STUDIES ON BEYPORE ESTUARY: TRACE METALS DISTRIBUTION AND PHYSICO-CHEMICAL CHARACTERISTICS

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CERTIFICATE

This is to certify that this Thesis is an authentic record of research work carried out by Mr. M.N.Muraleedharan Nair under my supervision and guidance in the Centre for Earth Science Studies for Ph. D. Degree of the Cochin University of Science and Technology and no part of it has previously formed the basis for the award of any other degree in any University.

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PREFACE

Kerala located along the southwest coast of India, has 41 west flowing rivers and as many as 32 estuaries. The estuaries of Kerala sprawling along the entire coastal length play a crucial role in the socio-economic development of the state, owing to their potentialities for aquaculture, navigation, commercial fishery, recreation and tourism. Some of the estuaries in Kerala, like Vembanad lake, has been studied in detail from an environmental stand point. However, studies are meagre in many others. Beypore estuary is one such estuary, wherein systematic studies on physico-chemical aspects are sparse. This estuarine system is formed at the confluence of the third largest west flowing river, the Chaliyar. The study presented in this thesis pertain to the physico-chemical processes in Beypore estuary, sediment inputs, sources and levels of trace metals, their transport within the estuary, dispersal characteristics and fate.

The thesis comprises of Five chapters. The first chapter begins with an introduction to the problem. A brief literature review on the national and international scenario of estuarine studies in the field/subjects concerned are given. Descriptions of the study area along with climate, drainage and geology are presented. The chapter also lists the objectives of the investigation.

Hydrography and dissolved constituents of the estuary are the themes dealt in Chapter 2. Followed by an introduction and methods, results on various parameters are presented and discussed. To understand the short term temporal changes and its effects on pollutants dispersal, variation of hydrographic parameters, such as, temperature, salinity, currents, water level, etc., over a tidal cycle at a fixed station repeated monthly for one year are depicted. Similarly, hydrographic data including DO collected from 9 stations along the longitudinal section of the estuary during every month for a duration of one year are also presented. Dissolved trace metals concentration along the river profile up to the estuarine mouth forms part of the work. Attempt is made to bring out the seasonal changes in the longitudinal distribution of nutrient and pollutant concentrations in the estuary.

The nature and distribution of suspended sediments in the Beypore estuary are given in the Third chapter. Spatial and temporal aspects of suspended sediment, distribution over tidal cycles and along the estuaries course are presented. Here, apart from using suspended sediments as a natural tracer to determine the circulation, the trace metal chemistry is examined in order to infer the source and sink of metallic pollutant in the system. These are comprehensively discussed in this chapter.

Chapter Four deals with the types of bottom sediment and its chemistry. As the sediment reservoir of the estuary plays an important role to elucidate the processes occurring in the system, the granulometric and geochemical parameters of the sediments are analysed and presented. This provides a base line information pertaining to both the actual metal concentration and factors that control these concentration. The data on grain size, organic carbon, CEC, major (Al_2O_3, MgO & CaO) and trace (Cu, Ni, Zn, Rb, Li, Cd, Mn, Ba, Bi, Cr, Co, Ti, Be, Mo & Sr) element concentrations along with the results of sequential extraction to fix the contributions of various sedimentary components are integrated to understand the pathways of these metals and also the chemical status of the estuarine system from a pollution point of view.

Chapter 5 summarises the work with a view to unravel the interactive role of water and sediments, and the fundamental processes thereon. Based on the various aspects discussed in the above chapters, conclusions are synthesised.

In connection with this study, the following research papers were published.

Nair, M.N.M., Harish, C.M. and Premchand, K. 1987 Vertical suspended sediment distribution in Beypore estuary. Proc. Natl. Sem. Estuarine Management (Ed: Nair, N.B.K.): 38-43.

Premchand, K., Harish, C.M. and Nair, M.N.M. 1987 Hydrography of the Beypore estuary. Proc. Natl. Sem. Estuarine Management (Ed: Nair, N.B.K.): 44-48.

Nair, M.N.M. 1994 Residual mercury in sediments of Beypore estuary. Proc. 6th Kerala Science Congress, Thiruvananthapuram: 60-61.

Nair, M.N.M., Ramachandran, K.K and Harish, C.M. 1995 Granulometric control over the distribution of certain trace metals in the sediments of Beypore estuary, Kerala. Proc. 7th Kerala Science Congress, Palaghat: 70-72.

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CHAPTER I

INTRODUCTION

Tropical coastal regions exhibit multitudinal features. As an integral part of all coastal zones, the estuaries play a critical role in dynamically evolving adjacent land forms and nearshore geographical settings. Hydrological and ecological studies of estuaries are important as these regions are fertile and most productive ecosystems of this planet. Despite estuaries being useful to man in different ways, of late, they are being subjected to serious deterioration as a result of urbanisation, industrialisation, etc. In most cases, the delicate ecological balance of the system is upset causing alarming environmental disturbances.

Estuary comes from the Latin word `*aestus*', meaning tide. The Oxford Dictionary defines it as "*the tidal mouth of a great river where the tide meets the current*". Geomorphologists and physical geographers fix the upper limit of the estuary as the upper limit of tidal action while chemists fix it as the innermost boundary of water mixing.

Pritchard (1967) defined an estuary as "*a semi-enclosed coastal body of water which has a free connection with the open sea and within which sea water is measurably diluted with fresh water from land drainage*". This definition of estuary is widely accepted. Fairbridge (1980) in his review on the definitions of estuaries argues that the tidally affected fresh water region should be considered an integral part of any estuary. The estuaries grouped under these definitions have a salinity significantly lower than the open sea and are termed positive estuary. Negative estuaries are those where evaporation exceeds river flow plus precipitation and hyper saline condition exist. It could also be said that an estuary is a semi-enclosed arm of the sea merging with a river valley that is influenced by tides and by the mixing of fresh and saline water.

In the geological time scale, an estuary is of comparatively recent origin. There are estuaries in non-tidal seas and in some exceptional cases, there exists pseudo estuaries in non-marine environments such as in Lake Baikal. The estuary can be regarded as a dynamically evolving land form that undergoes a life cycle from valley creation, followed by a drowning phase, and ending with progressive infilling (Fairbridge,1980).

The salinity difference between river and sea water is ≃35.00 and as a result the density difference is 2%. Since the density variation caused by temperature difference is small, salinity could be used as a good indicator for estuarine mixing and water circulation. According to Dionne (1963), an estuary could be divided into 3 sectors: (a) a marine or lower estuary in free connection with open sea, (b) a middle estuary, subjected to strong salt and fresh water mixing and (c) an upper or fluvial estuary characterised by fresh water, but subjected to daily tidal action.

Estuaries are divided into three geomorphologically defined categories (1) Fjord type, (2) Bar built type and (3) Coastal plain estuary. Fjords are generally deep with relatively large volume of semi enclosed sea water below a brackish surface layer. Bar built estuaries are generally associated with depositional coasts and have characteristic bars across their mouth. The coastal plain estuary is a submerged extension of a river valley opening towards the sea. The majority of estuaries that have been studied fall in the third category, and even with in this group, large differences are seen in the circulation pattern, density stratification and mixing processes. Chemistry of estuary should be considered in the context of the physical processes of water circulation which occur in them, since the distribution of dissolved and particulate substances are controlled by the circulation and mixing of their waters (Aston, 1980). Consequently, a better classification would be the one based on the salinity distribution and flow characteristics within the estuary. The interaction between processes arising from river discharge on one hand and tidal currents on the other results in a variety of estuarine circulation patterns [Dyer, 1973; Officer, 1976 and Bowden,1980]. At one extreme is the salt wedge type estuary in which the influence of water discharge is dominant and fresh water flows out of the estuary as a surface layer above and intruding wedge of sea water. At the other extreme, when tidal currents are dominant, the water is almost completely mixed vertically and there is little variation in salinity with depth. The partially mixed type estuary is an intermediate case in which there is a gradual increase of salinity from surface to bottom with a net sea ward flow in the upper layer and upstream flow below it.

Based on mode of formation of basin, the estuaries are classified as (a) drowned river valleys, (b) fjord estuaries, (c) bar - built estuaries and (d) estuaries produced by Tectonic processes (Pritchard, 1967). Classification of estuaries based on circulation patterns is of much greater value in understanding the estuarine processes. Water movement in estuaries are due to wind, tide and river flow. Based on the difference in the circulation within the estuary caused by variations in river discharge and tidal range, it is possible to classify estuaries as Salt Wedge, Partially mixed and Well mixed estuaries (Pritchard, 1952; Dyer, 1973).

1.1. **The estuarine environment**

Estuary is one of the most productive environments. Nutrient content is high in estuaries facilitating healthy growth of plants and benthic organisms. Estuaries are unique ecological systems because of their spatial relationship to land and sea. Their structure and functions are controlled not only by internal processes but also by adjacent land and sea. Estuary and shelf are interconnected in many different complex ways.

Historically, coastal areas have been important as sheltered sites of habitation that provide access to both land and sea. Some of the larger population centres all over the world have developed in or adjacent to estuaries (eg. Boston, Philadelphia, New York, Washington, New Orleans, London, Hamburg, Alexandria, Bombay, Calcutta, Cochin, etc.). Estuaries are considered as areas of commercial, industrial, recreational and navigational importance and play an important role in the life cycle of aquatic organisms. Various developmental activities are being carried out around estuaries leading to significant economic advancement and social changes. Coupled with various developmental activities, severe environmental problems also eschew. Construction of weirs, dams, bunds etc., upstream of the estuary disrupt free flow of water and upset the ecological balance. Man introduces many things in larger volumes to this system (such as detergents, pesticides and industrial wastes having organic and inorganic toxicants) and in many cases the environment is not in a position to absorb the same. This results in far reaching adverse consequences leading to the impairment of this productive environment. Man has made estuaries as a dumping place for his waste materials which are varied in nature. Aquatic organisms has the ability to concentrate these toxic materials in their body and transmit to human beings through the marine food chain. Depending on the physical and chemical characteristics of the various estuarine systems, such as mixing, flushing time and nature of the waste, the capacity to assimilate the waste load with in the system varies from estuary to estuary. It provides natural food resources rich in protein. These multiple features are often incompatible.

The ecology of the estuary is delicately balanced. Natural calamities are quite common but the system adjusts itself and soon returns to normal. Great pressure of population, industrialization in adjacent areas and on the river banks which joins the system and hazards arising out of urbanisation are the main threats faced by estuaries.

The general factors which influence life in estuaries are tides, waves, currents and influx of fresh water. Tides are critical to many benthic organisms as they may get exposed along with shallow parts of the estuarine floor during ebb tide. The estuarine organisms are thus subjected to wider ranges of temperature than marine organisms. Waves contribute to the mixing processes in estuaries. Further, waves help to bring sediments in suspension that choke life. Depending on shoreline configuration and weather, the wave conditions vary. Wind induced current promote mixing of water mass and bottom rolling which can lead to re-suspension and distribution of sediments and particulate organic matter. Such mixing and re-suspension can promote air/water/gaseous exchange as well as a number of chemical processes. Precipitation increases the amount of fresh water. Generally, run off brings in significant amounts of dissolved and particulate matter. Additional fresh water may induce or intensify circulation patterns. However, some local influence, natural or man made are also considered to be important.

Fresh water input causes stratification in estuaries. Because of its lower density, fresh water lie above the denser saline water. Fresh water has profound influence on the inter-tidal biota. Nature of population in each zone of estuary is influenced by local water characteristics. Much of the particulate and dissolved materials brought in by rivers are transmitted to the open sea through the estuary. River borne material include suspended and dissolved inorganic and organic matter as well as living organisms. Some of these materials are coarse and certain chemical species remain in them for extended periods. Whereas, dissolved species and fine particulate matter may pass quickly to the open sea. Most materials which enter the system become physically or chemically altered. Substances such as silicate minerals may pass through without any appreciable change.

Information on tides, salinity, fresh water flow, sedimentation and water characteristics are important as they provide general quality of an estuarine system. Direction and velocity of estuarine flow is needed for predicting dispersion of pollutants. Circulation pattern in an estuary is very important in determining the sediment movement. Quantity of suspended material transported by the rivers through the estuaries to the marine environment is quite high. Holeman (1968) gave an estimate of 2×10^{16} gm of suspended load draining through rivers every year. Estuaries receive suspended materials primarily from land. It can also receive suspended matter from the inshore sea water and from re-suspension of settled sediments within the estuary. A small quantity can also come from atmosphere. The bottom sediments in an estuary commonly consist of an admixture of mineral particles eroded from the continents, biogenic debris derived from indigenous organisms, and various human and industrial waste products. Inorganic terrigenous detritus account for most part of the sediments deposited. Amount of Organic carbon in the sediments dictates the volume of inorganic pollutants retained by the estuarine sediment to a great extent.

Nutrients (silicate, nitrate, nitrite and phosphates) are introduced into an estuarine system by natural as well as anthropogenic means. Silica is an important nutrient to certain organisms such as diatoms and radiolaria. The dissolved silica is removed by such organism to build their skeleton. Natural input of phosphorus to estuaries is by weathering of rocks and by land drainage in suspended (phosphate minerals) and dissolved forms. Phosphorus is also introduced into the system from domestic sewage and industrial effluent discharge. Nitrogen is supplied in both elemental and compound form to estuaries in many ways. The main form of combined nitrogen is dissolved nitrates derived from weathering of rocks. Nitrogen compounds are also derived from agricultural run off owing to the practice of applying nitrogenous fertilizers. Optimum levels of nutrients are essential for primary and secondary production in an estuary. But, excess nutrients in estuarine systems may lead to eutrophication.

Pritchard (1952) classified estuaries as *positive* where sea water is diluted with fresh water (run off plus precipitation) and *negative* where evaporation exceeds run off plus precipitation. Those estuaries where a relative balance between evaporation and fresh water supply are termed as *neutral* estuaries. Generally estuaries are classified based on (1) the mode of formation of the basin and (2) the physical processes taking place in the water body.

1.2. **Estuarine Pollution**

The health of the estuary is dependent on the nature and quantity of various contaminants and potentially toxic pollutants it receives. The main contaminants are sewage, synthetic organics, petroleum hydrocarbons, pesticides, toxic heavy metals and radionuclides. Sewage is the product of municipal drainage systems containing domestic wastes with or without the addition of discharges from industry, storm water and surface run off. The sewage may reach the estuary untreated or partially treated. The major constituents of sewage are organic matter, nutrients, detergent, microorganisms and parasitic worms. Oil and metals are usually associated with industrial effluent discharges. The high nutrient content in sewage leads to eutrophication which has got far reaching consequences on the estuarine ecosystem.

Due to human intervention, several hazards are being caused to the aquatic environment. This is happening mainly due to rapid industrialisation and modernisation.

Several activities such as installation of new industries, expansion of navigational water ways, deforestation, urbanisation of life, ruthless discharge of industrial effluent, etc. are posing serious threats to the health of these water bodies. In many of the estuarine systems of the world, it has become difficult to use the estuarine water for irrigation, desalination and extraction of resources, etc. Various poisonous products are getting in to man's food chain causing serious concern. The recreational role of the estuarine systems is declining at a faster rate due to pollution.

Residual PCBs and DDT which are brought into the system have deleterious effects on the marine ecosystem. At high concentration, its effect ranges from mortality to retardation of growth, impairment of reproduction and reduction of natural compensatory reaction to stress and disease.

Certain metals such as Hg, Cd, Cu, Zn, Co, Mn, Mo, Ni, Pb, Fe, As, Al, Cr, Sn, Ti, V, Ag, Bi, Be, Se, Te, etc. when introduced into the aquatic environment are found to have toxicity effects on aquatic organisms. Dominant pathways through which trace metals enter the system as a result of natural processes and human activities are rivers, land run off, dumping and atmospheric fall out.

Some trace metals when introduced into the system do not remain in the water column. They may be concentrated on the surface film or become adsorbed to suspended matter so that they sediment out on the bottom of the estuary. Even though the sediments are sinks, the trace metals may reenter the water column by various physical, chemical and biological processes. In this way the sediment acts as a buffer and may be able to keep the metal concentration above the back ground level in water and biota even after the input is removed. The metals introduced into the system after interaction with various other components already present alters their physico-chemical characteristics. Certain trace metals when converted to a particular form becomes more toxic. For example inorganic mercury when converted to methyl mercury becomes highly toxic.

1.3. Heavy Metals in Estuarine Environment

In recent years there has been a rapidly growing interest on the heavy metallic content in estuaries and on the nature and the pathways by which they are introduced into the system. Well known estuaries of the world Viz., Dervent estuary (Tasmania), Sör Fjörd (Norway), Restrongut estuary (U.K.) and Rio Tinto estuary (Spain) are the region most heavy polluted by heavy metals (Forstner and Wittmann, 1981). The physico-chemical processes which act on rocks and soil of the catchment area normally control the concentration of trace metals in the fluvial and estuarine sediments. Due to anthropogenic input, abnormal concentration of heavy metals in both dissolved and particulate phases result. These high inputs can also affect the adjoining coastal waters due to exchange. Addition of these undesirable heavy metals in excess quantities can disrupt the delicate balance which exist between biomass and trace metals. When it exceeds tolerance level, certain species in aquatic organisms will perish. Certain aquatic organisms have the ability to concentrate toxic metals many fold in their body which ultimately passes on to human beings through marine food web causing deleterious after effects. The Minamata Bay incident in South Western Kyushu, Japan is one such incident in which more than 52 lives were lost and many permanently disabled due to mercury poisoning through consumption of contaminated fish. A regular monitoring of sediments and water for heavy metals is required in order to protect human health from the consumption of contaminated marine products.

Rivers transport trace metals to ocean in dissolved, colloidal and particulate forms. In estuaries, where coastal and river water mix, strong gradients in the physical and chemical properties occur since dissolved and particulate suspended components have different transport mechanisms within estuarine and coastal regions (Postma, 1967). It is important to understand the effects of estuarine processes on trace metals for predicting the geochemical behaviour of each individual element and its possible effect on organisms.

