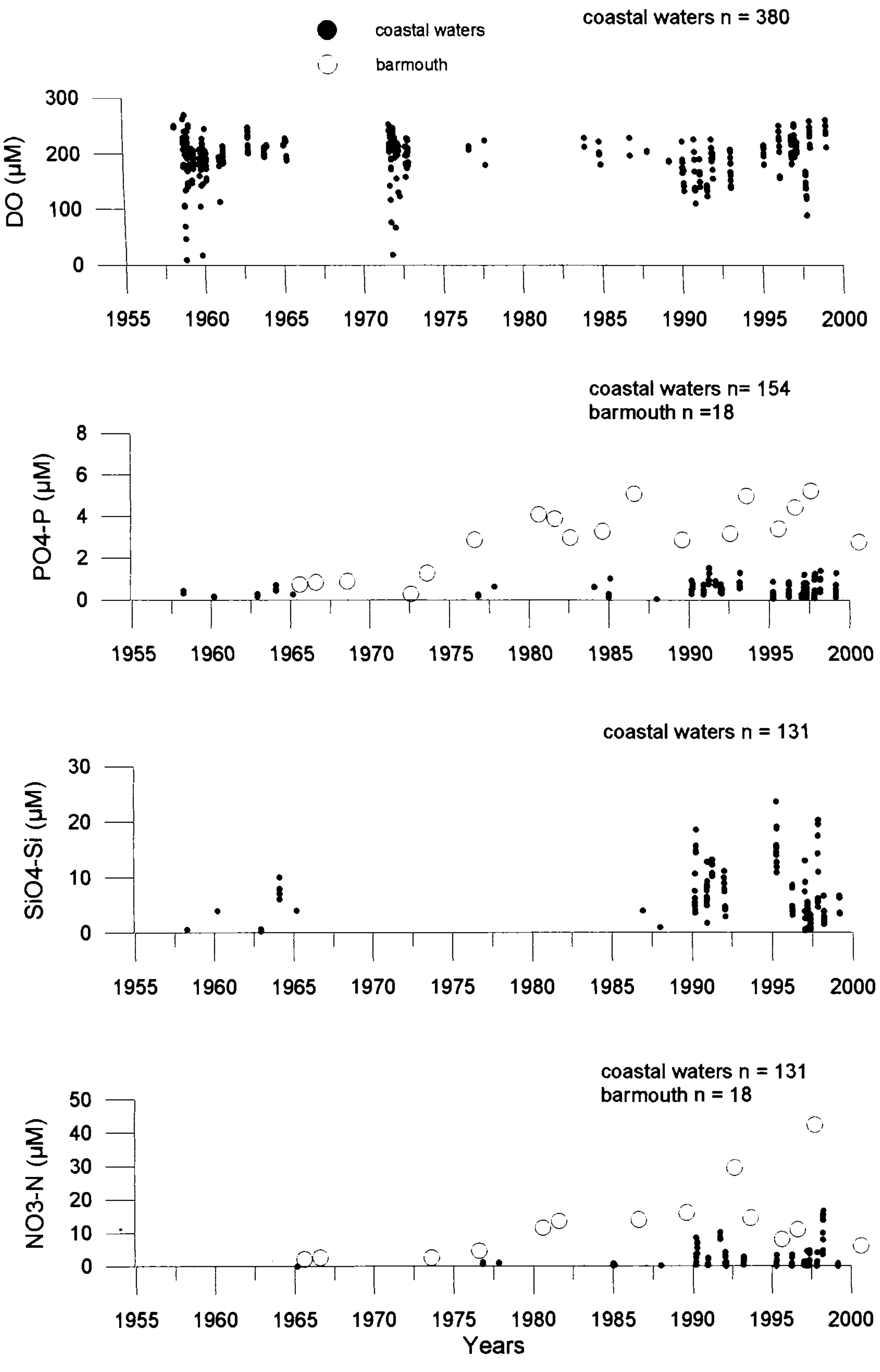


Fig. 5.2. Long-term trends in dissolved oxygen and nutrient levels in the coastal waters of Cochin.

DO ($^{-}$0.53, $^{-}$0.22 µM), PO_4-P (0.007, 0.005 µM), SiO_4-Si (0.10, 0.07 µM) and NO_3-N ($^{-}$0.03, 0.04 µM) respectively.

Although the above approximations furnish only the trend observed in the 41 years, limitations are there to assess how much of the variability is due to the different water masses and the adjoining backwaters fertilizing the coastal waters of the study region. Studies conducted by Naqvi and Jayakumar, (2000) show that the surface waters of Arabian Sea did not contain higher nutrient concentrations now than they used to have decades ago. Similar studies conducted elsewhere have successfully delineated the different water masses through systematic water-quality modeling (Gerlach, 1988). It is evident from the Table.5.3 that the long-term data collected and the data from present study give more or less comparable values for all the parameters studied (Fig. 5.2). But, as we look into the data more critically, there is a cause for concern in that, a marginal increase in nitrate and phosphate concentrations could be noticed in the coastal waters, though it is not to the level observed at the Cochin barmouth. The period since 1990 is seen with fluctuating levels of phosphate, nitrate and silicate. Wide variations are inherent, to a certain extent, with coastal waters as they are dynamic and hence turbulent. Moreover, the mudbanks observed in the southern and northern part of the region also play an important role in the nutrient dynamics of the region. How far these mudbanks and the discharges through the Cochin backwaters are regulating the nutrient dynamics of the coastal waters is not yet very clear. Only then, whether natural or anthropogenic processes control the coastal waters could be ascertained.

Now, are the nutrients transported by freshwater responsible for this ? Though reliable data are scarce, there is enough circumstantial evidence for the statement that rivers from densely populated areas, containing wastewater, sewage and sludge dumping are responsible for transporting substantial amount of nutrients, especially during and immediately after the monsoon months. Progress regarding our understanding of changes over time requires

Table 5.3 Mean and coefficient of variation (%) of different parameters in the coastal waters

		T	pH	DO	SAL	NO2-N	NH4-N	NO3-N	PO4-P	SiO4-Si
October	S	29.65	8.19	3.81	30.52	0.31	0.53	0.86	0.65	6.91
	C.V(%)	2.53	1.22	19.42	7.60	151.60	200.00	152.32	70.77	56.44
	B	27.94	8.14	3.23	34.07	0.57	0.31	2.74	1.01	6.61
	C.V(%)	4.71	1.47	2.47	29.72	82.46	75.18	242.00	45.99	69.31
February	S	30.22	8.05	4.88	31.41	0.19	1.29	2.88	0.52	4.50
	C.V(%)	2.25	3.97	13.93	0.86	78.95	146.51	71.87	40.38	57.78
	B	29.74	8.13	13.93	31.74	0.46	0.93	3.49	0.57	4.38
	C.V(%)	2.42	1.35	1.10	14.79	91.30	61.03	169.89	46.35	35.09
November	S	29.92	8.07	4.17	34.58	0.25	0.87	1.18	0.53	4.83
	C.V(%)	1.10	1.36	10.33	1.88	48.78	122.02	77.63	42.52	50.08
	B	29.86	8.06	3.58	35.00	0.82	1.09	1.52	1.27	6.39
	C.V(%)	1.10	1.36	1.88	10.33	48.78	77.63	122.02	50.08	42.52

monitoring data in the same way as weather forecasting. Improved modeling and verification of models along our coastal sea circulation is necessary including the modeling of small-scale effects of freshwater discharge. Likewise, there are many questions yet to be answered such as the fate of 19 million m^3 of water discharged annually to this coastal environment (Srinivas, 2000). A better understanding of the fate of nutrients in the particulate phase is also required. The role of denitrification, remineralisation in the sediment and excretion by grazers has to be identified to get a better estimate. The interactions between nutrients and phytoplankton have to be clarified. Only by improving our understanding on such basic sciences, a proper addressing of coastal eutrophication processes could be made possible. Whether such marginal enrichment in respect of phosphate and silicate, and reduction in nitrate and dissolved oxygen has affected the phytoplankton community over the years could provide new dimensions to studies related to ecological balance of the coastal waters. In the absence of simultaneous primary productivity data, it can be only concluded that the developmental activities in and around Cochin region has not altered the oxygen saturation, but there is some change with respect to coastal water fertility. In a broader sense, it can be said that while Cochin backwaters are dominated by anthropogenic influences, the coastal waters of Cochin do not reflect many of its impact and is still governed by the natural oceanographic processes.

5.3. Elemental distribution across the study region

When trace metals enter the estuaries, they are exposed to an environment in which chemical and physical properties like pH, redox and ionic strength may be changing rapidly. A number of significant processes will affect the proportion of the metal remaining in solution. Most important are the precipitation, adsorption and desorption reactions. Iron and manganese will precipitate as hydroxides and in the process scavenge other metals also. With more than 90 % of riverine particulate matter is deposited in estuaries and coastal zones and only a small percentage of the trace metals will reach the open sea, the ultimate sink of most trace metals discharged into the aquatic environment is the sedimentary deposit.

The elemental concentrations in the sediments sampled during November 2000 from the Cochin backwaters and the coastal regions of Cochin (station No. 26 to 36) are provided in table.(5.4) and that for each element is also given in Fig.(5.3) against distance in kilometers from barmouth. The negative sign is given to the estuarine region and positive sign to the coastal region. It is observed that Pb, Fe, Zn, Cu and Mn are enriched in estuarine region while Cr and Ni are impoverished. Co does not convey as such any trend across the region. In the case of textural distribution also, percentage of clay inside the estuary is lower than compared to that of the coastal sediments. Organic carbon in sediment is however higher inside the estuary, probably trapping the estuarine materials without escaping to the coastal zone. The enrichment of estuarine sediment with Zn is the most significant observation among the metals.

As the concentrations of metals in sediments depend on large number of factors, quantification of metal contamination in sediments is difficult and uncertainties are inherent to any methodology employed. The simplest and most frequently used method of assessment of metal accumulation is to compare the values with those of the global shale of Turekian and Wedepohl (1961). The ratio however suffers from errors due to mismatching of genesis of matrix, which plays a crucial role in metal contaminants. Albiet, this procedure is often preferred and the assessment is made by expressing the ratio of the observed concentration with the concentration of the same metal in the global shale (Fig.5.4). It is obvious from the fig that the metal ratios with respect to global shale for sediments from coastal region of Cochin show various degrees of enrichment. The values are more than one for most of the trace metals inside the estuary (Fe, Zn, Pb and Mn). Copper, nickel and cobalt show relatively low enrichment even inside the estuary, probably due the dilution of sediment by suspended load containing low levels of these able. 5.4 Gradient in elemental distribution from estuary to the Coastal region (Reference : Barmouth)

Estuary ← [BM] → Coastal region

Distance(Km)	-9	-6	-4	0	7	14	21	23
Pb(µg/g)	43	29	29	21	23	25	27	20
Ni(µg/g)	61	50	35	16	65	54	56	29
Co(µg/g)	21	17	13	6	19	19	17	13
Cr(µg/g)	74	68	81	15	177	136	155	109
Fe(mg/g)	49	47	31	14	25	31	22	18
Cu(µg/g)	52	34	17	5	29	24	24	13
Zn(µg/g)	1076	679	278	92	86	62	66	61
Mn(µg/g)	287	234	303	151	187	150	166	138
Sand (%)	21	28	38	65	12	5	15	33
Clay(%)	63	45	28	25	66	70	55	32
Silt(%)	16	27	34	11	22	25	30	35
OC(mg/g)	43	36	26	12	28	31	21	-

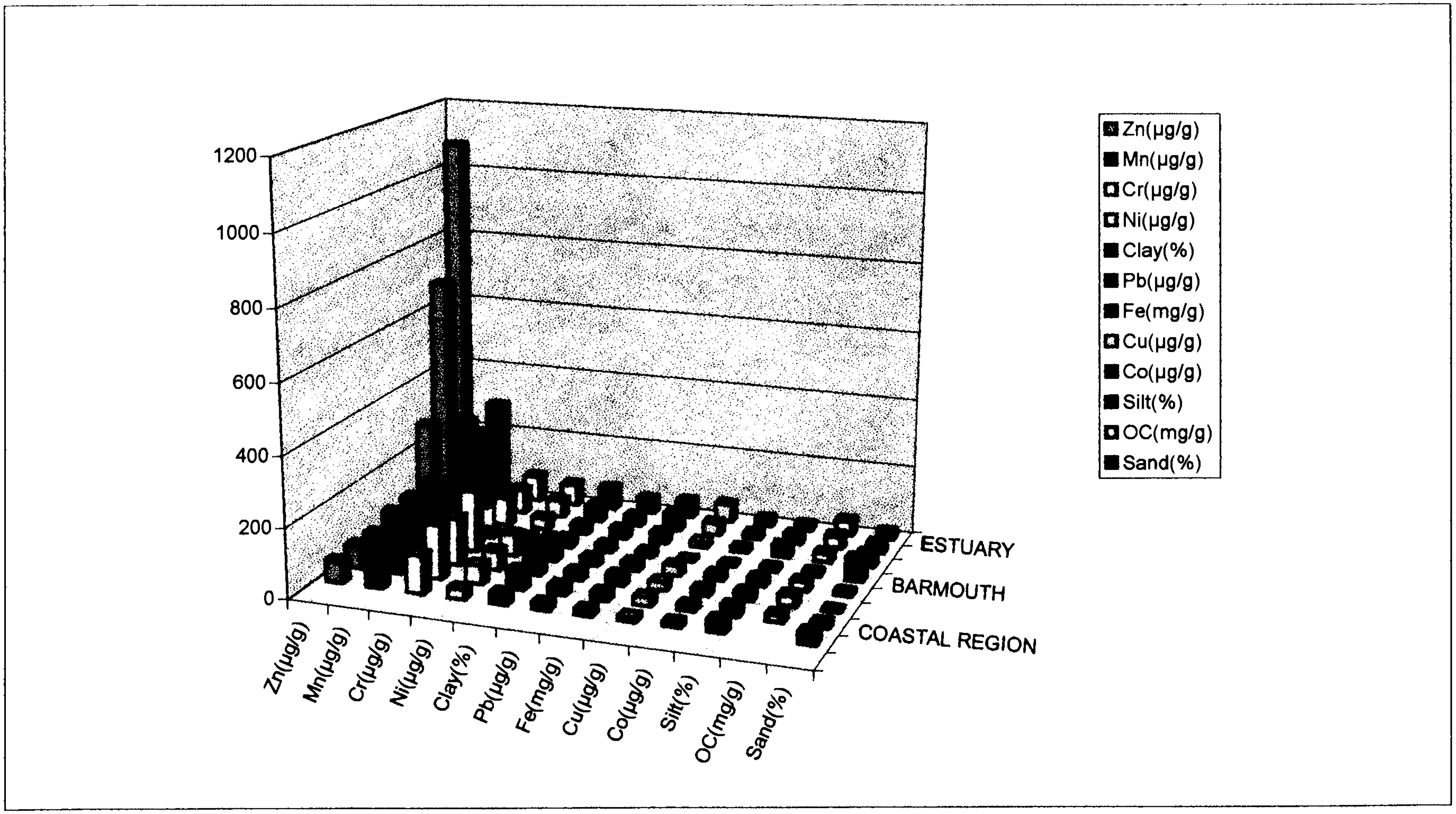


Fig. 5.3 Gradient in the distribution of texture and trace elements across the study region (backwaters to coastal region) during Nov.2000

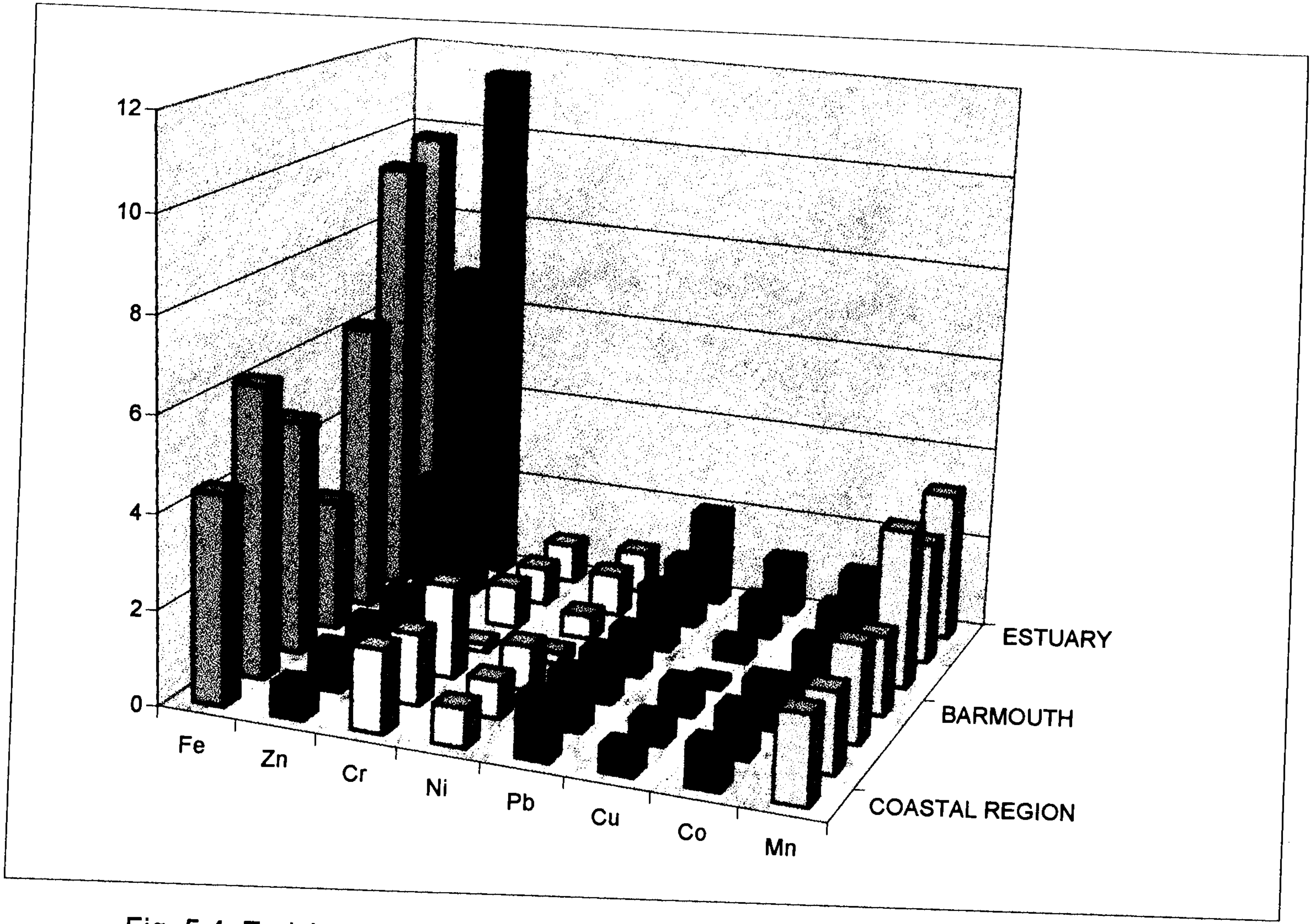


Fig. 5.4 Enrichment factor for trace elements from estuary to coast, Nov. 2000

elements. In contrast, Zn, Fe, Mn and Pb exhibit decreasing ratio from the upstream sections (9 km from barmouth) to >30 m zone in the coastal region. Iron and manganese are found to be the most enriched metals in the study region as they are present an order of magnitude higher than the global shale. However, the behavior of zinc is typical, with the coastal sediments showing ratio < 1 upto the barmouth and abruptly increasing upstream, where the enrichment factor as high as 11.4 is shown at 9 km upstream from the barmouth. Upstream contamination of sediments with zinc is reported earlier (Nair et al., 1991; Shibu et al., 1995). Organic carbon, which is high inside the estuary, seems to be influencing the locking of metals inside the estuary, in effect, preventing the pollutants from being exported out into the sea.

Trace metal data collected at off Cochin for last ten years have been pooled together for 5 m level and 15 m level respectively and presented in (Table.5.5) and Fig.(5.5). It can be seen that there is a progressive decrease in metal levels from 5 to 15 m for most of the metals from '90 onwards. The present study shows comparable values with the earlier concentrations from this region and corroborate that there is no increase in trace metal levels, eventhough the variations with respect to seasons are recurring associated with sediment restitution.

It is clear from the above study that trace metals do not seem to constitute a threat to the marine environment other than in estuaries. The difference between the natural concentration and that at which acute effects are observable is normally several orders of magnitude. Though the use of trace metals has declined over the years, their remaining uses are unlikely to find substitutes in the foreseeable future. However, the trace metals are natural constituents of the earth and man's input on these geological cycles is relatively small. Consequently, the release of metals into the coastal zone through anthropogenic activities are adequately dealt with by the sea's natural control mechanisms resulting in minimal biological impact.

Table 5.5 Inter-annual variability in trace metal distribution in sediments off Cochin (1990-2000)

At 5 m depth

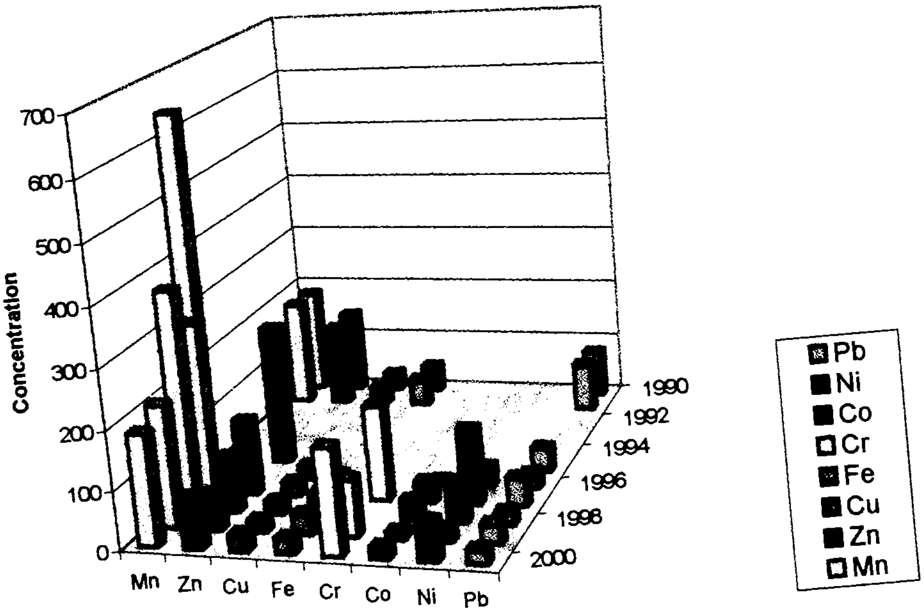
	Pb	Ni	Co	Cr	Fe	Cu	Zn	Mn
	(μg/g)	(μg/g)	(μg/g)	(μg/g)	mg/g	(μg/g)	(μg/g)	(μg/g)
Nov-90	79	--	--	--	46	29	143	182
Apr-91	80	--	--	--	46	29	140	184
Mar-95	40	--	--	--	--	28	237	--
Mar-96	24	32	6	--	--	9	--	--
Dec-96	19	33	4	--	--	23	--	--
Feb-97	26	48	26	58	35	15	128	375
Apr-97	29	63	24	74	40	18	97	645
Oct-97*	47	126	33	160	37	23	83	293
Feb-98	20	66	33	--	37	21	94	373
Feb-99*	32	17	12	94	34	20	61	207
Nov-00*	23	65	19	177	25	29	86	187

At 15 m depth

	Pb	Ni	Co	Cr	Fe	Cu	Zn	Mn
Nov-90	31	--	--	--	39	31	120	139
Apr-91	26	--	--	--	38	30	111	146
Dec-92	38	--	--	--	53	30	101	140
Mar-95	41	--	--	--	--	38	171	--
Mar-96	19	20	3	--	--	10	--	--
Dec-96	24	33	3	--	--	23	--	--
Feb-97	71	94	30	108	47	33	187	272
Apr-97	42	86	24	83	44	20	121	348
Oct-97*	43	135	31	149	38	25	90	241
Feb-98	31	85	38	--	43	28	111	172
Jan-99	30	8	11	--	24	11	33	121
Feb-99*	46	3	14	--	43	29	57	183
Nov-00*	25	54	19	136	31	24	62	150

* Present study

at 5m level



at 15m level

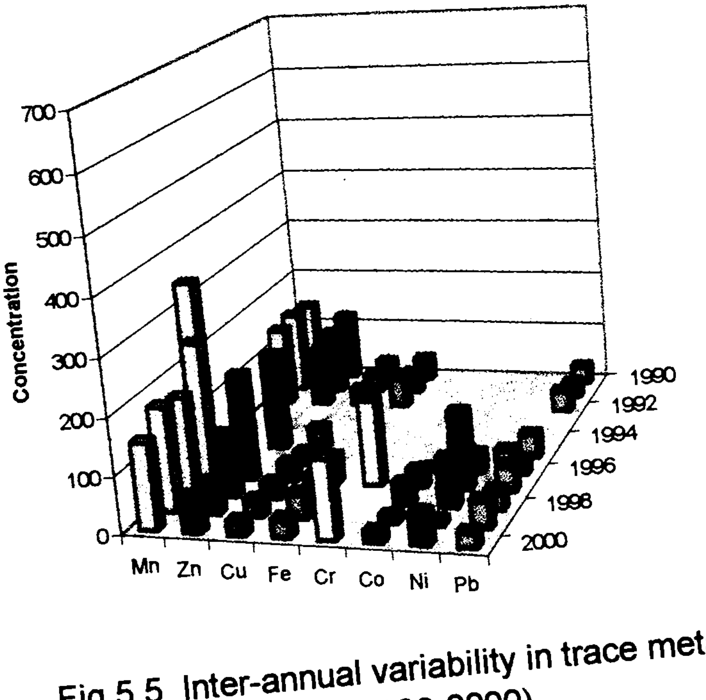


Fig.5.5 Inter-annual variability in trace metal distribution off Cochin(1990-2000)

5.4. Future concerns

As per the objective of this study, the water and sediment qualities of both estuarine and coastal region have been monitored to understand the present status of environment. The chemical oceanographic studies reveal that in spite of transformations in respect of environmental deterioration that had happened to Cochin backwaters, the coastal water of Cochin remained unaltered. Being a part of Arabian Sea, the natural oceanographic processes control this coastal region, and any type of increased human influences that have taken place in the Cochin backwaters is yet to affect this coastal environment.

Then, what is happening to the increased inputs through the backwaters into the coastal sea? Are they completely utilsed by primary producers? Or else, where are these pollutants finding their way? The present observations are incapable to answer these questions completely.

In the introduction, it has been mentioned that Arabian Sea is a delicately balanced system owing to the presence of suboxic and denitrifying water column and any alterations in the sub surface oxygen demand may bring about large changes in chemical fluxes. Recent reports by Naqvi et al, (2000) and Jayakumar et al., (2001) are eye openers to the above scenarios as to where our coastal inputs are getting concentrated. They have reported the intensification of one of the largest low-oxygen zones in the ocean, which develops naturally over the western Indian continental shelf during late summer monsoon along west coast (from Quilon to Mumbai). These are attributed to the increased inputs of nutrients to the coastal zones by human activities causing eutrophication and bottom-water hypoxia. These "dead zones", so called because of a drastic depletion of marine life, have tripled in number over the last three decades. While the ecological and socio-economic impacts of hypoxia in coastal waters have received much attention, little is known about their potential contribution to global change. Their observations made over a period of three years (1997-99) have identified this hypoxic zone, by far the largest and most intense found in the ocean. This zone appears to have intensified in recent years, and is characterized by record high accumulations of H_2S, N_2O and methane for the open coastal waters. Their studies cautions that a global expansion of hypoxic environments may lead to disproportionately large emission of N_2O from the ocean in shallow, rapidly denitrifying waters. The geographical extent of the zone of severe hypoxia ($0_2 < 0.5$ ml/l) is estimated to be ~ 1,80,000 km^2, covering almost entire shelf (Naqvi, et al., 2000).

The most important observation causes concern was the presence of H_2S, which have not been reported so far. Although suboxic conditions associated with high nitrite and low nitrate concentrations, reflecting the prevalence of denitrification, were observed even at that time, H_2S was not detected. If sulphate reduction in the water column is a recent phenomenon, it is not entirely clear what has triggered its onset. They observe that, over the past few decades there has been a substantial increase in the consumption of nitrogen and phosphorus based fertilizers in the western coastal plain that is intensively cultivated during the monsoon. In Goa, nitrogen based fertilizers has risen from 400 to 3700 tonnes (1962 – 1999). In Kerala, the consumption of nitrogen and phosphorus fertilizers is estimated to be 93,675 metric tonnes during 1986 (Kunjukrishna Pillai, 1991). Although the magnitude of anthropogenic nutrient loading is much smaller, its impact is expected to be larger since the system is already O_2 depleted. Alternatively, slight hydrographical changes related to freshwater runoff or in the circulation pattern could also have brought about a flip-over from suboxic to anoxic conditions. Any further changes, particularly the global warming, are expected to produce an even larger effect. The enhanced rate of denitrification and its potential impact on the global N_2O budget (as a greenhouse gas) can be quite significant.

In conformity with this observation, Jayakumar et al., (2000), have reported highest saturation values for methane (110 – 2521 %) along the inner shelf of Arabian Sea during the southwest monsoon (1997). They have attributed the enrichment of methane saturation in surface waters which caps the upwelled water to the insitu production, supply from the sediments and inputs from the coastal wetlands. Conditions conducive for the biological production of methane in sediments and at sediment-water interface appear to exist along the shelf off the west coast of India due to copious supply of organic carbon from land as well as overlying water column (Paropakari et al., 1987) where very high rates of primary production are supported by coastal upwelling during the southwest monsoon.

The above observations reported recently for Arabian Sea cautions that anthropogenic activities are indirectly being concentrated towards the oxygen minimum zone of the system, disturbing its delicate biogeochemical balance. It has already shown signs of outbursts off Bombay during late monsoon with the development of H_2S along with hypoxic zone. This hypoxic zone, though without H_2S, was found extended upto 9° N (Quilon), which included the present study area also (Naqvi et al., 2000). The oxygen depleted zone identified in the present study also falls under the same late monsoon period underlines the possible adverse effect imparted by anthropogenic activities to the coastal waters in recent years. Hence it is important to consider the fluxes of both nitrogen and phosphorus fractions into the coastal zone because both plays vital role in oceanic nutrient budget.

In view of the response of Arabian Sea to the increased waste discharges, concerted efforts should be made with immediate implementation of regulations to control untreated effluent discharges through Cochin backwaters. All the industrial and domestic sewage should be strictly subjected to proper treatment prior to discharge to the backwaters. Special places should be selected to process the domestic and sanitary wastes, which are presently not taken care of. The increased use of fertilizers in agricultural fields should be optimized, thereby minimizing nutrient losses through leaching and also saving expenditure. Proper management policies should be imparted to minimize sand mining from the upstream sections and sediment transport to the estuary and coastal environment. The catchment's area should be protected from soil erosion by improving natural habitat. While we cannot expect to enlarge the area of Cochin backwaters, we should at least refrain from further reducing its volume by indiscriminate reclamation.

CHAPTER 6

SUMMARY

The main aim of the present dissertation is an attempt to understand some of the chemical oceanographic processes of the coastal waters and the backwaters of Cochin. The importance of this study lies in the fact that there has been an increasing concern on the environmental degradation of Cochin backwaters with respect to water and sediments due to various anthropogenic activities. Considering the economic importance of Cochin, the second biggest harbour city along the west coast of India after Mumbai, the economic activities in the region are likely to increase in future. Since the backwaters are connected to the sea, the study on the influence of the backwaters on the coastal waters assumes significance. The increased transport of nutrients and toxic metals through the backwaters are likely to disturb the coastal water ecology. It is also important in relation to the Arabian Sea, which has been identified as one of the highly vulnerable regions because of its sub-surface oxygen minimum layer and associated denitrification. Therefore, a critical evaluation of the status of the coastal waters including the nature and quantum of inputs to the coastal waters and their fate becomes necessary. So far, such a study has not been undertaken in this region. Hence, a detailed chemical oceanographic study of the coastal waters of Cochin has been undertaken covering three different seasons. Two hydrographic surveys in the lower reaches of Cochin backwaters are also carried out to understand the impact of anthropogenic influences on the coastal waters.

The thesis is presented in six chapters. The first chapter gives a general introduction, oceanographic settings of the west coast and the Arabian Sea. Also a brief description of the mudbanks, which comes under the study region (between 9° 12’ and 10° 12’ N Lat., 76° and 76° 24’ E Long.), of the estuarine processes and of earlier studies carried out in the Cochin backwaters and Arabian Sea has been dealt with in this chapter.

Chapter 2 presents the sampling strategy and analytical methods adopted in the study. The water quality parameters covered are temperature, salinity, dissolved oxygen, pH, nitrite, ammonia, nitrate, phosphate, silicate, chlorophyll 'a', particulate organic carbon, suspended particulate matter and dissolved trace metals such as copper, zinc and iron. The sediment qualities include textural characteristics, organic carbon and trace metals like lead, copper, cobalt, nickel, chromium, manganese, iron and zinc. The statistical analysis is carried out to understand the specific and interactive effects of nutrients on chlorophyll 'a', particulate organic carbon and suspended particulate matter and the results are also presented in appropriate sections. The predictive model applied for chlorophyll 'a' for nine environmental parameters is discussed in the subsequent chapter.

Chapter 3 presents the results of the chemical oceanographic surveys of the coastal waters during different months of the years (October 1997, February 1999 and November 2000). The first survey represents transition period (October), while the second and third ones pertained to pre-monsoon (February) and post-monsoon (November) seasons respectively. The horizontal distributions are presented for each parameter at surface and bottom waters, and sediments.

The oceanographic studies carried out in the coastal waters of Cochin during the three months delineate the changing hydrochemistry in response to each season. The transition period (October) observation evinces the presence of upwelled water characterized by lower temperature, higher salinity with low oxygen and high nutrients in the coastal waters, especially at the bottom. The freshwater runoff during this season forms a cap of low saline water at the surface causing stratification of the coastal waters preventing the upwelled water reaching the surface. The sub-surface water, which is deficient in dissolved oxygen, as it advances towards the shallow regions, is further depleted in dissolved oxygen levels by the increased demand for oxidation of organic matter and biological utilization. The freshwater containing high levels of nutrients transported through the Cochin inlet or barmouth, thus makes a significant contribution to the nutrient budget of the coastal waters. This kind of enrichment in nutrients and low dissolved oxygen might be the first observation along the coastal waters of Cochin, which has got more relevance when linked with the recent reports on eutrophication and intense anoxia along the west coast during late monsoon.

During pre-monsoon season (February), the coastal waters are vertically mixed and saturated with oxygen. The entire region is occupied by less saline water of 31 to 33 psu, which may probably be due to the northerly coastal current along the west coast of India, bringing in low saline waters from the Bay of Bengal during this period. The phosphate concentrations do not show any significant horizontal or vertical variation in the water column. However, higher concentrations of ammonia, nitrate and silicate are observed at a few stations towards the coastal regions. It is difficult to point out a definite source to these high nutrient values during this period, as the fresh water discharge is minimum. This could be possibly due to the active regeneration, which is taking place in the coastal sediments, especially in mudbank areas as reported by earlier workers.

Observations during post-monsoon season (November) also show homogenous layer with moderate salinity in the area of study. While the physical characteristics are more or less stable, there is considerable variability with respect to nutrient distribution and chlorophyll 'a' concentration. The dissolved oxygen levels in sub-surface layers are low with an increase in nitrite, phosphate and silicate concentrations. Ammonia, nitrate and particulate organic carbon are also high at some stations along the southern transects. The decrease in dissolved oxygen can be attributed to the increased rate of oxidation of particulate organic matter during the period. The elevated nitrite levels around Cochin may be due to the input through the backwaters, which receive substantial quantity of nutrients through various anthropogenic sources. The co-existence of nitrite with nitrate in the offshore waters of Pallana indicates that the nitrite production is mostly due to assimilatory reduction. This is further substantiated by the higher concentration of chlorophyll a along these transects. Similarly, the enrichment of the coastal waters with phosphate has been related to the regenerative activity of sediments and its contribution from mudbank area. Eventhough the discharge through the Cochin backwaters brings in substantial amount of phosphorus to the coastal waters, the sediments of the shallow coastal region including the mudbanks also play an important role in fertility of the overlying waters.

Chlorophyll a values during this study are by far the highest reported from this region, the maximum chlorophyll a concentration recorded being 14 mg/m^3 during each observation. Higher chlorophyll values are associated with higher nutrient levels, especially phosphate and increased carbon production.

The predictive model applied to chlorophyll ‘a’, particulate organic carbon and suspended particulate matter with other environmental parameters reveals that the nine environmental factors play selective roles, either as controlling or limiting factors and their interaction effects are quite decisive in chlorophyll production. The interaction effect of phosphate with nitrate determines the outcome of interspecific competition at different nutrient concentrations because the intake of these parameters is species specific to a great extent. As the present studies do not reflect this interaction effect, it could be assumed that the pigment productions in these coastal waters are not controlled by their interaction i.e., availability of both these nutrients are not restricted. Temperature is obtained as an important factor for this model in February and November, suggesting that temperature sets the condition for optimal metabolic activity with increase in the abundance of flagellates and succession of diatom species and confirm the view that primary productivity has been a function of surface irradiance. In some cases, limiting factors are found to be more important than controlling factors. Since the interaction between nitrite and nitrate is obtained as one of the controlling factors in November, it follows that the growth of phytoplankton is often controlled to a certain extent, by the supply of ammonium excreted by zooplankton and members of other trophic levels.

Since nitrogen compounds and dissolved oxygen are obtained as important factors, it means that they are also brought into the medium by decomposition of particulate organic carbon. The interaction effects of ammonia with pH, nitrite, dissolved oxygen, temperature and nitrate are also controlling factors in primary production. Similarly pH and salinity are also found to be dominant and interactive factors in the present study region. But this has not been observed for a similar study in the Arabian Sea. This may probably be associated with the greater land-sea interaction and also due to the fact that the biological production induced by chemical changes in the coastal zones far exceed that of the oceanic region. It is worth mentioning here that while this predictive model for the Arabian Sea could explain only less 25 % of the variability in primary production, the same analysis in the present study (especially in November and February) could explain more than 70 % of the variability. Higher variability explained implies a more stable environment. This shows that the predictive model is more significant when applied for the coastal waters than for oceanic region because, the high variability explained for the predictive model for chlorophyll a is suggestive of a more stable coastal waters. This also consolidates the view that, inspite of seasonal fluctuations associated with monsoon, the coastal waters are pre-conditioned for the primary production during most of the time. The unexplained variability for the model may be due to other factors like rate of mineralisation, grazing rate, transparency, turbidity, upwelling etc. and inclusion of these factors will improve the efficiency of this predictive model.

In October, the textural characteristics of the sediments show that clay and silt fractions dominate the coastal sediment; clay being particularly concentrated in 10 to 20 m zone, to southeast coastal region. The silt fraction is also high (30 to 40 %) in the same region. During this survey, all the metals studied are at elevated levels in the study region. The distribution of trace metal concentrations show that there is no definite gradation in the metal distribution from the shallow to the deeper regions and, the sediments lying between 10 and 20 m depth are relatively low in certain metals. The distribution pattern appears to be in tune with the low saline front observed during this period. Iron is found to be the most abundant element with its enrichment around the barmouth as well as towards the deeper regions of southwest and northwest areas. Manganese is the next most abundant element, followed by Cr > Zn > Ni > Cu > Pb > Co. Manganese shows higher concentrations towards the northern coastal region and does not show any definite distribution in the remaining region. The elevated levels and irregularity in the metal distributions are attributed to the strong estuarine discharges indicating the source from land.

The metal concentrations are the lowest in February and show a definite decrease from the shallow to deeper regions. Sediments with > 70% clay occupy the stretch extending from northwestern part of the study region, which extend down upto the coast of Kannamali. The sand dominates the coastal and middle regions of Andhakaranazhi to the central and southwest offshore regions. Around the central area of Andhakaranazhi, silt is found to be high (> 70 %). South of this region and extending offshore, silt fraction upto 50 % is observed. High organic carbon (25 to 30 mg/g) levels are observed around the middle section of the region between Kannamali and Edavanakkad and in the mid-shelf of Azhikode transect. However, the western regions of Cochin and Alleppey to Pallana are lower in carbon content.

In November, the freshwater input to the coastal region is low as compared to other months and correspondingly a decrease in suspended load reflecting the textural characteristics of the sediments of the region are observed. The metal levels, though not upto the level observed in October, still show a gradient from inshore to the offshore region for all the elements concerned. Two areas of accumulation of metals are clearly observed; first between Kannamali and Edavanakkad and the other, between Chethi and Alleppey. These two environments represent entirely different sedimentary sources, which are ultimately remobilized and settled within the 30 m depth zones.

Another strong but much smaller effect is produced by some of the metals, which are present in low levels at stations situated near the Cochin barmouth, and the coastal sediments between Chetti and Pallana, indicating that the enrichment of these metals in the coastal sediments are controlled by some other processes also. It is to be mentioned here that, over the past several years, the navigational channels of Cochin harbour region are dredged regularly for maintenance as well as for deepening the channels. The two dumping sites for the dredged materials are situated at about 10 to 12 m depth, each on the south and north side of the entrance channel. The distribution reveals that the dredge-spoil dumped sediments instead of getting uniformly dispersed by coastal currents, tend to spread along the mid-shelf north of Cochin and southeast regions near Kannamali. In addition, the shallow coastal regions from Azhikode to Pallana are also known for the formation of mudbanks during monsoon season. In the outer shelf, heavy metal concentrations are very close to those determined for unpolluted sediment.

The processes by which trace elements are preferentially segregated are explained by sketching the matrix obtained through linear correlation analysis. The principal crystal lattice is constructed clubbing all elements having significant positive correlations ($r > 0.7$) and secondary layer for elements with decreasing correlation ($0.7 < r > 0.5$)

and the elemental distributions are simplified into a schematic representation. This representation clearly shows that the elemental concentrations in the study region are chiefly regulated by its binding efficiency with other elements, their textural characteristics, and the organic carbon.

The lower concentrations of Ni, Cr, Co and Zn in February are mainly due to its lack of association with organic carbon and clay. Both October and November observations show moderate relationship for Zn, Co and Ni with organic carbon and clay indirectly. Hence, the comparative enrichment of these 3 elements during October may be due to its contribution through the silt fraction, which has a moderate correlation with organic carbon. In February, a relative enrichment of zinc in water may be associated with desorption from sediment leading to its low concentration in sediment. Similarly, the higher concentration of Cu in February when compared to other two surveys could be explained due to its moderate positive correlation with organic carbon. High dissolved Cu in bottom waters in February also possibly implies its greater accumulation in sediments during the period.

Being most abundant, Fe is the binding element controlling the distribution of other elements, and shows maximum interaction, especially with organic carbon and clay. The distribution of Fe in sediment and overlying waters, in general, behaves complementing each other in that, when there is an enrichment of dissolved Fe, correspondingly the sediments are impoverished in Fe content.

The organic association as well as binding efficiency with other elements controls the geochemistry of lead in the sediments. In October, the significant correlation with Cr, Ni, Co and Cu ($r > 0.6$) and moderate association with organic carbon and silt through iron make Pb concentration the highest among the three surveys. The distribution slightly changes in February since Pb is no longer in the principal lattice, which is occupied by Fe-Zn-Cu-Co. The association of organic carbon is moderate during this month and compensates its association in sediments in February. In November, eventhough all the elements maintain moderate correlation ($r < 0.6$) with Pb, it is not as high as that in October. Moreover, the lack of correlation of Pb with organic carbon and clay substantially alters its distribution. Either or a combination of these two mechanisms seems to explain the distribution of Pb in November.

Mn exhibits a different geochemistry along this coast. In October, though Mn shows the highest concentration along with all other elements, it fails to establish any relationship with other metals, organic carbon, sand, silt and clay. The absence of correlation with organic carbon and clay make the distribution of Mn more even during the other two months. Manganese and iron constitute the most enriched metals in sediment.

Chapter 4 is presented with the results of water and sediment qualities of Cochin backwaters during two surveys. The hydrographic studies conducted through tidal cycle observations of spring and corresponding neap tide at 4 stations in the Cochin backwater extending upto 9 km from the barmouth indicate that the environmental quality is of moderately polluted condition. Wide variability is observed in the case of nutrients owing to their upstream discharge. Dissolved oxygen, a good indicator for aquatic life always remains well above saturation levels and it can be presumed that eventhough the backwaters receive significant load of nutrients through anthropogenic activities, there is no cause of concern with respect to oxygen depletion. The backwaters are found to play a significant role by serving as a sink for the nutrients, thus regulating their transport to the sea.

Physical, chemical and biological processes affect distribution of nutrients in the estuary and the major source of inorganic nutrients is upstream discharge. Correlation studies between the different parameters show that during the spring tide, salinity exhibits a good negative correlation with silicate, nitrate, phosphate and ammonia. Neap tide observations show lower, but significant correlation with silicate, nitrate, phosphate and ammonia. The significant negative correlation between salinity and nutrients within the estuary indicates that the nutrient levels within the estuary are controlled by the upstream discharges. In the coastal waters, it is seen that salinity did not show any correlation with these nutrients, confirming that coastal waters behave independently and once the nutrients enter the coastal waters, the natural processes inherent with the coastal waters govern it from time to time.

The trace metal concentrations in recently deposited sediments of Cochin backwaters show both natural and anthropogenic signals. Basically, most of the metals considered in this study are significantly enriched in lower reaches, especially in the northern parts of the estuary. The high values are due to anthropogenic inputs from industries and sewers situated on the banks of the river Periyar. Compared to the metal levels of other regions and the earlier reported values for the same region, it can be seen that Cochin barmouth and harbour region are not enriched in metals to greater levels, but the northern parts of the estuary, where the influence of effluent discharges are predominant, an enrichment of metals, especially zinc is evident.

The variability in the metal content of present study is compared with the earlier reported values for the same region as well as for different coastal waters. The ranges in concentrations of these studies are comparable with the present study. For the Cochin backwaters, seasonal hydrographic changes play a predominant role in regulating the metals in the sediments. Generally, the post-monsoon period is associated with the build-up of metals, which become enriched in the accumulative phases of the sedimentary material. The absence of significant correlation of metals with organic carbon and clay is indicative of metal enrichment through inorganic processes. High values of zinc observed in the mid-estuarine region are due to industrial discharge through the river Periyar.

The correlation studies indicate that none of the metals have significant relationship with organic carbon and clay fraction in the sediment. Significant correlation obtained for iron with all other metals except manganese suggests that precipitation of iron followed by organic association may be the principal process of elemental accumulation in sediments. The significant correlation between all metals except manganese shows the common source of metals. The absence of any significant correlation for manganese may be due to its sedimentary origin, identical to the observation for the coastal sediments. Hence, it is presumed that natural processes control the distribution of most of the metals studied in the estuary, while that of zinc and lead is controlled by anthropogenic input.

The model developed to predict the metal enrichment in the sediments of Cochin backwaters follows a pattern similar to that obtained for the coastal environment in November. Here also iron form the principal lattice bound strongly with Ni, Cu, Co, Zn, Cr and Pb exhibiting significant correlation within their matrix. Mn is having a moderate correlation only with Cr. Organic carbon, through its moderate correlation with Fe, Ni and Cu, form the secondary layer is indicative of metal association through Fe precipitation. The absence of correlation between organic carbon and Zn, and to a certain extent, Pb suggests the abiological processes by which these elements are deposited in this region. The interaction of organic carbon and clay with other elements seems to be a main factor differentiating the trace metal distributions in the coastal and estuarine sediments.

Chapter 5 discusses in detail about the environmental changes of the backwaters as well as that of the coastal waters of Cochin on a long-term basis. Thus, the above description outlines the common environmental conditions of Cochin backwaters characterized by well-oxygenated and nutrient-rich water column under-laid with organic-rich clayey sediments. A comparison of the earlier works and the present study shows that there is an accumulation of nutrients in the water and metals in sediments in the middle region of the estuary. Surface concentrations of phosphate and nitrate recorded at the barmouth during the non-monsoon months for the period 1965 to 2000 clearly indicate that phosphate and nitrate concentrations at the barmouth has shown considerable increase over the years. The trend also indicates that the nitrogen and phosphorus fractions show a build up after 1975 and from 1980 onwards, the concentrations remained high. However, this enhanced nutrients are not causing any oxygen depletion associated with eutrophication, possibly because the river discharge and tidal exchange through the barmouth may be sufficient enough to renew the estuarine waters by flushing and thereby preventing deoxygenation even during lean fresh water discharge period. Thus, the estuary acts as a sink for the nutrients, flushing out only a portion of the pollutant load that it receives. The enhancement with respect to these nutrients in Cochin backwaters shows the signs of eutrophication.

One of the noticeable changes that has happened to this estuary is that there has been a considerable reduction in the exchange volume of water with coastal waters. The tidal transport, which was between 80 and 125 Mm3/tidal cycles during 60s, has been reduced to about 35 Mm^3/tidal cycle in 80s of the last century, and no further reduction has been reported after that. The reduction in transport volume has reduced the flushing characteristics of the backwaters. In the present study also, during the neap tide, considerable build up of nutrients is observed at the barmouth (station.I) and at station II. These observations suggest a possible relationship between the diminishing flushing rate and estuarine build-up of materials. Considerable shrinkage of the Cochin backwaters has reduced the tidal expanse of this system. The response of such events is complex, as the suspended sediments and estuarine waters, instead of flushing out into the sea, is pushed inward and ultimately is retained within the lower estuary itself favoring metal accumulation. The response of the backwaters was slow initially, but it is now recognized that the deterioration with respect to environmental quality has already taken place and there has been considerable reduction in estuarine fishery.

An attempt has been made to evaluate linear trends on some of the water quality parameters in the coastal waters of Cochin for the period 1958 to 1999. The results show that the influence of the anthropogenic inputs through the Cochin backwaters has not significantly affected the coastal waters, as their behaviors are more or less consistent when compared to the trends observed at the barmouth. The dissolved oxygen concentrations indicate that over the 41 years, there is only a very slight reduction in oxygen levels (< 10 %). The trends for the nutrients are however found to be varying. While silicate shows periodic enrichment in the coastal waters after 1990, phosphate and nitrate seem to deviate slightly from being consistent.

As we look into the data more critically, there is a cause for concern, in that, a marginal enrichment in nitrate and phosphate concentrations could be noticed in the coastal waters, though it is not as conspicuous as at the Cochin barmouth. The period since 1990 is seen with fluctuating levels of phosphate, nitrate and silicate. Wide variations are inherent, to a certain extent, with coastal waters as they are dynamic. Moreover, the mudbanks formations in the southern and northern parts of the region also play an important role in the nutrient dynamics of the region.

Within the limitations of this study, it can be safely concluded that the developmental activities in and around Cochin region have not altered the oxygen saturation, but there is some change with respect to coastal water fertility. In a broader sense, it can be said that while Cochin backwaters are dominated by anthropogenic influences, the coastal waters of Cochin do not reflect many of their impact and are still governed by the natural oceanographic processes.

The elemental concentrations of sediments sampled from the Cochin backwaters and the coastal regions of Cochin are pooled together to understand the estuarine impact on metal distribution of the coastal zone. It is observed that Zn, Fe, Pb, Cu and Mn are enriched in estuarine region, while Cr and Ni are low. Cobalt as such, does not convey any trend across the region. In the case of textural distribution also, percentage of clay inside the estuary is lower than compared to that of the coastal sediments. Organic carbon content in the estuarine sediment is comparatively higher, probably trapping the estuarine materials without escaping to the coastal zone. The enrichment of estuarine sediment with Zn is the most significant observation among the metals studied.

As the concentrations of metals in sediments depend on large number of factors, quantification of metal contamination in sediments is difficult. The simplest method of assessment of metal accumulation is to compare the values with those of the global shale value. It is observed that the metal ratios of sediments from coastal region of Cochin show various degrees of enrichment with respect to global shale. The values are more than one for most of the trace metals inside the estuary (Fe, Zn, Pb and Mn). Copper, nickel and cobalt show relatively low enrichment even inside the estuary, probably due to the dilution of sediment by suspended load containing low levels of these elements. On the contrary, Zn, Fe, Mn and Pb exhibit decreasing ratios from the upstream sections (9 km from barmouth) to greater than 30 m zone (23 km from barmouth) in the coastal region. The behavior of zinc is typical, with the coastal sediments showing ratio less than 1 upto the barmouth and abruptly increasing upstream, where the enrichment factor as high as 11.4 is shown at 9 km upstream from the barmouth. Organic carbon, which is high in the estuary, seems to be influencing in trapping of metals inside the estuary, in effect, preventing the pollutants from being transported into the sea.

Trace metal history off Cochin when pooled together for 5 and 15-meter depths from 1990 to 2000 show a progressive decrease from 5 to 15 m depths for most of the metals from 1990 onwards. The present study reveals comparable values with the earlier concentrations from this region and corroborate that there has been no trend of an increase in trace metal levels, though variations with respect to seasons are recurring associated with sediment restitution.

It is clear from the above discussion that trace metals at the existing levels do not constitute a threat to the marine environment except in estuarine or hydro dynamically restricted areas. The difference between the natural concentration and that at which acute effects are observable is normally several orders of magnitude. Though the use of trace metals has declined over the years, their remaining uses are unlikely to find substitutes in the foreseeable future. However, the trace metals are natural constituents of the earth and man's input on these geological cycles is relatively small. Consequently, the releases of metals into the coastal zone through anthropogenic activities are adequately dealt with by natural control mechanisms resulting in minimal biological impact.

The 5th chapter concludes with the findings that coastal waters of Cochin is fairly clean and sediments remain unpolluted indicating that natural oceanographic processes are still capable of controlling the assimilative capacity of this coastal region. However, the long-term trend shows that there is an increase with respect to the coastal water fertility, as signals are given by an increase in phosphate concentrations from 1960 to 2000. This is corroborated with recent reports of anoxia and increased nitrous oxide production along the west coast of India during monsoon, induced by the elevated anthropogenic influences. One has to be reminded that even the moderate input of nitrogen and phosphorus compounds into the coastal zone is prone to upset the Arabian Sea ecosystem and its coastal region, as the system is already suboxic at subsurface levels. Any perturbation towards the oxygen minimum zone is predicted to bring about a flip-over from suboxic to anoxic conditions.

The 6th chapter gives the conclusions of the thesis. A detailed bibliography follows the chapter 6. The published works of the candidate are also appended.

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Estuarine Response of Fluoride - Investigations in Azhikode Estuary

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Concentrations of fluoride in Azhikode estuarine region were measured as a function of chlorinity during the different seasons. The type of behaviour indicated that fluoride was regulated by sea water incursion alone. Fluoride behaved conservatively during the postmonsoon season. However, during the premonsoon season 25 % removal of fluoride was observed due to estuarine mixing. The possible mechanisms for the removal are explained.

INTRODUCTION

Fluoride has long been considered as an acute pollutant to natural environment because of its detrimental effects upon marine biota even by concentrations as low as1.5 mg/L. The optimum level of fluoride in the drinking water for the prevention of tooth decay is 1 mg/L while fluoride concentrations in excess of 4 mg/L can cause molted stained teeth and fluorosis (De Souza, 1988). Though extensive work has been done on the behaviour of fluoride during estuarine mixing (Sankaranarayanan *et al.* 1986; De Souza, 1988) no such information on the behaviour of fluoride is available in Azhikode estuary. The present investrgation was undertaken to understand the distribution of this element in Azhikode estuary during different seasons, and to find an explanation for any anomaly that may exist. Azhikode estuary is formed by the major arm of the periyar river opening out at the Azhikode barmouth (Figure 1). The annual input of fresh water in this estuary is about 2.7 x 10^9 m^3 / year, of which 60 % is contributed by Periyar river and the rest by Chalakudy river (Pylee, 1990).