The adsorption/desorption experiments carried out by Kharker et al.(1968) and the interpretation of estuarine bottom sediment data (Groot, 1966, Groot and Allersma, 1975) throw light upon the significant release of trace metals from river borne suspended matter once in contact with sea water.

The chemical behaviour of a trace metal during its transport within the estuary is determined mainly by its chemical form in which it is transported. It could be either (1) in solution as inorganic ion or (2) adsorbed on to surfaces, (3) solid organic particles, (4) coating on detrital particles after co-precipitation with and sorption on to mainly iron and manganese oxides, (5) in lattice positions of detrital crystalline material, or (6) precipitated as pure phases, possibly on detrital particles.

This scheme allows clear distinction of trace metal fractions as

(1) readily available (dissolved and adsorbed),

(2) fraction that are available after chemical changes (organically bound and iron oxide coating) and

(3) forms which are not at all available for release (in crystal structures).

The solubility of an element depends on its oxidation state, pH, oxygen concentration and the presence of organic or inorganic ligands. Hydrous metal oxides of Mn and Fe are important for the transport of trace metals in natural waters. Trace metals adsorbed on the freshly precipitated Mn and Fe oxides is considerably larger than on aged precipitates.

Clay minerals with its comparatively high cation exchange capacity also play an important role in mobilizing the trace metals. But laboratory experiments carried out on the adsorption of trace metals on clay minerals have shown that their contribution in retaining trace metals in sediments is very small (Lee, 1975) . Their importance is attributed in acting as the nucleation centres for Fe and Mn oxides in fresh water region and estuarine mixing as well as centres for the flocculation and precipitation of dissolved and colloidal organic matter during estuarine mixing .

Organic matter in natural waters is capable of modifying the solubility, redox potential and the precipitation behaviour of metals. A larger part of dissolved organic matter is humic substances which are macromolecules of phenolic carboxylic acids. The anodic character of these macromolecules enable them to interact with trace metal cat ions and linkages by ion exchange, surface adsorption and chelation. The associations of trace metals with Fe and Mn hydrous oxides, organic matter and clay minerals decreases in the order of MnO_2 > humics > $Fe(OH)_3$ > clay minerals.

1.4. **Scope of the present study**

Kerala is located along the southwest coast of India. It has 41 west flowing rivers and as many as 32 estuaries. An outstanding feature of Kerala coast is the wide spread presence of estuaries and lagoons representing the submergent and emergent aspects of the Kerala coast. The evolution of the estuarine tracts is closely associated with the evolution of the western ghats (Subramanian, 1987). Kerala has an inland water area of 3,36,000 ha. The back water system consisting of estuaries of river, their lower part having tidal influx, the brackish water lakes etc. contribute to 2,42,600 ha, which amounts to about 68% of the inland water resources of the state (Sukumaran, 1987).

One peculiarity of estuaries in Kerala is that more than one river opens into a single estuary (e.g. Vembanad lake). The coastal waters of Kerala are greatly influenced by the estuaries since they empty large volumes of fresh water from rivers. The estuarine environment is the breeding and nursery ground for various commercially important fish species which adds to the economy of the state. The estuaries of Kerala play a crucial role in the socio economic development of the state. Due to rapidly increasing population, Kerala state is not in a position to provide adequate food material. If the estuaries in Kerala are managed judiciously the rich fisheries resources can be sustainably exploited.

Due to industrialisation and modernisation in recent times in the state, it has become imperative to protect the estuaries from various hazards emanating out of human intervention.

It is estimated that there are about 200 major and medium scale industries and 2000 small industries discharging their effluent to the aquatic environments causing serious concern over the water quality. Effluent enriched in nutrient content causes eutrophication which ultimately leads to depletion in dissolved oxygen content due to biodegradation.

Environmental studies have been carried out in detail in some estuaries in Kerala, but meagre in many other estuaries. The Beypore estuary, which is situated on the lower part of Chaliyar river, where systematic studies are sparse. The Beypore estuary has been subjected to severe pollution due to effluent discharge from the Mavoor Gwalior Rayons Factory causing severe damage to the fishery resources of the estuary. It has a major port and a fisheries harbour. A ship breaking unit also is situated on its bank. The rayon factory (when in operation) alone discharges 40,800 m^3 untreated or partially treated effluent to this estuary in a day (Prasad et al. 1976).

1.5. **Objectives**

The present work aims to understand the metal pollution in the Beypore estuary both in the sediment and water. The influence of season on the distribution of these metals in the environment will be assessed. Different path ways by which trace metals are introduced into the system and physical and chemical parameters which are responsible for the retention/distribution of trace metals in the sediment/water column would also be investigated. Textural characteristics, elemental composition and organic carbon in sediments are also proposed to be investigated in order to ascertain their influence on the trace metal levels. Magnitude of anthropogenic inputs of metallic pollutants in the estuary is to be assessed by comparing with base line values. Study of bio-availability of metals in sediment forms the part of the investigation. The hydrographical features like temperature, tide, salinity, DO and water current are also proposed to be monitored. The data thus generated would indicate the quality status of the estuary and would throw light upon future changes.

1.6. Physiographic features:

The Chaliyar River is one of the major rivers in Kerala. It originates from the Ilambalari hills in Gudalur Taluk of Nilgiri district in Tamil Nadu at an elevation of 2066 m above mean sea level. The longitudinal setting is depicted in figure 1.1. The Chaliyar river flows through Nilambur, Mampad, Edavana, Areacode, Vazhakkad and Feroke before it joins the Arabian sea through Beypore estuary. It has a drainage area of 2923 km^2 of which 388 km^2 is in Tamil Nadu. The important tributaries which joins the main stream are: Chalipuzha, Punnapuzha, Pandiyar, Karimpuzha, Cherupuzha, Kanhirampuzha, Kurumbanpuzha, Vadapurampuzha, Irinjipuzha and Iruthillipuzha (Fig. 1.2)

Three distinct physiographic zones exist in this basin. (1) The highland region covering the Western Ghats 75 m above mean sea level. (2) The midland region lying between 7 m and 75 m above mean sea level. (3) The lowland region lying below 7 m.

1.7. Geology of the region

A generalized geological map of the study area is given in figure 1.3. From the geological point of view, this river basin can be classified into (a) eastern zone (ghat area) consisting of mainly crystalline rocks of Archaean group; (b) central zone consisting mainly of residual laterites and (3) western coastal zone consisting of sandy alluvium and silt. The western coastal belt is a narrow strip of land bordering the sea. The laterites found in the central zone are of two types viz. vermicular and pelite. The crystalline rocks found in the ghat area consist of hornblende biotite genesis, generally grey or greyish white in colour.

1.8. Rainfall and Climate:

Rainfall received during the southwest and northeast monsoons are the main controlling factors of the basin. The average annual rainfall of Kerala is about 300 cm. of which 75% occurs during the southwest monsoon (Ananthakrishnan et al., 1979). The climate

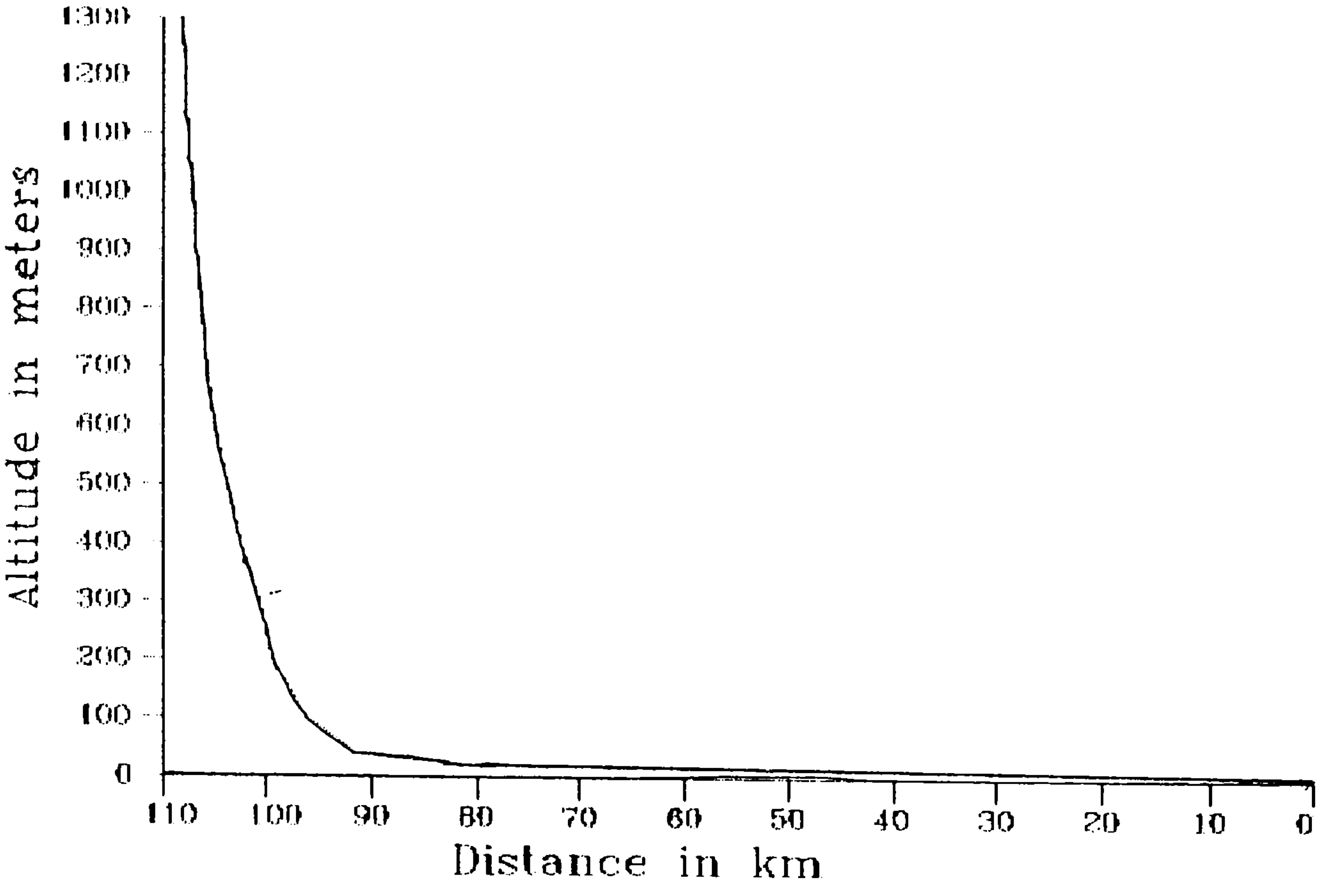


Fig. 1.1 Longitudinal Profile of Periyar river

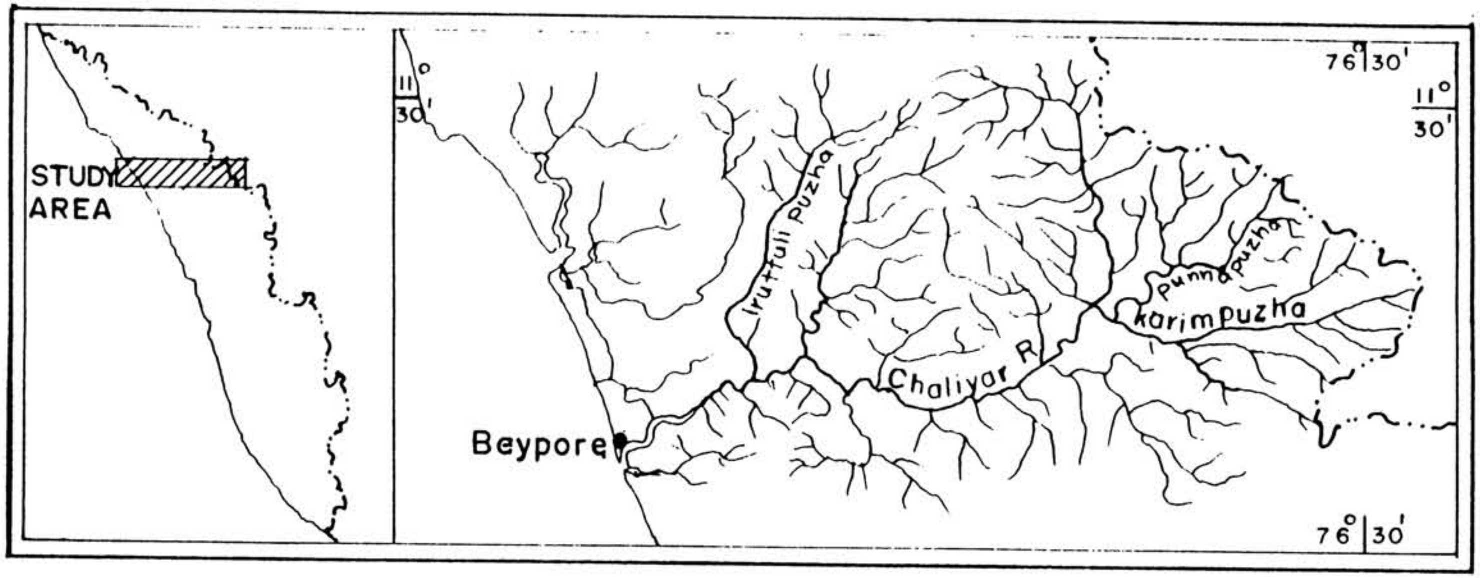


Fig. 1.2 Study area with drainage pattern

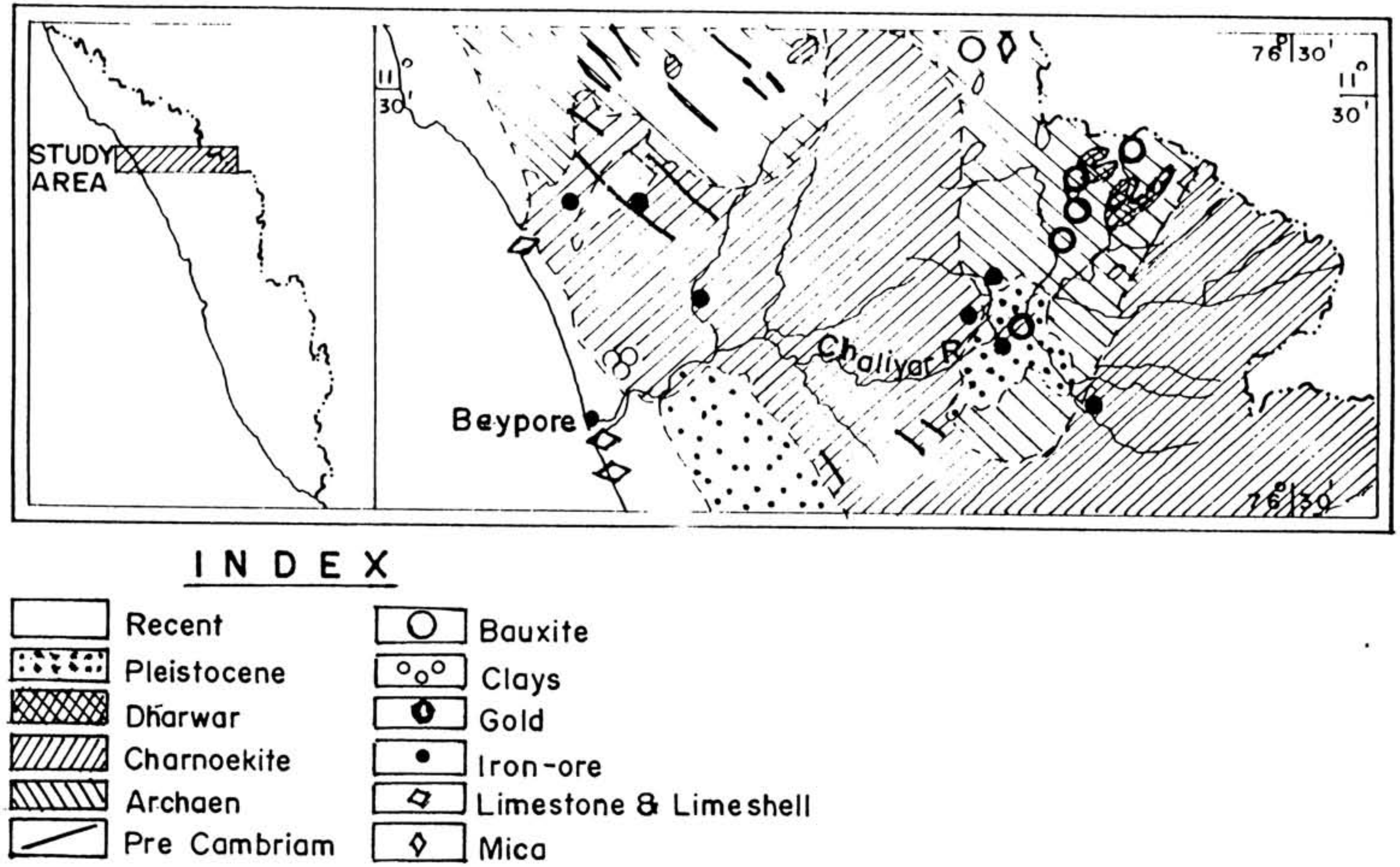


Fig. 1.3 Generalised geological map of the study area

of the basin is generally moderate. The coastal belt is humid and damp and the humidity percentage decreases towards the eastern portion of the basin. The mean annual temperature varies between 18.5°C and 28.5°C in different zones of the state.

CHAPTER II

HYDROGRAPHY

2.1 **Introduction**

The knowledge on the hydrographic parameters of an estuarine environment is of great importance while attempting to characterise its general features, distribution pattern of various pollutants, salinity intrusion, abundance of nutrients etc. The main factors which influence the hydrographic conditions of an estuary are the saline water intrusion associated with tides and influx of fresh water brought in by the rivers. The bottom topography and geographical shape also play an important role in controlling the hydrographic regime of an estuary. Generally the diurnal variation in salinity is found to be in pace with flood and ebb tides. The influence of tides decrease with distance from the estuarine mouth. It is important to have a comprehensive data set on the seasonal variations of hydrographic features and suspended sediment load characteristic in an estuary. Study on the dynamics of the estuary is important for the planning of various developmental programmes. Hydrographic features such as temperature, pH, flow patterns, dissolved oxygen (D.O), BOD, salinity, nutrients etc. are greatly influenced by the topographical as well as climatic conditions. Main dynamic features of an estuary are (1) the horizontal gradient of density which increases from the point of river influx towards the sea and (2) the tidal currents with periodic ebb and flood between the sea and the estuary.

Estuarine systems play important roles in the exchange of materials (nutrients, carbon, etc.) between sea and river. Thus one of the major goals of estuarine research is to establish the source/sink characteristics of an estuarine system by investigating the exchange between the estuary and the adjacent coastal waters. Smith (1979) has shown that these exchanges can occur over a broad range of time scales. As far as an estuary is concerned, the local tidal oscillations are the best means of flushing.

Tide is found to be one of the most important physical factors governing the hydrography of an estuary. Hence it is essential to obtain the information on the range of variation of the hydrography with the tidal rhythm. Knowledge on the fluvial and estuarine systems are essential in order to understand their impact on the near shore region. Hydrographic features show wide variations from estuary to estuary and hence every estuary is unique. Drastic variations in parameters are noticed in the same estuary during different seasons.

2.2 Previous work

A good amount of work has already been carried out to monitor the hydrographic features and influencing parameters of important estuaries world over. Influence of topographical features on estuarine characteristics were investigated by Barthurst et al. (1977). The effect of wind on estuarine circulation was studied in detail by Pickard and Rodjers (1959) and Rattray and Hansen(1962) Kjerfve (1975(and Smith (1977). Current-salinity relations were studied in various estuaries by Hansen (1965), Dyer (1974), Lewis (1979), Hughes and Rattray (1980), Uncles et.al. (1985) and Jonge (1991). Many attempts have been made to study the physico-chemical parameters at selected locations over short periods in estuaries in India, but comprehensive surveys of larger area over longer periods are much limited.

Das et al. (1972) made extensive investigations on the hydrography, circulation and suspended sediment distribution of the Zuari and Mandovi estuarine systems. Cherian et al. (1975) made investigations in Zuari estuary on the seasonal and temporal variations in hydrographic conditions in relation to tidal currents. The influence of tide over hydrographic parameters such as DO, temperature and salinity was investigated in Mandovi estuary by Singbal (1976). Physical and hydro-biological features of Zuari and Mandovi estuaries were monitored by various workers. De Sousa (1977) carried out studies on the stratification aspects and nutrient load and arrived at the conclusion that the change in physico-chemical parameters in the estuary is largely due to the monsoon rains. Rao (1981) reviewed the physical aspects of estuaries in Goa region. De Sousa et al. (1986a,b) carried out investigations on the salinity dependence of oxygen solubility in the Mandovi Estuary and by De Sousa and Gupta (1986) in Zuari estuary .

A number of studies have been reported on the hydrographical characteristics of Cochin backwaters. Ramamirtham and Jayaraman (1963), Qasim and Reddy (1967), Qasim et al. (1968), Qasim and Gopinathan (1969), Sankaranarayanan and Qasim (1969) and Cherian (1973 have made significant contributions on the hydrographic aspects of this estuarine system. The effect of tidal currents on the hydrography of the Cochin backwater system was studied by Narayana Pillai et al. (1973). Nair et al. (1984) studied seasonal changes in temperature, light penetration, pH, salinity, DO and nutrients in Kadinamkulam estuary. The deterioration in water quality caused by the coconut husk retting was also explored by them. Change in water quality parameters due to industrial waste disposal from a paper factory was assessed by Balachand et al. (1986) by carrying out studies in the tidal zones of Muvattupuzha river. Sankaranarayanan et al. (1986) carried out studies pertaining to saline water intrusion and flushing characteristics of Cochin estuary after computing the fresh water fraction at different locations. Investigations were also conducted by Sankaranarayanan et al. (1986) at the lower reaches of Periyar river to assess the longitudinal intrusion of saline water into the system during different seasons and also its effect on various pollutants discharged by industries. Physical aspects of Azhikode estuary were reported by Revichandran et al. (1987) and Abraham Pylee (1989). Joseph and Kurup (1989, 1990) examined the stratification and distribution of salinity in relation to tide and fresh water discharges.

Observations on the hydro-biological characteristics of Hoogly estuary were carried out by Datta et al. (1954) and Roy (1955). Mahanadi estuary was studied in detail by Ray et al. (1981). Chandramohan (1963), and Chandramohan and Rao (1972) studied the Godavari estuary. Physical and biological characteristics of Vellar estuary were monitored and reported by Krishna Moorthy (1961) and Ramamoorthy et al. (1965). Studies carried out in Purna river estuary on its pollution status and flushing characteristics by Zingde et al. (1986) reveals that the estuary is a shallow, well mixed one with excellent flushing characteristics and devoid of any serious pollution threats.The variations in physico-chemical parameters of Vishakapatnam harbour waters were reported by Ramaraju et al. (1987). Various contributing factors for variations in water temperature, DO, salinity and suspended sediment in Vasishta-Godavari estuary were explored by Saisastry and Chandramohan (1990).

Studies on the physical aspects of Beypore estuary are limited. Ramachandran (1973) made a qualitative survey of fresh water input into Chaliyar river and reported considerable flow of fresh water throughout the year. Prasad et al. (1976) monitored the water quality parameters from a pollution point of view and reported that due to reduction in water flow through the river, flushing is minimum during summer months causing considerable variations in the water quality parameters. Saraladevi et al. (1983) collected hydrographic data from Beypore, Korapuzha, Kallai and Mahe estuaries and made a comparative study. Circulation, mixing and pollutant dispersion in the estuary were studied by James (1982). Further James and Sreedharan (1983) attempted to compute the transport of salt and longitudinal mixing in the Chaliyar river. Salinity intrusion and freshwater discharge studies were carried out by James and Sreedharan (1983). Premchand et al. (1987) studied the hydrographic features in detail and observed a salt-wedge during the month of September. Effects of salinity intrusion on flora and fauna was investigated by Nirmala et al. (1990) and noticed that variations in salinity as well as other hydrographic parameters have significant bearing on the ecology of the estuary.

Though several researchers have attempted studies in Beypore estuary and Chaliyar river on several aspects, the inferences are drawn from a few location specific short-term data set. For a proper understanding of the hydrographic features, detailed spatially coherent temporal data set is essential. This is imperative to examine the pollutant dispersion patterns as well. Hence, the present work aims at understanding the seasonal changes of hydrographic parameters in the longitudinal section of the estuary. Apart from this, the study also attempts to decipher the hydrography over a tidal cycle at a fixed station repeated monthly for one year.

2.3 **Materials and Methods**

2.3.1 *Sampling procedure:*

Hydrographic data were collected from seven fixed stations in the estuary for the period June 1987-May 1988 (Fig 2.1). The details of the stations are given in Table 2.1. A fibre glass boat fitted with an outboard engine was used for the sample collection. Tidal cycle observations were made from a fixed station near the fisheries harbour (1.8 km upstream). Parameters such as, temperature and current were monitored at sub surface, middle and near bottom levels. Sampling was made 3 hours prior to the high tide and was repeated every month at same locations. Apart from these, surface water sampling was carried out up to 15 km upstream occupying 15 stations. Stations were fixed based on prominent land marks. For tidal cycle observations, hourly measurements of salinity, water temperature and current direction and speed were made. Water samples from the surface were collected using a clean plastic bucket. A Van Dorn water sampler was used for collection from mid depth and near bottom. Samples for dissolved oxygen analysis were taken in glass stoppered 125 ml bottles taking care not to get any air bubbles during sampling. Dissolved oxygen was fixed immediately by the addition of Winkler A ($MnCl_2$) solution followed by Winkler B (alkaline potassium iodide + sodium azide) solution. Water samples for the determination of salinity were collected in ultra clean polythene bottles.

Water temperature at the surface was measured using a bucket thermometer and at sub-surface depths using STD meter of SEA model which has an accuracy of 0.1°C. Current measurements were made using a direct reading current meter of SEA model which has an accuracy of ±1.0 cm/sec. for speed and 5° for direction.

2.3.2 *Analytical Methods*

Salinity:

Salinity was determined by Mohr Knudson titration method in which a known volume of the sample was titrated against standard silver nitrate solution using potassium chromate as indicator and the chlorosity is found out which upon multiplication by a factor of 1.80655

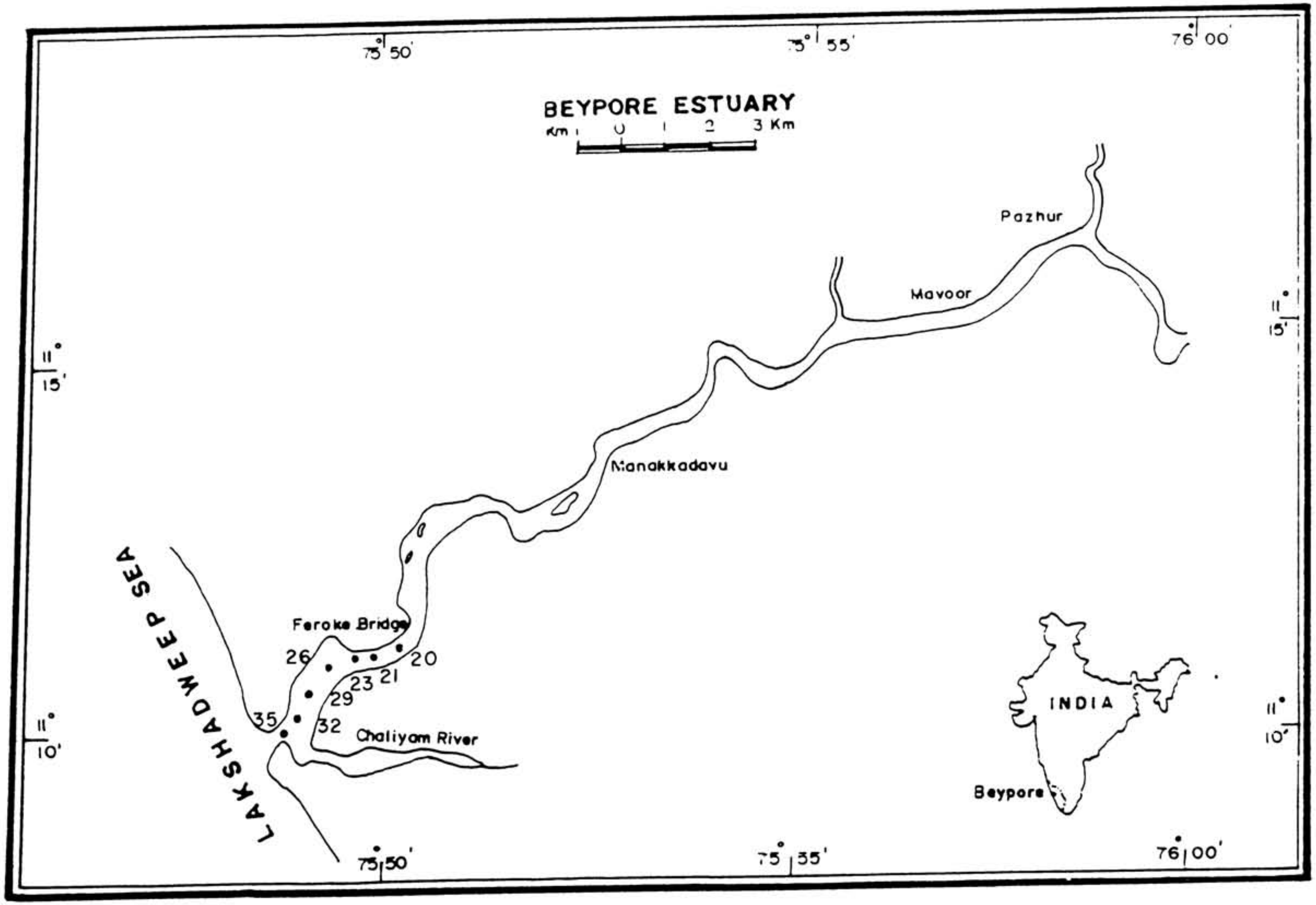


Fig 2.1 Location map of the study area

Table 2.1 Details of the sampling stations

Sl. No.	*Station No.*	*Description*	*Distance from barmouth (kms.)*
1.	1	Eruvanji puzha	28.55
2.	2	PHED Pumping station	27.70
3	3	Bund	25.50
4.	4	Gwalior Rayons Factory	24.85
5.	5	H.T.Line	22.65
6.	7	Cherupuzha Junction	20.55
7.	8	Akode Pallikadavu	18.65
8.	9	G.R.Effluent discharge	17.80
9.	10	Chungapalli	16.50
10.	11	Puttikadavu	15.15
11.	12	1 km. upstream of III H.T tower	13.80
12.	13	III H.T. Manekakadavu	12.10
13.	14	Island bifurcation sown stream	10.50
14.	15	II H.T. line	8.45
15.	16	I H.T. line	7.00
16.	18	Last tile factory	5.95
17.	20	Road bridge down stream	4.80
18.	21	Rail bridge down stream	4.05
19.	23	Tile factory	3.15
20.	26	Green Island	2.65
21.	29	Fisheries Harbour	1.80
22.	32	Port Office	1.00
23.	35	Light House	0.55
24.	38	Bar mouth	0.00

gives salinity. The silver nitrate used is standardised using standard sea water obtained in sealed glass ampules from The Institute of Oceanic Sciences in Wormley, Godalming, Surrey, (U.K). The possible sources of errors in the method discussed by Grasshoff (1983) were well taken care of.

Dissolved Oxygen:

Dissolved oxygen was determined by the Winkler method as detailed by Strikland and Parsons (1972). The outline of the method is as follows:

Dissolved Oxygen in water reacts with manganese (II) hydroxide in strong alkaline medium to form manganese(III) hydroxide $MnO(OH)_2$ which dissolves to liberate Mn^{+3} ions which is a strong oxidising agent in acid medium. Mn^{+3} reacts with iodide present in the media to liberate equivalent free iodine which is titrated against standard thiosulphate solution using starch as indicator. From the titre values the dissolved oxygen present in the water sample is calculated.

2.4 **Results and Discussion**

2.4.1 *Hydrographic variation over tidal cycle*

Monthly variations of water level, temperature, salinity over a tidal cycle are given in table 2.2. Figure 2.2a gives variation of the parameters for June 1987. It clearly depicts a flood followed by an ebb with water level difference of nearly 1.3 m. Surface salinity was very low whereas mid-depth and bottom salinities followed the tidal rhythm, but with a phase lag. As the salinity increases temperature registered a decrease, not so prominent in the surface levels. In July as well as in August I survey (fig. 2.2b & c), the same features were observed. However during II survey in August (Fig. 2.2d), the tidal cycle was not so prominent as indicated by marginal water level fluctuations (0.7 m). The temperature pattern showed a mixed nature and salinity was drastically lowered (almost fresh water < 0.1 ppt salinity) at all levels. Coinciding with a flood tide, slight improvement in temperature as well as in salinity was observed (Fig. 2.2e) during September I survey, but during the following ebb, salinity

Table 2.2 Monthly variations of hydrographic parameters over tidal cycles

TIDAL CYCLE OBSERVATIONS Jun-87

Time	Salinity (ppt)			Temperature°C		
	S	M	B	S	M	B
645	0.19	2.68	6.33	30.3	29.8	29.4
740	3.41	6.08	6.57	29.6	29.8	29.8
840	3.14	9.74	21.66	30.4	29.1	28.7
940	3.16	17.52	30.1	30.4	29.6	27.3
1040	3.48	26.53	33.34	30.8	28.5	27.1
1140	3.69	30.16	31.4	30.4	27.6	27.1
1240	5.6	32.13	34.07	30.5	27.7	27.1
1340	4.38	26.04	31.64	31.6	29.5	28
1440	2.68	26.14	30.42	31.9	28.5	28
1540	1.95	25.07	27.75	31.9	29.1	28
1640	1.46	20.3	20.8	31.3	29.4	29.1
1740	1.95	9.98	13.87	30.9	30.3	29.3
1840	1.2	7.05	8.52	30.8	30.1	29.9
1940	1.88	7.06	8.76	30.6	29.8	29.6

TIDAL CYCLE OBSERVATIONS Jul-87

Time	Salinity (ppt)			Temperature°C		
	S	M	B	S	M	B
630	2.76	7.66	22.66	30.1	29.9	26.9
730	9.18	10.27	27.26	29.7	29.3	26.2
830	3.39	22.97	31.27	29.5	27.1	24.7
930	3.98	25.73	30.63	29.5	26.3	24.8
1030	5.82	32.78	34.16	29.1	25.2	24.5
1130	7.66	33.69	33.16	28.8	24.69	24.5
1230	3.98	33.08	33.16	27.8	24.6	24.6
1330	4.29	32.16	33.08	31.1	25.1	24.9
1430	3.98	32.16	33.08	30	25.2	25
1530	2.76	31.23	32.16	30.9	25.6	25.5
1630	3.39	28.79	31.85	30.7	25.6	25.1
1730	1.84	21.79	24.18	30.5	27.3	25.9
1830	3.06	21.13	26.34	30.3	27	25.7

TIDAL CYCLE OBSERVATIONS Aug-I-87

Time	Salinity (ppt)			Temperature°C		
	S	M	B	S	M	B
630	3.37	1.68	12.9	30.1	29.9	28.8
730	3.09	7.01	7.57	29.3	29.3	29.1
830	2.24	7.01	11.5	29.7	29.4	29.4
930	3.09	5.61	10.86	30.7	29.9	29.4
1030	9.54	20.48	26.65	29.9	28.9	27.2
1130	7.85	26.09	22.72	29.3	27.6	25.7
1230	16.55	34.23	33.83	28.9	27.6	26
1330	16.55	33.66	33.66	28.8	26.2	26.2
1430	15.99	33.66	35.61	27.7	26.5	26.3
1530	14.03	33.94	33.6	28.9	26.5	26.9
1630	9.82	30.02	32.26	28.9	27.5	26.9
1730	7.29	21.04	30.02	30.6	29.2	29.4
1830	7.57	19.08	22.72	29.1	29.2	27.1
1930	7.57	18.79	23.28	29	29.1	27

Table 2.2 Continued.....