MATERIAL AND METHOD

Two stations one at Azhikode (barmouth) and the other at Kottapuram at a distance of about 6 km upstream from the river mouth were selected for sampling. Water samples at 2 hourly intervals were collected from the surface, mid - depth and near bottom of the water column during October '93 and May '94 (postmonsoon and premonsoon, respectively) for a complete tidal cycle. Sampling was also done from a station at the fresh water region where there is no sea water effect. Surface samples were collected using a clean bucket and the subsurface and the bottom samples using Niskin samplers. All samples were filtered using Whatman GF/C filter paper. The salinity was measured with an electrodeless induction type salinometer (DIGI - AUTO. model 3G, Tsur - umic Seiki, Japan). The fluoride was estimated by the alizarine - complexone method of Greenhalgh and Riley (1961).

Table 1. *Variation of fluoride - chlorinity in Azhikode estuary*

Chlorinity x 10^{-3}	Fluoride, mg/L	(F/C)x10^{-5}
0.01-0.10	0.02-0.11	200.0-129.55
0·10-1.00	0.08-0.12	110.65-14.29
1.00-5.00	0.10-0.41	8.55-8.22
5.00-10.0	0.41-0.79	8.17-7.93
10.00-14.0	0.86-1.02	7.83-7.66
14.00-19.0	1.03-1.19	6.97-6.66

RESULT AND DISCUSSION

The highest chlorinity was observed during the premonsoon observations with a maximum of 19.37 x 10^{-3} at both stations. However, the influence of the high saline water mass was restricted to 2 hr coinciding with the high tide at Kottapuram, whereas this water mass persisted for 6 hr at Azhikode barmouth. During this period, the chlorinity values at Azhikode varied between 13.12 and 19.37 and at Kottapuram it varied from 8.42 to 19.37 x 10^{-3}. The surface to bottom chlorinity gradient was minimum during this period showing vertical homogenity of the water column. The tidal variations of fluoride at both the stations followed the same pattern of distribution as that of chlorinity. This type of distribution indicates that fluoride is

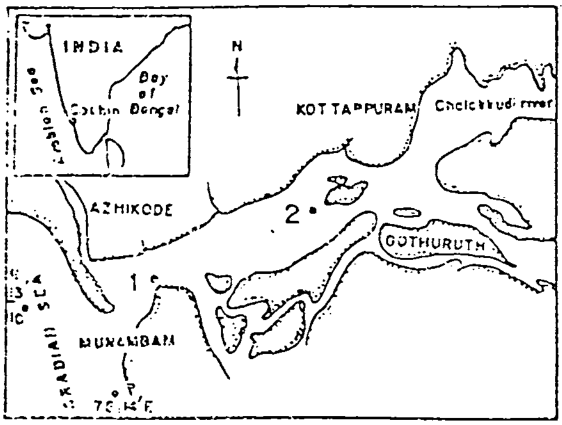

Figure 1. *Study area with location of stations*

regulated by the sea water incursion. The fluoride levels at Azhikode barmouth increased gradually with tide from 0.82 at low tide to a concentration in the range of 1.2 to 1.31 mg/L. At Kottapuram, the changes were found to be more pronounced with a rise in fluoride level from 0.42 to 1.31 mg/L.

During October, the influx of fresh water was at its maximum and the incursion of sea water into the estuary was restricted. This is reflected in the fluoride and chlorinity distributions. The chlorinity values varied markedly from 3 5 to 18 x 10^{-3} at Azhikode and 1.1 to 16.8 x 10^{-3} at Kottapuram. The fluoride concentrations ranged from 0.20 to 1.22 mg/L at Azhikode and 0.08 to 1.20 mg/L at Kottapuram. At both the stations, fluoride content observed was less than that observed in May. In both seasons, the average fluoride concentrations in river water was found to be in the range 0035 to 0.15 mg/L.

Fluoride - chlorinity relationship

Plots of chemical constituents versus chlorinity or salinity have been used to demonstrate removal, addition or conservation of a given constituent within an estuary (Liss, 1976). Figure 2 are plots of fluoride against chlorinity for both the stations during October and May, respectively. The regression analysis shows a highly significant positive correlation (r = 0.98, r = 0.97) in both the observations. The F - Cl % relationship for Azhikode and Kottapuram during October was linear given by :

$$F = 0.066 \text{ Cl } \% + 0.068, r = 0.98$$

It was observed that fluoride behaves conservatively during the month of October when there is fresh water influx. This linear relationship shows that its concentration is governed by physical processes of mixing and tidal variations and is not affected by any other geochemical factor. But during premonsoon season (May), a significant deviation was observed from theoretical dilution line (TDL drawn by joining the concentration of fluoride at zero chlorinity with that in coastal sea water) between chlorinity 2 - 14 x 10^{-3} indicating removal. The extent of removal of fluoride has been calculated to be 25 % (+ 8) which is comparable to the earlier reports (25 - 28 %) from Mandovi and Zuari estuaries (De Souza and Sen Gupta, 1988) and Baltic Sea (17 - 30 %) and other rivers flowing into it (Kullenberg and Sen Gupta, 1973). Figure 2 shows that deviation from the TDL is experienced below chlorinity 13 x 10^{-3}. The removal may be attributed to some geochemical mechanism which predominates in this chlorinity range during premonsoon season. The studies on sediment dynamics in Azhikode estuary have shown that during premonsoon season, there was formation of a turbidity maximum at a distance 6 - 9 km upstream from barmouth (Revichandran, 1993). The character

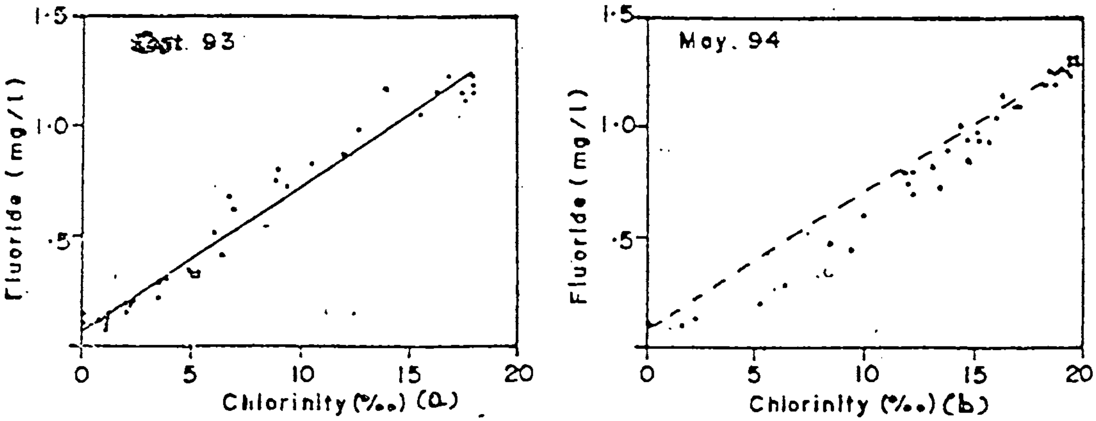

Figure 2. *Fluoride - chlorinity relationship during Sept* 93, *May* 94

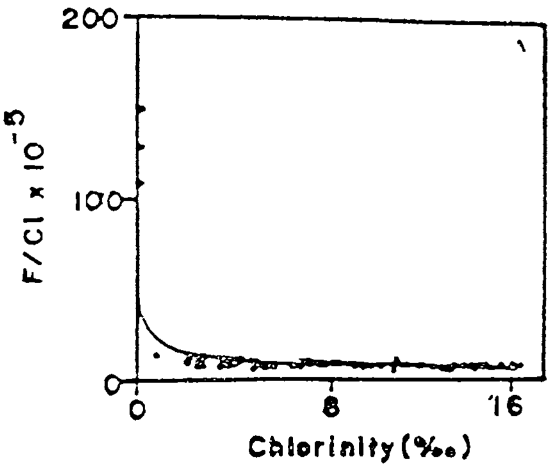

Figure 3. *Variation of fluoride chlorinity ratio with chlorinity in the Azhikode estuary*

the suspended sediment distribution strongly sugsts that there existed a third source of material r mixing in the estuary and this source is sedimts which are resuspended within the turbidity ximum.

an estuary, ionic strength of dissolved material d surface charges on particulate material rapidly anges in turbulent mixing zones. Such conditions celerate reaction between dissolved species and spended particles (Liss, 1976). Thus fluoride y be absorbed on to the particles in suspension the first step in the removal process. Similar obsations of geochemical removal of fluoride have en reported earlier (Carpenter, 1969; Kullenberg d Sen Gupta, 1973; De Souza and Sen Gupta, 88). Table 1 presents the range and mean conntrations of fluoride and F/Cl ratio in different chlnity ranges (Figure 3). These values are in close eement with reported values of fluoride to chlori/ ratio for ocean water (Riley, 1965; Brewer, l., 1970; De Souza and Sen Gupta, 1988).

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Non-conservative Controls on Distribution of Dissolved Silicate in Cochin Backwaters

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Abstract

Cochin backwater system was studied with regard to dissolved silicate (DSi) to understand its seasonal distribution and behaviour during estuarine mixing. Silicate had a linear relationship with salinity during the high river discharge period. During premonsoon period, a sharp decrease of silicate with distance in the middle regions between salinity range of 4 to 22 x 10^{-3} in the estuary was observed. River discharge was found to modulate both estuarine residence time and the DSi supply. The substantial removal of DSi (approximately 50 %) during premonsoon was attributed to enhanced biological utilization, caused by the development of null zones in the middle areas of the estuary.

Introduction

Distribution of dissolved silica (DSi) in estuaries differs om other major micronutrients, since the main DSi source is ver discharge coupled with an insignificant contribution from ;cycling by dissolution of siliceous diatoms (Patterson *et. al.*, 975; Anderson, 1986). Silica utilization is normally by hytoplankton in synthetic processes and by inorganic removal nto suspended matter (Liss and Spencer, 1970). Although a :w published informations are available on the distribution of ilicate in this area (Sankaranarayanan and Qasim, 1969; ankaranarayanan, Joseph, Jayalakshmi and Balachandran, 984; Sankaranarayanan, Varma, Balachandran, Pylee and oseph, 1986) and other estuaries of India (Borole, rishnaswamy and Somayajulu, 1977; Sarin, 1985; Burton, Liss nd Venugopalan, 1970b) an exhaustive study on the silicate ehaviour during the estuarine mixing is lacking. An attempt as been made here to study the behaviour of DSi in this stuarine system during different seasons of the year.

Materials and Methods

Water chemistry observations were made within 48 hrs as many as 20 stations in the mid-channel of the estuary etween river mouth and the freshwater boundaries of northern eriyar and southern Muvattupuzha rivers during the flood tide. lonthly hydrographic studies were made for two years from ly 1989 to May 1991. Water samples collected from surface 0.5m) and 0.5m above the bottom were filtered through hatmann filter paper no.1. Salinity was estimated using ductive laboratory model salinometer (Tsurumi Seiki Model G DIGI AUTO, accuracy 0.01 x 10^{-3}. Silicate was measured silicomolybdate method as given in Grasshoff 983)(accuracy + 4µg at/l).

Results and Discussion

mporal and spatial variations

In order to understand the temporal and spatial variations in DSi, the study period is divided into 3 seasons *viz.*, Premonsoon (February - May), SW monsoon (June- September) and postmonsoon (October- January). The salinity intrusion in the northern and southern limbs of the estuary responds closely to the variations in river discharge. The intrusion of salt water into the estuary was deep, the distance being 25 km in Muvattupuzha and 21 km in Periyar from the barmouth (1989-90). For monsoon months the saline intrusion is limited to 10 km. During the premonsoon, the estuary becomes dominated by neritic waters leading to near vertical homogenity. During monsoon season, the entire estuarine water is flushed out and replaced by freshwater. There is a short fall in river discharge between September and October when again the northeast monsoon brings in moderate precipitation from late October to January resulting in considerable river discharge, though much less than that in the SW monsoon period. During this period, the estuary behaves as partially mixed one until December. The extent of saline intrusion was more in the southern part as compared to the northern part throughout the year. This is probably due to a higher river discharge through river Periyar compared to Muvattupuzha. Levels of silicate in the present study varied from 4.43 to 139.4µg at/l at the surface and 6.14 to 133.4 µgat/l at the bottom. In Muvattupuzha, the average silicate concentration varied between 4.03 and 138.15µ g at/l, while in Periyar it ranged between 5.20 to 140.1 g at/l Monsoon and postmonsoon peaks in silicate content for both rivers indicated that the silicate source to this estuary is by river run off, which is in clear agreement with earlier works (Sankaranarayanan and Qasim, 1969; Sai Sastry, 1990; Gouda and Panigraphy, 1992).

Plots of chemical constituents *vs.* salinity have been used to demonstrate uptake, addition or conservation of a given constituent within an estuary (Liss, 1976). These concepts were extended by Patterson, Conomos *et.al.*, 1975). DSi - salinity relations of the Cochin backwaters during monsoon, postmonsoon and premonsoon seasons are given in Figs.1 a,b

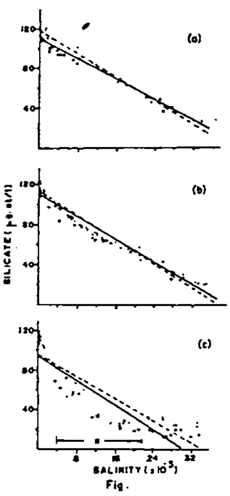

Fig 1. Dissolved Silicate - Salinity relationship during different seasons for two years in the Cochin backwater system as a whole. (a) DSi vs. S% during monsoon 1989 and 1990.(b) DSi vs. S% during postmonsoon 89 and 90, (c) DSi vs. S% during premonsoon 1990 and 91.

and c respectively. For this the individual values were averaged out for each season and plotted. The DSi-salinity (S) relationship during monsoon 1989 and 90 is linear given (Fig.1a) by

DSi = 119.16 - 2.98 S Correlation coefficient r = - 0.97 and

DSi = 109.81 - 2.65 Sr = - 0.98 L

inear relation between DSi and salinity is also observed duringpostmonsoon season

DSi = 110.33 - 2.91 Sr = - 0.98 and

DSi = 107.51 - 2.76 Sr = - 0.98

for 1989 and 1990 respectively (Fig.1b). It is thus clear that dissolved silicate bears a linear relationship with salinity during monsoon and postmonsoon seasons. A linear distribution of this kind indicates that mixing rates between river and seawater dominate over non-conservative processes (Patterson *et.al.*, 1975). During premonsoon season, however, the DSi-Salinity relationship is not linear (Fig.1c), but forms a curvilinear shape. The relation is best explained by the exponential equations, DSi = 95.32 * $e^{-0.05131\,S}$ and DSi = 99.82 * $e^{-0.06868}$ S.

For years 1990 and 91 (Figs.2 a & b). Premonsoon DSi-salinity relationship thus implies that the estuary behaves as a sink for river-supplied dissolved silicate. Let us examine whether such removal of DSi is by inorganic or organic process. Experimental studies by Wollast and Peter, 1976; on silicate changes at light and dark condition and Borole *et.al.*, 1977 at different salinity ranges have ruled out the possibility of silicate removal onto suspended matter. In the present study, since the amount of DSi removed is far too high (approximately 50%), inorganic removal alone cannot account for the anomaly. According to Li Faxi (1979), the degree of DSi removal may depend on hydrographic and biological conditions of the particular estuary. We believe that the principal factors influencing the loss of DSi from this estuary are the development of watermass with high residence time during premonsoon which favours enhanced primary productivity. The peculiar topography of this estuary with the two perennial rivers entering the estuary from opposite directions, a system of canals connecting the two and the seaward opening at right angle to their direction of flow makes the hydrodynamics of estuarine circulation complex. As the river discharge decreases, the estuary is gradually dominated by tidal influence which forces the neritic water into the upper reaches of the estuary, against a weak river discharge. In such conditions, there develops a non tidal mean flow representing a body of water column with a high residence time compared to other seasons, called "null zone" (Patterson *et.al.*, 1975). The sections adjacent to this zone (both upstream and downstream) will be having a residual flow towards the zone, thus enriching the zone with nutrients. Flushing time of the estuary in general increases resulting in a net accumulation of any material discharged into the estuary towards the null zone. Available information also supports the view that primary productivity in this estuary remain high during premonsoon season and with occassional bloom of phytoplankton during the rest of the period (Joy, Balakrishnan and Joseph, 1990; Nair *et.al.*, 1975; Qasim, 1979; Gopinathan, 1984; Nair *et.al.*, 1988; Joseph and Pillai, 1975). The standing stock of Chlorophyll 'a' pigments (54.5 mg.m^{-3}) and biomass recorded are highest during this season (Joy *et.al.*, 1990) and are mainly constituted by diatoms and dinoflagellates (Joseph and Pillai, 1975), which are the main consumers of silicon in the water.

In the light of above conditions, we can explain the salient features pointed out earlier. During monsoon and postmonsoon seasons, moderately high rate of supply of DSi through river discharge compensates the removal, if any, from the estuary explaining the near-linear relationship between DSi and salinity(Fig 1a and 1b). During premonsoon period, the river discharge becomes low, decreasing the rate of supply of DSi. The productivity can be increased due to enrichment of N and P fractions into the null zone. But the primary nutrients necessary for primary productivity are N, P and Si, of which the last is not in surplus. This leads to utilization of DSi from the river input, at a greater rate than its addition through river discharge. The net result is, an observed removal of DSi from the estuary between salinity range 4 - 22 x 10^{-3} marked by the zone 'B' in Fig. 1c. Within the limitations of our field surveys carried out, we find that this 25 km stretch of Cochin backwaters with salinity range of 4 to 22 x 10^{-3} behaves as a biologically active zone, during the premonsoon period of 1990. Another noticeable feature is that the null zone was found to extend more towards the southern side than towards the north. This can be explained by difference in the river discharge through these two rivers. The southern portion of the estuary is also charactarised by seaward increase of cross channel area.

The fractional loss of DSi within an estuary (G)

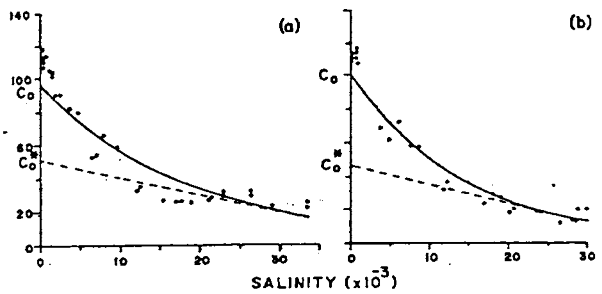

Fig 2. Fractional loss of DSi in Cochin backwaters duimg premonsoon asons of (a) 1990 and (b) 1991. C_0 = Fresh water end concentration of DSi and C_0^* = Extrapolated value of lower estuary DSi concentration to zero salinity

proximated by the method of Hydes a and Liss (1977) and tended by Officer (1979) for this estuary is given as G = (C_0 C_0 *) / C_0, where C_0 * is the extrapolated silicate value rresponding to zero salinity of the linear lower estuary silicate stribution and Co as the freshwater end point DSi ncentration. This fractional loss for the Cochin backwaters = 45.4% and 53.1% during premonsoon seasons of 1990 and 91 respectively (Fig.2) are comparable with with the values ported by Callaway and Specht, 1982, but high compared to values reported by Liss (1976).

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We are thankful to Dr.E.Desa, Director, N.I.O, Goa for s keen interest. Technical assistance rendered by Miss. ssamma Sebastian is gratefully acknowledged.

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Estuarine Characteristics of the Lower Reaches of the River Periyar (Cochin Backwater)

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Lower reaches of river Periyar were studied to assess longitudinal extent of salt water intrusion into the system during different seasons and also its effect on the flushing of pollutants introduced by the industries. During SW monsoon season due to the influx of a large volume of fresh water longitudinal salinity gradient could be noticed only up to a few stations upwards from the barmouth. During postmonsoon season the estuary behaved like a partially mixed estuary with the saline intrusion extending further upstream up to 17 km. In the premonsoon season the intrusion length extended further upstream beyond 21 km. A steady down stream dilution of any pollutant introduced could be expected during these seasons. Fluoride concentration showed high values (>1.5 $mg.l^{-1}$) during Nov. to May and minimum from July to Sept. The high values observed may be due to the effect of pollutants containing fluoride discharged into the river.

The Cochin backwater estuarine system is a part of the lower reaches of the river Periyar, which is one of the largest perennial rivers of this region. The hydrographic studies[1-4] so far made are on physical and biological aspects and mainly centred around the Cochin harbour. However there is no attempt to evaluate the extent and nature of the salt water intrusion into the estuarine region and its variation from season to season with respect to varying tidal prisms at the Cochin harbour inlet and fresh water influx into the estuarine system. The present study pertains to intrusion of salt water into the estuarine region, assessment of its longitudinal extent in different seasons, and its effects on the flushing of pollutants introduced into the system from the industrial belt. As very little information is available[5,6] on the distribution of fluoride in Indian waters, in this study the fluoride concentration is estimated in the Cochin backwater system and the river Periyar.

Materials and Methods

Monthly surveys (1982-83) were conducted from the Cochin harbour mouth towards upstream, a distance of about 21 km (Fig. 1), during the spring tide. From each of the 13 stations water samples were collected at the peak of high tide for the estimation of salinity, inorganic phosphate[7], fluoride[8] and dissolved reactive silicate[7]. The direction and speed of the currents were measured at 1 m interval from surface to 1/2 m above bottom after anchoring the boat at all the stations. Also current measurements were made from sts 9 and 13 at hourly interval during the spring tide for 1 complete tidal cycle.

This estuarine system is largely influenced by the influx of fresh water, which, in turn, is controlled by the rainy season facilitating the division of the observation period into 3 distincts periods, viz. premonsoon (Feb.-May), monsoon (June-Oct.) and postmonsoon (Nov.-Jan.).

Results

Distribution of saline water entering into this region is depicted in Fig. 2. Major incursion of saline water occurs from Jan. to May when the salinity is $>30 \times 10^{-3}$. Even at a distance of about 18 km from the

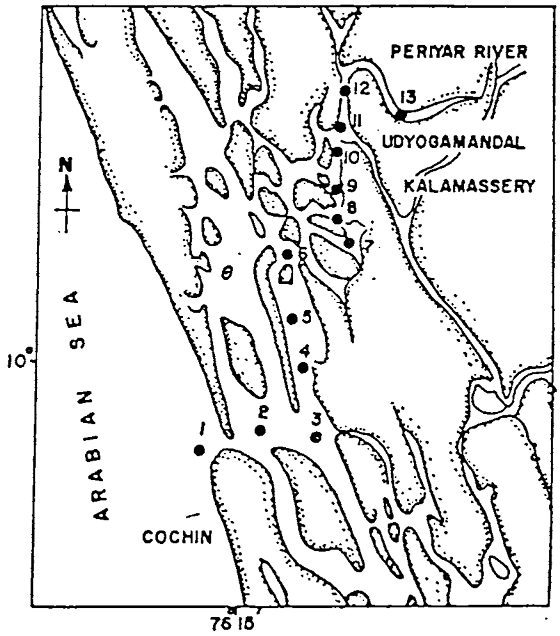

Fig. 1—Station positions

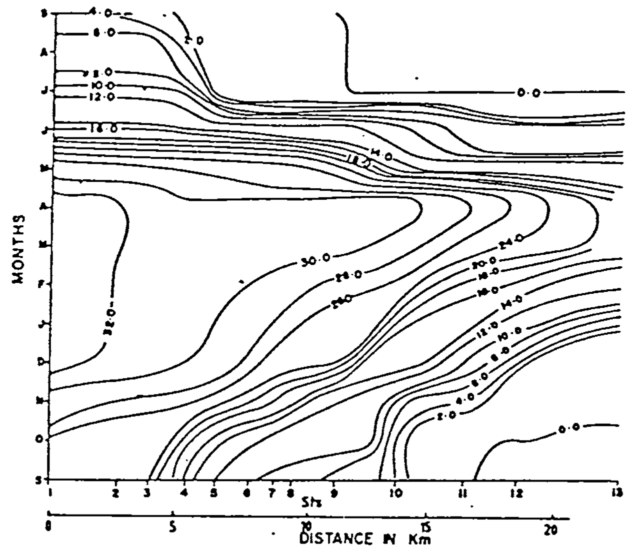

Fig. 2—Extent of saline water penetration from the estuarine mouth (Isohalines give the salinity of 2×10^{-3} intervals)

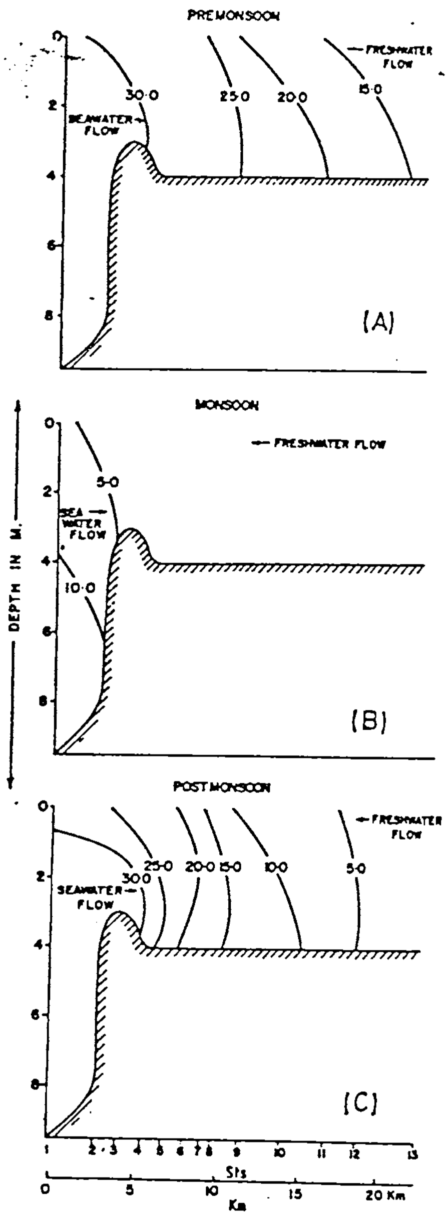

Fig. 3—Occurrence of seawater and fresh water flow in longitudinal section along the Cochin backwater system dur different seasons (Values indicate salinity $\times 10^{-3}$)

barmouth and beyond this high saline water can be traced to a distance of > 25 km from the barmouth. At st 1 salinity value remains high ($> 25 \times 10^{-3}$) just after the monsoon. However at st 13 the salinity value shows only a gradual increase from 0 to $> 20 \times 10^{-3}$ from Dec. to May. The vertical salinity gradient is very small ($< 3 \times 10^{-3}$) during this season.

With the onset of the monsoon fresh water or very low saline water of $< 1 \times 10^{-3}$ salinity is traceable even to a distance of 5 km from the barmouth. While the salinity at st 1 varies from 19 to 3×10^{-3}, the salinity at st 13 is 0 most of the period except in early June. During this period actually a fresh water regime would be established towards the head of the estuary after 5 km from barmouth (Fig. 3B). The vertical salinity gradient at stations near the barmouth is $> 10 \times 10^{-3}$ showing saline incursion through the bottom during high tide.

During the postmonsoon period a gradual increase in salinity could be noticed at all stations as the season progresses. While at st 1 salinity value increased to nearly 30×10^{-3}, at st 13 it increased from 0 to 2×10^{-3}. Similar gradual increase of salinity took place at all the intermediate stations (Fig. 3C). The salt water intrusion was restricted to a distance of about 19 km during this season.