TIDAL CYCLE OBSERVATIONS Aug II-87

Time	Salinity (ppt)			Temperature°C		
	S	M	B	S	M	B
600	0.06	0.06	0.06	24.8	24.6	25
700	0.06	0.06	0.06	25	24.8	24.9
800	0.06	0.06	0.06	25.2	25	25.1
900	0.03	0.06	0.06	25	25.2	25.2
1000	0.06	0.06	0.06	25	25.1	25.2
1100	0.06	0.06	0.06	25.5	25.2	25.1
1200	0.03	0.06	0.09	25.5	25.3	25.2
1300	0.06	0.03	0.06	25.7	25.5	25.3
1400	0.06	0.06	0.06	25.6	25.5	25.4
1500	0.06	0.06	0.06	25.5	25.7	25.5
1600	0.06	0.06	0.06	25.5	25.8	25.7
1700	0.03	0.06	0.06	25.5	25.7	25.6
1800	0.06	0.06	0.06	25.3	25.5	25.5

TIDAL CYCLE OBSERVATIONS Sep I-87

Time	Salinity (ppt)			Temperature°C		
	S	M	B	S	M	B
900	0.23	1.02	3.37	28.6	28.4	28.4
1000	0.16	1.33	2.75	28.6	28.8	28.6
1100	0.24	1.8	3.53	28.4	28.2	28.4
1200	0.08	1.33	2.98	28.4	28.4	28.6
1300	0.39	1.18	2.12	28.6	28.7	28.6
1400	0.47	1.1	1.96	28.6	28.6	28.5
1500	0.31	0.51	1.49	28.4	28.6	28.4
1600	0.23	0.55	1.1	28.2	28.4	28.2
1700	0.16	0.31	0.35	28	28.1	28
1800	0.08	0.08	0.08	27.8	27.4	27.4
1900	0.08	0.08	0.08	27.6	27.2	27.4
2000	0.08	0.08	0.08	27.2	27.2	27
2100	0.08	0.08	0.08	26.6	26.6	26.5
2200	0.08	0.08	0.08	26.6	26.4	26.3
2300	0.08	0.08	0.08	26.6	26.5	26.7
2400	0.08	0.08	0.08	26.8	26.6	26.6
100	0.08	0.08	0.08	26.7	26.6	26.8
200	0.08	0.08	0.08	26.6	26.6	26.6
300	0.08	0.08	0.08	26.4	26.2	26.2
400	0.08	0.08	0.08	26	25.8	26
500	0.08	0.08	0.08	26	25.8	25.8
600	0.08	0.08	0.08	26	25.8	25.8
700	0.08	0.08	0.08	25.9	25.8	25.8
800	0.08	0.08	0.08	26.2	216.2	26.2
900	0.08	0.08	0.08	25.8	26	25.8

Table 2.2 Continued.....

TIDAL CYCLE OBSERVATIONS Sep II-87

Time	Salinity (ppt)			Temperature°C		
	S	M	B	S	M	B
900	0.32	0.78	2.43	28.25	28	28
1000	0.39	0.86	2.51	28.2	28	28
1100	0.31	0.86	2.91	27.3	28	28.1
1200	0.63	1.49	2.75	28	28.3	28.5
1300	0.63	1.49	2.51	28.3	28.6	28.7
1400	0.55	1.49	3.76	28.3	28.7	228.7
1500	0.7	1.56	2.35	28.5	28.5	28.4
1600	0.55	0.71	0.62	28	28.2	28.2
1700	0.39	0.39	0.39	28	28	28
1900	0.08	0.16	0.16	27.2	27.2	27.2
2000	0.08	0.16	0.16	27	26.9	26.9
2100	0.07	0.08	0.08	26.5	26.5	26.5
2200	0.08	0.08	0.08	26.3	26.5	26.5
2300	0.08	0.16	0.08	26.5	26.6	26.6
2400	0.08	0.08	0.16	26.5	26.8	26.8
100	0.08	0.08	0.08	26.6	26.6	26.7
200	0.08	0.08	0.16	25.2	26.3	26.5
300	0.08	0.2	0.08	26.2	26.2	26
400	0.08	0.08	0.08	25.8	25.8	25.8
500	0.08	0.08	0.08	25.7	25.6	25.6
600	0.08	0.08	0.08	25.4	25.4	25.4
700	0.16	0.16	0.16	25.3	25.2	25.2
800	0.08	0.16	0.16	25.5	25.5	25.4
900	0.16	0.16	0.16	25.6	25.7	25.7

TIDAL CYCLE OBSERVATIONS Oct-87

Time	Salinity (ppt)			Temperature°C		
	S	M	B	S	M	B
730	0.45	1.33	1.48	28.9	28.8	28.8
830	0.3	1.11	1.49	29	28.8	28.8
930	0.15	1.02	1.29	29.2	29	29
1030	0.21	1.36	1.72	29.4	29.2	29
1130	0.21	1.06	2.02	29.6	29.4	29
1230	0.09	0.24	0.86	29.8	29.4	29.1
1330	0.09	0.48	0.91	29.8	29.6	29.3
1430	0.12	0.69	1.6	30	29.9	29.8
1530	0.15	0.69	1.67	30	29.8	29.6
1630	0.18	1.39	1.9	29.8	29.6	29.4
1730	0.27	1.24	1.97	29.6	29.4	29.2
1830	0.48	0.72	0.84	29	28.9	28.7
1930	0.18	0.75	0.94	29	28.8	28.6

Table 2.2 Continued.....

TIDAL CYCLE OBSERVATIONS Jan-88

Time	Salinity (ppt)			Temperature°C		
	S	M	B	S	M	B
915	22.46	28.08	28.08	Jan-00	29.5	29.6
10	23.06	27.19	28.38	29.6	29.6	29.6
1055	22.76	27.19	27.19	30.2	29.8	29.7
1155	22.76	29.85	29.56	30.2	30	29.8
1250	21.73	29.71	30.15	30.8	29.8	29.6
1355	21.28	29.26	30.15	30.6	29.9	29.8
1455	17.29	27.78	27.78	31	29.9	29.8
1550	16.4	24.98	26.31	30.8	30.2	30
1650	18.33	23.94	24.24	30.6	30.4	30.3
1745	17.88	22.17	23.35	30.6	30.4	30.3
1850	16.26	19.51	20.99	30.4	30.4	30.2
1950	15.37	17.88	20.99	30.2	30.2	30.2
2035	16.7	21.58	27.2	29.8	30	29.6

TIDAL CYCLE OBSERVATIONS Feb-88

Time	Salinity (ppt)			Temperature°C		
	S	M	B	S	M	B
800	23.65	26.45	26.45	31	30.8	30.6
900	23.5	25.57	26.31	31.5	31.2	31.2
1000	21.28	24.29	24.53	31.9	31.8	31.9
1100	20.1	23.5	24.53	32.2	32	32
1200	22.61	24.68	24.98	32.2	32.1	32
1300	23.9	26.9	27.49	32.3	32.2	32.1
1400	27.97	31.92	32.22	32.2	32	32
1500	32.96	32.98	33.11	32.2	32	31.8
1600	33.11	33.11	33.7	32.2	32.1	31.8
1700	33.25	33.4	33.4	32	31.8	31.4
1800	33.11	33.25	33.25	31.8	314	31.2
1900	33.11	32.96	33.25	31.2	31.2	31
2000	32.81	33.4	33.4	31.2	31	31

TIDAL CYCLE OBSERVATIONS Mar-88

Time	Salinity (ppt)			Temperature°C		
	S	M	B	S	M	B
815	25.78	27.28	28.93	31.8	31.6	31.6
915	24.13	25.63	25.48	31.8	32	31.8
1015	23.08	25.18	25.93	32	32.8	31.6
1115	26.35	27.28	27.83	32.2	32.2	32.2
1215	28.47	28.33	29.22	32.4	32.2	31.8
1315	28.77	31.63	31.95	32.8	31.8	31.8
1415	31.53	32.07	32.47	31.6	31.6	31.4
1515	31.95	32.53	32.83	31.8	31.8	31.8
1615	31.48	32.68	32.83	32	31.6	31.5
1715	31.68	32.22	32.82	31.8	31.6	31.6
1815	32.38	32.68	32.98	31.8	31.4	31.4
19.15	29.97	32.08	32.32	31.4	31.2	31.2

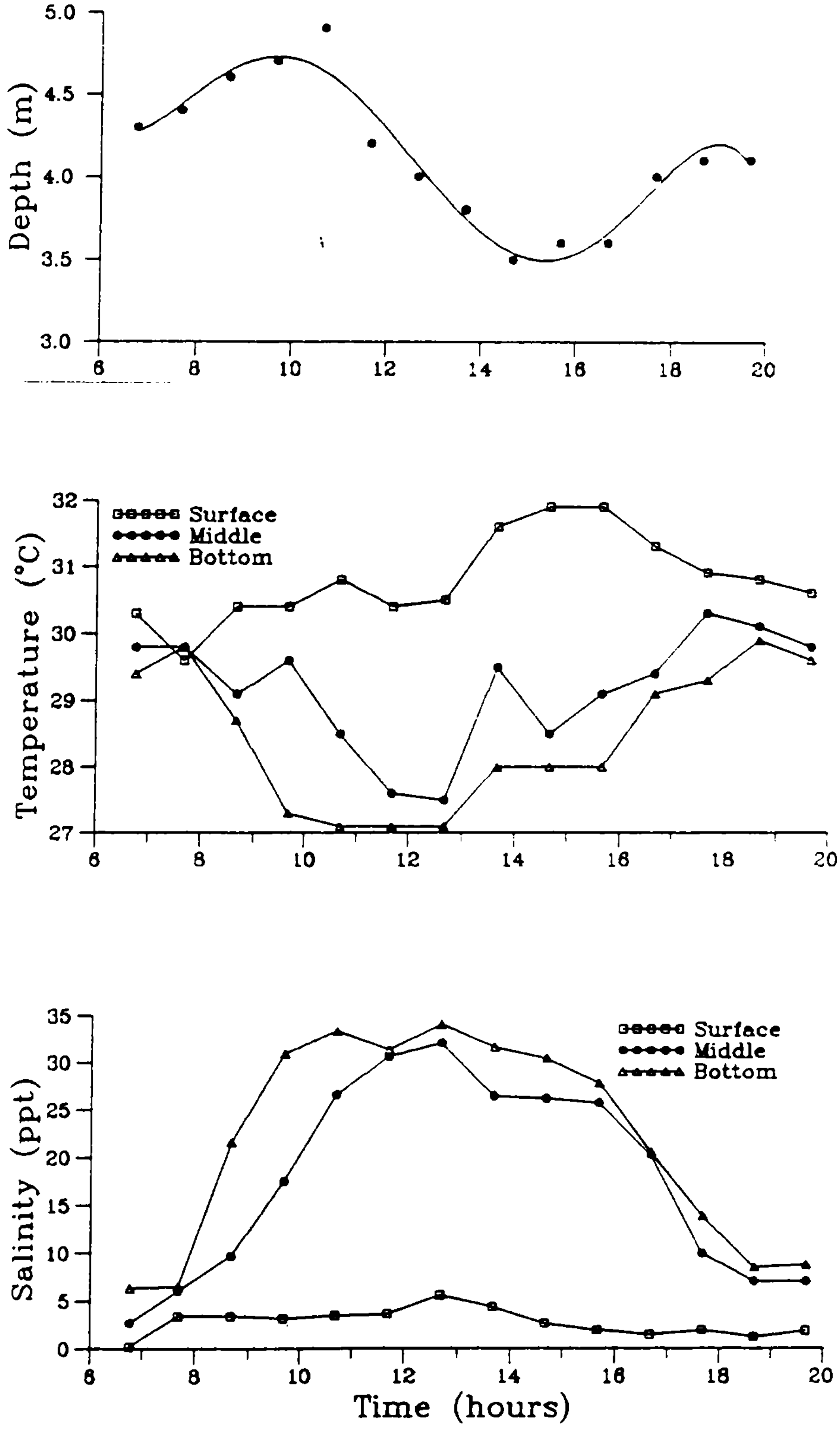


Fig. 2.2a Hydrographic variation over tidal cycle during June 1987

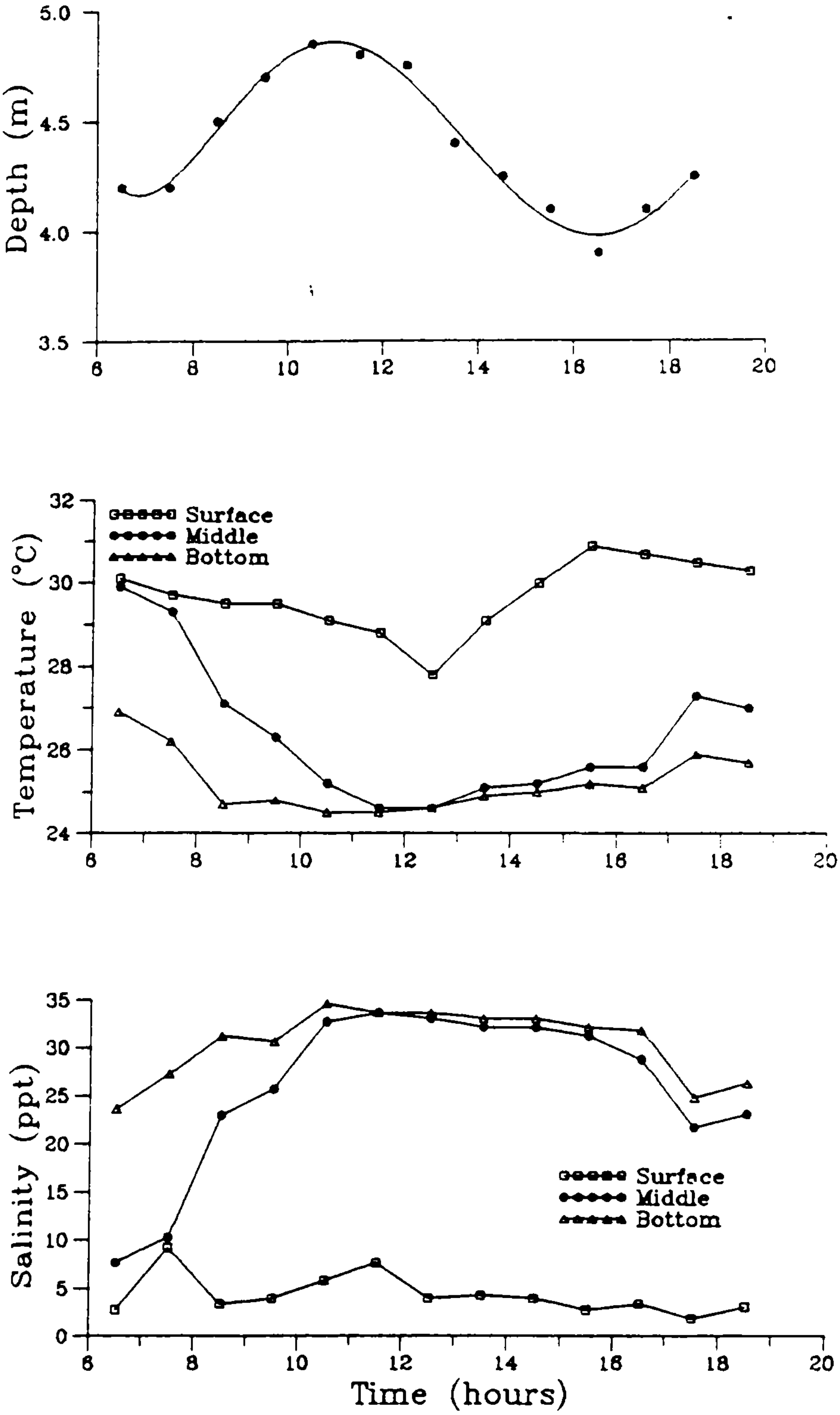


Fig. 2.2b Hydrographic variation over tidal cycle during July 1987

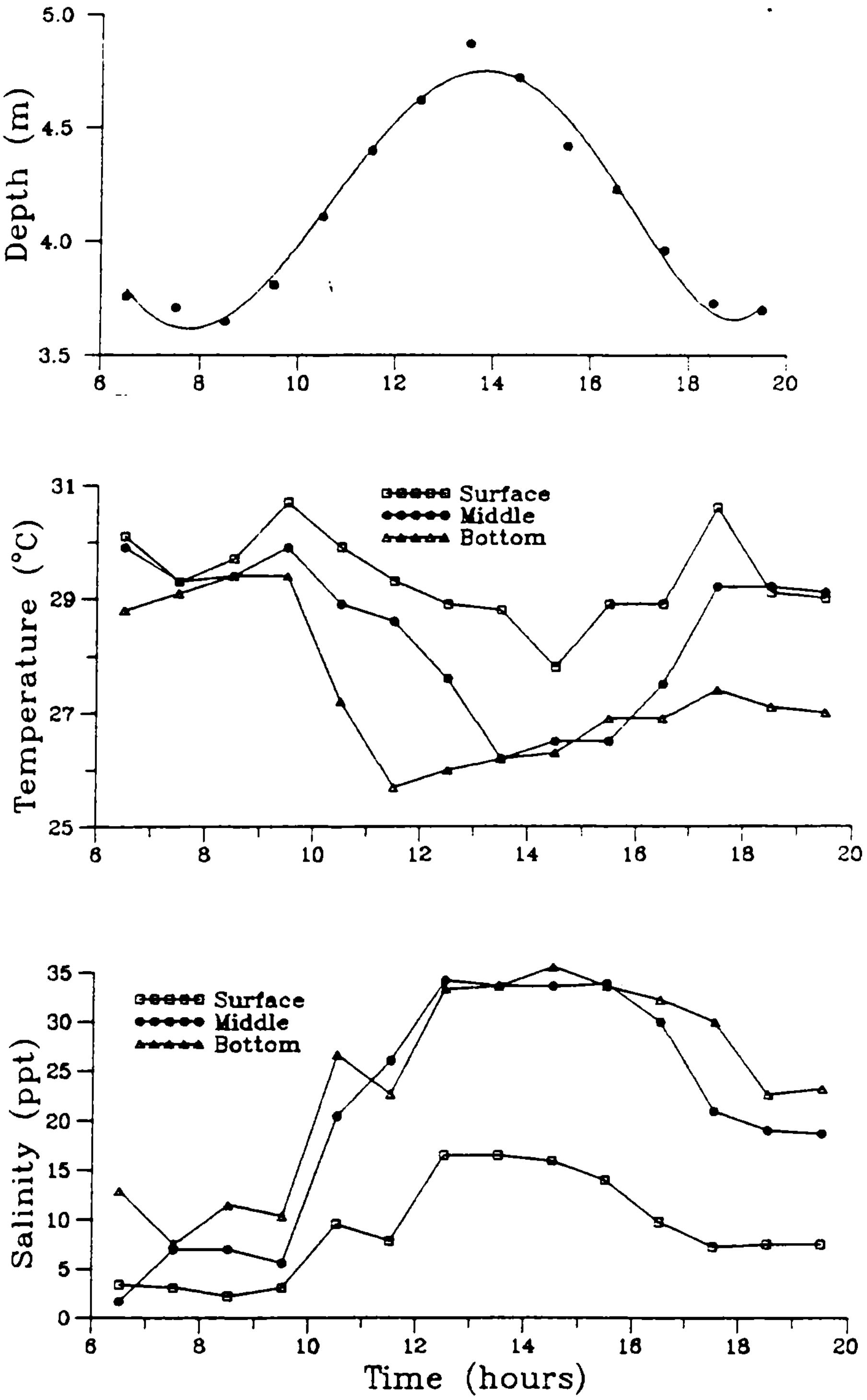


Fig. 2.2c Hydrographic variation over tidal cycle during August I 1987

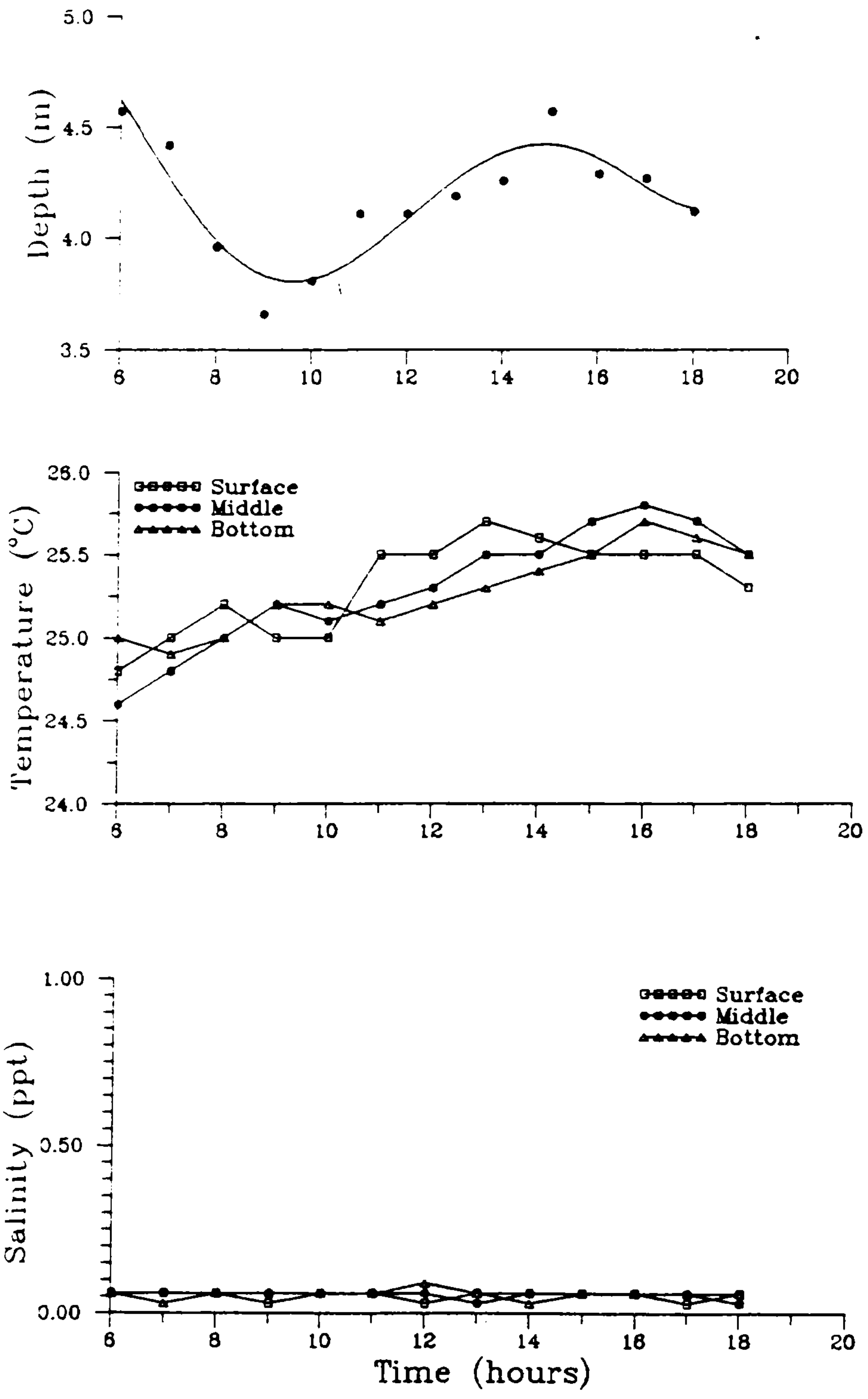


Fig. 2.2d Hydrographic variation over tidal cycle during August II 1987

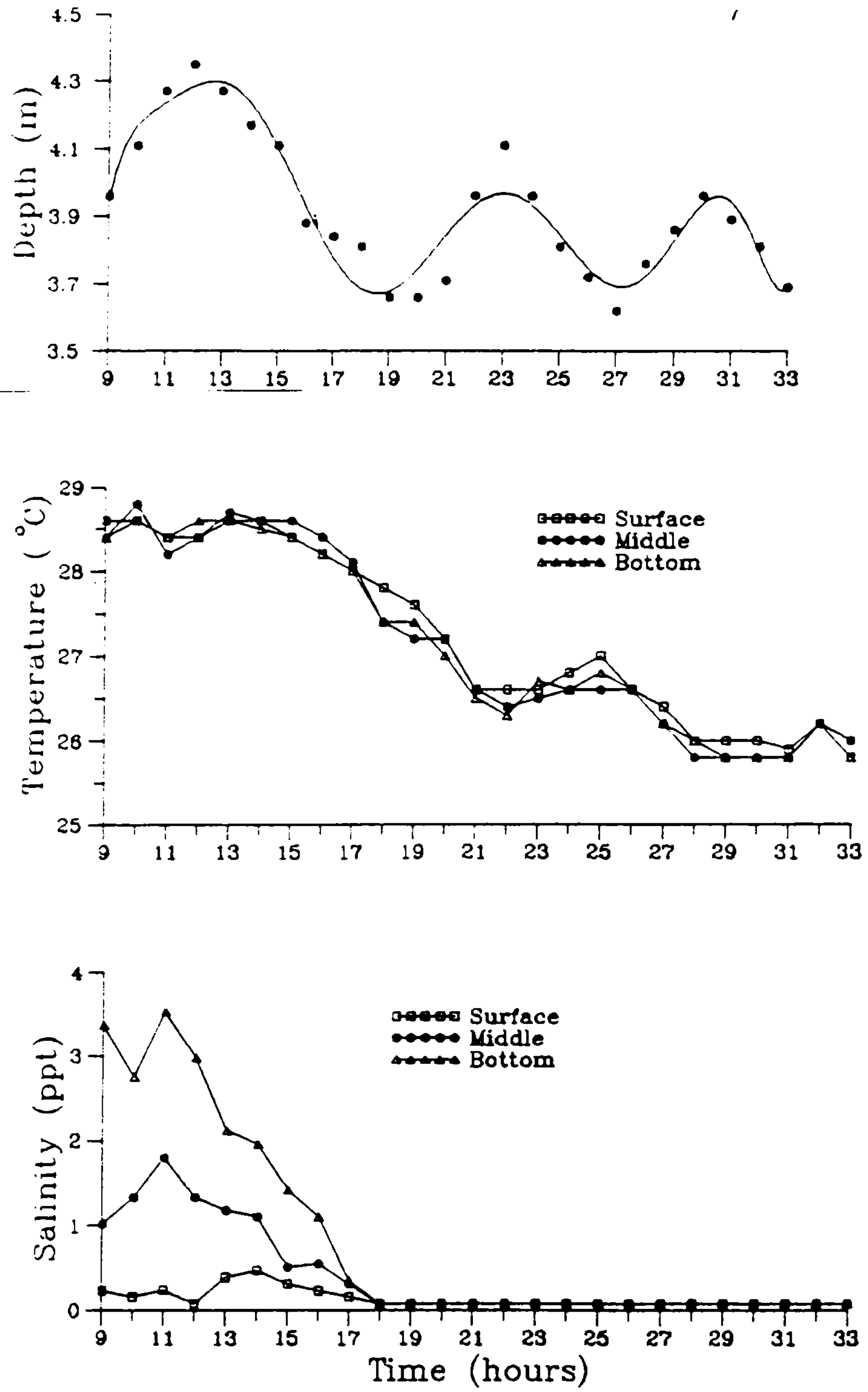


Fig. 2.2e Hydrographic variation over tidal cycle during September I 1987

structure collapsed with a corresponding reduction in temperature. This scenario was found to get repeated during II survey in September (Fig. 2.2f). In the following month (October), salinity and temperature did show specific trends corresponding to the tidal fluctuations, though the water was less saline (Fig. 2.2g). January marks a distinct deviation from the preceding monsoon months with a water level difference of 1.05 m between flood and ebb. Pattern of salinity and temperature variation also depict clear demarcation (Fig. 2.2h). February and March follow a similar structure (Fig. 2.2i &j).

The overall variations manifests 3 distinct sets of salinity and temperature structures over tidal cycle during the study period extending from June 1987 to March 1988. Obviously June, July and I survey in August with a low salinity surface water mark the initial phase of dilution due to precipitation. However the surface levels seems to be intact responding to the sequentiality of tidal movement. Temperature shows an inverse relationship during this period indicating low temperature of sea water that floods into the estuary. Distribution of temperature in an estuary is dependent on the temperature of the incoming river and sea water, mixing processes and exchange of heat through the surface. During the warmer, months the river water gets hotter than the sea water due to the greater heat capacity of the sea and its slower response to the heating and cooling processes. This testifies the above observation. Whereas a converse relationship between temperature and salinity was observed from August II survey onwards. During the period salinity and temperature vary sympathetically. This could be mainly due to the monsoonal precipitation effects. Even the non-stratified nature of salinity structure was because of the high influx fresh water owing to torrential precipitation. October onwards a low stratification was observed in salinity which again varies according to the tidal influx, but with a phase lag. The temperature profiles vary inversely with the salinity trend. This is again attributable to the differential response of river and sea waters to heating and cooling processes.