The flow pattern studied, at the peak of the high tide, shows that the direction of current is towards the estuary at all the stations during the 3 seasons. However the current observations taken at sts 9 and 13 for a complete tidal cycle showed the complete reversal of the tidal current according to the tide. The speed of the current varied from 10 to 42 cm.sec^{-1} at different regions of the estuary during the 3 seasons. Maximum speed was recorded near the narrow regions of the estuary especially at sts 7, 8 and 13. Generally the speed increased from surface to 1-2 m depth layers and th reduced to the bottom. The water in the estua remains partially mixed when the river water run-c was small and moderate. At high fresh water influx t stratification is pronounced at sts 1 to 5.

Dilution and flushing—The amount of fresh water at any given location in the estuary in terms of salini (S) at the same location is given[9]—

$$f = \frac{S_o - S_n}{S_o}$$

where S_o is salinity of the coastal seawater and $S_$ salinity at any location inside the estuary. The fres water fraction at different stations along the estuar was calculated for different seasons (Fig. 4). The fresh water fraction was very large during the monsoon at almost all stations except at 1 and 2 where it was 0.69 and 0.89. During the postmonsoon seasoons the fresh water fraction increased from 0.17 at st 1 to 0.86 at st 10 in a gradual way and is maximum there after. In the premonsoon season there was a gradual increase from 0.04 at st 1 to 0.63 at st 13 and was very low as compared to other seasons.

The dilution factor, inverse of the fresh water fraction, showed during premonsoon conditions a gradual decrease from 14.28 at st 4 to 1.58 at st 13. During monsoon period this factor was 1.47 at st 1 and 0 at st 13. During postmonsoon period it was 5.88 at st 1 and gradually decreased to 1.02 at st 11 and 0 at st 13.

Distribution of inorganic phosphate—During premonsoon high concentration of inorganic phosphate (Fig. 5) was seen at sts 13 (81 μmol.l^{-1}) and 12 (63 μmol.l^{-1}) and from st 12 down the estuary there was reduction in the concentration and reached a value of 3 μmol.l^{-1} at st 1. During monsoon the distribution was irregular. While very low values below 10 mol.l^{-1} could be observed at sts 10 and 13, between s 9 and 3 values above 17 μmol.l^{-1} reaching a value f approximately 50 μmol.l^{-1} at st 8 could be corded, and after that at stations near to barmouth e concentration was below 10 μmol.l^{-1}. In the ostmonsoon months, a picture almost similar to that premonsoon could be noticed with a difference that e maximum value (88 μmol.l^{-1}) was at st 11 instead st 13. The phosphate level showed a gradual crease from st 11 to st 1.

Silicate—Average silicate concentration varied m 0.37 to 5.96, 0.21 to 4.73 and 0.03 to 2.66 mg.l^{-1} pectively in monsoon, postmonsoon and pre-msoon seasons from barmouth to upstream (Fig. 6). ere was a general decrease in the silicate content m Oct. to May. In the upper reaches of the river ere the salinity influence is less the silicate levels e relatively uniform throughout the year. The jor changes in the silicate content of estuarine ers are due to the difference in dilution and the hest concentration is observed during the SW soon season when the fresh water discharge is imum. During premonsoon season when the river harge is minimum the longitudinal variation in the ate content was minimum (0.03-2.66 mg.l^{-1}). karanarayanan *et al.*[10] observed atypical viour of dissolved silicate in this region. They also reported substantial removal of silicate by pitation at different salinity ranges as compared ther areas.

uoride—There is a general increase in the fluoride

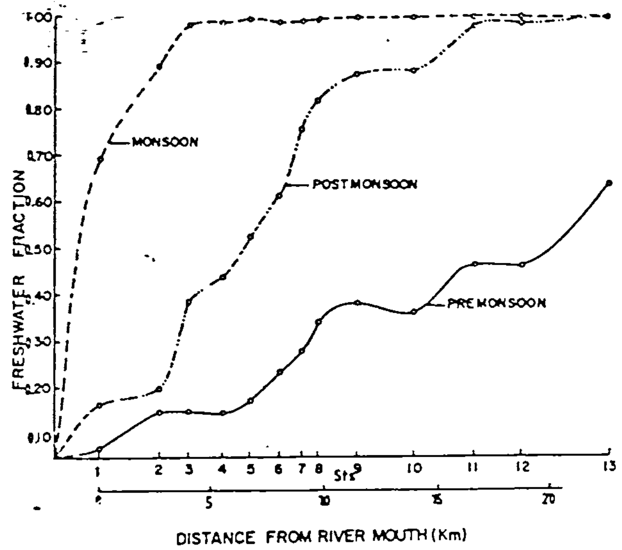

Fig. 4—Distribution of fresh water fraction during different seasons

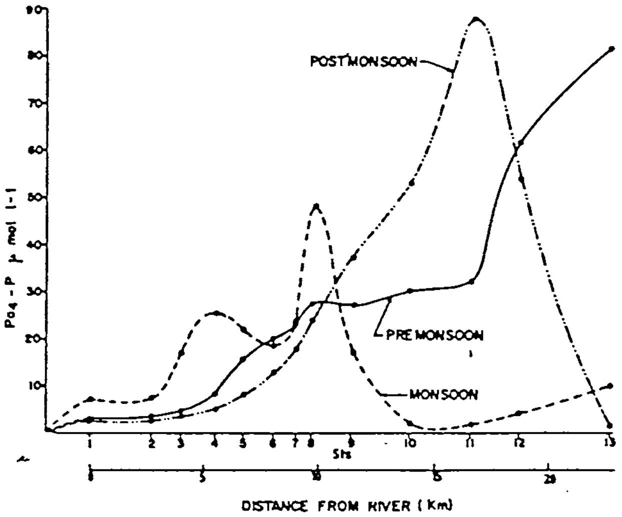

Fig. 5—Concentration of phosphate in a longitudinal section along the Cochin backwater system during different seasons of the year

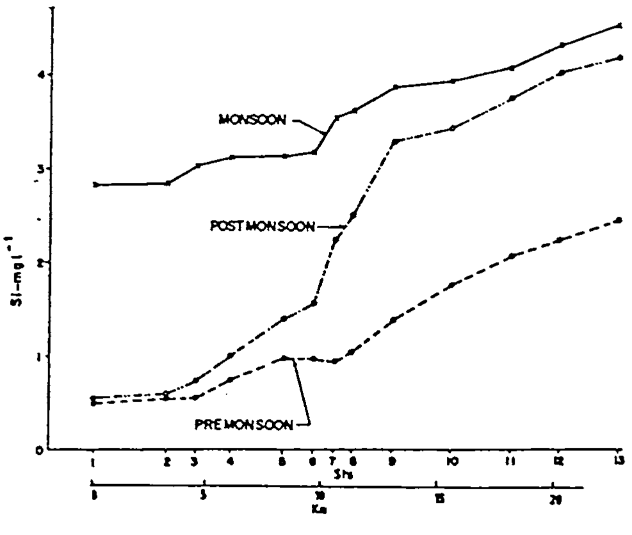

Fig. 6—Concentration of silicate in a longitudinal section along the Cochin backwater system during different seasons of the year

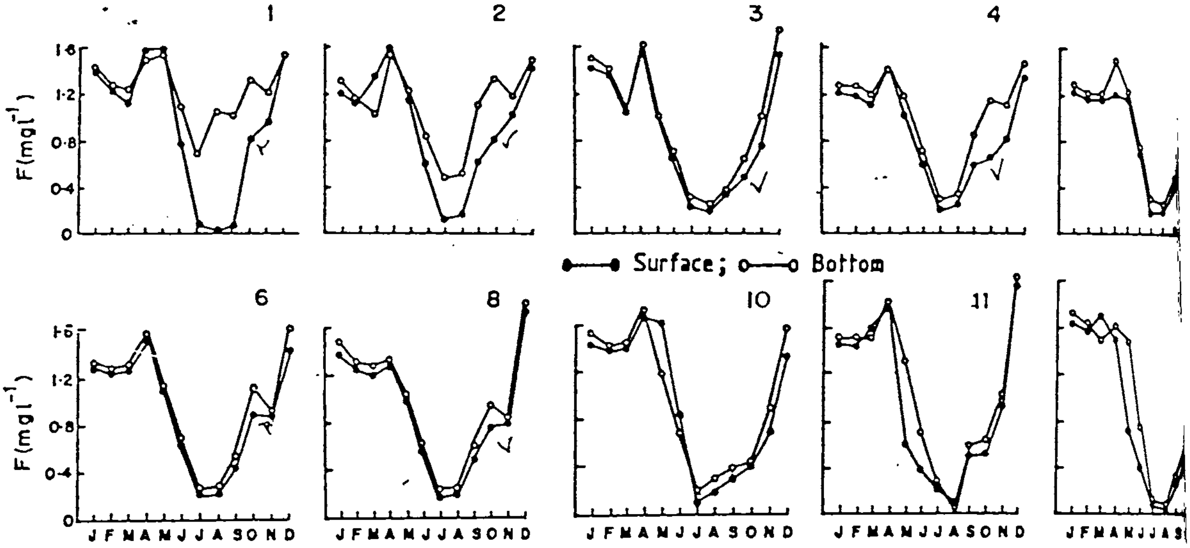

Fig. 7—Distribution of fluoride at various stations during different months

(Fig. 7) concentration (0.5 to >1.5 mg.l^{-1}) from Oct. at all stations. Maximum concentration is observed during Dec. to April. From May the values begin to decrease and minimum concentrations (<0.5 mg.l^{-1}) are observed at all stations except at st 1 during July to Sept. At st 1 fluoride content is high (>0.5 mg.l^{-1}) at the bottom. During this season the fresh water influx through the river is maximum. The extent of seawater incursion into the estuarine system during different months of the year considering the index of seawater penetration as 1×10^{-3} is shown in Fig. 3. Fluoride values at sts 8 to 13 are markedly high (>1.5 mg.l^{-1}) during Dec. to April (Fig. 7) and there is a general decrease in the concentration towards the river mouth. High concentration of fluoride observed is due to the effect of pollutants discharged from the fertilizer factory situated upstream near to st 13. It is also believed that the Aluminium Factory, which is also in the vicinity of the fertilizer factory, uses cryolite as one of the raw materials and this may be contributing fluoride substantially to the environment. The effect is conspicuous during the time of the year when the fresh water discharge through the river is minimum. Station near to the river mouth also shows higher levels than the usual seawater concentration except during March, but the values are less than the values observed at stations upstream. This indicates clearly the contribution from the river and afterwards dilution by the time the effluent mixed water reaches the river mouth.

Fluoride content of the river water at zero chlorinity collected from the upstream of the industrial belt showed a concentration from 0.18 to 0.24 mg.l^{-1}. This value is slightly higher than what has been reported for the river water from other regions[5,11]. As already discussed there is a higher concentration of fluoride at station downstream of the industrial belt during to April. Absence of higher values at these sta during May to Oct. is due to the greater dilutio fresh water flow.

Fluoride data from the estuary and the river w plotted against chlorinity showed no defi relationship. A linear relationship between fluo and chlorinity was reported from the estuary when fresh water containing no fluoride mixes w seawater[11]. Water samples of lower chlorinity sho a marked variation showing a higher fluor chlorinity ratio than chlorinities above 15×1 indicating contributions from the river.

The secondary maximum observed at chlorini between 10 and 14×10^{-3} is also believed to be du the effect of fluoride containing pollutant at upstream stations during Dec. to April, when chlorinity values increased from 0 to $>10\times10^{-3}$ to the decrease in the fresh water flow.

Discussion

Changes in the characteristics of this estua system reveal its dependence on the monsoonal c of this region. SW monsoon season accompanied b large volume of fresh water influx into the estuar system creates stratification at the mouth of estuary during the flood tide. At stations nearer to barmouth the direction of flow was controlled by nature of the tide. Seawater dominated up to st 2 a from there onwards fresh water dominated. Qasim a Sen Gupta[12] observed a salt wedge extending up t distance of 10 km in Mandovi and 12 km in Zu rivers during monsoon which is totally absent in th system during this period. The horizontal salini gradient could be noticed only up to a few statio upwards from barmouth. Eventhough the inorgani phosphate concentration was generally low compared to the other seasons, there was an accumulation, between sts 3 and 9. This also depicted in the fresh water fraction which does not show much variation between these stations. This showed that eventhough the pollutant introduced near st 11 gets diluted, the flushing was less during the season, because seawater dilution factor was very negligible beyond st 3 towards the head of the estuary reaching zero value. Therefore any pollutant introduced into the estuary from factories located near sts 11 and 12 would only get diluted by the fresh water influx and would be cradled back and forth according to the tidal current up to st 3 near to barmouth, where it would get progressively mixed with seawater and get diluted further and flushed out of the estuarine system. High concentration of phosphate and fluoride observed between the sts 4 and 9 may be due to the effect of cradling of river water mixed with the effluent discharge in between tidal regimes.

During the postmonsoon period, the salinity gradient along the longitudinal axis of the estuary increases (fresh water fraction curve in Fig. 4). This showed that with the reduction in the river discharge intrusion of saline water was taking place more interior into the estuary (up to 17 km from barmouth). The slight vertical gradient of salinity with an upstream current from surface to bottom showed that the estuary behaved as a partially mixed estuary during the season. The fresh water fraction curve and the phosphate distribution also showed that there was partial mixing of river water and seawater. From the steep gradient of phosphate curve after st 11 up to st 4, it was evident that there was a progressive dilution downstream after the discharge point.

Comparatively high horizontal gradient of salinity from the barmouth to st 13 and beyond and less vertical gradient, with the flow pattern showing a steady upstream current from top to bottom at all the stations, showed that the estuary during the premonsoon condition is a mixed estuary. This is also quite evident from the distribution of phosphate and fresh water fraction from st 13 downstream. A steady dilution of any pollutant introduced at sts 11 and 12 could be expected downstream up to barmouth.

As the estuary is a tide dominated one it is responding to the vagaries of the monsoon in a great way. The deepening of the harbour entrance channel has increased the tidal prism resulting in greater incursion of seawater into the estuary during the flood tide. Indiscriminate reclamation of the estuarine water area near the harbour entrance for various activities of the harbour has also helped in the horizontal extension of seawater into the river Periyar thereby increasing the salinity of the system considerably.

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Atypical Behaviour of Dissolved Silicate in the Cochin Backwater & Periyar River

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Dissolved silicate was determined for 1 y (1982-83) covering a wide range of salinity from the estuarine mouth to the fresh water region. Silicate concentration ranged between 0.03 and 4.75 mg l^{-1}. Silicate - salinity relationship was linear and inverse in the salinity ranges 0-5 × 10^{-3} and 5-35 × 10^{-3}. Since variability in the distribution of silicate explained by the significant linear regression model was small in the subranges of salinity 5-20 and 20-30 × 10^{-3}, a curvilinear regression model was fitted and it gave a good fit at 5% level ($P > 0.05$). The expected removal of silicate at salinity range 0-5 and 5-35 × 10^{-3} given by linear relationship was 28.8 and 51.1% respectively. In 5-20 and 20-30 × 10^{-3} at 5 and 20 × 10^{-3} salinity the expected removal as given by curvilinear relationship was 31.94 and 6.068% respectively.

Distribution of dissolved silicate in the sea has been tudied extensively. Several workers have studied the ehaviour of silicate during the estuarine mixing[1-4]. Very little information is available[1] on the silicate istribution in the Indian estuaries, though it is of nterest to note its behaviour during the estuarine ixing processes.

This paper presents the behaviour of silicate in elation to salinity in the Cochin backwater and in eriyar river.

aterials and Methods

Water samples were collected from Cochin ackwater and Periyar River at monthly intervals uring 1982-83 from marine zone to fresh water region overing a wide range of salinity (Fig. 1). The station epths varied between 2 and 7 m. Samples were ollected from the surface and bottom and stored in olyethylene bottles and analysed immediately. issolved silicate by spectrophotometric method[5], and linity by titration method[6] were estimated. A linear gression model was fitted and its significance tested sing ANOVA technique[7], based on the significance of near correlation.

Salinity ranges in 0-35 × 10^{-3} were combined and rouped into 2 as 5-20 × 10^{-3} and 20-35 × 10^{-3}. For e 2 groups separately and for the whole the same near regression model was fitted and its significance sted as above. Since linear relationship was not nificant for the subranges a curvilinear model was ted for 2 groups. The fitted equation[8] was

$$= Y_i + \frac{X^2}{a_0 + a_1 X + a_2 X^2}$$

ere Y_i = silicate concentration at the i^{th} salinity el; $i = 5,20$; Y = silicate; X = salinity; a_0, a_1, a_2 are curvilinear regression coefficients. This model was fitted for the average of silicate and salinity concentration in each interval of 5 units in each range. The fitted model was found to be good fit using χ^2 statistic at 5% level. For linear and curvilinear relationships, the expected removal of silicate at 0 salinity in different ranges was computed.

Results and Discussion

There is a vast change in the salinity conditions at all stations except at the estuarine mouth where the salinity changes are less during the year (Table 1).

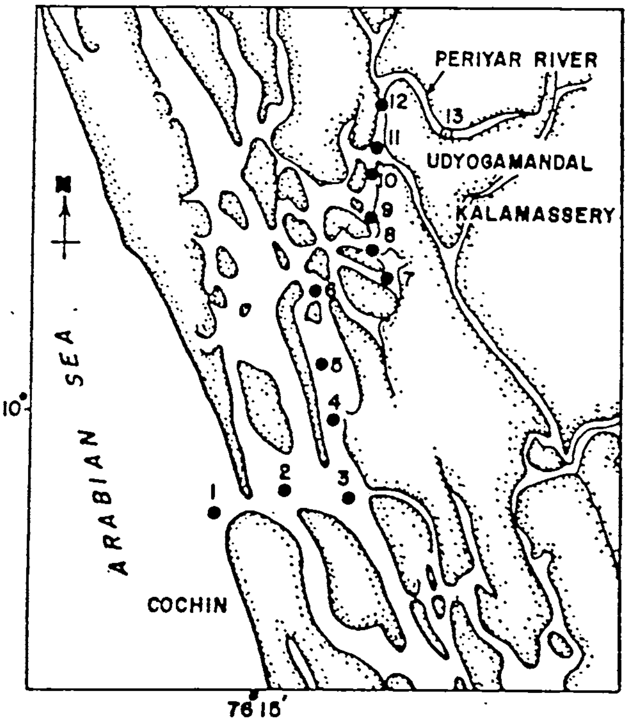

Fig. 1—Cochin backwaters and Periyar river showing station positions

Table 1—Salinity (× 10^{-3}) at Different Stations during Different Months

St		1982							1983				
		June	July	Aug.	Sept.	Oct.	Nov.	Dec.	Jan.	Feb.	March	April	May
1	S	0.45	1.45	27.78	29.27	18.25	24.12	32.69	32.52	33.08	33.15	33.87	28.4
	B	16.26	29.18	25.80	33.07	33.33	33.15	33.33	33.24	32.16	34.32	34.14	30.6
2	S	0.54	1.26	0.72	25.47	11.18	26.10	29.81	29.18	29.10	29.54	30.89	27.2
	B	17.61	8.04	3.64	9.39	32.88	33.06	32.79	33.35	29.63	32.88	32.43	29.1
3	S	0.36	0.63	0	8.58	9.12	17.43	24.12	29.18	29.72	31.34	31.34	26.9
	B	0.18	0.54	0	10.12	14.27	30.53	33.15	31.25	30.17	31.16	31.79	27.0
4	S	0.27	0.05	0	9.30	8.94	13.73	24.03	28.00	30.35	30.71	32.88	26.9
	B	0.18	0.09	0	--	28.01	29.36	30.62	28.45	30.53	30.80	33.06	26.8
5	S	0.18	0.05	0	—	9.76	11.15	22.04	27.46	29.63	30.17	31.98	24.8
	B	0.18	0.05	—	—	16.44	13.10	26.47	27.64	29.63	30.26	32.16	24.8
6	S	0	0.09	0	7.86	6.87	9.67	17.98	26.20	26.83	29.99	31.34	19.7
	B	0	0.09	0	9.21	15.54	10.48	21.68	26.28	26.83	29.90	31.52	19.7
7	S	0	0.05	0	2.44	1.63	6.02	13.19	24.75	25.47	29.36	30.53	17.1
	B	0	0.05	0	5.51	5.60	7.00	17.79	24.75	25.56	29.26	30.89	17.1
8	S	0	0.05	0	0.14	0.38	2.35	10.39	22.04	22.76	27.10	28.54	8.7
	B	0	0.05	0	2.35	0.38	7.72	18.88	22.76	23.12	27.73	29.08	17.1
9	S	0	0.05	0	0.09	0.42	0.42	6.05	20.41	21.23	24.66	27.46	6.5
	B	0	0.05	0	0.05	0.43	3.88	15.27	20.41	22.22	26.65	28.81	17.2
10	S	0	0.05	0	0.05	0.29	1.72	6.05	10.80	20.59	25.20	27.64	6.77
	B	0	0.05	0	0.05	0.33	4.07	12.01	11.25	21.77	27.10	28.63	25.9
11	S	0	0.05	0	0.05	0.27	0.81	1.00	16.62	20.96	19.96	19.15	6.77
	B	0	0.05	0	0.05	0.29	0.72	1.63	17.61	21.77	26.65	25.92	20.3
12	S	0	0.05	0	0.05	0.22	0.90	4.21	12.65	20.14	20.96	23.48	7.2
	B	0	0.05	0	0.09	0.25	0.81	0.69	12.92	21.14	26.47	29.27	18.16
13	S	0	0.05	0	0.05	0.20	0.09	0.78	2.44	15.81	19.20	17.56	7.9
	B	0	0.05	0	0.05	0.15	0.18	0.84	5.33	20.68	23.10	22.80	12.2

S = surface, B = bottom

There is a general increase in the silicate concentration from the mouth of the estuary to upstream (Table 2). Average silicate concentration (mg l^{-1}) varies from 0.37 to 5.96, 0.21 to 4.73 and 0.03 to 2.66 respectively in monsoon, postmonsoon and premonsoon seasons from the barmouth to upstream. Highest silicate concentration is observed at the surface. There is a general decrease in the silicate content from Oct. to May. In the upper reaches of Periyar where the salinity influence is less, the concentration is comparatively uniform throughout the year. All samples have been collected at a similar stage of tidal cycle. Nevertheless the major changes in the silicate concentration observed are due to differences in dilution and the concentration is maximum when the fresh water flow is maximum. The silicate distribution appears to be largely governed by the river water discharge. Maximum concentration of silicate (1.7 to 6.7 mg l^{-1}) occurs during SW monsoon when the river water discharge is maximum. But during the premonsoon season when the river discharge is minimum the variation and the concentration of silicate are minimum (0.03-2.66 mgl^{-1}).

Variation in the concentration of salinity decreases steadily from 195 to 3 %. Whereas in silicate, it reaches to a maximum of 443 % in the salinity range 10-
× 10^{-3} and falls to a minimum of 47 % in the lower (
× 10^{-3}) and higher (30-35 × 10^{-3}) ranges. Correlati
coefficient is negative in all cases except in the salin
range 10-15 × 10^{-3} and it is significant only in
× 10^{-3}. It is further suggested that dilution
significant inverse effect at 5 % level only in the salin
range 0-5 × 10^{-3}.

The fitted linear regression equation for differ
salinity ranges (× 10^{-3}) are:

$$Y = -0.4445\ X + 3.3808 \text{ for } 0\text{-}5$$
$$Y = -0.2566\ X + 4.0231 \text{ for } 5\text{-}10$$
$$Y = 0.1222\ X - 0.0049 \text{ for } 10\text{-}15$$
$$Y = -0.2099\ X + 5.1256 \text{ for } 15\text{-}20$$
$$Y = -0.0136\ X + 0.8482 \text{ for } 20\text{-}25$$
$$Y = -0.0055\ X + 1.0587 \text{ for } 25\text{-}30$$
$$Y = -0.1029\ X + 4.0212 \text{ for } 30\text{-}35$$

where Y is silicate and X is salinity.

The fitted linear regression model was signific
only in salinity range 0-5 × 10^{-3} (F ratio 30.25;
< 0.05) and variability explained was only 7.382
Since linear regression model was not significant
the remaining ranges, they were all combined a

redivided into 2 ranges 5-20 × 10^{-3} and 20-35 × 10^{-3}. The correlation coefficient was calculated and the same model was again fitted for the 2 separately and together.

The fitted equations for the 2 salinity (× 10^{-3}) ranges and the combined one are:

$$Y = -0.0508\,X + 2.3203 \text{ for } 5\text{-}20$$
$$Y = 0.0147\,X + 0.3594 \text{ for } 20\text{-}35$$
$$Y = -0.0556\,X + 2.3234 \text{ for } 5\text{-}35$$

Since linear model was significant only for the salinity range 5-35 × 10^{-3} (F ratio = 59.1776; $P < 0.05$) the fitted linear equation in this range was extended to salinity 0 and the expected removal was estimated as 51.1%. The variability explained was only 19.57% (Table 3). Therefore the unexplained variability may be due to different types of relationships between silicate and salinity; in the salinity sub-ranges 5-20 × 10^{-3} and 20-35 × 10^{-3}. Since linear relationship did not hold good for these 2 ranges, a curvilinear model was fitted and it was:

for sal. 5-20 × 10^{-3}

$$Y = 1.047 + \frac{X^2}{-211.4349 + 13.8129\,X + 2.7041\,X^2}$$

for sal. 20-35 × 10^{-3}

$$Y = 0.6163 + \frac{X^2}{-46048.107 + 1748.5109\,X + 0.9746\,X^2}$$

The model was fitted using the average values of silicate and salinity in each interval of 5 units in each range. The fitted model gave a good fit for both ranges

Table 2—Silicate (mg.l^{-1}) Distribution at Different Stations

St		1982							1983					
		June	July	Aug.	Sept.	Oct.	Nov.	Dec.	Jan.	Feb.	March	April	May
1	S	4.46	3.86	3.64	0.61	1.47	0.97	0.24	0.53	0.76	0.37	0.61	0.26
	B	2.49	0.95	3.55	0.37	0.68	0.39	0.21	0.44	0.69	0.61	0.70	0.31
2	S	4.71	3.87	5.96	0.75	1.31	0.69	0.38	0.50	0.66	0.41	0.78	0.25
	B	3.14	3.25	3.26	1.67	0.42	0.43	0.25	0.60	0.77	0.36	0.79	0.30
3	S	3.85	4.57	3.73	2.79	1.61	1.09	0.72	0.63	0.81	0.45	0.84	0.27
	B	2.70	4.99	3.73	1.91	1.45	0.60	0.43	0.43	0.74	0.42	0.80	0.27
4	S	4.90	6.07	1.94	1.77	1.66	0.64	0.94	0.76	0.86	0.62	0.91	0.41
	B	2.93	6.53	3.97	2.00	2.14	2.01	0.43	0.69	0.85	0.67	0.89	0.48
5	S	2.59	4.13	3.97	—	2.31	1.55	0.99	0.70	0.91	0.89	1.18	0.89
	B	4.12	4.24	—	—	1.89	2.06	0.78	0.67	0.87	0.82	1.42	1.06
6	S	4.08	4.03	3.40	2.14	2.87	2.15	1.03	0.77	0.71	0.88	1.22	1.15
	B	3.90	4.38	3.78	2.42	2.08	2.76	1.08	0.49	0.61	0.74	1.17	0.99
7	S	4.70	3.75	3.59	4.05	3.85	2.72	1.42	0.61	0.65	0.74	1.37	1.34
	B	2.74	2.83	3.69	3.16	3.10	3.61	1.43	0.16	0.57	0.65	1.34	1.22
8	S	3.61	4.26	3.59	4.33	4.05	3.04	1.81	0.54	0.11	0.31	1.30	2.23
	B	3.96	2.65	3.59	4.05	3.77	4.73	1.19	0.66	0.34	0.46	1.49	1.69
9	S	4.94	6.70	3.68	4.31	4.05	3.70	2.83	0.30	0.03	0.55	1.34	2.55
	B	4.09	3.76	3.69	4.33	4.23	3.79	1.73	0.04	0.27	0.66	1.70	1.79
)	S	4.71	3.44	3.50	4.33	3.86	3.93	2.16	0.19	0.10	0.39	1.59	2.67
	B	3.72	3.75	3.40	4.23	4.05	4.08	1.46	0.89	0.24	0.78	1.95	1.82
1	S	2.10	3.30	3.69	4.70	3.85	4.12	3.47	0.79	0.22	0.12	0.22	2.66
	B	2.08	3.78	3.78	4.98	3.96	4.64	3.47	1.82	0.38	0.72	0.84	1.80
!	S	2.51	3.26	3.69	4.14	3.96	4.45	3.94	1.41	0.12	0.31	0.49	2.10
	B	2.62	2.47	2.84	4.05	4.10	3.42	3.75	0.50	0.28	1.20	1.28	1.34
;	S	3.00	3.61	3.40	3.95	3.96	1.55	3.84	0.48	0.10	0.33	0.31	6.80
	B	2.69	3.62	3.31	4.05	4.12	3.51	4.22	0.41	0.54	0.64	0.76	3.22

=surface, B = bottom

Table 3—Removal of Silicate for All Salinity Ranges and Variability Explained by Linear Regression Model

	Sal. range (× 10^{-3})			
	0-5	5-20	20-35	5-35
rcent silicate removed at l. × 10^{-3})	28.83 at (0)	31.94 at (5)	6.068 at (20)	51.09 at (0)
plained variability (%)	7.38	—	—	19.57

by χ^2 test at 5% level ($P > 0.05$). Therefore the reduction in the variability explained by the linear regression model in the salinity range $5\text{-}35 \times 10^{-3}$ can be attributed to different types of curvilinear relationships existing between silicate and salinity in the salinity ranges $5\text{-}20 \times 10^{-3}$ and $20\text{-}35 \times 10^{-3}$. Using these 2 equations the expected removal of silicate at 5 and 20×10^{-3} salinity is 31.94% and 6.068% respectively (Table 3). Burton *et al.*[9] observed only values 2% less than the measured concentration for the test estuary and thereby ruling out the possibility of any silicate removal by precipitation when the freshwater mixes with seawater. Substantial removal of dissolved silicate from river water entering the Mississippi Delta has been suggested by Bien *et al.*[2]. Burton[1] has reported 10% removal of dissolved silicon in the upper estuary of the Vellar river. The variation in the concentration observed over the year in the estuarine mouth have been associated with the biological factors such as high phytoplankton production occurring in these waters[10]. In other regions of the estuary the biological effect on the distribution of silicate seems to be minor.