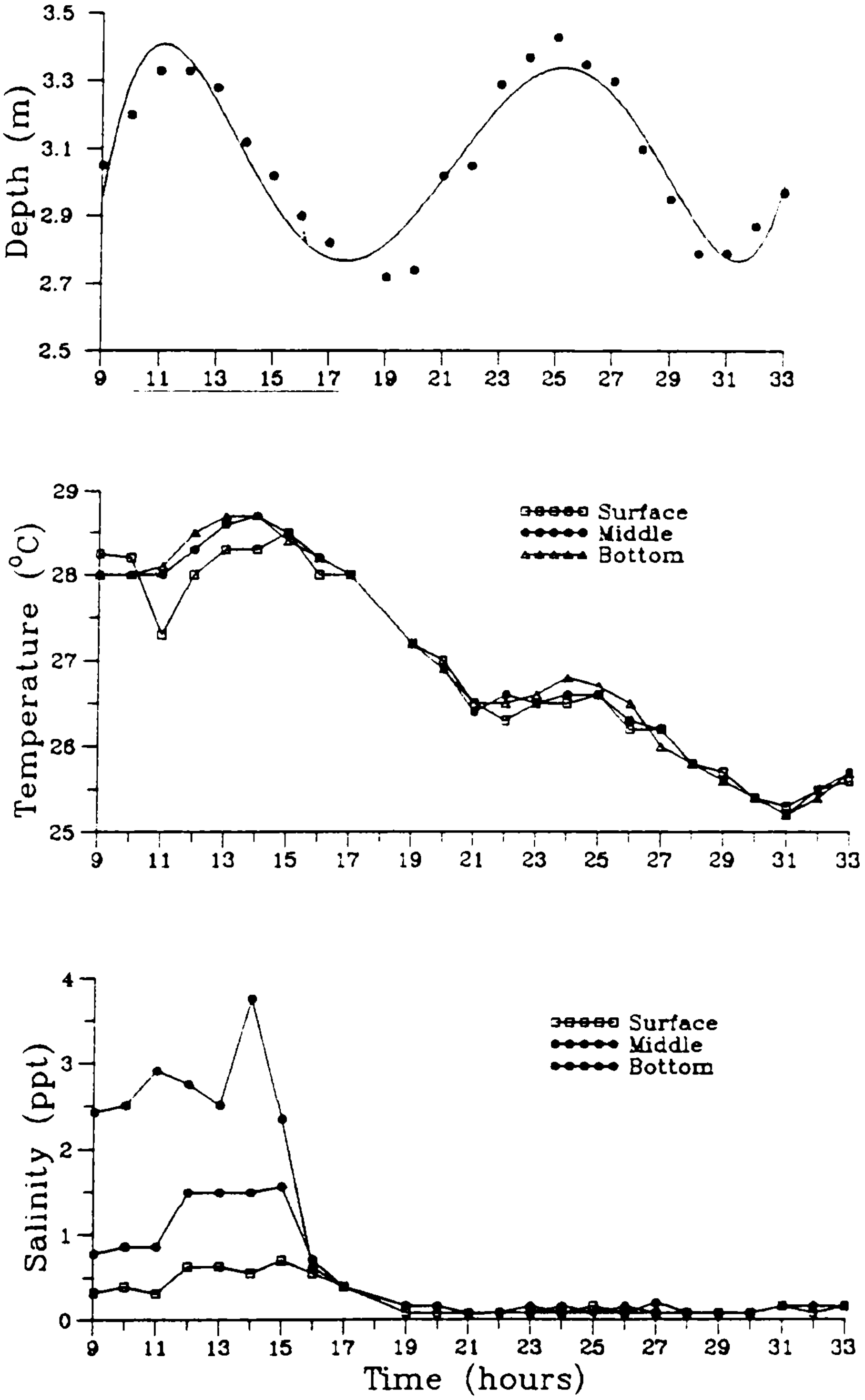


Fig. 2.2f Hydrographic variation over tidal cycle during September II 1987

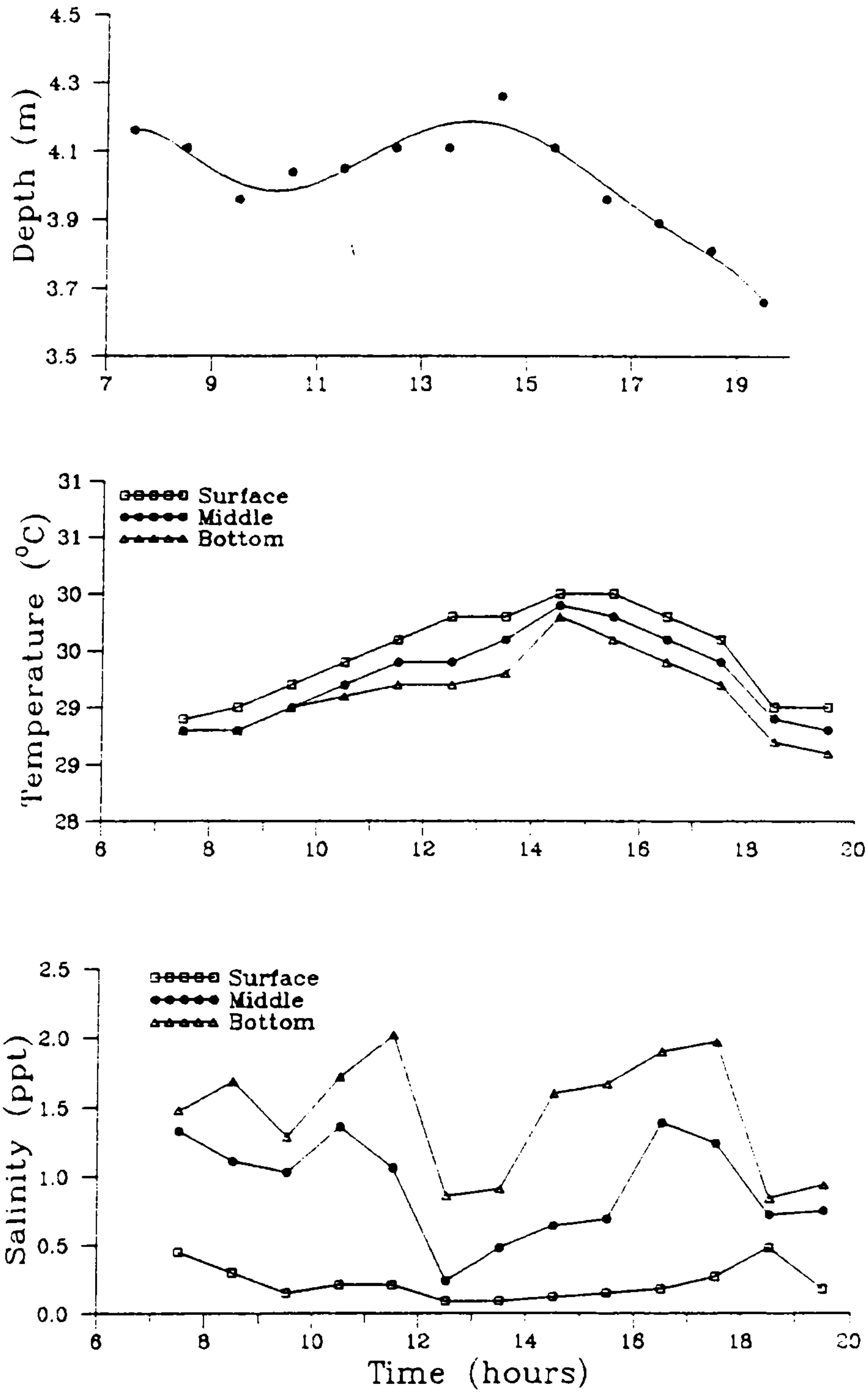


Fig. 2.2g Hydrographic variation over tidal cycle during October 1987

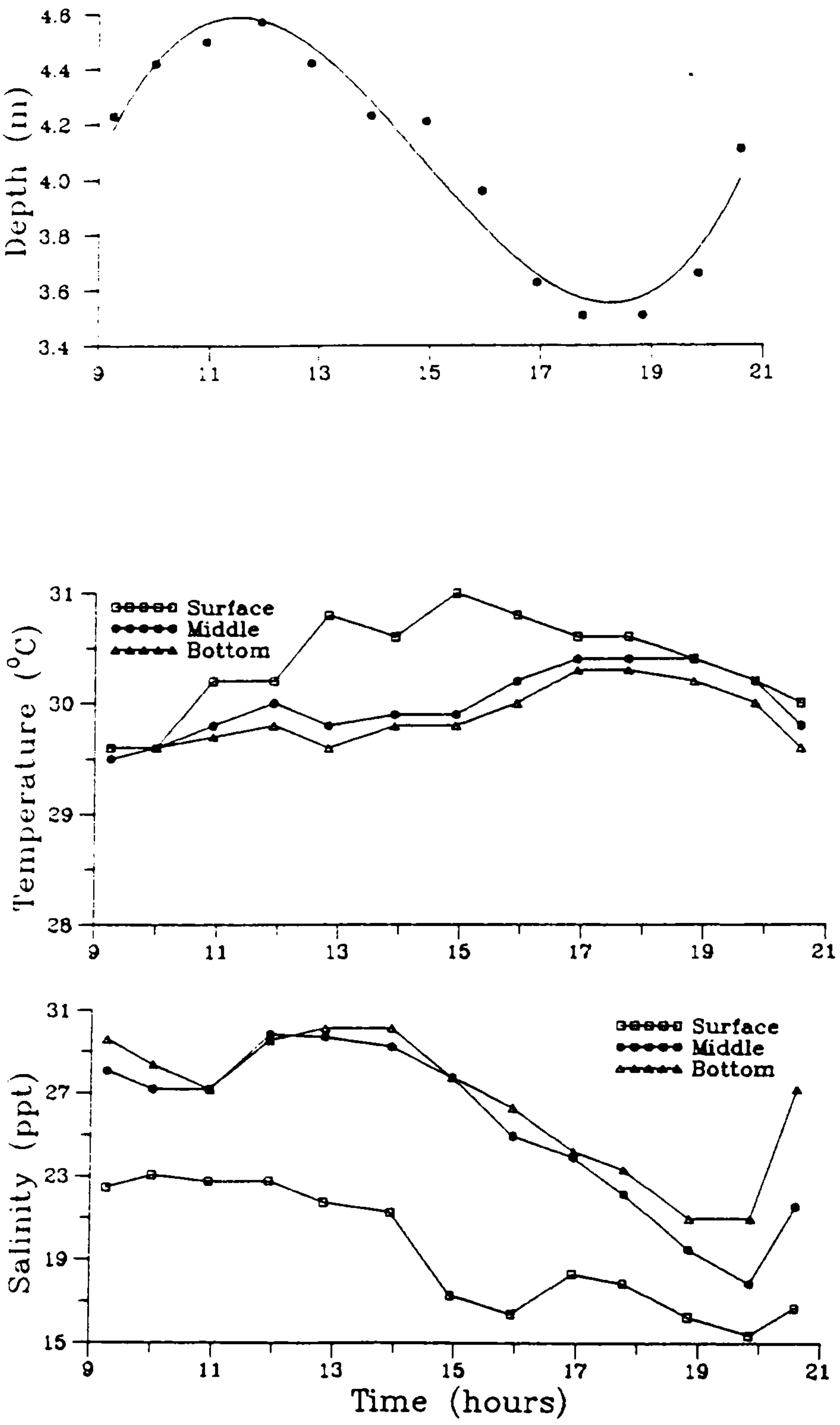


Fig. 2.2h Hydrographic variation over tidal cycle during January 1988

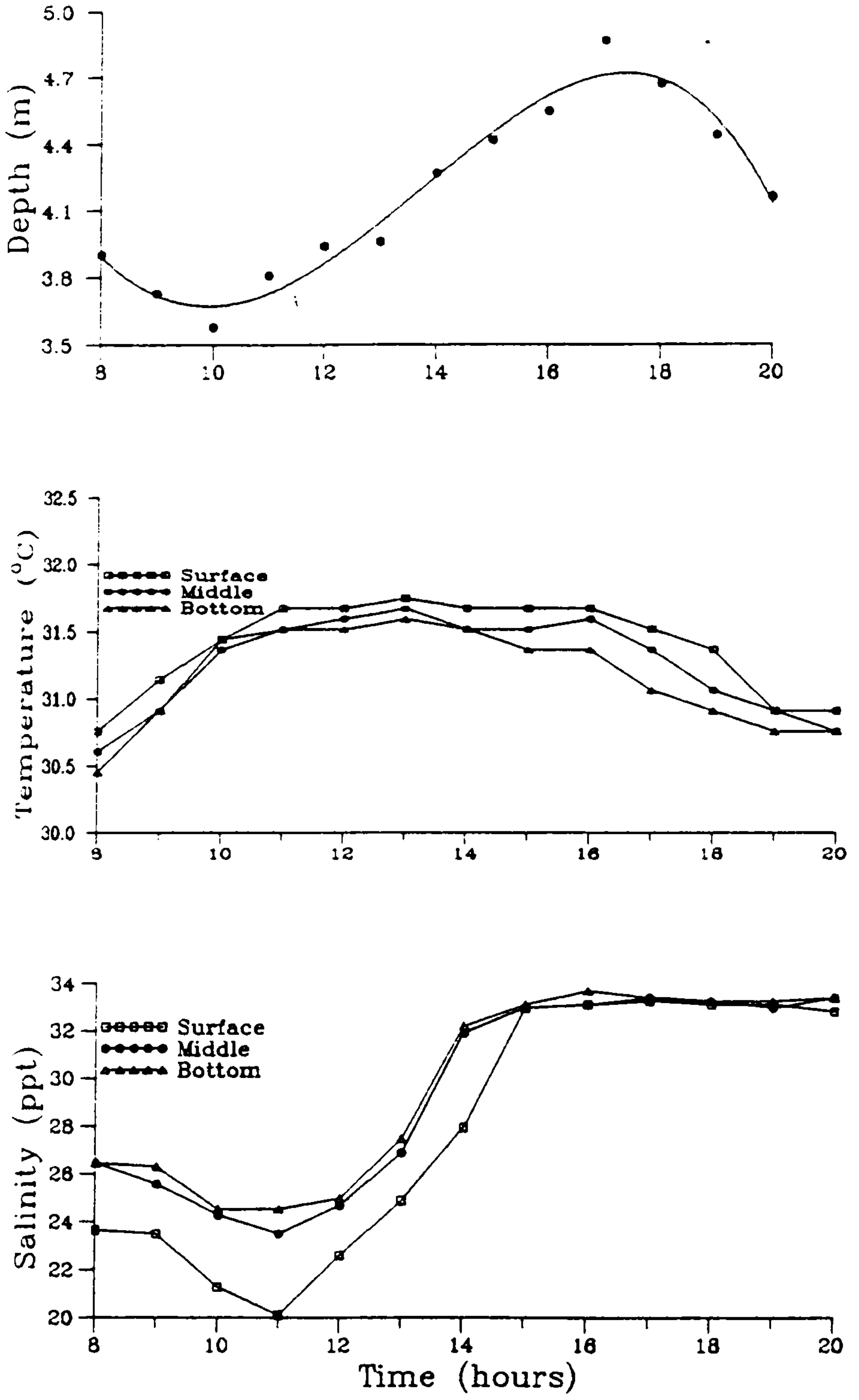


Fig. 2.2i Hydrographic variation over tidal cycle during February 1988

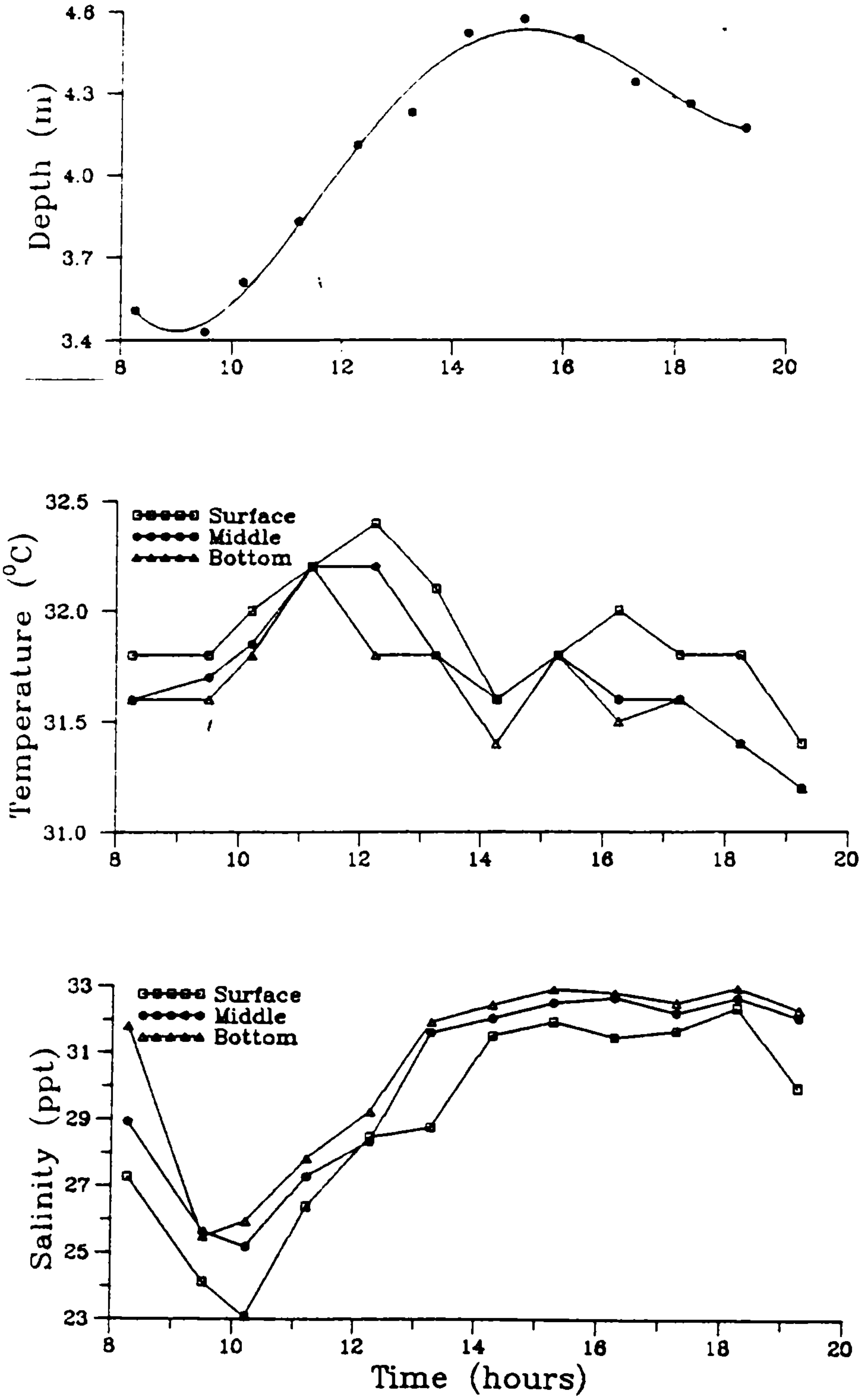


Fig. 2.2j Hydrographic variation over tidal cycle during March 1988

2.4.2 Longitudinal variation of hydrographic parameters

Temperature :

The distribution of surface, mid-depth and bottom temperatures at different locations during the period of survey is given in table 2.3. Time series of temperature at different levels are given in figures 2.3a-c. Average variations are given in Table 2.4. During the study period, a maximum of 33.75°C was noticed in the surface in May while the minimum recorded was 26.5°C during the second survey in August. The maximum annual average temperature at surface was noticed at the station near road bridge (4.8 km upstream: 30.35°C) while the average minimum was recorded at station near bar mouth (29.3°C). Generally the water temperature was found to be dependent on the solar radiation. The diurnal effect is most important factor in controlling the temperature rather than the tidal effect. The annual average minimum value in mid-depth (28.7°C) was observed at bar mouth station and the average maximum value of 29.85°C was registered at station near road bridge, the average variations between stations being 1.1°C. The average temperature values at bottom waters show an almost steady decrease from stations upstream to barmouth and ranges between 31.31°C and 28.72°C.

A decrease in temperature was noticed during the monsoon months compared to the pre- and post-monsoon periods. During the second survey in August, an uniform distribution of low water temperature of 25.75°C was noted. Relative lower temperature observed in the estuary during monsoon months was attributed to the influx of upwelled water into the estuary (Premchand et al., 1987). However, this could also be due the less heating by solar radiation as the sky was mostly overcast. They also noticed a vertical gradient of 7.6°C at the barmouth during monsoon months. During pre- and post monsoon months, surface and sub-surface temperatures depicted negligible differences.

According to De Sousa (1977) the temperature fluctuations in the water column in estuaries was governed by the atmospheric conditions. It is observed that the distribution of temperature in the estuary is greatly influenced by the inflow of freshwater and the intrusion

Water temperature -surface

Date	Distance from barmouth						
	0.55	1	1.8	2.65	3.15	4.05	4.8
26.6.87	30.8	29.8	30.6	31.1	31	31.2	31.4
25.7.87	26.9	26.1	26.8	27.7	30.1	30.8	31.2
11.8.87	28.5	27.4	27.2	27.6	29.2	29.4	29.5
28.8.87	25.752	26.5	26.5	27	26.6	26.6	26.7
10.9.87	29	29.2	29	29.1	29.5	29.6	30
23.9.87	29.5	29.4	29.7	29.4	29.6	29.6	29.8
6.10.87	30	30	30	28	28	28.1	28.1
28.10.87	29.7	29.8	29.6	29.6	29.4	29.6	30.6
27.11.87	28.2	28.2	28.8	28.4	28.2	28.4	28.4
31.12.87	28	27.8	27.8	29	28.8	29	28.7
21.1.88		30	30	30.4	30.2	30.4	30.5
24.2.88		31.8	31.6	31.8	31.8	32.8	33
21.3.88	32.1	32.1	32.4	32.6	32.6	32.8	33
26.5.88	33.1	33	33.5	33.5	33.5	33.75	33.75
Average	29.3	29.35	29.51	29.67	29.89	30.16	30.35

Water temperature-middle

Date	Distance from barmouth						
	0.55	1	1.8	2.85	3.15	4.05	4.8
26.6.87	30.4	30.7	30.5	31	31.2	30.7	31.5
25.7.87	25.4	25.7	25.6	27.7	29.9	28.9	28.8
11.8.87	26.8	26.7	27.1	27	27.7	27.4	28.4
28.8.87	25.75	26	26.5	26.5	26.5	29.5	26.5
10.9.87	26.75	26.5	29	29	29	29	29.5
23.9.87	29.7	29.3	29.34	29.4	29.6	29.6	29.6
6.10.87	29.5	29.5	29.7	28	28	28.1	28.1
28.10.87	29.7	29.8	29.6	29.6	29.6	29.6	28.8
27.11.87	28.2	28.2	29.3	28.4	28.4	28.4	28.4
31.12.87	28	28.2	28.4	28.8	29	29.3	29.8
21.1.88		29.9	29.6	30.2	30	30.1	30
24.2.88		31.6	31.5	31.6	31.4	31.8	32.4
21.3.88	32	32.4	32.4	32.8	32.6	32.4	32.8
26.5.88	32.9	32.9	33	33.5	33.5	33.5	33.3
Average	28.75	29.1	29.46	29.45	29.76	29.6	29.85

Water temperature-Bottom

Date	Distance from barmouth						
	0.55	1	1.8	2.65	3.15	4.05	4.8
26.6.87	30.2	30.4	30.5	30.8	31.1	30.1	31.2
25.7.87	25.2	25.5	26.5	26.2	27.3	26.9	25.8
11.8.87	26.5	26.6	27	27	27.7	27.2	27.4
28.8.87	25.8	26	26.5	26.5	26.5	26.5	26.5
10.9.87	26.5	26.5	27	28.5	28.5	28.2	27.5
23.9.87	29.6	29.5	29.4	29.5	29.5	29.5	29.6
6.10.87	29.5	29.5	29.7	28	28	28.1	28.1
28.10.87	29.7	29.8	29.8	29.6	29.6	29.6	29.8
27.11.87	29	29.1	29.3	28.2	28.4	28.2	28.4
31.12.87	28.1	28.3	28.6	28.9	27.9	29.3	29.6
21.1.88		29.8	30.2	29.9	29.9	29.9	30
24.2.88		31.6	31.6	31.5	31.6	31.8	32.6
21.3.88	32	32.4	32.4	32.4	32.6	32.3	32.5
26.5.88	32.5	32.9	32.9	32.25	33.25	33.25	33.25
Average	28.72	29.14	29.39	31.31	29.42	29.35	29.45

Table 2.3 Longitudinal variation of temperature at different levels (°C)

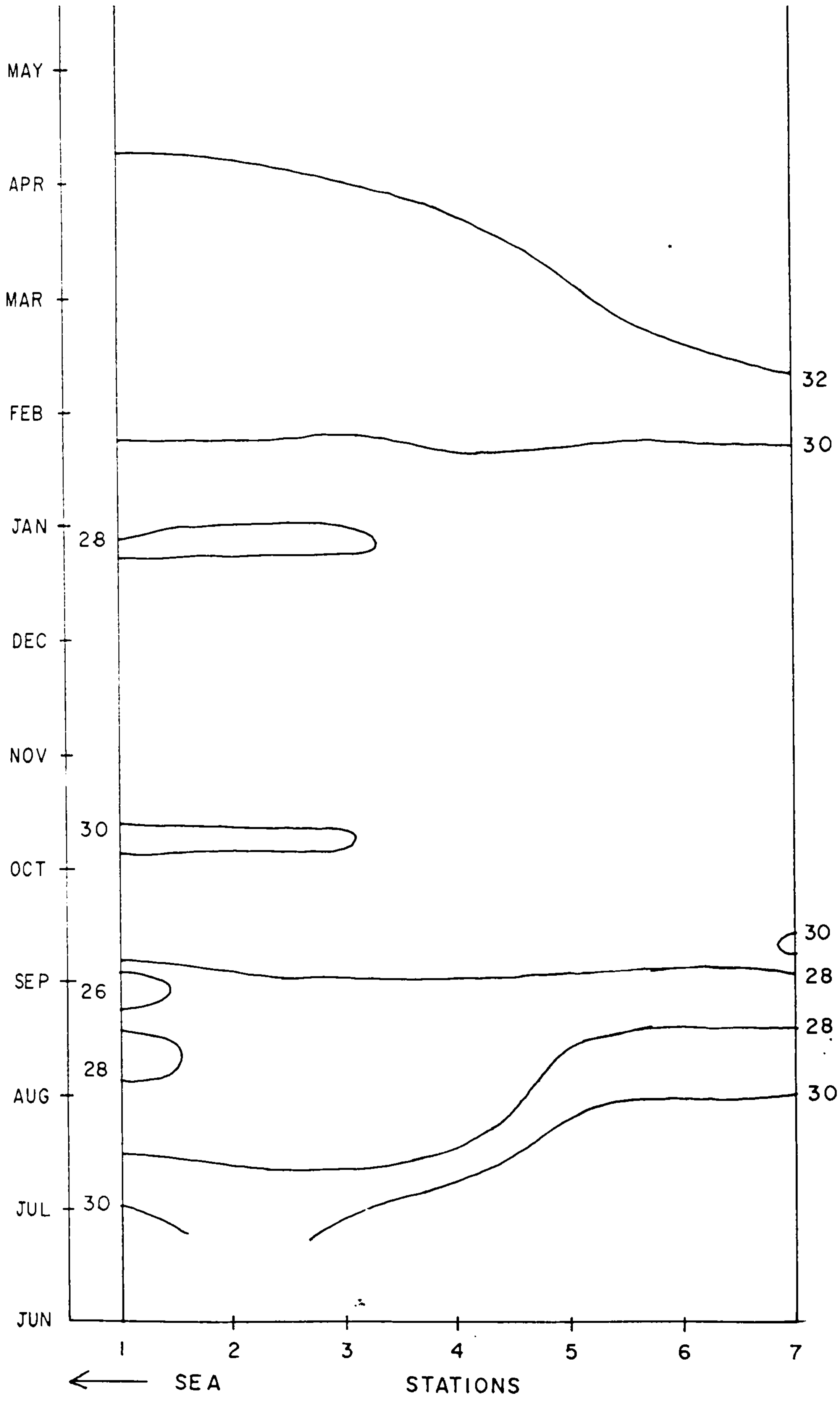


Fig. 2.3a Time series for temperature at the surface °C

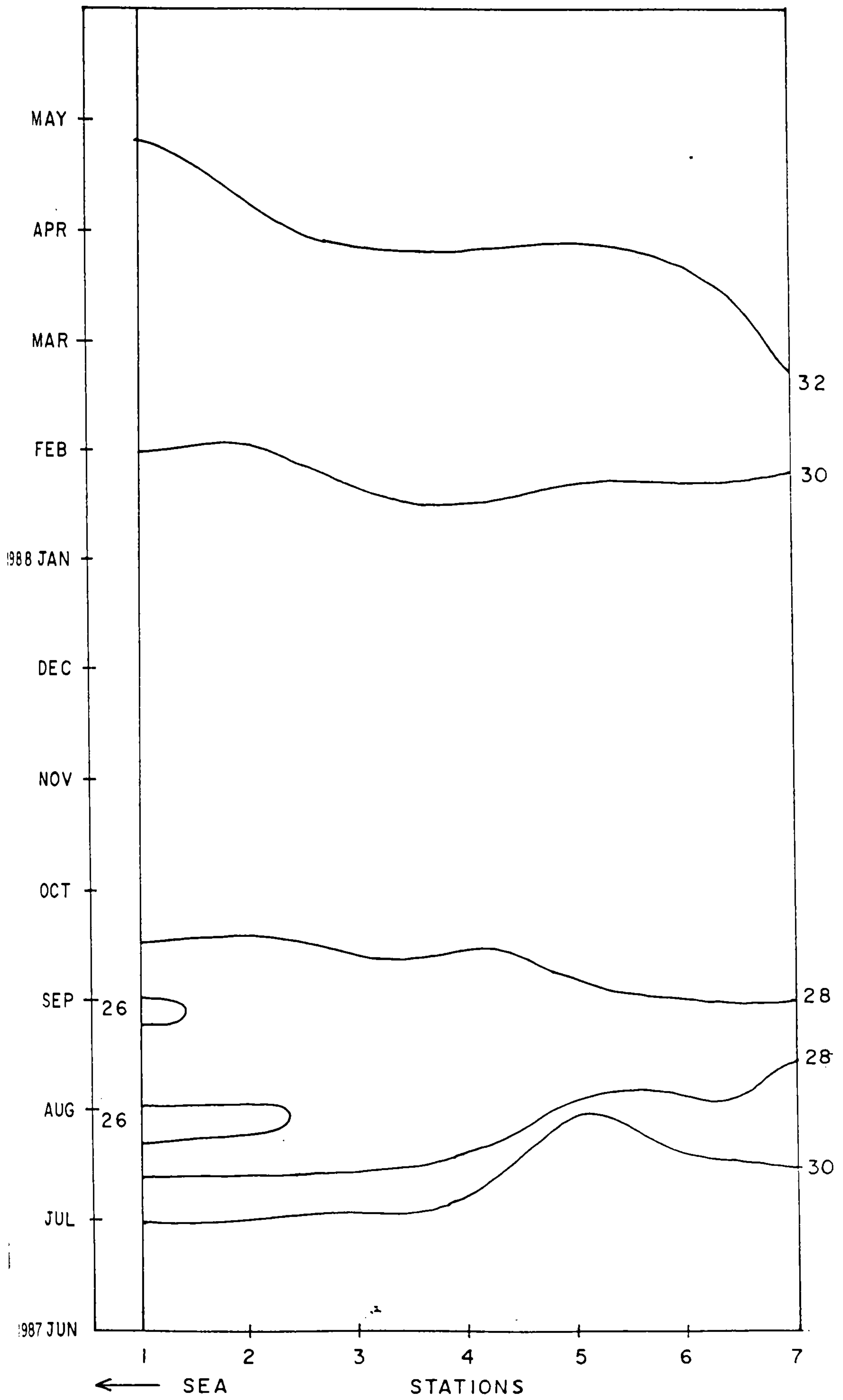


Fig. 2.3b Time series for temperature at mid depth °C

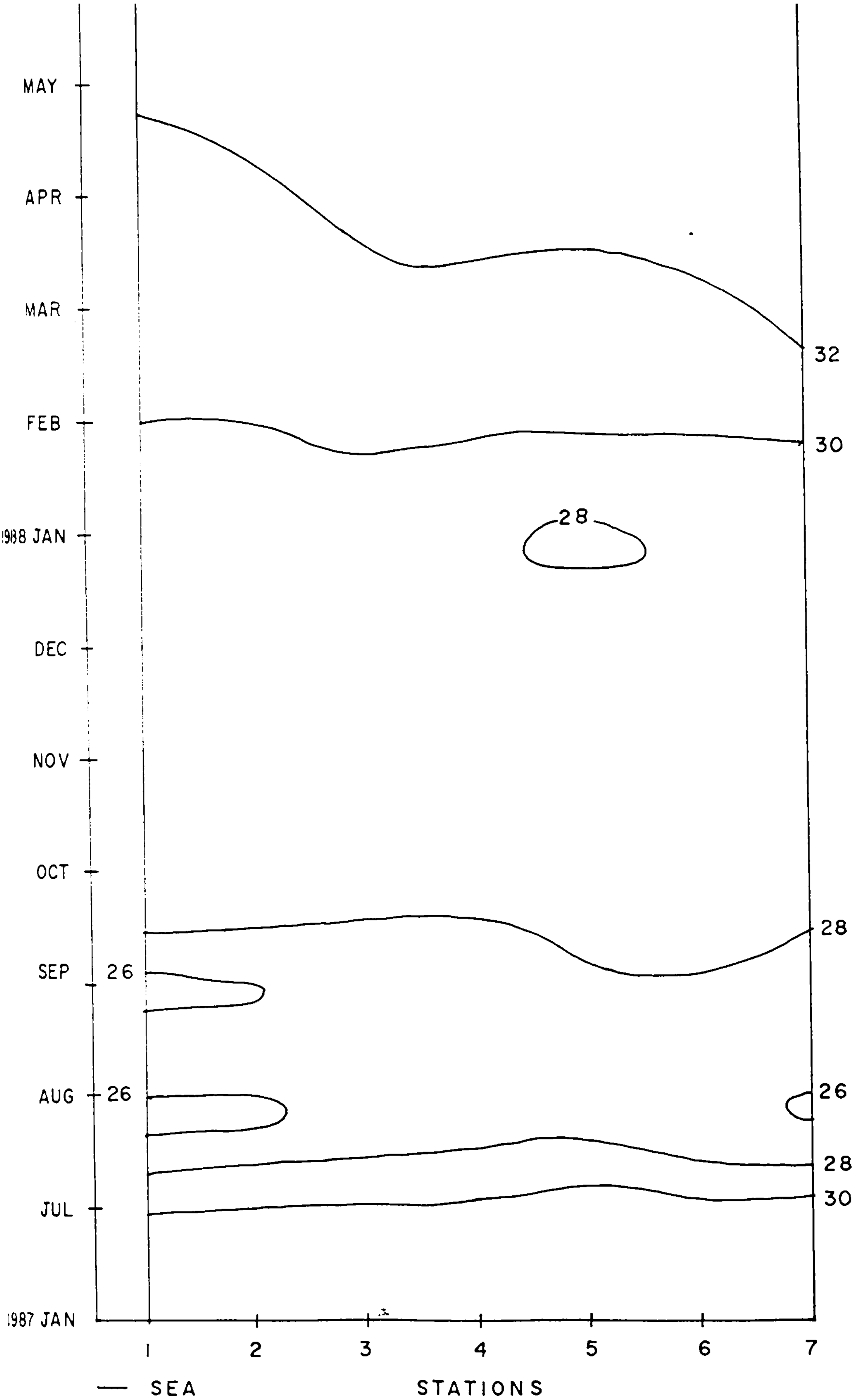


Fig. 2.3c Time series for temperature at the bottom °C

Table 2.4 Average longitudinal monthly variation of hydrography

AVERAGE MONTHLY VALUES

	Salinity (PPT)			Temperature°C			Dissolved oxygen (mg/l)		
Month	S	M	B	S	M	B	S	M	B
Jun-87	2.74	9.48	12.78	31	30.6	30.6	4.32	4.23	4.17
Jul-87	15.96	22.88	31.98	28.5	27.4	26.2	4.94	4.22	4.04
Aug.I-87	17.02	25.46	29.13	28.4	27.3	25	4.66	3.71	3.36
Aug.II-87	0.12	0.12	0.18	26.5	26.3	26.3	5.98	5.92	5.71
Sept.i-87	3.86	14.63	29.34	29.3	28.3	27.5	4.89	3.79	3.62
Sept.ii-87	9.04	22.31	29.51	29.6	29.5	29.5	5.16	4.9	4.55
Oct.i-87	3.78	16.08	25.21	28.9	28.7	28.7	5.45	5.02	4.3
Oct.II-87	0.04	0.32	1.53	29.7	29.5	29.7	5.54	5.36	4.94
Nov-87	3.07	7.95	10.6	28.3	28.4	28.6	5.56	5.94	5.55
Dec-87	13.09	25.52	28.13	28.4	28.7	28.7	5.56	5.43	5.4
Jan-88	26.31	29.41	29.61	30.1	30.1	29.9	6.15	6.3	5.5
Feb-88	30.44	30.54	31.52	31.8	31.8	31.2	5.29	5.43	4.46
Mar-88	32.7	33.95	34.8	32.5	32.5	32.3	4.75	4.54	4.35
May-88	34.43	34.43	34.51	33.4	33.4	33	4.55	4.05	3.75

of saline water due to tidal current. Similar results were obtained by Sankaranarayanan et al. (1969) on observations made on the temperature distribution in the Cochin estuary.

Investigations in Vasishta-Godavari estuary by Saisastry and Chandramohan (1990) have shown that at the lower part of the estuary, temperature was influenced by the incursion of cool neritic water while at the upper reaches it was dependent on insolation, increasing depth of water column, movement of water with changing tide and occasional addition of farm drainage after cessation of annual floods. It is well known that during monsoon months (June-September) nutrient rich, low oxygenated cold water due to upwelling phenomena is fairly widespread along the west Indian coast (Sharma, 1968). The incursion of such cold water in to the estuarine systems along west coast results in the lowering of water temperature in the lower reaches of estuarine systems. The upwelling sets in earlier in the south and progressively spreads towards north (Reddy and Sankaranarayanan, 1968). The lowest temperature recorded in Beypore estuary at all levels during the August second survey could be due to this effect of upwelling. Incursion of upwelled water in Cochin backwaters was reported by Ramamirtham and Jayaraman (1963) and Sankaranarayanan and Qasim (1969). Effect of upwelled water was also noticed in the Mandovi and Zuari estuaries (Sankaranarayanan and Jayaraman, 1972).

In the Beypore estuary, the river discharge greatly influences the temperature distribution. Maximum river discharge to the estuary was reported during the southwest monsoon months and very little discharge during March-April (James and Sreedharan, 1983). The temperature gradually increases from February to May and then decreases during southwest monsoon and thereafter increases steadily. This is in tune with the observations made in other estuaries (Qasim and Sen Gupta, 1981; Cherian et al., 1975; Haridas et al., 1973). During the month of August, a temperature difference of 5°C between surface and bottom waters was noticed, whereas such marked differences are lacking for the other months.

To conclude, in Beypore estuary the temperature regime showed seasonal cycle with increasing temperature during pre- and post monsoon period and low temperature during southwest monsoon period. Surface to bottom temperature difference were marked only during the month of August compared to other months of observation. The cold water regime observed during the month of August could be due to the incursion of upwelled water in to the estuary.

Salinity:

The spatial distribution of salinity in surface, mid-depth and near bottom water samples during the period of study is given table 2.5 and in time series (Fig. 2.4a-c). The longitudinal variation for different months are illustrated in graphs (Fig. 2.5). The maximum landward extend of salinity intrusion due to tidal forcing was noticed up to 22 km upstream during April-May period.

Salinity varied widely in space and time. In the beginning of June, except for the first two kilometer zone from the bar mouth the estuary becomes fresh water dominated with increasing river discharge. During June 1987 the surface salinity at different stations was more or less 5% while the bottom salinity near bar mouth was 25%. The saline water intrusion due to tidal force was found only up to 3 km upstream. Stratification was more pronounced near to the bar mouth and the vertical salinity gradient was 20%. Studies by James and Sreedharan (1983) in the estuary during monsoon have shown the extend of salinity intrusion up to fisheries wharf (1.8 km upstream), which is in full agreement with the present observation. In July, saline water incursion was up to green island (2.65 km upstream). Here again, stratification was pronounced near to the bar mouth region. During the first survey period in August, clear stratification was observed up to Road Bridge (4.80 km upstream) with a vertical salinity gradient of 20%. But during the second survey in August, the estuary was totally fresh water dominated, owing to high fluvial discharge.