Eventhough linear model was found to be significant in $0\text{-}5 \times 10^{-3}$ salinity the explained variability is very low. This may be due to precipitation. Similarly, in the salinity range $5\text{-}35 \times 10^{-3}$ the explained variability is little more, but much less than 50%. Since curvilinear relationship gave a good fit in the subsalinity ranges $5\text{-}20 \times 10^{-3}$ and $20\text{-}35 \times 10^{-3}$, a part of the unexplained variability may be due to removal but at a lower rate.

Acknowledgement

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Hydrochemical Characteristics of Chaliyar River Estuary

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Hydrochemistry of Chaliyar river estuary was studied for a period of one year taking tidal observations across 4 sections along 15 km distance. The important factors affecting the general hydrography were rainfall, freshwater inflow and seawater intrusion. Nitrate - N source was found to be due to land drainage and the source of inorganic phosphate as seawater. An inverse relationship was observed between inorganic and organic nitrogen fractions.

INTRODUCTION

Estuarine ecological environments are complex and highly variable compared to other marine environments. In an estuary, mixing occurs between natural waters of very different chemical composition and physico - chemical properties. Differences in the nature of the fresh and saline mixing components produce gradients and transitions of various parameters within this region. Estuaries receive highest inputs of nutrients through land drainage and industrial pollution. What happens to this large quantity of nutrients that enter the estuary is not only of ecological interest, but also relevant to water quality management. The Chaliyar river is one of the major west flowing rivers of the Kerala State. It originates from the Western Ghats and joins the Arabian Sea at Bevpore, near Kozhikode in the south west coast of India. Earlier, a few studies have been conducted in this estuary on salinity intrusion (James and Sreedharan, 1983) and general hydrography (Premchand *et al.*, 1987). In the present work the distribution and seasonal variation of different hydrochemical parameters, such as pH, salinity, dissolved oxygen and nutrients in the estuary are discussed. The studies was mainly directed at identifying the sources and sinks of nutrients and defining the important geochemical and biochemical pathways of these nutrients in the estuary.

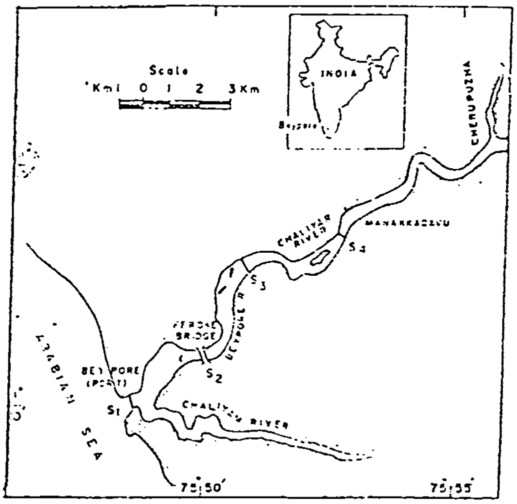

Figure 1. *Study area*

MATERIAL AND METHOD

Study area

Intensive sampling and analyses were made at 4 sections in Chaliyar river estuary. The study area with the 4 observation sections, namely S1, S2, S3, and S4 are shown in figure 1. S1 is near to the river mouth and the upstream sections are at 5, 10 and 15 km distances from S1. Two stations were selected along each section across the river which are almost equidistant from the shore, one on the northern side and the other on the southern side. Depths along these sections varied with tide and season, so that mean values and exceptions are stated below. The physical dimensions of the sections are :

Section	Width, m	Mean depth, m
S1	390	2.45 to 2.95
S2	294	2.99 to 3.50
(The northern side is deeper with depth approx. 7.00 m)		
S3	200	4.00 to 4.54
S4	243	2.52 to 3.06

Sampling and analysis

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Monthly surveys were conducted in the estuary for a period of one year. 13 hr tidal observations were made simultaneously at 2 sections on consecutive days. Water samples were collected at 2 - hourly intervals from the surface, mid - depth and bottom of the water column. Hydrochemical parameters determined for each station included pH, salinity, dissolved oxygen, nitrite - N, Ammonia - N, nitrate - N, phosphate - P, total - N and total - P. Organic - N and organic - P are obtained by substracting the inorganic fractions from corresponding total fractions. The pH measurements were conducted *Insitu* using a portable pH meter (Philips model PP 9046) and salinity was measured using an electrodeless induction type salinometer (Digi - Auto model 3G, Tsurumi Seiki, Japan) after proper calibration. DO was determined by Winkler's method as described in Grasshoff (1983). NH_4 - N was measured using the indophenol blue method, NO_2 - N by sulphanilamide diamine mathod, NO_3 - N determined after reduction to nitrite and phosphate using the molybdenum blue method (Grasshoff, 1983). Total N and P were determined by simultaneous oxidation procedure using alkaline persulphate described in Grasshoff (1983).

RESULT AND DISCUSSION

Resuts of the present study on the hydrochemical characteristics of the estuary are summarised below. Based on rainfall, the period of study was divided into 3 seasons, namely Oct - Jan as post monsoon, Feb - May as pre monsoon and June - Sept as monsoon season.

General hydrography

The hydrogen ion concentration (pH) is an important indicator of the chemical condions of the estuarine waters. Spatial variations in pH during each month of observation is shown in figure 2. The pH values were found decreasing from the marine towards the riverine end of the estuary. Tidal averages varied between 8.2 and 6.9 during post monsoon, 8.4 and 7.3 during pre monsoon and 7.8 and 6.7 during monsoon. The low pH values observed during the monsoon months are clearly due to the heavy fresh water inflow into the estuary. The increased pH values during pre monsoon and post monsoon seasons and the gradual increase in pH towards the marine end of the estuary are due to greater sea water intrusion. Spatial distribution of salinity during each month of observation is shown in figure 3. Salinity was mainly controlled by freshwater discharge through the river. During the monsoon months (June - July), when the rainfall and river discharge were maximum, saline intrusion was felt upto a distance of about 5 km from the river mouth. Sea water intrusion increased during post monsoon and the estuary was found to be marine dominated during premonsoon. These observations on salinity distribution lead to the classification of the estuary to be salt - wedge type during monsoon, a partially mixed type during post monsoon and a well mixed type during pre monsoon season.

Spatial variations in dissolved oxygen during each month of observation is shown in figure 4. Generally, dissolved oxygen concentration was higher during monsoon and comparatively low during the pre monsoon months. The variations in dissolved oxygen may be attributed to the variations in fresh water inflow, tidal ingress and water temperature. Although vertical differences in oxygen values were not conspecuous due to the shallow nature of the estuary, surface values were slightly higher than the bottom values. This may be due to the oxidation of organic matter at sub - surface levels. Thus the important factors affecting the general hydrography of Chaliyar river estuary were rainfall, freshwater inflow and seawater intrusion through the river mouth.

Distribution of nitrogen fractions

Ammonia - N : Seasonal variations in the integrated mean values of ammonia concentration in the 4 sections of the estuary are shown in figure 5. Ammonia concentration varied from non - detectable amounts during the monsoon months at certain sections to a gradual build up during the monsoon months and high concentrations (> 5.0 µg at/L) during the post monsoon season. Isolated high concentrations (> 15.0 µg at/L) were noticed in the month of January in the 2 upstream sections. Otherwise the ammonia concentration decreased gradually to lower values in the months of February to May.

Nitrite - N : Seasonal changes in the integrated mean values of nitrite concentration are shown in figure 6. Nitrite distribution did not followed a clear definite pattern. Very low concentrations (1 µg at/L) were observed throughout the estuary during the period of study with a few exceptions. The maximum value observed (1.9 µg at/L) was at the

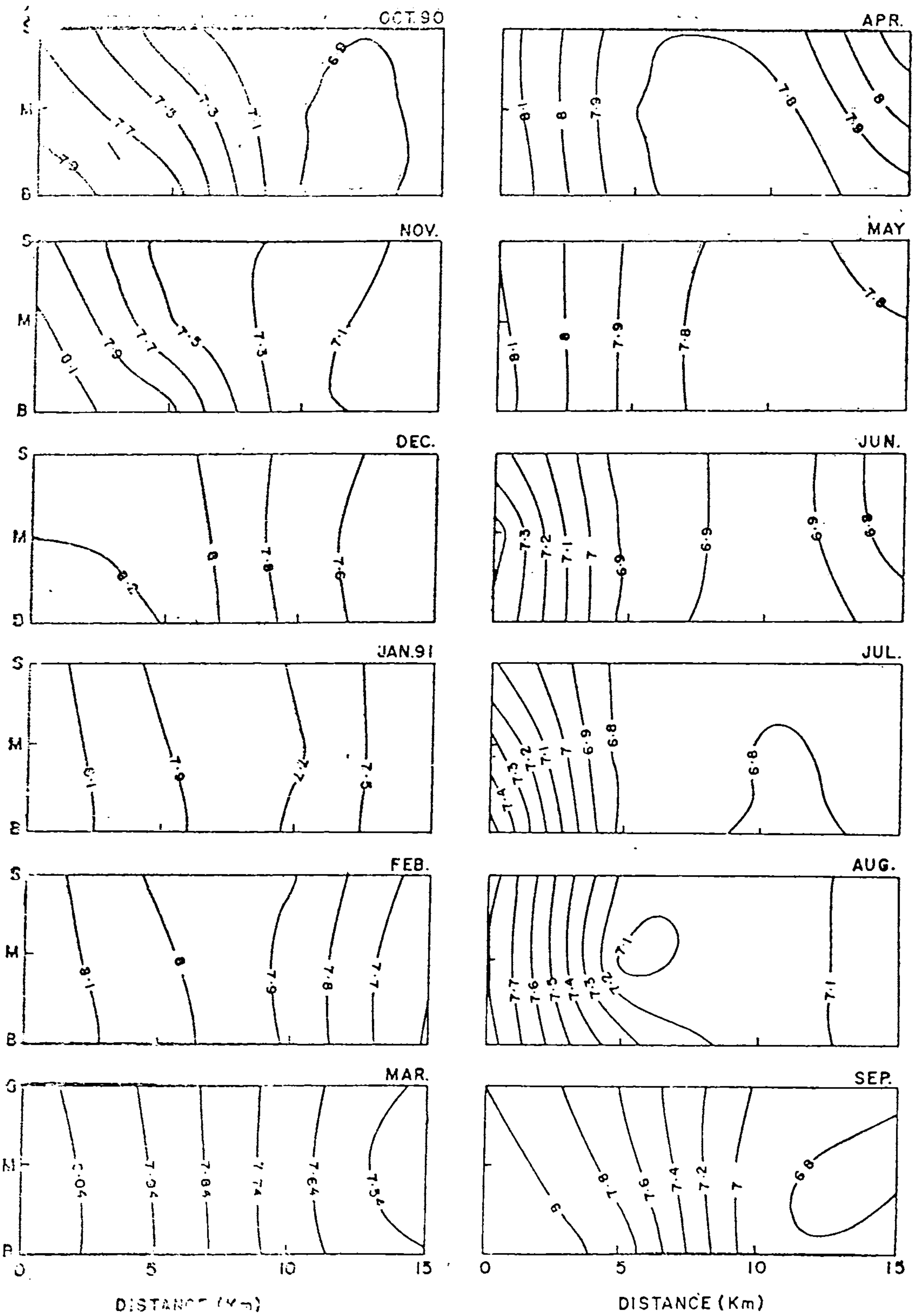

Figure 2. *Spatial variations in pH during each month of observation*

ver mouth during June. A second maximum was bserved during October at section 2.

Itrate - N : Seasonal changes in the integrated mean concentration of nitrate at 4 sections in the estuary are shown in figure 7. The annual cycle showed minimum nitrate concentrations at all sections during the premonsoon followed by high conce-

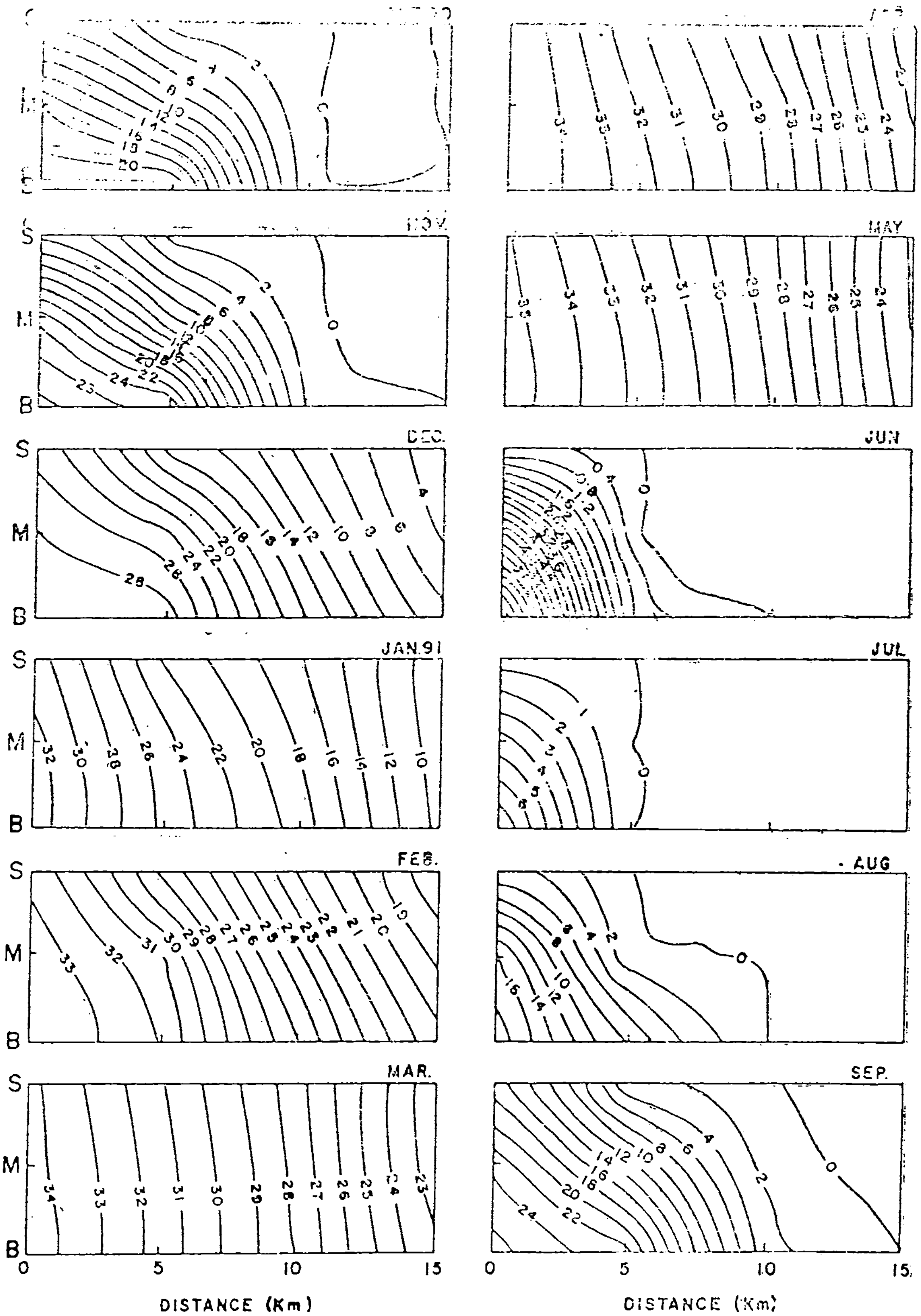

Figure 3. *Spatial distribution of salinity during each month of observation*

ntrations during the monsoon and a decrease in levels during the post monsoon.

Organic - N : Seasonal variation in the Integrated mean values of organic nitrogen in the estuarine waters (Figure 8) showed an inverse trend with that of nitrate - N.

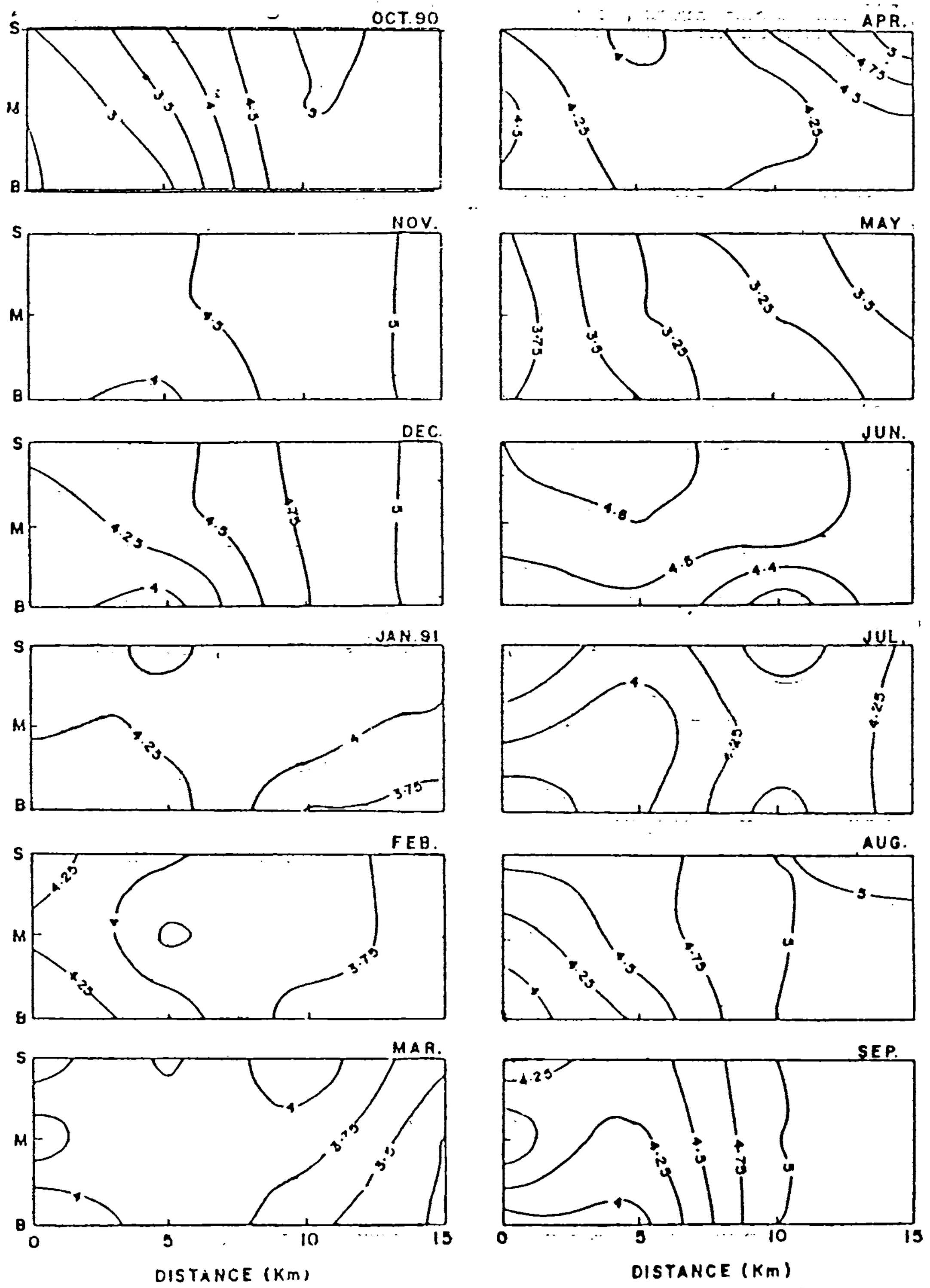

Figure 4. *Spatial variations in dissolved oxygen during each month of observation*

A discussion of the seasonal variation in the distribution of various nitrogen fractions in the estuary will help in understanding the nutrient chemistry of the estuary. The degree to which phytoplankton nitrogen uptake processes affect estuarine nitrogen concentration varies between different estuarine systems (Mc Carthy, 1981). Several factors including external environmental conditions, such as temperature light, nutrient concentration and physiological state of the phytoplankton ultimately regulate the rate of nitrogen uptake in the estuary. The effect of these uptake processes on ambient nitro-

Table 1. *Percentage of various nitrogen fractions*

Season	NO_2-N + NO_3-N	NH_4^+-N	Org-N
Premonsoon			
S-1	13.80	4.80	81.40
S-2	10.60	7.60	81.80
S-3	13.80	9.80	76.40
S-4	10.00	1.50	88.50
Monsoon			
S-1	65.90	10.00	24.10
S-2	72.30	8.20	19.50
S-3	85.00	7.10	7.60
S-4	85.70	6.10	8.20
Postmonsoon			
S-1	32.00	27.20	40.80
S-2	38.60	18.60	42.80
S-3	54.40	28.90	16,70
S-4	48.80	26.60	24.60

Table 2. *Interstitial nutrients of sediments at various sections in Chaliyar river estuary, in µg at/L*

Sections	NO_2-N	NO_3-N	NH_4^+-N	PO_4-P
Premonsoon				
S-1	1.70	13.09	559.90	14.44
S-2	1.92	12.35	681.70	12.43
S-3	3.59	73.90	106.20	2.46
S-4	1.93	17.35	69.30	8.20
Monsoon				
S-1	1.75	16.41	770.00	22.20
S-2	3.29	29.72	480.00	23.70
S-3	1.64	42.28	118.40	1.20
S-4	1.48	36.85	86.20	1.64
Postmonsoon				
S-1	2.37	15.52	425.90	11.08
S-2	1.45	13.16	226.60	9.51
S-3	1.33	61.62	51.52	3.25
S-4	1.88	24.92	27.80	4.92

gen distributions are determined by the physical charectaristics, such as flushing rate and circulation in the estuary (Pennock, 1987). Tidal mixing of the water column appears to be one of the factors responsible for the differing responses of phytoplankton populations to nutrient inputs observed in estuaries (Monbet, 1992). Microbial transformations of nitrogen may be as important as phytoplankton uptake of inorganic nitrogen in determining the distributions of nitrogen among the major dissolved forms (Horrigan *et al.*, 1990).

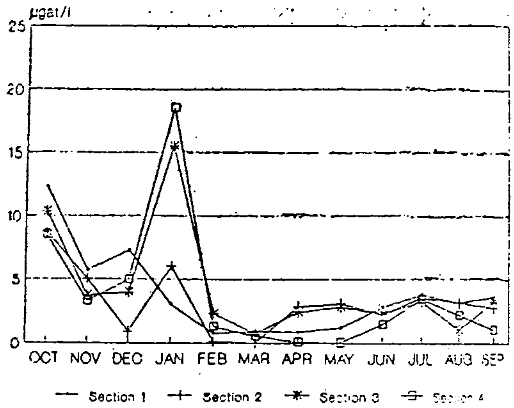

Figure 5. *Seasonal changes of the integrated mean concentration of ammonia - N at four stations in the estuary*

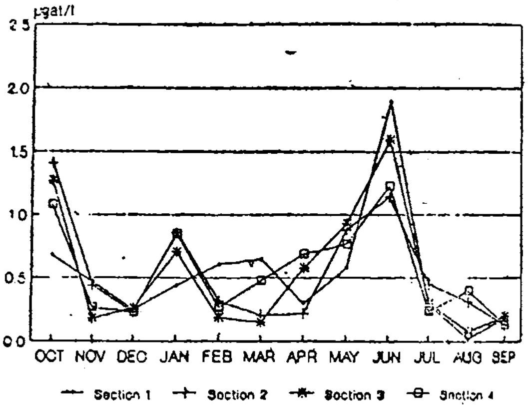

Figure 6. *Seasonal changes of the integrated mean concentration of nitrate - N at four sections in the estuary*

The distribution of various nitrogen fractions in the estuary was affected by physical, chemical and biological processes. The contribution of various nitrogen fractions to the total nitrogen pool of the estuarine waters was found to vary spatially and temporaly. The major source of inorganic nitrogen was through river discharge which was indicated by their maximum concentration during monsoon. During the pre monsoon months when the riverine contribution was very little, percentage of inorganic nitrogen in the estuarine waters was found to be the minimum and the major form of nitrogen was organic. During post monsoon season, the contribution of both these components were almost equal in the estuarine waters eventhough there existed a predominance in the inorganic form. Generally, dissolved nitrogen compounds are present throughout the estuary during all seasons of the year in one form or other and so nitrogen was not a limiting nutrient in the estuary.

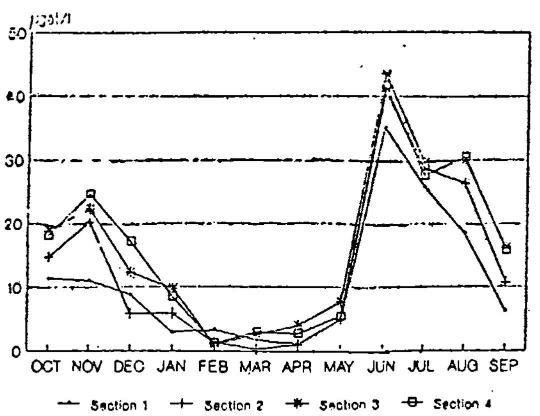

Figure 7. *Seasonal cbanges of the integrated mean concentration of nitrate - N at four sections in the estuary*

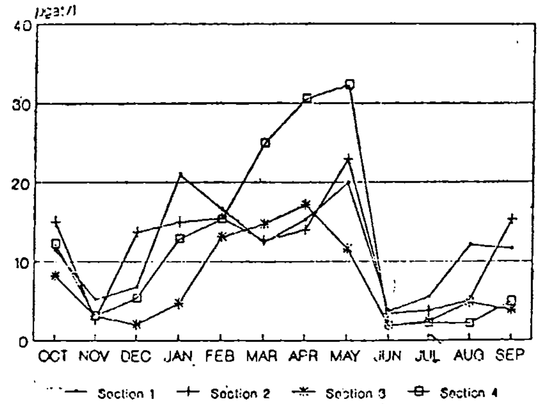

Figure 8. *Seasonal changes of the integrated mean concentration of organic nitrogen at four sections in the estuary*

Percentage of different nitrogen fractions at various sections in the estuary is given in table 1. Contribution of ammonia to the total nitrogen pool of the estuary was $\lesssim$ 10 % during the monsoon and premonsoon periods. Maximum accumulation of ammonia ($>$ 25 % of total N) occurred during the postmonsoon period when the opposing forces, namely river runoff and tidal incursion were moderate. Ammonia - N did not costitute a major component in the river water; therefore its concentration is subjected to little influence by river discharge. Ammonia distribution in the water column clearly indicated the process of ammonification in the estuarine and riverine part, which is the ultimate step in the autoepuration of organic matter. Added to this also the transfer of ammonia from the interstitial water in the bottom sediments which was rich in ammonia (Table 2). An examination of ammonia data in the interstitial water at various sections during different seasons (Table 2) indicated that it is minimum during the post monsoon season and the values are lowest at sections 3 and 4. But the ammonia concentrations are uniformly high in the water column with maximum values at the upstream sections. The transfer of ammonia to the overlying water can only be minimal at sections 3 and 4 where the interstitial water values are low. Therefore, it strengthens the argument that the high amount of ammonia encountered can only be due to ammonification in the water column.

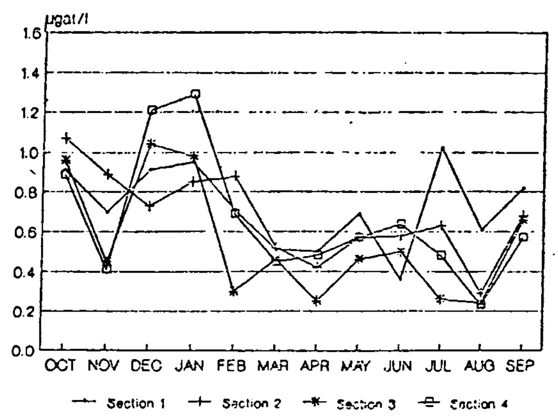

Figure 9. *Seasonal changes of the integrated mean concentration of inorganic phosphate at four sections in the estuary*

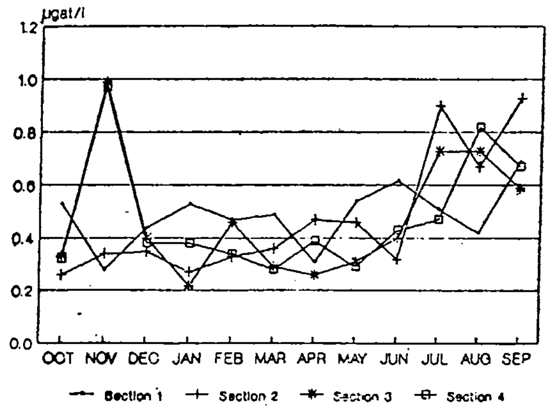

Figure 10. *Seasonal changes of the integrated mean concentration of organic phosphorus at four sections in the estuary*

Nitrite concentration was found to be significantly high only during the postmonsoon season. A close look at the tidal variations during this period showed the sequence of a peak concentration of ammonium followed by an increase in nitrite at all sections (Jose K. Xavier, 1993). This was indicative of nitrification in the water column as reported by several workers, like Ward and Twilley (1986) and Fan and Jin (1989). Here nitrifying bacteria can play an important role because they are able to oxidise ammonium to nitrate with nitrite as an intermediate. Nitrite may als be formed in the reduction of nitrate and denitrification. Heavy rainfall and consequent land drainage was observed to be the main source of nitrate in the estuary. High nitrate concentration in the run - off waters can be related to the large amount of nitrogenous fertilizers used in agriculture. Nitrates are not well retained by the soil and if not utilised quickly are leached away along with land drainage. Since nitrates are highly water - soluble, most of it may be leached away during the initial runoff period and this could be the reason for the decrease in nitrate concentration during July and August eventhough the river discharge was high. A second nitrate peak observed during November is due to the influence of river runoff during the north - east monsoon. A gradual decrease in concentration was observed downstream and the fluctuations observed at the barmouth section was according to the phase of tide. Much of the nitrate was washed out of the estuary during the period of high runoff without being assimilated, due to short residence time and slow uptake rate of nitrate by phytoplankton.

Nitrate concentration decreased during December and January due to the decrease in contribution from the land source and increased uptake by primary producers. During the premonsoon months from February to May, the entire estuary was marine dominated and the contribution of nitrate from fresh water was practically absent. This together with the high biological activity brought nitrate concentration to a minimum. But during this period, there was an increase in organic - N concentration. The reduction in the inorganic nitrogen accompanied by a substantial increase in the percentage of organic - N indicated that the major source of organic - N in this system is not the river runoff. Organic - N was positively correlated with salinity during monsoon and post monsoon ($r = 0.40$ to 0.61). This indicated that the source of this nutrient during this period was from the sea. Dissolved organic compounds in the sea water come from the decay of organic matter produced in the body of water itself, from the excreted waste products of living organisms or by diffusion from the bodies of certain phytoplankton (Rao and Rao, 1974).

During the monsoon period, when land drainage and river discharge were maximum, 80 - 90 % of the total nitrogen pool in the estuary was contributed by nitrate alone. On the other hand during the premonsoon period, when the estuary was marine dominated, 75 - 85 % of the total nitrogen pool was organic - N. Generally an inverse relationship was observed between the inorganic and organic forms of nitrogen in the estuary. Such an inverse relationship has been reported in the waters of western English Channel (Butler *et al.*, 1979). A sharp rise in organic - N accopanied by a depletion of inorganic nitrogen during pre and post monsoon seasons is indicative of phytoplankton productivity and nutrient enrichment due to favourable physicochemical conditions.

Distribution of phosphorus in the estuary

Dissolved inorganic phosphate : Seasonal variation in the integrated mean concentration of phosphate is shown in figure 9. The seasonal trends observed in the phosphate distribution were less marked compared to the nitrate distriburion. Phosphate concentrations were relatively low (< 1.0 μg at/L) throughout the estuary with a few exceptions. The peak values observed were at the upstream sections during Dec - Jan. The peak value noticed at the river mouth was during July.

Organic phosphorus : Seasonal variation in the integrated mean concentration organic phosphorus in the water column at different sections of the estuary are shown in figure 10. The temporal and spatial variation of inorganic phosphate differed from that of nitrogen fractions. The concentration that was generally low during the pre monsoon period picked up with the advent of monsoon and recorded the highest mean concentration during the post monsoon at all sections in the estuary. Except during December, January and June, higher concentrations of inorganic phosphate was found at the rivermouth section. Organic phosphorus was higher at the rivermouth except during November.

Therefore the source of inorganic phosphate as well as organic - P was mainly from the sea. Regeneration from sediments was found to be a major source during post monsoon season. The monsoon floods contributed only small amounts of phosphate to the estuary, which was apparent from the slight increase of phosphate concentration during June. The concentration was very low at sections 1 and 2 during this period and it can be correlated with the high values of interstitial phosphate. Jitts (1959) showed that 80 to 90 % of the phosphate in solution might be adsorbed to the estuarine silt and this process is more under conditions of high terrestrial runoff. Higher interstitial phosphate concentrations at sections 1 and 2 during monsoon (Table 2) reveal this. High values of inorganic phosphate observed at the rivermouth during July and August could be due to the intrusion of upwelled water. The high concentrations observed during December and January can be accounted as due to local regeneration under favourable physico - chemical conditions. Pomeroy *et al.* (1965) pointed out that the exchange of phosphate consisted of a 2 step ion exchange process between clay minerals and water, plus an exchange between terrestrial micro - organisms and water. Further he suggested that the exchange rate and capacity of the sediments were ecologically important factors in maintaining the phosphate concentartion at an optimum level favourable for plankton production.

It has been found that total productivity in aquatic biological communities is directly limited by the concentration of available phosphorus and that several geochemical processes are involved in regulating the availability of phosphorus in the nutrient cycle. One of these important processes in the aquatic environment is the incorporation of phosphorus into the sedimental phase, either by sorption mechanisms or by the formation of insoluble inorganic phosphate minerals (Storm and Biggs, 1982). The biological removal of phosphate in estuaries include uptake by both phytoplankton and bacteria (Lebo, 1990). The 'buffering' of phosphate concentrations in esuaries has been described as an equilibrium process where phosphorus is adsorbed or released from particles to maintain a constant concentration.

CONCLUSION

The important factors affecting the general hydrography of Chaliyar river estuary were rainfall, freshwater inflow and intrusion of sea water through the river mouth. Observations on salinity distribution lead to the classification of the estuary to be a salt-wedge type during monsoon, a partially - mixed type during postmonsoon and a well - mixed type during premonsoon.

The distribution of various nitrogen fractions in the estuary was found to vary spatially and temporaly. Concentration of inorganic nitrogen compounds were high only during periods of heavy freshwater runoff. Nitrate - N was the predominant form among inorganic species and it showed a negative correlation with salinity. High nitrate concentration in the runoff waters can be related to the large amount of nitrogenous fertilizers used in agriculture. Nitrates are not well retained by the soil and are leached away along with land drainage. Organic nitrogen showed from the sea.

The distribution and seasonal variation of phosphorus in the estuary differed from that of nitrogen fractions. The source of phosphorus in the estuary was found to be mainly from the sea. Contribution from land drainage was very small and a significant contribution during postmonsoon was observed to be regeneration from the bottom sediment.

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Changes in water quality at Cochin harbour dredging site, south west coast of India

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The water quality in the vicinity of the dredging did not show any appreciable change. All dissolved nutrients recorded sharp changes in the water column. After 20 minutes and 2 hours, the conditions at the dredging were much different from the pre-dredging site. As the surge in the nutrients was confined only to the end stage of the dredging, the possibility of any extensive water quality deterioration at the site or in its vicinity was remote.

The proposal to deepen the navigational channel of Cochin to 12.2 - 12.8 m draft level would increase he annual extend of dredging to 10×10^6 m^3 from he present level of 6×10^6 m^3. Deepening of the hannel might lead to a greater incursion of salt rater and silt into the harbour region and that may ffect the benthic community. The release of the etritus and silt and their re-deposition over biota ay even cause mass mortality. As part of a etailed study to establish prevailing conditions of e water body, with an aim to provide a scientific asis for future integrated management of the arbour area, a field experiment was devised to onitor the effect of extreme perturbation caused y dredging.

The dredging operations for deepening the annel for super tanker entry started in nakulam channel (Fig. 1) during October 1992. e field study was conducted on 15th December, 92 in the Ernakulam Channel while dredging as operational. Observations were made just fore the dredging, immediately after the edging operations, after 20 minutes and 2 hours dredging respectively. From the vicinity of the edging site, sea water samples were taken for the alysis of dissolved nutrients and other chemical ameters with a clean plastic bucket and the surface samples by a 1.71 Niskin water mpler. The ammonial nitrogen was analysed by Indophenol blue method[1] and the nitrate, nitrite phosphate were done as in Grasshoff *et al.*[2] *In situ* turbidity measurements were made with a OSK Model FN5 Turbidity meter and the light penetration in the water column by a sechi disk. The salinity is measured by an Inductive Salinometer. Water samples from three levels (surface, mid-depth and bottom) for salinity, dissolved oxygen and nutrient analyses and water samples from every 1m levels for sediment load were collected from the site. The transparency,

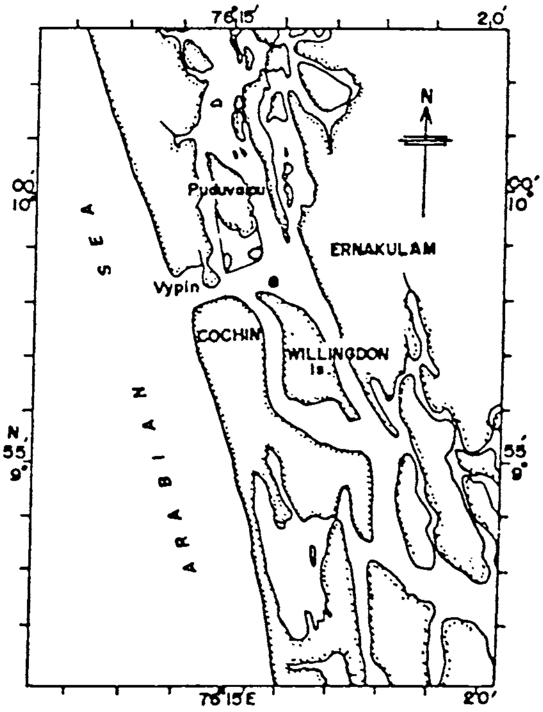

Fig. 1—Location of study

turbidity of the water column were measured. A small neutrally buoyant float was put into the sediment cloud formed at the dredging site with the hauling up of dredger and the movement of the patch and float was followed at a distance making least disturbances to the sediment patch immediately after dredging.

During the dredging operations (tidal ranges were between 1 and 1.3 m), and the water in the vicinity of the dredging had a sechi disk reading of 50 cm, turbidity of 10-15 ppm in the surface layer, 15-25 ppm at mid depth and 48.55 ppm just above the bottom. The suspended load in the surface water layer was 10-20 mg.l^{-1}, 15-30 mg.l^{-1} in the mid layer and 35-50 mg.l^{-1} in the bottom layer during the dredging. As soon as the column of suspended sediment was introduced into the navigational channel along with dredger head lifting, it started to move away from the site by the average large scale tidal current, while at the same undergoing mixing by small scale turbulent eddies. On lifting up of dredger head, the sechi disc reading dropped to 5 cm, the turbidity reached 150 ppm at the surface, 900 ppm at the mid-depth and 1300 ppm in the bottom layer. The suspended load in the surface water reached to 120 mg.l^{-1} and the bottom water recorded 1150 mg.l^{-1} of sediment load. The sediment cloud formed during the lifting of dredging gear was extended to the bottom. The mixing process causes the initial sediment column to grow with time, thereby reducing the concentration within the sediment cloud.

The chemical features of the water column during the operation period were quite close to the average values of the parameters recorded for the month of October. A strong density stratification and a two layer structure of the water column was evident from the salinity and silicate distribution (Table 1). Phosphate profiles had a small vertical gradient within the range (0.50-0.71 *μM*). Nitrate recorded a decrease from the surface to the bottom within the range 0.2-0.54 *μM*. Ammonia was generally absent except at the surface where its concentration was 0.41 *μM*. Silicate varied inversely with salinity and decreased from 55.70 *μM* at the surface to 14.39 *μM* at the bottom.

Immediately 1 minute after the hauling of the dredging head, the sediment cloud patch was uniformly spread over the water column. All the nutrients in the water increased substantially. Phosphate levels increased four times, nitrite levels had doubled and ammonia levels underwent a five

Table I—Distribution of chemical properties during the final stages of the dredging

Depth m	Salinity *μM*	Phosphate-P *μM*	Nitrite-N *μM*	Ammonia-N *μM*	Silicate-Si *μM*
Pre-dredging					
S	16.10	0.50	0.54	0.41	55.70
M	22.42	0.67	0.28	000	44.41
B	31.91	0.71	0.24	0.00	14.39
Immediately after dredging					
S	19.31	1.89	0.65	0.21	48.06
M	24.62	3.35	0.75	5.03	39.36
B	33.52	3.02	0.58	4.25	10.92
20 minutes after dredging					
S	17.77	0.55	0.52	0.00	50.38
M	31.90	0.75	0.28	0.00	15.31
B	33.26	1.22	0.22	3.49	11.24
Two hours after dredging					
S	15.74	0.67	0.60	0.00	55.19
M	18.90	0.75	0.54	0.00	46.63
B	19.80	0.71	0.52	0.00	45.20

S=surface, M=mild layer, b=bottom

fold jump. Within 20 minutes after dredging, the water column regained its vertical density stratification. The phosphate and nitrite levels had returned to the pre-dredging ambient levels. But the ammonia and phosphate in the bottom layer still remained high. Normal suspended load values were attained within 30-45 minutes.

After 2 hours of dredging, the sediment plume completely mixed with the surrounding waters. Nitrite and phosphate had reverted to their pre-dredging levels. It could be seen that the disturbance due to the dredging was confined to a short span and to a limited area and was unlikely to cause any intense environmental damages to the entire system. The environment may be considerably affected increase of frequent lifting of dredging gear and total collapse/ failure of the system of dredging or accidental release of dredged material in the channel on its route in the designated dumping site.

This study forms a part of EIA study prior to deepening of the navigational channel, sponsored by Cochin Port Trust.

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Heavy metals in fishes from coastal waters of Cochin, southwest coast of India

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The concentration levels of copper, zinc, manganese and iron have been determined in marine fishes from Cochin area which is one of the major fishing zones along the west coast of India. The concentration of heavy metals varied from species to species. Copper, Zn, Fe and Mn showed increased levels in the gills and alimentary canal compared to the muscle. Difference in heavy metal concentration in various species studied is attributed to the varying feeding habits. The observed levels were below the toxic limit.

Accumulation of certain toxic metals in different organs of marine organisms and their subsequent transfer to man through the food chain is of great concern[1]. Fish musculature is a major path through which heavy metals can enter the human body and therefore, it has been investigated more than other organs. The present study was confined to the assessment of the level of some heavy metals in the muscle, liver, alimentary canal and gills of fishes collected from the inshore waters of Cochin in the south west coast of India.

Fish samples for analysis were collected from the Chinese dipnets deployed off Cochin during the summer 1992. Most of these fishes were confined in their distribution to shallow waters which subsist on phytoplankton and zooplankton strained from the surrounding waters by the well developed and feathery gills[1]. The fish samples of same size were weighed individually and dissected to remove the various tissues which were washed in double distilled water. The alimentary canal was first removed carefully to avoid any contamination. The samples were dried to constant weight at 40 - 50°C, powdered and stored. The composite samples were digested in aquaregia using teflon bombs. Parallel replicate measurements were made on all the samples and the mean value has been tabulated. This method was calibrated by analysing one BCSS-1 standard reference material supplied by the National Research Council, Canada. The standard deviation found for each metal are Cd (±7%), Cu (±5%), Zn (±11%), Fe (±19%) and Mn (±15%) respectively. Determination of heavy metals were performed with a flame atomic absorption spectrophotometer (Perkin-Elmer 2380).

The details of the concentration of various metals in fourteen different species fishes are given in Table .1. Though the concentrations of metals in different tissues of fishes varied widely, the musculature which forms the edible part showed much lower concentration than other tissues. The concentration of Cu in the muscle tissue of *Sphyrna zygaena* was 1.54 $\mu g.g^{-1}$, while in the case of liver it was 35.49 $\mu g.g^{-1}$. This corresponds to an average enrichment ratio of about 1:23 in respect of liver as compared to the musculature. Similarly, the enrichment ratio for Zn and Mn in the same species were 1 : 26 and 1 : 3 respectively.

In the case of *Chirocentrus dorab* the liver to muscle ratio for Cu, Zn, and Fe were 11 : 1, 38 : 1 and 2 : 1 respectively. The enrichment ratio for each element between the pair of organs for different species of fishes varied considerably. The absolute increase of heavy metals in muscle tissue of contaminated fish is often much lower than in other organs and as mentioned earlier, it becomes enriched by metals only when the contamination is extremely high.

The estimated concentrations of Cu, Zn and Mn in the muscle tissue compared well with those of reported values in fishes from different parts of the western Indian Ocean[2-5]. Elevated levels of Zn were observed in the alimentary canal and gills of *Stolephorus devisi, Chirocentrus dorab, Sardinella longiceps, Rastrelliger kanagurta, Mini maculata* and *Mugil cephalus*. It is generally believed that fish activity regulates Zn concentration in their muscle tissue and as a result do not reflect changes in

Table 1—Heavy metal concentration in different tissues of fish from coastal waters of Cochin (µg. g^{-1} dry weight).

Species	Common name	Tissue	Cu (SD)	Zn (SD)	Fe (SD)	Mn (SD)
1 *Sardinella longiceps (14)*	Indian oil Sardine	M	1.54 (±0.09)	20.52 (± 1.80)	148.50 (± 32.0)	ND
		AC	6.94 (±0.41)	63.42 (±11.10)	2255.40 (±609.0)	6.14 (±1.10)
		G	2.72 (±0.11)	110.83 (±12.02)	428.39 (± 68.0)	16.39 (±2.40)
2 *Dussumieria auta (8)*	Rainbow sardane	M	1.59 (±0.06)	24.63 (± 1.66)	57.97 (± 9.5)	ND
		AC	9.92 (±0.65)	64.45 (± 9.20)	376.81(± 80.1)	8.19 (±1.10)
		G	ND	58.25 (± 6.67)	224.63(± 40.4)	2.73 (±0.60)
3 *Stolephorus devisi (18)*	Anhovy	M	2.20 (±0.15)	29.90 (± 3.20)	119.04(± 18.0)	ND
		AC	27.00 (±0.56)	123.15 (±16.09)	443.84(± 96.0)	ND
		G	ND	172.41 (±15.50)	1009.32(±122.0)	64.40 (±8.20)
4 *Rastrelliger kanagurta (4)*	Mackerel	M	2.01 (±0.12)	14.99(± 1.60)	127.59(± 21.0)	ND
		AC	9.28 (±0.32)	71.25(± 6.50)	3773.30(±540.0)	14.68 (±2.10)
		G	ND	117.87(±12.00)	419.25(± 85.4)	11.70 (±1.20)
5 *Chirocentrus dorab (3)*	Wolf herring	M	1.52 (±0.08)	6.56(± 0.42)	33.77(± 6.6)	ND
		L	16.53 (±0.74)	247.62(±31.00)	72.46(± 14.5)	4.39 (±0.62)
		AC	4.63 (±0.21)	462.64(±64.00)	144.92(± 36.0)	20.90 (±3.50)
		G	6.17 (±0.35)	396.96(±55.00)	318.84(± 72.0)	62.84 (±11.00)
6 *Mini maulata (6)*		M	4.63 (±0.21)	38.58(± 2.90)	250.00(± 51.0)	6.83 (± 1.02)
		AC	15.43 (±0.69)	159.68(±18.00)	536.25(± 98.0)	6.98 (± 1.50)
		G	4.92 (±0.32)	137.52(±16.00)	692.03(±125.0)	25.95(± 2.10)
7 *Megalaspis cordyla- (9)*	Torpedo trevally	M	1.43 (±0.07)	19.29(± 2.10)	362.32(± 70.0)	1.36 (± 0.22)
		AC	7.71 (±0.46)	90.72(± 8.70)	833.33(±178.0)	2.73 (± 0.50)
		G	4.60 (±0.25)	83.74(± 9.20)	347.82(± 68.4)	17.75 (± 2.11)
8 *Psuedosciaena diacoantis (11)*	Sciaenids	M	1.55 (±0.06)	19.70(± 2.50)	79.71(± 11.2)	ND
		AC	6.17 (±0.29)	68.14(± 9.50)	166.66(± 33.3)	ND
		G	ND	82.58(± 8.70)	306.90(± 55.0)	ND
9 *Johnllies sp. (4)*	Jew fish	M	1.50 (±0.04)	18.06(± 1.80)	112.31(± 20.0)	ND
		AC	9.25 (±0.46)	67.73(± 8.00)	239.13(± 49.5)	ND
		G	ND	66.05(± 7.00)	306.32(± 61.5)	ND
10 *Sphyrna zygaena (2)*	Shark	M	1.54 (±0.08)	13.13(± 0.90)	90.58(± 16.2)	1.26 (± 0.19)
		AC	15.43 (±0.84)	58.55(± 5.20)	173.91(± 35.0)	4.29 (± 0.73)
		G	3.70 (±0.14)	54.67(± 2.50)	49.13(± 2.1)	3.27 (± 0.33)
		L	35.49 (±2.01)	341.97(±49.00)	94.20(± 11.5)	4.09 (± 0.80)
11 *Mugil cephalus (4)*	Grey mullet	M	1.51 (±0.04)	26.68(± 1.20)	72.46(± 17.9)	ND
		AC	24.69 (±1.89)	137.93(±18.60)	167.00(± 26.4)	17.75 (± 3.20)
		G	2.72 (±0.15)	140.53(±11.00)	479.54(± 86.0)	26.51 (± 4.00)
12 *Petrica filamentosa (3)*	Silver bellies	M	ND	33.66(± 4.40)	144.92(±22.5)	ND
		AC	40.12 (±3.11)	110.01(±20.10)	166.30(±40.4)	30.05 (± 4.40)
		G	1.54 (±0.08)	84.03(± 7.20)	262.14(±45.6)	2.41 (± 0.50)
13 *Gobius plassa (5)*	Goboid	M	ND	18.06(± 2.10)	101.44(± 17.0)	ND
		AC	12.34 (±0.78)	100.16(±13.00)	264.49(± 42.3)	4.09 (± 0.60)
		G	2.72 (±0.15)	138.36(±14.00)	1419.44(±320.0)	24.10 (± 3.19)
14 *Parastromateus niger (3)*	Black pomfret	M	3.08 (±0.16)	15.18(± 0.60)	45.29(± 5.5)	9.56 (± 1.50)
		AC	7.71 (±0.48)	12.15(± 0.90)	91.66(± 14.0)	20.49 (± 4.90)
		G	9.25 (±0.44)	91.54(±11.00)	398.55(± 70.4)	24.59 (± 3.20)

M - muscle, AC - alimentary canal, G - gill, L - liver (SD) - standard deviation for triplicate analysis
(Values in paranthesès give the no. of samples analysed)

ambient available levels of this element in the environment[6]. Therefore, the high levels of Zn concentration reported here infers that the regulation of this element may not be complete. In all the species, Fe was found to be the most abundant of the metals analysed. Acceptable limits for other elements for human consumptions are: Zn (150ppm), Cu (10ppm) and Pb (1.5ppm) wet weight, respectively[7]. No maxima is specified for Mn.

Dussumiera acuta, Chirocentrus dorab, Mini maculata and *Megalaspis cordyla* contained trace metal levels in the order of alimentary canal > gill > musculature, while in the others the order was gill > alimentary canal > musculature. The possible explanation for the latter trend is that the principal mode of uptake of metal is through the gills. As the gills are constantly exposed, the mucus exposed to seawater acts as a surface adsorption sheet for either selective or general accumulation of metals[1].

The variation in concentration of metals in different tissues may be attributed to the feeding habits. In detrital feeders like *Mugil cephalus* which feed by grazing on submerged materials and plant surfaces or by sucking the surface layer of the mud, ingestion of sediment which could be enriched with heavy metals as a result of contamination, would probably lead to the ingestion of greater quantities of heavy metals by the fishes[8].

From the data it is clear that the concentration of all the metals analysed were within the prescribed limits for human consumption.

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CHLOROPHYLL 'a' AND PARTICULATE ORGANIC CARBON IN RELATION TO SOME PHYSICO-CHEMICAL PARAMETERS ALONG SOUTHWEST COAST OF INDIA

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ABSTRACT

Chlorophyll 'a', Particulate Organic Carbon and other environmental parameters were studied along Kerala coast during October 1987 and 1988. High chlorophyll 'a' content at surface water and decreasing trend towards offshore was observed. Spatial gradient in the Chl 'a' and POC distribution exhibited appreciable difference in the nearshore and offshore region. Gaylor and Hopper conditions tested to apply Satterthwaites approximation for unequal sets of sample observations showed that chlorophyll 'a' and environmental parameters except NO_2-N varied spatially, while POC and NO_2-N diurnally. For total and 60 µm size fractioned chlorophyll 'a' a negative relation of high gradient with salinity while, for 20 µm size fraction a positive relation of low gradient was observed. Inverse relation was observed between size fractioned chlorophyll 'a' and other parameters.

INTRODUCTION

BIOMASS of phytoplankton in the seas in terms of chlorophyll 'a' concentration is one of the most widely accepted methods in the study of primary production. Chlorophyll 'a' indicates total plant material available in the water at primary stages of food chain. An assessment of particulate organic carbon provides a more meaningful estimation of the available energy to the next trophic level where herbivore grazing is proposed to control phytoplankton within the limits set by nutrient concentration. The control of phytoplankton production by nutrient availability in the euphotic zone is the basis of any geochemical model calculation of bioreactive element cycling, particularly in the coastal and estuarine systems dominated by detrital material. Further, it is increasingly recognised that the physico-chemical characteristics prevailing in the water column play an important role in selecting the size structure of the phytoplankton community (Malone, 1980; Platt, *et. al.,* 1983; Charez, 1989; Legendre and Le-Ferre, 1989). The spatial and temporal gradients in environmental parameters offered by the inshore/offshore waters make this ecosystem suitable for examining the relationship between physico-chemical parameters and phytoplankton pigment (size fraction) which forms the main objective of the present study.

Lot of information is available regarding the productivity and related parameters from the southwest coast of India. But all these are confined to a particular region or season, but the present work concentrates on the entire southwest coast of India.

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MATERIAL AND METHODS

This study is based on the samples collected along the southwest coast of India extending from Kasargod to Cape Comorin during the 187th and 204th cruises of RV *Gaveshani* during October, 1987 and 1988 respectively. The stations along the continental shelf (< 200 m depth) were taken as near shore and those on the continental slope (> 200 m depth) were classified as offshore stations. During October 1987, 12 nearshore stations, including 6 anchor stations were occupied covering 43 day and 26 night observations and also 6 offshore stations covering 3 day and 3 night observations. Collection during October 1988 included 18 nearshore stations, with 6 anchor stations covering 44 day and 21 night collections and 9 offshore stations covering 4 day and 5 night observations. Each anchor station was sampled 3 hourly intervals. Surface water was analysed for hydrographic parameters like temperature, salinity, DO and nutrients such as phosphate, nitrite, nitrate and silicate. Chlorophyll 'a' and Particulate Organic Carbon were determined by standard methods (Strickland and Parsons, 1968). For numerical interpretations the data of the two cruises were pooled and 7 anchor stations viz; Kasaragod, Cannanore, Calicut, Cochin, Quilon, Vizhinjam and Cape Comorin, 6 nearshore non-anchor stations and 6 offshore stations were considered. The numerical analysis include intraparameter association, box model for Chlorophyll 'a' distribution over the parameters POC, temperature, salinity, DO, PO_4-P, NO_2N, NO_3-N and SiO_4-Si (Snedecor and Cochran 1967, Fisher and Yates 1963), critical ratio test and student's *t* test for single sample and student's two sample test for comparison of independent samples (Federer, 1967), two way nested analysis for testing significance of difference between offshore, nearshore and anchor stations and difference between day and night with respect to the concentration of parameters stated earlier using Gaylor and Hopper conditions for Satterthwaites approximation, Kruskal-wallis non parametric test for comparing day and night collections of offshore, nearshore and anchor stations (Sokal and Rholf, 1981). Based on these results day and night collections were combined together or not according as the difference was not significant or otherwise, for further analysis. Duncan's multiple range test was applied to determine the highly different shore types and significant differences are presented in the form of a Trellis diagram for each parameter (Sanders, 1973). For size fractioned chl 'a' studies, total water sample, 60 µm, and 20 µm size filters were used (Arantza Iriartee, 1993).

RESULTS AND DISCUSSIONS

Environmental features: A slight increase in temperature was observed towards offshore during both years showing an upward gradient from nearshore to offshore. Salinity and dissolved oxygen did not show much variations. Well oxygenated conditions prevailed throughout the study period. Of the four micronutrients only phosphate showed a wide range (0-2µg atom/1) in the near shore regions during October 1987 and most of the values were less than 1 µg at/1. Nitrate was found in trace level in most of the collections. Nitrate showed considerable increase during October 1987 compared to 1988. Moderate values for silicate content was noticed during both cruises. The values ranged between 1.01 and 26.21 µg at/1 and mostly the values were between 5 to 10 µg at/1 irrespective of space and time.

Distribution of chlorophyll 'a' and Particulate Organic Carbon: In October 1987, Chl 'a' during day ranged between 0.007 to 3.32 mg/m^3, lowest being near Cochin and

TABLE 1. Mean, Standard Deviation (SD) & Coefficient of variation (C. V. %) of the parameters

	Chl 'a'	POC	T°C	S%	D.O.	PO_4-P	NO_2-N	NO_3-N	SiO_4-Si
OFFSHORE : a) DAY									
$\bar{X}$	1.311	0.564	29.410	35.070	4.440	0.199	0.091	0.934	2.130
SD	1.113	0.531	0.290	0.391	0.760	0.173	0.224	1.302	1.831
CV	84.89	94.15	0.98	1.11	17.12	86.93	246.15	139.40	85.96
b) NIGHT									
$\bar{X}$	1.561	3.144	29.110	34.880	4.549	0.248	0.144	0.726	2.685
SD	1.989	4.892	0.383	0.370	0.303	0.137	0.264	0.322	2.457
CV	127.42	155.60	1.32	1.06	6.66	55.24	183.33	44.35	91.51
NEARSHORE : a) DAY									
$\bar{X}$	1.625	16.386	29.409	34.030	4.757	0.413	0.068	0.619	3.550
SD	2.076	14.496	0.685	1.741	0.447	0.560	0.136	0.574	5.265
CV	127.75	88.47	2.33	5.12	9.40	135.58	199.85	92.77	148.31
b) NIGHT									
$\bar{X}$	1.134	0.980	28.700	34.870	4.518	0.300	0.032	0.584	3.068
SD	0.518	0.371	0.405	0.277	0.226	0.188	0.064	0.809	2.759
CV	45.68	37.86	1.41	0.79	5.00	62.67	200.00	138.53	89.93
ANCHOR STATIONS									
1. KASARAGOD : a) DAY									
$\bar{X}$	4.291	0.615	28.730	34.260	5.125	0.464	0.052	0.651	3.305
SD	4.593	0.419	0.989	0.811	0.553	0.335	0.149	1.211	0.360
CV	107.38	68.13	3.44	2.37	10.79	72.20	286.54	186.03	10.89
b) NIGHT									
$\bar{X}$	2.996	0.762	29.350	33.450	4.824	0.214	0.304	0.200	0.196
SD	4.426	0.280	0.608	0.762	0.218	0.307	0.279	0.213	0.104
CV	147.73	36.75	2.07	2.28	4.52	143.46	91.78	106.50	53.06
2. CANNANORE : a) DAY									
$\bar{X}$	22.490	0.818	29.40	33.18	5.177	0.351	0.016	0.454	6.957
SD	22.01	0.412	0.745	1.574	0.455	0.214	0.048	0.269	5.730
CV	97.86	50.37	2.53	4.75	8.79	60.97	300.00	57.97	82.36

Table 1. Contd.

b) NIGHT									
X̄	10.300	0.773	29.720	33.710	5.107	23.860	0.271	0.416	6.047
SD	48.86	0.585	0.732	1.260	0.257	0.127	0.044	0.243	8.186
CV	144.27	75.68	2.46	3.74	5.03	0.53	16.23	58.41	135.37
3. CALICUT : a) DAY									
X̄	4.118	1.169	29.69	32.570	4.447	0.271	0.032	0.779	4.959
SD	2.527	1.668	0.507	1.891	0.381	0.303	0.064	0.999	4.623
CV	60.20	143.169	1.71	5.81	8.57	111.81	200.00	128.20	93.22
b) NIGHT									
X̄	2.815	1.765	29.22	32.34	4.441	34.25	0.00	1.013	2.420
SD	2.005	1.808	0.472	2.626	0.337	0.335	0.00	1.340	3.617
CV	71.23	102.44	1.63	8.12	7.59	0.98		132.28	149.46
4. COCHIN : a) DAY									
X̄	1.561	1.788	29.16	33.74	5.614	0.185	0.156	0.457	3.691
SD	0.696	2.253	0.465	1.604	0.515	0.082	0.238	0.517	4.168
CV	44.59	126.01	1.59	4.75	9.17	44.32	152.56	113.13	112.92
b) NIGHT									
X̄	1.174	0.986	28.96	34.58	5.543	0.213	0.00	0.534	4.149
SD	0.383	1.231	0.333	0.529	0.283	0.071	0.00	0.612	3.682
CV	32.62	124.85	1.15	1.53	5.11	33.33	—	114.65	88.74
5. QUILON : a) DAY									
X̄	1.954	1.103	28.66	34.63	5.596	0.187	0.063	0.387	6.187
SD	1.275	1.055	0.526	0.573	0.316	0.131	0.164	0.382	6.842
CV	65.25	95.65	1.84	1.65	5.65	70.05	260.32	98.71	110.59
b) NIGHT									
X̄	1.727	0.600	28.40	34.80	5.339	0.219	0.00	0.713	4.046
SD	1.086	0.492	0.340	0.282	0.284	0.149	0.00	0.454	4.434
CV	62.88	82.00	1.20	0.81	5.32	68.04	—	63.67	109.59
6. VIZHINJAM : a) DAY									
X̄	0.288	1.167	29.250	35.450	4.512	0.397	0.195	1.040	0.162
SD	0.149	1.018	0.126	0.063	0.244	0.121	0.209	0.531	0.030
CV	51.33	87.23	0.43	0.17	5.41	30.48	107.18	51.06	88.52

Table 1. Contd.

b) NIGHT									
$\bar{X}$	0.227	1.403	29.22	35.28	4.247	0.330	0.490	2.060	0.227
SD	0.005	1.180	0.023	0.133	0.103	0.053	0.078	0.071	0.040
CV	20.70	84.11	0.08	0.38	2.43	16.06	15.92	3.44	17.62
7. CAPE COMORIN : a) DAY									
$\bar{X}$	1.407	0.357	29.10	34.70	4.392	0.512	0.00	0.497	5.478
SD	0.126	0.211	0.100	0.251	0.206	0.149	0.00	0.215	3.679
CV	8.95	59.11	0.34	0.72	4.69	29.10	—	45.26	67.16
b) NIGHT									
$\bar{X}$	1.550	0.423	28.53	34.76	4.557	0.387	0.00	0.16	6.123
SD	0.120	0.239	0.206	0.035	0.098	0.180	0.00	0.057	2.760
CV	7.74	55.16	0.72	0.10	2.15	46.51	—	35.63	45.19

highest near Quilon. The values during night were low ranging between 0.02 and 1.99mg/m^3, minimum being near Cape Comorin and maximum near Quilon. The day and night Chl 'a' concentration of the offshore region varied from 0.27 to 2.01 mg/m^3 and 0.05 to 6.5 mg/m^3 respectively. The particulate organic carbon of the nearshore region ranged between 0 and 6.60 mg/m^3 and 0.22 and 4.14 mg/m^3 during day and night respectively. High POC values were recorded near Cochin, Quilon and Vizhinjam and low values at Kasaragod and Calicut. In the offshore region, the values ranged from 0.11 to 6.6 mg/1 during day and 0.22 to 4.15 mg/1 during night. The mean Chl 'a' values for the 9 observations of the anchor stations ranged between 0.3 and 1.76 mg/m^3 during day and 0.21 to 1.48 mg/m^3 during night. From Kasaragod to Quilon Chl 'a' content was almost the same except a high value at Quilon (3.32 mg/m^3) and from Vizhinjam to Cape Comorin low chl 'a' <1 mg/m^3 was noticed. POC was low at Kasaragod and Calicut and high at Cochin.

During october 1988, chl 'a' of the nearshore region ranged between 0.17 and 66.65 mg/m^3 during day and 0.88 to 10.99 mg/m^3 during night, both at Calicut. In the offshore region the values ranged between 0.21 and 3.51 mg/m^3 during day and between 0.32 and 2.18 mg/m^3 during night. POC in the nearshore ranged between 0.12 and 1.81 mg/1 during day and between 0.24 and 1.89 mg/l during night and in the offshore it ranged between 0.22 and 1.64 mg/l during day and 0.28 to 3.84 mg/l during night. The average chl 'a' value for the anchor stations ranged between 1.33 and 36.44 mg/m^3 during day and 0.95 and 22.26 mg/m^3 during night. The peak value of both were observed at Calicut and lowest value at Quilon. Comparatively high values were noticed at Kasaragod, Cochin and Vizhinjam irrespective of time. Cannanore and Quilon showed low levels of pigment concentration. Mean POC values were almost low at all anchor stations, the peak value 2.77 mg/l being at Vizhinjam (Table 1). Based upon the combined data, it was observed that mean chl 'a' ranged between

TABLE 2. Relative importance of parameters in the box model

Parameters	Offshore		Nearshore		Kasaragod		Cannanore		Calicut		Cochin		Quilon		Vizhinjam		Cape Comorin	
	Day	Night	Day	Night	Day	Night	Day	Night	Day	Night	Day	Night	Day	Night	Day	Night	Day	Night
Temperature	1.37	1.15	2.40	0.03	0.61	0.29	1.11	1.61	2.19	166.88	0.55	0.01	0.68	0.44	0.05	0.01	0.17	0.31
Salinity	0.47	0.18	0.10	0.06	0.36	0.04	4.35	0.17	0.26	798.99	0.17	0.24	0.23	0.38	0.03	0.18	0.32	0.11
D.O.	0.15	0.77	0.04	0.32	0.67	0.02	3.92	2.22	2.29	65.52	1.33	0.64	0.90	0.25	0.53	1.27	1.68	2.52
PO_4-P	1.07	3.08	0.25	0.30	0.36	0.58	0.89	3.89	43.83	11.12	0.08	1.06	1.86	0.91	4.61	1.62	1.68	29.37
NO_2-N	2.80	0.22	0.35	4.31	0.13	0.10	8.26	1.34	1.00	0.00	0.56	0.00	2.22	0.00	2.70	8.89	0.00	0.00
NO_3-N	3.15	1.80	2.17	1.65	0.08	0.36	9.51	2.64	1.03	415.64	0.63	0.95	0.90	0.50	4.61	5.42	0.63	26.39
SiO_4-Si	0.80	0.76	0.06	2.90	0.38	0.35	17.16	4.93	0.10	61.92	1.50	1.33	0.35	0.01	3.64	39.55	0.07	16.82
POC	0.63	0.36	0.15	0.14	0.18	0.28	4.11	11.98	0.47	198.70	0.88	1.78	0.94	0.55	10.02	28.40	1.91	17.78

0.23 (Vizhinjam, day) to 22.490 (Cannanore, day) with c.v.(%) ranging between 7.74 (Cape Comorin, night) to 147.73 (Kasaragod, night), Higher variations for all parameters were observed for night collections taken from offshore and nearshore stations whereas for the day collections taken from anchor stations. NO_2-N is the parameter with the maximum variations (Table 1). Also in the offshore region, the set of parameters, (temperature, silicate, (.763)), (NO_2-N, NO_3-N, (.999)) were highly associated during day and (salinity, silicate, (-.803)) and (chl 'a', POC, (.904)) were significantly correlated during night. In the nearshore region, during day, (POC, Chl 'a', (-.528)), (salinity, POC, (-.594)), (POC, PO_4, (.580)) and (POC,Temp, (-.596)) which are highly correlated while *r* of (Chl 'a', temp., (-,967)), (DO, NO_2-N, -.926)), (DO, salinity, (-.893)) and (NO_2-N, NO_3-N, (.974)) during night were also high. In the nearshore anchor stations, intraparameter relationships were all highly significant except at Calicut and Vizhinjam during day and at Cape Comorin during night (Table 5).

The box model fitted to the normalised data of chl 'a' and other parameters showed that silicate was the relatively most important factor (being the factor with the highest value or the next highest value for partial regression coefficient), in controlling the total chl 'a' concentration, the primary production at anchor stations Quilon, Calicut and Cape Comorin and at other non anchor nearshore stations during night.

Nutrients were also found to be contributing substantially in controlling the distribution of chl 'a' in the offshore, nearshore and at the anchor stations viz. Calicut, Cape Comorin and Cannanore during day. Similarly nutrients play a prominent role in limiting chl 'a' distribution in the nearshore stations and anchor stations, namely Kasaragod, Calicut, Cape Comorin and Cannanore during night. This implies that availability of several elements particularly nutrients, control phytoplankton production at different oceanic locations whereas nonavailabilty generally limited primary production in coastal environments. The prominency of NO_3-N in Chl 'a' distribution implies that it is used in the formation of phytoplankton biomass on a global ocean basis. It has been observed that the physical process that control NO_3-N supply to the euphotic zone also controls the magnitude of primary production. The functional relation between phytoplankton and NO_3-N is however the result of the processes that occur to the food chain after NO_3-N has been introduced into the euphotic zone and it is evident at all trophic levels of the marine ecosystems. The high negative correlation between chl 'a' and DO during day at Cochin indicates high respiratory demands for oxygen by the biota (Yakobi, *et.al.,* 1993) (Table 2).

Gaylor and Hopper conditions were tested to apply Satterthwaites approximation when the sample sizes are unequal. It showed that chl 'a' distribution is significantly different between offshore, nearshore and anchor stations with more or less same form of distribution during day and night. But in the case of POC, day and nigh difference was high irrespective of the region. Temperature, salinity, DO PO_4-P, NO_3-N and silicate distribution varied between regions irrespective of the time of collection whereas NO_2-N concentration was almost same at all regions, being more during day than night (Table 6).

The non-parametric Kruskall-wallis test showed that chl 'a', salinity, POC, temperature, DO and silicate distribution are more or less in the same pattern throughout the investigation whereas the nutrients differed between day and night, irrespective of the shore type (Table 3.)

The disparity in the distribution pattern obtained by parametric and non-parametric analysis reveals that the assumption of normal distribution and additivity property for treatment effect is satisfied only for the parameters temperature, chl 'a', salinity (except nearshore), DO and silicate while for nutrients such as PO_4-P and NO_3-N and for POC, the observed data is to be subjected to Tukeys test of additivity to satisfy the additivity property by suitable transformations for treatment effects in nested two way ANOVA.

TABLE 3. Difference between day and night by Kruskal-wallis test H' corrected for ties

Parameters	Offshore	Nearshore	Kasaragod	Cannanore	Calicut	Cochin	Quilon	Vizhinjam	Cape Comorin
Chlorophyll	0.0134	0.0981	0.6746	1.6095	0.7103	1.7245	0.2400	2.4202	2.0336
POC	0.6598	1.2666	0.9747	0.2384	0.0494	0.1668	1.3039	0.1513	0.0678
Temperature	0.2158	2.8716	1.4021	0.7753	1.5022	0.6665	1.0453	0.0678	0.8235
Salinity	0.2756	-7.7590	3.0067	0.0858	-0.5716	0.5245	0.3760	2.8403	0.0000
D.O.	0.6831	0.5614	0.4771	0.1172	0.0178	2.9075	3.2267	2.4000	2.0167
PO_4-P	0.4281	0.2439	2.6536	1.0552	-0.5994	0.4040	0.3760	0.4274	1.0756
NO_2-N	0.7941	0.1329	2.9026	-4.8020	1.7000	4.0300	1.9000	3.3793	0.0000
NO_3-N	2.2364	2.5350	1.5261	10.4500	0.3342	-8.6073	1.8182	5.4454	3.2667
SiO-Si	0.2736	0.8769	2.6508	0.7724	2.0211	0.2053	0.1068	3.8136	0.0000

Based on the informations gathered from Kruskal-wallis test, day and night data were combined for temperature, chl 'a', salinity, DO and silicate to test the difference between the regions using the same test and for the rest of the parameters day and night data were treated seperately. The test showed that in the case of POC and silicate, difference between the regions was within the significance limit (Table 4). The result based on non-parametric test is to be considered because, it is better to use the distribution-free test when transformation is required.

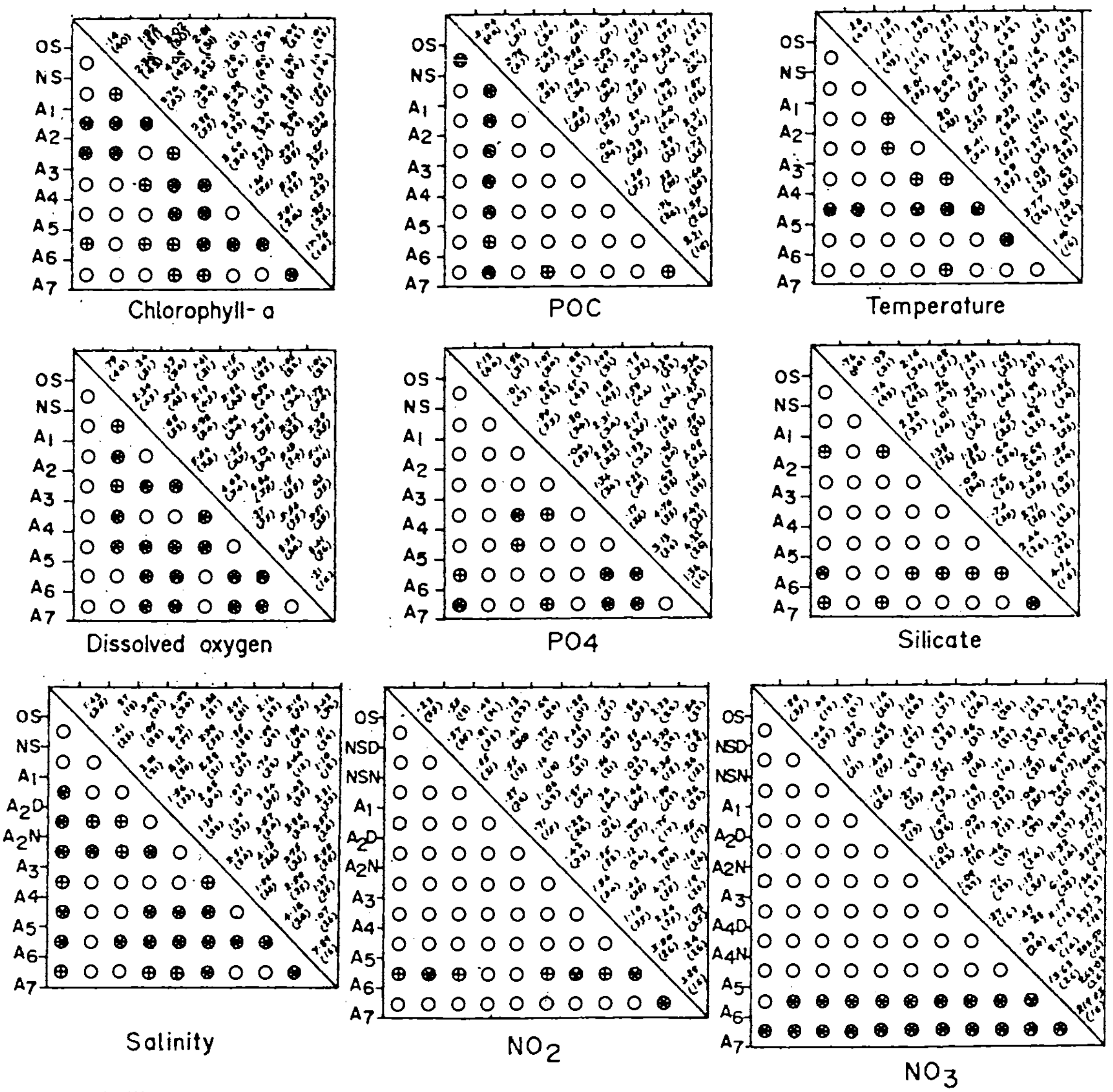

FIG. 1. Trellis diagram showing the similarity between offshore, nearshore and anchor stations with respect to (a) chl 'a' (b) POC, (c) temperature, (d) salinity, (e) dissolved oxygen, (f) PO_4-P (g) NO_2-N, (h) NO_3-N and (i) SiO_4-Si, O-'t' Not significant, ⊕ 't' significant at 5% level, ⊕ 't' significant at 1% level.

Multiple range test was applied based on the results of the nested two way ANOVA and similarity index in terms of student's range statistic, 't' is presented in the form of a Trellis diagram. High similarity was observed at all regions except Trivandrum for NO_2-N, Cape Comorin and Cannanore for NO_3-N and Calicut for POC with respect to their concentrations (Fig. 1).

TABLE 4. Kruskal-wallis test statistic (H^+) for significance of the difference between the shore types

Parameters	H^+	N	Remarks
Chlorophyll 'a'	44.914	9	*
POC	13.422	9	—
Temperature	28.569	9	*
Salinity	61.078	10	*
D.O.	80.917	9	*
PO_4-P	17.904	9	*
NO_2-N	19.106	11	*
NO_3-N	22.776	12	*
SiO_4-Si	14.937	9	—

* — Calculated H^+ is significant at 5% level, $P < 0.05$

From the relation between chl 'a' and salinity at different size fractions and total, it was observed that total chl 'a' ranged between 0 and 10 mg/m^3, lowest values were recorded at salinities ranging between 34 and 35 ppt, nearly 18.54% of the samples, mostly that collected from Cannanore and Calicut fall in the lowest range of chl 'a' (<1 mg/m^3) and salinity the range 29 to 33.9 ppt. In the 60 μm size fraction, chl 'a' ranged between 0 and 3.5 mg/m^3 and salinity ranged from 31.6 to 35.5 ppt. Most of the values were between 34 and 35.6 ppt of salinity. In the size fraction 20 μm, chl 'a' ranged between 0 to 3 mg/m^3 and salinity between 34.4 to 35.6 ppt. For total and 60 μm, a negative relationship of high gradient with salinity while for the 20 μm size fraction, a positive relation of low gradient with salinity was observed.

The size fraction of chl 'a' when plotted with respect to DO, observed ranges for chl 'a' were 0-5, 0-2.5, 0-3 mg/m^3 which vary with DO in the ranges 3.75 to 6, 4.1 to 6 and 4.1 to 5 ml/1 with inverse relation but prominent only in the lowest size fraction. Silicate-chl 'a' relation showed 3 narrowing ranges viz; 0 to 5, 0 to 2 and 0 to 1mg/m^3 for chl 'a' and 0 to 15, 0 to 6 and 0 to 8 for silicate concentration for total, 60 μm and 20 μm size fractions respectively. However the relationship between the two, in the lowest range of silicate (0 to 1), was not significant and it constituted about 22% of the samples. Only in the range of 1 to 10 μg at/l for silicate, inverse relation was observed. Inverse relation was also observed between chl 'a' and nitrite + nitrate, and chl 'a' and phosphate with high values of chl 'a' falling in the lower range 0-2 of $NO_2 + NO_3$ and in 0 to 0.5 of phosphate. The ranges for chl 'a' were 0 to 5, 0 to 3.5 and 0 to 3 in the case in $NO_2 + NO_3$ relation and 0 to 8, 0 to 3.3 and 0 to 3 in the case of phosphate for total, 60 μm and 20 μm size fractions respectively.

The positive relationship of chl 'a' with salinity observed in 20 μm size fraction is likely to reflect the obligate regress for high amounts of ions (Waturburry *et. al.* 1986). Phyco erythrin containing *Synechococcus* spp. in agreement with this observation. But the negative relationship of chl 'a' with salinity observed for total water sample and 60 μm size fraction as against the positive relation in 20 μm size fraction suggests that these discrepancies could be a reflection of strain specific variation in salinity tolerance. It was also observed that small size phytoplankton rarely attain concentration of bloom level (> 10 mg chl 'a' /m^3) ; ie; concentration is more tightly controlled and less frequently subjected to larger variations and it can be suggested that it is mainly the variations in the abundance of the larger phytoplankton that determine the size structure of phytoplankton communities.

The major changes in chl 'a' content are associated with varying nutrient levels in the euphotic zone and appears to be necessary adaptation to provide these slowly growing population at low nutrient concentration. High chlorophyll 'a' content at surface water and a

TABLE 5. Significant correlation between parameters

DAY	NIGHT
Anchor Station 1 (Kasaragod) (C, DO) = .616 (T,Si) = .724 (S, P) = .651 (S,Si) = .559 (T.P) = -.639 (S,DO) = .580 (S,NO_2) = -.617 (P,Si) = .693	(C,T) = -.943 (C,P) = .980 (C,Si) = -.947 (P,NO_3) = .967 (S,Si) = -.976 (P,Si) = -.909
Anchor Station 2 (Cannanore) (C,Si) = .743 (S,Si) = .930	(C,Si) = .929 (P,Si) = .863
Anchor Station 3 (Calicut) (C,Si) = -.707 (T,D.O) = .701 (S,NO_3) = -.684 (P,NO_3) = .905 (C,DO) = -.700 (S.P) = -.735 (Si,DO) = -.651	(C,S) = .717 (C,NO_2) = -.770 (P,NO_2) = .737 (S,NO_2) = -.953 (P,NO_3) = .750 (C,P) = -.771 (P,POC) = .738 (S,P) = -.954 (S,NO_3) = -.874 (POC,S) = -.773
Anchor Station 4 (Cochin) (S,DO) = .620 (S,NO_3) = -.819 (Si,DO) = .707 (P,NO_2) = .620 (DO,NO_3) = -.632 (NO_3 Si) = -.617	(C,POC) = .868 (POC,DO) = -.866 (T,P) = -755 (T,Si) = -.821 (P,NO_2) = .894 (NO_2 NO_3) = .876 (POC,S) = -.772 (T,DO) = .841 (T,NO_2) = -.755 (Si,DO) = .894 (Si,P^2) = .876 (Si,NO_2) = .876
Anchor Station 5 (Quilon) (Si,DO) = .632 (NO_2. NO_3) = .727	(T,NO_3) = -.766 (S,DO) = .680 (DO,NO_2) = -.946 (T,Si) = -.749 (DO,P) = -.946 (Si, NO_3) = .876
Anchor station 6 (Vizhinjam) (POC,Si) = .842 (DO,S) = .940 (S,Si) = -.838 (T,NO_2) = -.879 (S,NO_2) = -.862(DO,NO_2) = -.914	(POC,Si) = -.998 (P,NO_2) = .999
Anchor station 7 (Cape Comorin) (S,DO) = -.842 (S,NO_2) = -.935 (P,Si) = .951 (Si,NO_2) = .951 (S,PO_4) = -.935 (S,Si) = -.925 (NO_2,NO_3) = .951	(C,T) .998 (Si,DO) = -.998 (P,NO_2) = -.998

decreasing tendency towards offshore as noticed in the present study was also reported by Radhakrishna *et. al.* (1977). They also could not observe any relation between POC and chl 'a'. The coastal and nearshore waters of westcoast of India are enriched by heavy rainfall and land runoff from June to September every year (Bhargava *et. al.* 1978). Devassy (1983) noticed high concentration of chl 'a' (10.2 mg/m^3) at the surface during October and November in the southwest coast of India. Bhargava *et. al.* (1978) reported an average chl 'a' value of 6.44 mg/m^3 and 10.6 mg/m^3 during October and December respectively, when the concentration of nutrients were also high along this coast. Balachandran *et. al.* (1989) reported high values (8 mg/m^3) during October 1987 and 1988 in the inshore waters of Cochin. They stated that the variation in the observed values during 1987 and 1988 can be attributed to the intensity of freshwater discharge. The spatial gradients in the chl 'a' and POC exhibited appreciable difference in the nearshore and offshore region. This difference in the distribution can be taken as due to the variations in depth, currents prevailing in the area, sinking of water masses and other oceanic phenomena such as convergence and divergence as stated by earlier workers (Bhattathiri and Devassy 1977). Krey (1976) opined that variability in temporal distribution and heterogeneity in spatial distribution which are naturally inherent in oceanic biological parameters make comparison of data rather troublesome.

TABLE 6. Showing the significance of the difference between shore type and between day and night using 2 way ANOVA for unequal number of samples.

Parameters		Shore type		Day and night	
		F.value	d.f.	F. value	d.f.
Chlorophyll 'a'	(a)	8.0388*	(8,132)	1.1326	(9,132)
	(b)	7.8068*	(14,6)		
POC	(a)	3.8746*	(8,132)	3.0756*	(9,132)
	(b)	3.3056	(14,7)		
Temperature	(a)	2.3893*	(8,132)	1.7589	(9,132)
	(b)	2.1533	(14,7)		
Salinity	(a)	10.1250*	(8,132)	0.6424	(9,132)
	(b)	11.7908*	(8,4)		
D.O.	(a)	23.4512*	(8,132)	0.7771	(9,132)
	(b)	25.2920*	(8,5)		
PO_4-P	(a)	3.0731*	(8,132)	0.4968	(9,132)
	(b)	4.1368	(8,3)		
NO_2-N	(a)	1.4395	(8,132)	2.5176	(9,132)
	(b)	1.2485	(8,7)		
NO_3-N	(a)	2.4246*	(8,132)	0.7416	(9,132)
	(b)	2.6591	(8,5)		
SiO_4-Si	(a)	4.5855*	(8,132)		
	(b)	6.5916	(8,3)		

(a) — Actual F ratio for groups considered under shore type.
(b) — F ratio on applying Satterthwaites approximation.

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Hydrochemical Studies Along the Coastal Waters off Mangalore

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ABSTRACT

Environmental parameters such as temperature, salinity, dissolved oxygen, BOD_5, pH, nutrients, suspended load and chlorophyll 'a' were estimated in the coastal waters of Mangalore. Four transects, each consisting of four stations extending from old Mangalore port to Surathkal were monitored biomonthly and different parameters were compared seasonwise. Inorganic phosphate values registered high values at all the transects during September, with a maximum of 2.24 umol/l. Nitrite was found to be absent except during January. Low bottom values of dissolved oxygen with corresponding high inorganic phosphate were indicative of monsoonal upwelling along the Mangalore coast during September. This period was characterised by a drop in pH values, though not very significant. Low BOD values encountered indicated the absence of any organic pollution in the area.

Key words : Coastal waters, Nutrients.

Introduction

The nutrients determine the potential fertility of the water masses and therefore, it is important to understand their distribution and behaviour in different geographical locations and seasons. Some information on the spatial and seasonal distribution of nutrients is available in different estuarine and coastal environments of India. The earlier reports on the physico-chemical characteristics of the coastal waters of Mangalore are that of (Suresh *et al.*, 1978 and Rivonkar *et al.*, 1990). It is considered worthwhile to study the changes in the environmental parameters in the coastal waters of Mangalore, especially as the coastal belt is getting industrialised and this region supports a good fishery both pelagic and demersal. In the present investigation, spatial and temporal variations of different environmental parameters in the region between old Mangalore port and Suratkal are reported.

Materials and Methods

The study area covering coastal stretch of about 20 km is shown in Fig. 1. The area of investigation and station locations are shown in Fig. 1. Four transects were selected between old Mangalore Port and Suratkal at equidistant points. With four stations at 5,10, 15 and 20 meters depth. Surface, mid and near bottom water samples were collected from 16 stations for a year during rough monsoon months. Surface samples were collected using a clean plastic bucket and subsurface samples using Niskin water sampler. Bucket thermometer and reversing thermometers were used to measure the surface and subsurface temperatures respectively. In suit pH determinations done with a portable digital pH meter (Philips 9046). The nitrite, nitrate, phosphate and silicate were done as of (Grasshoff 1983) and dissolved oxygen, BOD_5 and Chlorophyll 'a' were estimated as in (Strickland and Parsons 1972). Known volume of samples for Chlorophyll 'a' were filtered through a GF/C filter paper at the shore laboratory and the filter papers were kept in the deep freezer until analysis.

Results and Discussion

The monthly means of the chemical parameters for each transect are shown in figures 2 and 3.

Water temperatures were high during March.

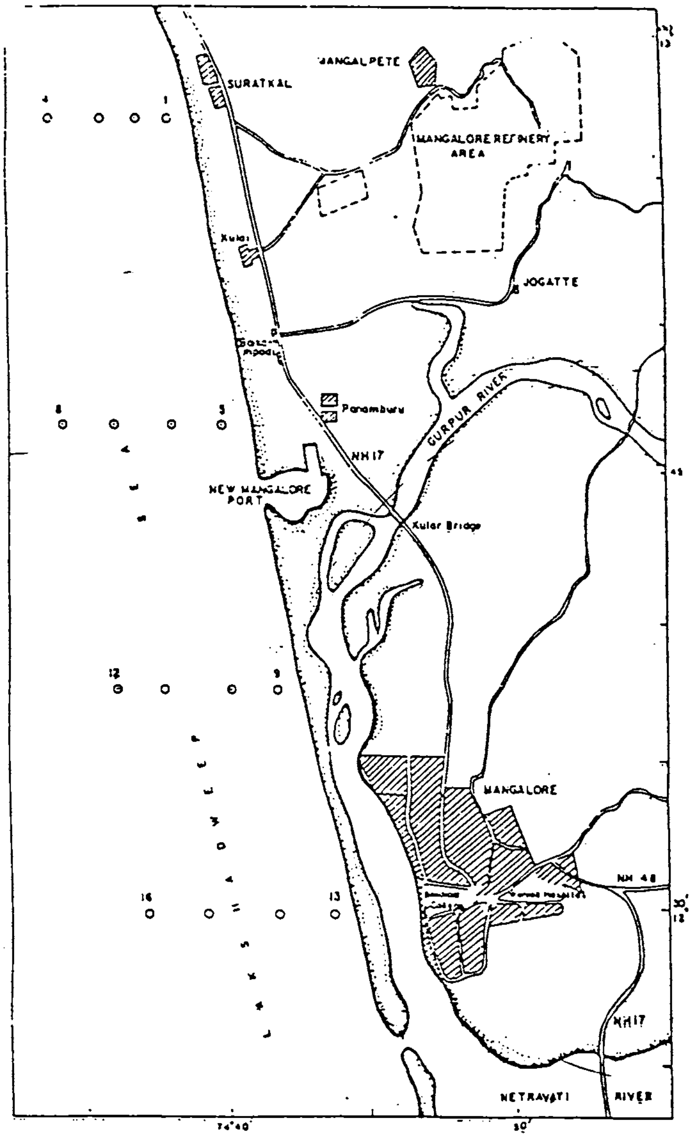

Fig. 1.

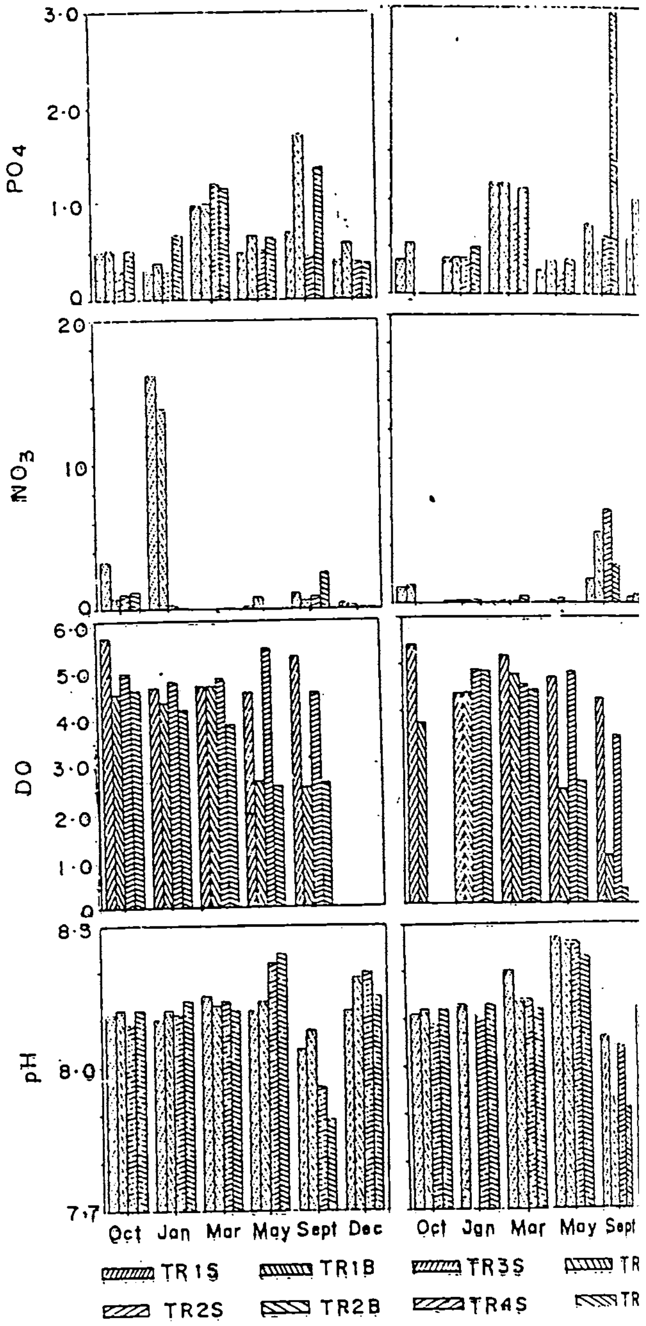

Fig. 2.

Surface temperatures ranged from 29.0° C to 31.2°C during this period and those at the bottom from 28.8 to 30.6°C. Relatively cooler conditions prevailed during the remaining period at all the transects. Lower temperatures were recorded during September (26 to 27°C for surface samples and 26.0 to 28.4°C for bottom samples).

Salinity values were found to vary in a narrow range at all the transects, surface values ranged from 27.02 × 10^{-3} (September, off old Mangalore port) to 34.8 × 10^{-3} (May, off Surathkal). The values at the bottom varied between 32.94 × 10^{-3} (September, off Suratkal) and 36.32 × 10^{-3} (October, off old Mangalore Port). Vertical gradient was either absent or small at all the transects which could be largely the result of strong turbulence favoured by the near shore geometry.

Maximum values of dissolved oxygen (DO) were recorded during premonsoon months (months) (4.79-5.12 ml/l) along all the transects. Generally surface waters were found to be well oxygenated. Very low levels of DO (0.31 to 1.00 ml/l) were recorded for bottom waters during the months of May and September. More pronounced reduction in DO content was noticed during September at transects 3 and 4.

pH values for the surface and bottom waters remained more or less same along all the transects. Comparatively low values of pH (7.9-8.27) observed

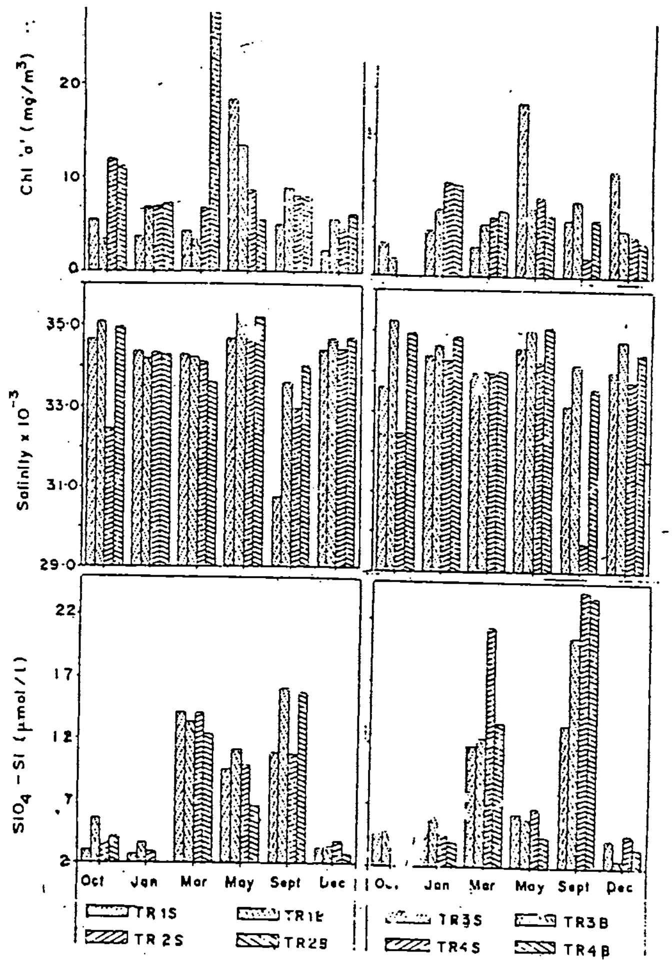

Fig. 3.

during September may perhaps be due to the dilution of the waters by the monsoonal discharge.

High values of phosphate (1.73-2.95 μmol/l at transects 4) were noticed during September at all stations. Minimum values (0.23-0.59 umol/l) were observed during post monsoon months (October, December and January). Higher concentrations were found to be associated with bottom waters at all transects. This may be due to the lesser uptake of this nutrient. The high values of inorganic phosphate at all the four transects were conspicuous during September. The oxygen depleted water column with high nutrient content is indicative of the occurrence of upwelled waters along the coast during this period. Seasonal changes in hydrographic parameters due to upwelling were prevalent in this region from May to September. Sastri and D' Souza (1972) observed that cyclonic circulations prevailed in this region during this period which can induce coastal upwelling. They concluded that from June to September this region is subjected to direct wind mixing and indirect effect of wind induced circulation, which probably brings the cold subsurface waters to the surface.

TABLE 1

Ranges of mean values of BOD_5 and suspended solids along the four transects

		BOD_5 mg/l	Suspended solids mg/l
Transect	1	S 0.11 - 2.88	17 - 238
		B 0.62 - 3.09	36 - 290
Transect	2	S 0.68 - 3.88	8 - 189
		B 0.34 - 2.15	13 - 176
Transect	3	S 0.94 - 3.32	14 - 241
		B 0.17 - 2.03	2 - 255
Transect	4	S 0.49 - 3.20	8 - 255
		B 0.31 - 1.95	13 - 233

Nitrate-N showed the fluctuation between surface and bottom waters. Nitrate remained low, but for a few exceptions. Nitrites were found to be practically nil at all the transects except during January, which could be treated as an exception. Seasonal changes in nitrate concentrations suggest that the availability of this nutrient is adequate to meet the required demand for primary production.

An inverse relation of silicate for surface waters with salinity during September was observed. Generally, during this period, silicate levels in surface water increased (5-254 umol/l). The erosion of loose solid strata from the catchment areas may be bringing in high silicate to the water column. A vertical gradient could be noticed only in September. Similar observations have been reported in this area by Rivonker *et al* ., (1990). Bottom waters during that time originated from deeper layers and permeated the area.

The BOD_5 values were below 3 mg/l along all the transects during most of the observation which indicated the absence of organic pollution in this area of study. High values noticed in September could be attributed to the extraneous input from land runoff (Table 1).

Monthly pattern of Chlorophyll 'a' distribution was found to be more or less the opposite of those of nitrate and phosphate suggesting that the seasonal reduction of these inorganic nutrients could be due to assimilation by phytoplankton.

The suspended solids ranged from 8 to 255 mg/l at the surface and from 8 to 290 mg/l at the bottom (Table 1). The higher suspended load was associated with the bottom water. The prevailing physical climate seems to control the quantum of suspended sediment by activating resuspension and settling cycles in time.

The various environmental parameters along the four transects between old Mangalore port and Suratkal encountered very little variations between each transects except along transect 4 during September, which could be the result of the fresh water discharge through the two rivers. During this period, comparatively higher values of phosphate, nitrate and silicate were encountered along transect 4 which could be due to the influence of the river Nethravati which opens to the sea closer to transect 4. The water remained well mixed due to turbulent mixing in this shallow coastal zone and thus the stability of the water column is maintained. The assessment of the impact of release of waste water on the marine environment becomes easier and reliable if baseline water quality is known against which the existing conditions can be compared.

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Short Communications

Residual fluxes and suspended sediment transport in the lower reaches of Muvattupuzha river, southwest coast of India

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Spatial and seasonal variation of different physical processes governing the transport of salt and sediment of the Muvattupuzha river are discussed. Salt and suspended sediment due to tidal pumping was directed upstream, salt transport due to vertical shear was upstream irrespective of seasons. Suspended sediment concentration was higher during flood tide.

Knowledge of the fluxes of suspended sediment, salt and water are important to understand the dynamics of the estuarine system[1]. In the present study, an attempt has been made to estimate and compare various dispersion mechanisms such as residual fluxes of water, Stokes drift and vertical shear in the tidal and residual current at 4 stations in the lower reaches of the Muvattupuzha river, under varying dilution intensities. Emphasis has been given to study intra-tidal variation of suspended sediment concentration with concurrent salinity and current observation.

The study area (Fig. 1) is characterised by the presence of the two large basins of the Periyar and Muvattupuzha rivers. The Muvattupuzha river empties into the Cochin backwaters, which is subjected to the tidal effects through the Cochin barmouth. Average depth of the study area is 5.5 m. Width of the cross section—I is 633 m and that of section-II is 1012 m. Tides in the region of study being- semidiurnal, synoptic field measurements for 13 h were made at 4 stations during May and August 1990, which respectively represent the low and high fresh water discharge period (data from Central Water Commission, Cochin). Measurement include vertical profiles of current speed, direction, salinity and suspended sediment concentration. Vertical profiles of current speed and direction were made using indigenous rotor current meter (accuracy for velocity $\pm 2\,\mathrm{cm.s^{-1}}$ and direction ± 2.68°, designed at NIO, Goa, India). Vertical profiles of salinity is accomplished by Beckman salinometer (accuracy 0.01×10^{-3}). Water level at the observation site was recorded using a graduated tide pole, suspended sediment concentration at surface, mid depth and bottom were determined by vacuum filtration of water samples through pre-weighed 0.45 µm millipore filter paper[2]. Cubic splines[3,4] were used to interpolate data at fixed fraction of the non-dimensional depth ($\eta = 0$ at the surface and $\eta = 1$ at bottom.

Basic properties of the stations are given in Table 1. Tide averaged depth was higher during August 1990 at all stations by an amount < 50 cm. Appreciable salinity gradient of $< 3 \times 10^{-3}$ was observed in the upstream direction. Vertical salinity gradient of 5 to 8 $\times 10^{-3}$ was observed during May at all stations.

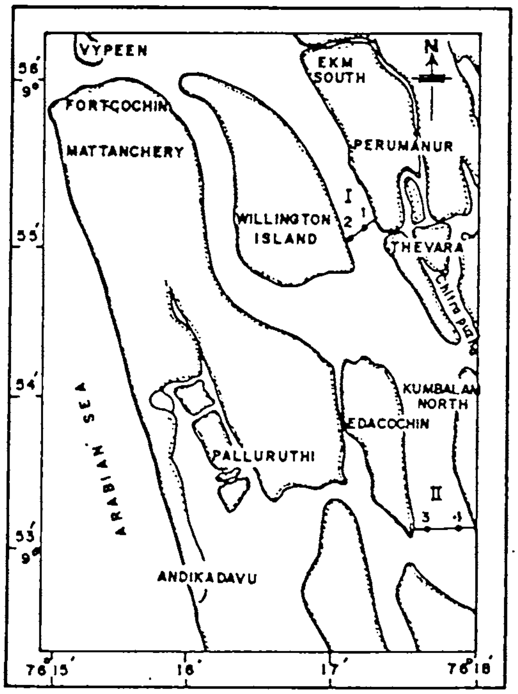

Fig. 1—Study area with location of stations

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Longitudinal salinity gradient did not exhibit seasonal fluctuation as it depends both on the tide and the river discharge. Higher vertical salinity gradient at section-I could be attributed to the influx of Chitrapuzha river which joins the system 1 km upstream of this section. Tide-depth average suspended sediment (Table 1) concentration did not vary much between May and August.

Residual flux of water—A summary of the observed residual fluxes of water is given in Table 2. Negative sign shows that transport is directed upstream and positive sign indicates the downstream transport. Eulerian residual flow (u_E, Table 2) was upstream at all stations during May and changes its direction towards downstream in August. Direction of the Stokes drift (u_S, Table 2) was upstream irrespective of the season. Stokes drift arises because of the partially progressive nature of the tide, resulting from the frictional dissipation of tidal energy in the estuary. Langrangian residual flow which is the sum of residual current and stokes drift follows the direction of the residual flow as the magnitude of Stokes drift was very low.

Residual fluxes of salt—Values of the observed fluxes of salt computed are given in Table 2. Residual transport salt due to residual discharge of water (F_L) was upstream during May and downstream during August. Generally the salt transport due to tidal pumping (F_{Tp}) was directed upstream. Magnitude of Stokes drift was higher at section-I due to the strong tidal infleunce available there, since its close proximity to the barmouth. Large transverse variation in F_{Tp} was observed in section-I. This indicates the predominant flood channel in the eastern flank of the estuary. Residual transport of salt due to vertical shear was directed upstream irrespective of the season. Net salt transport was upstream during May and August though the magnitude was less in August. Fischer[5] accredited this net upstream transport even during high freshets to the transverse shear.

Table 1—Basic properties of stations

St No.	H (m)	S ($\times 10^{-3}$)	T (°C)	F ($mg.l^{-1}$)	S_B ($\times 10^{-3}$)	S_S ($\times 10^{-3}$)
			May 1990			
1	6.40	26.94	30.33	103.49	29.05	24.28
2	6.40	26.96	30.25	90.36	28.54	23.79
3	6.92	23.35	30.85	91.36	27.04	19.32
4	5.05	23.70	30.75	80.06	26.70	18.35
			August 1990			
1	6.73	8.60	24.68	77.00	12.70	03.40
2	6.62	5.42	24.61	60.21	06.29	02.00
3	7.24	2.30	25.96	108.88	03.49	01.20
4	5.05	2.60	26.06	83.11	03.65	01.20

H : Tide averaged depth
T : Tide-depth averaged temperature
F : Tide-depth averaged suspended sediment concentration
S = Tide-depth averaged salinity
S_B, S_S : Tide averaged salinity at bottom and surface respectively

Table 2—Axial component of residual fluxes

St. No.	u_E^*	u_S^*	u_L^*	$F_L^{\$}$	F_{TP}	$F_V^{\$}$	$F^{\$}$	G_L^+	G_{TP}^+	G_V^+	G^+
					May 1990						
1	−09.5	−2.5	−12.0	−325	−146	−09.0	−489	−1340	−1734	83	−2991
2	−12.3	−3.4	−15.7	−423	−166	−09.0	−599	−1400	−1366	61	−2707
3	−03.8	−1.6	−05.4	−188	−166	−21.0	−255	−700	−985	281	−1404
4	−01.4	−2.9	−04.3	−97	−78	−28.0	−285	−304	−285	−16	−605
					August 1990						
1	7.2	−1.2	6.0	52	−150	−2.0	96	136	−1666	166	−1364
2	4.5	−1.1	3.3	17	−34	−4.0	−21	286	106	3	395
3	2.6	−1.1	1.5	3	−32	−7.0	−36	613	133	−222	524
4	3.3	−1.2	2.1	12	10	−9.0	−31	122	−563	131	−310

Units: $* = cm.sec^{-1}$, $\$ = 10^{-3}\ cm.sec^{-1}$, $+ = mg.l^{-1}.cm.sec^{-1}$
u_E—Depth averaged Eulerian residual current
u_S—Stokes drift
u_L—Langrangial residual flow of water
F_L (G_L)—Residual transport of salt (suspended sediment) due to residual flow of water
F_{TP} (G_{Tp})—Residual ransport of salt (suspended sediment) due to tidal pumping
F_V (G_V)—Residual transport of salt (suspended sediment) due to vertical shear in the tidal and residual current
F (G)—Net transport of salt (suspended sediment)

Residual transport of suspended sediment—Residual transport of suspended sediment due to the residual discharge of water was directed upstream during May and August (Table 2). Tidal pumping of suspended sediment was directed upstream during May, probably due to resuspension of bed sediment and associated upstream transport, whereas in August tidal pumping of suspended sediment was irregular both in magnitude and direction. Suspended sediment transport by the tidal pumping was in general high at section-I, in particular at st.1. This was possibly due to the easily erodable bed material at st.1 and the presence of flood channel described earlier in the salt transport mechanism. Suspended sediment transport associated with vertical shear was downstream at section-I during May and August. At section-II, direction of the vertical shear transport was not consistent.

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