Table 2.5 Longitudinal variation in salinity

Salinity-surface

Date				Stat;ions			
	L.H	P.O	F.H	G.I	T.F	R.B	RDB
26.687	3.65	3.16	2.68	3.16	2.92	1.95	1.7
25.7.87	35.21	29.09	16.23	19.91	4.9	3.37	3.06
11.8.87	26.82	26.7	26.93	11.22	9.26	11.22	7.01
28.8.87	0.12	0.06	0.12	0.19	0.19	0.06	0.12
10.9.87	5.96	5.96	4.39	3.82	2.51	1.58	2.51
23.9.87	11.92	11.51	9.42	6.28	5.96	4.39	13.81
6.10.87	2.2	3.45	9.1	2.2	1.26	0.62	0.62
28.10.87	0.1	0.09	0.03	0.03	0.03	0.03	0.03
27.11.87	8.26	6.67	3.07	1.17	1.32	0.73	0.29
31.12.87	17.48	16.28	18.13	16.67	8.92	7.75	6.43
21.1.88 ..		31.63	31.63	23.06	29.94	22.17	19.51
24.2.88	33	32.9	33.2	32.1	32.17	26.91	22.81
21.4.88	34.57	35.24	35.94	32.89	27.52	31.55	31.21
26.5.88	34.13	35.18	35.53	34.83	34.83	34.49	32.05
Average	16.52	17.5	16.17	13.4	11.5	10.5	10.08

Salinity - mid depth

Date				Stations			
	L.H	P.O	F.H	G.I	T.F	R.B	RDB
26.687	19.77	19.23	12.68	3.89	3.16	3.98	3.65
25.7.87	35.23	35.65	33.69	33.38	27.87	19.6	9.8
11.8.87	27.49	30.3	31.42	22	23	18.51	25.53
28.8.87	0.19	0.12	0.06	0.12	0.12	0.12	0.06
10.9.87	32.32	31.39	10.67	7.22	5.65	5.65	8.53
23.9.87	26.68	26.58	27.92	28.58	19.77	15.26	14.08
6.10.87	23.22	26.28	24.65	13.18	16.95	3.26	5.02
28.10.87	0.34	0.24	0.24	0.15	0.3	0.84	0.15
27.11.87	13.67	11.75	11.93	5.12	7.6	5.26	0.29
31.12.87	30.59	29.66	21.06	27.2	28.95	27.45	13.75
21.1.88 ..		32.07	31.78	30.15	28.97	27.78	25.72
24.2.88	33.5	33.05	32.85	32.66	32.32	30.42	18.98
21.4.88	36.25	35.58	35.24	32.89	32.91	32.23	32.55
26.5.88	34.83	34.53	34.83	33.41	35.18	34.49	33.79
Average	24.16	24.74	22.07	19.77	18.77	15.94	13.71

Salinity - bottom

Date				Stat;ions			
	L.H	P.O	F.H	G.I	T.F	R.B	RDB
26.687	26.77	26.77	18.65	3.89	4.13	5.01	4.22
25.7.87	33.38	35.22	34.3	33.69	31.24	26.64	29.4
11.8.87	33.66	31.98	31.98	31.14	25.25	23	26.93
28.8.87	0.06	0.12	0.06	0.12	0.06	0.06	0.12
10.9.87	29	29.2	29	29.1	29.5	29.6	30
23.9.87	29.5	29.4	29.5	29.3	29.6	29.6	29.8
6.10.87	31.71	31.71	27.58	22.29	21.3	20.2	21.99
28.10.87	2.81	1.06	1.86	1.84	1.45	1.57	0.15
27.11.87	14.35	13.75	12.24	5.7	9.21	14.62	4.39
31.12.87	29.97	30.59	26.61	29.61	28.95	27.78	23.42
21.1.88		32.22	31.28	30.78	29.85	28.67	24.81
24.2.88	33.8	32.76	33.05	32.66	32.76	31.15	24.5
21.4.88	35.58	34.91	33.9	33.56	35.89	34.23	35.58
26.5.88	34.83	35.22	34.83	34.49	34.49	34.49	33.79
Average	25.8	26.06	25.88	22.58	22.39	21.9	20.6

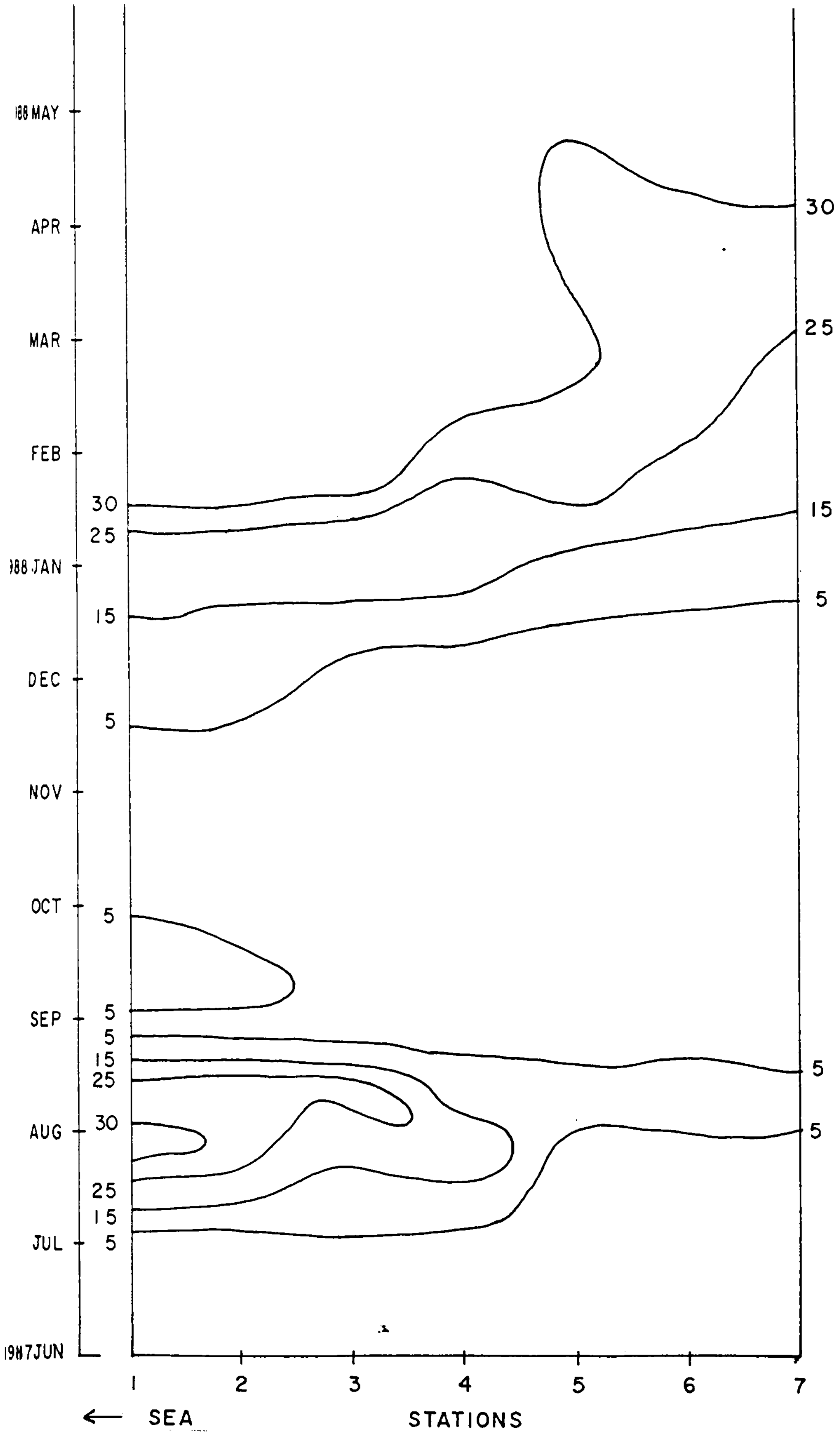


Fig. 2.4a Time series for salinity at surface (ppt)

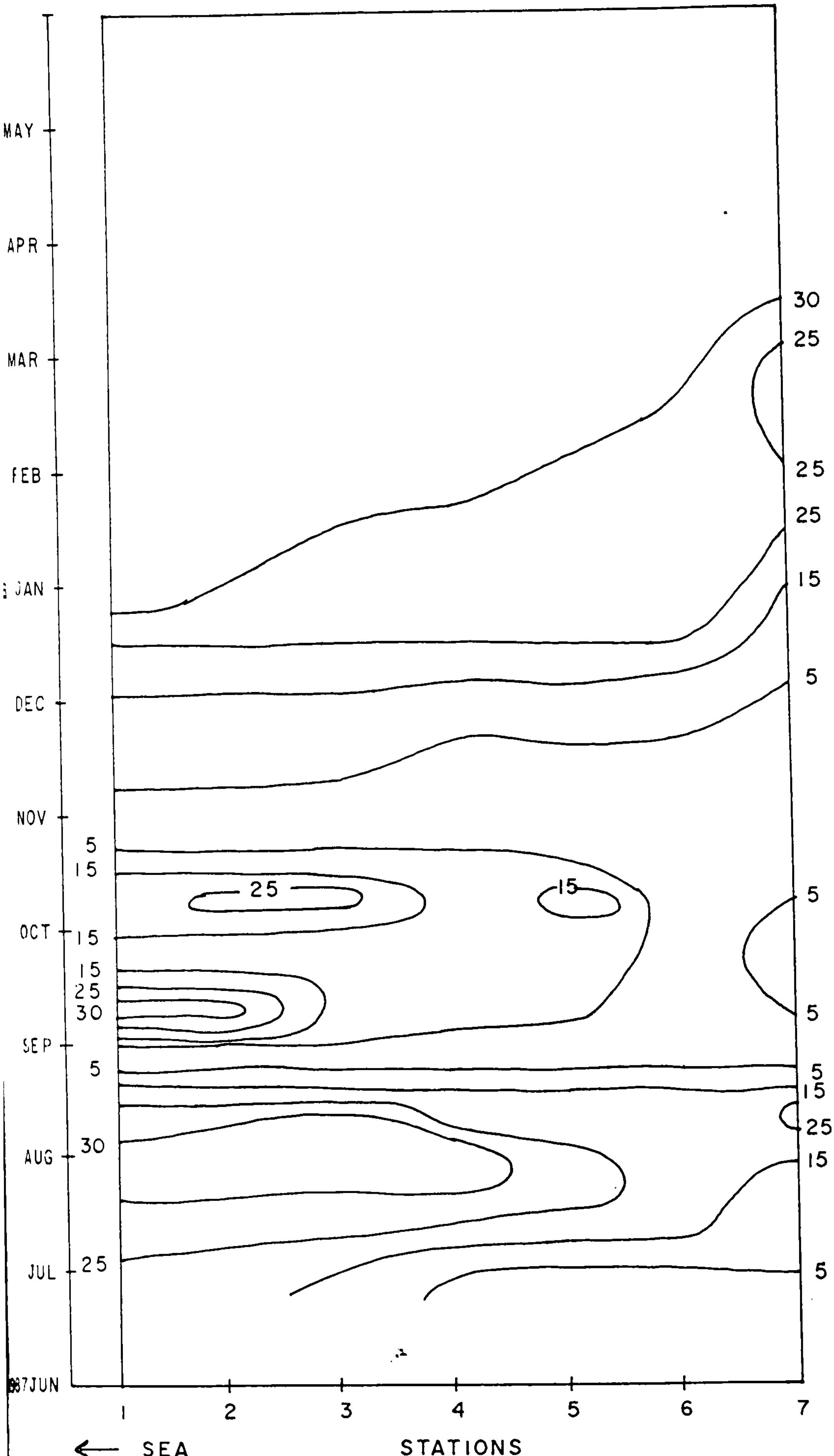


Fig. 2.4b Time series for salinity at mid depth (PPT)

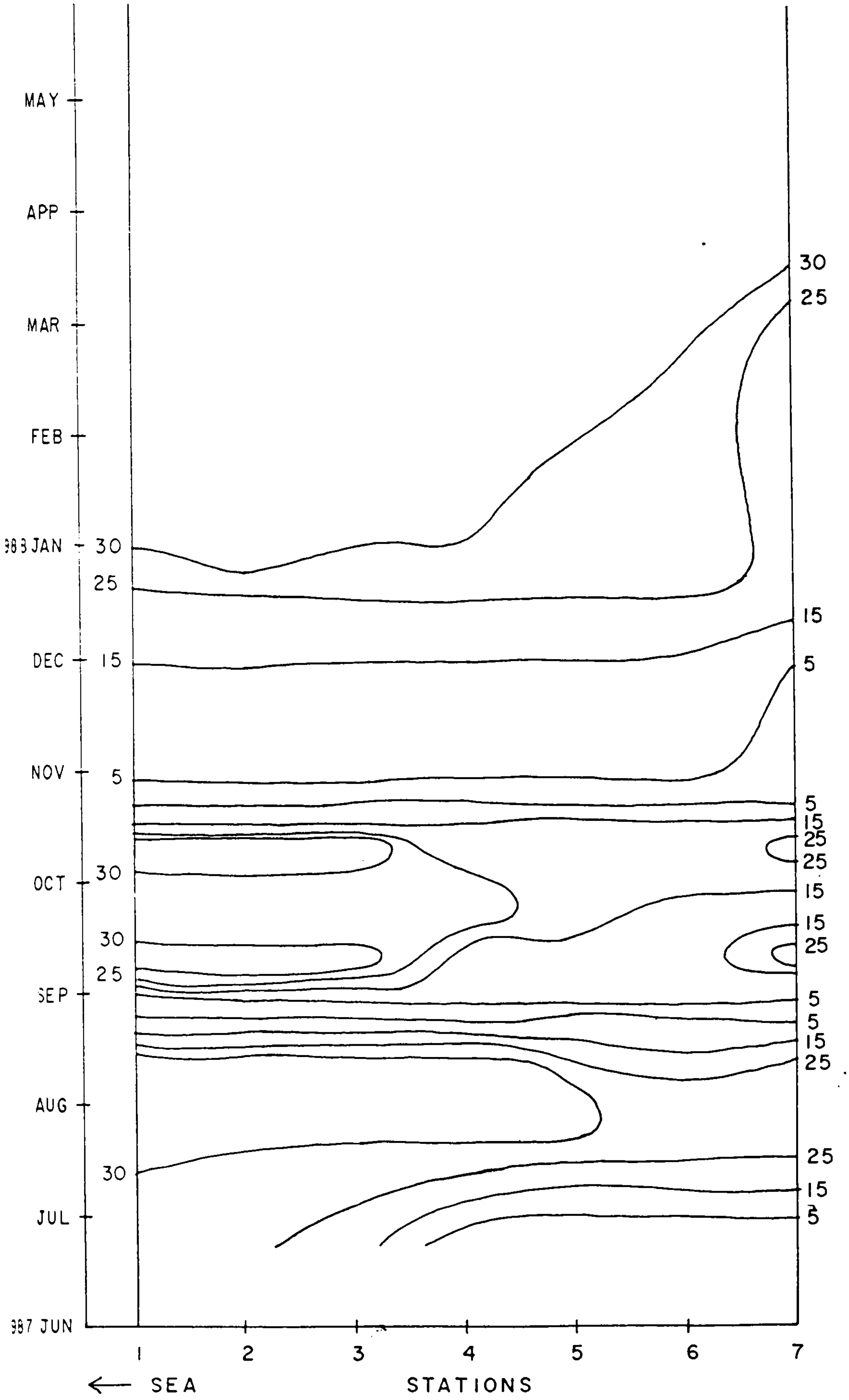


Fig. 2.4c Time series for salinity at bottom (PPT)

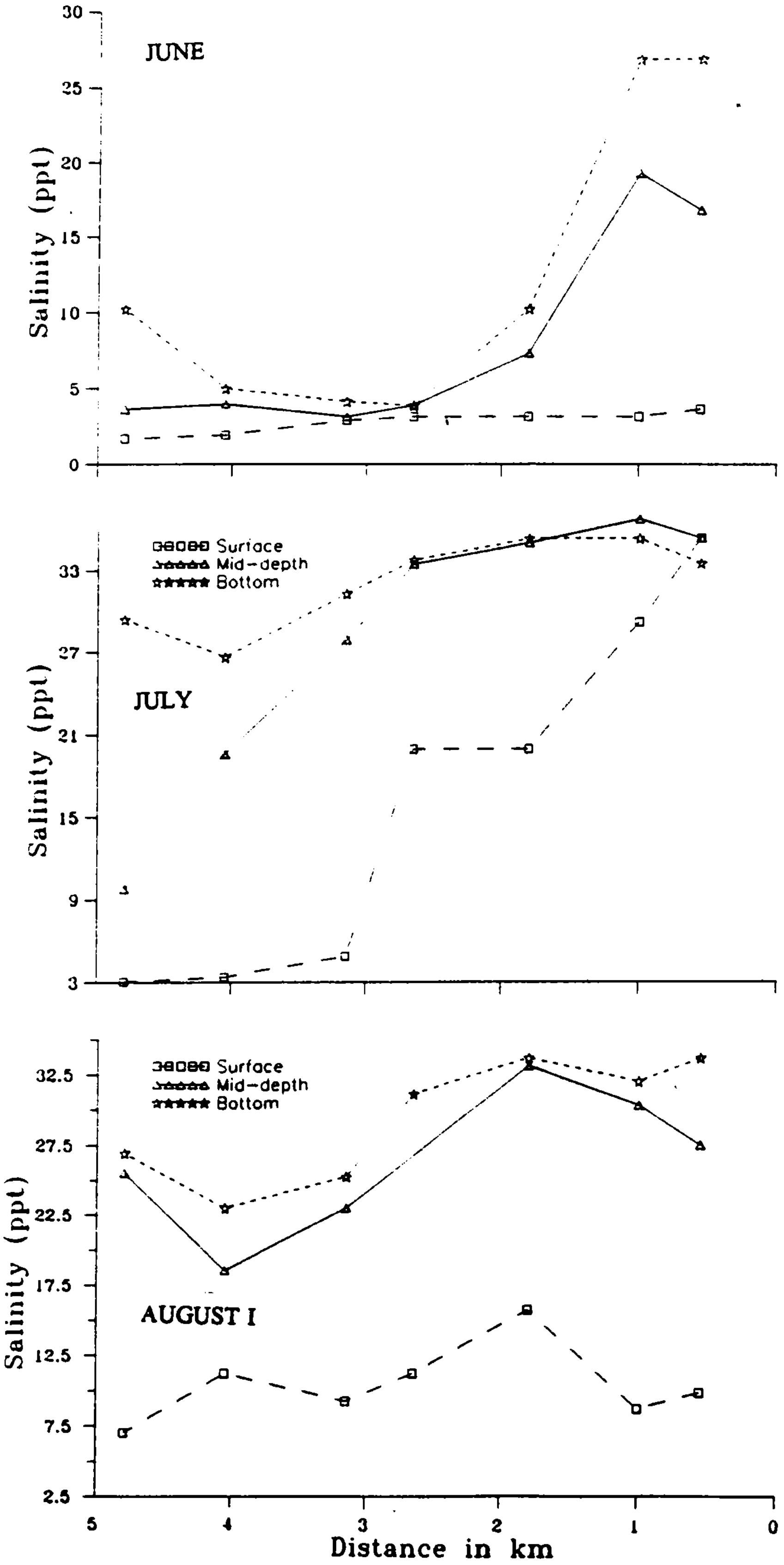


Fig. 2.5 Longitudinal variation of salinity during different months

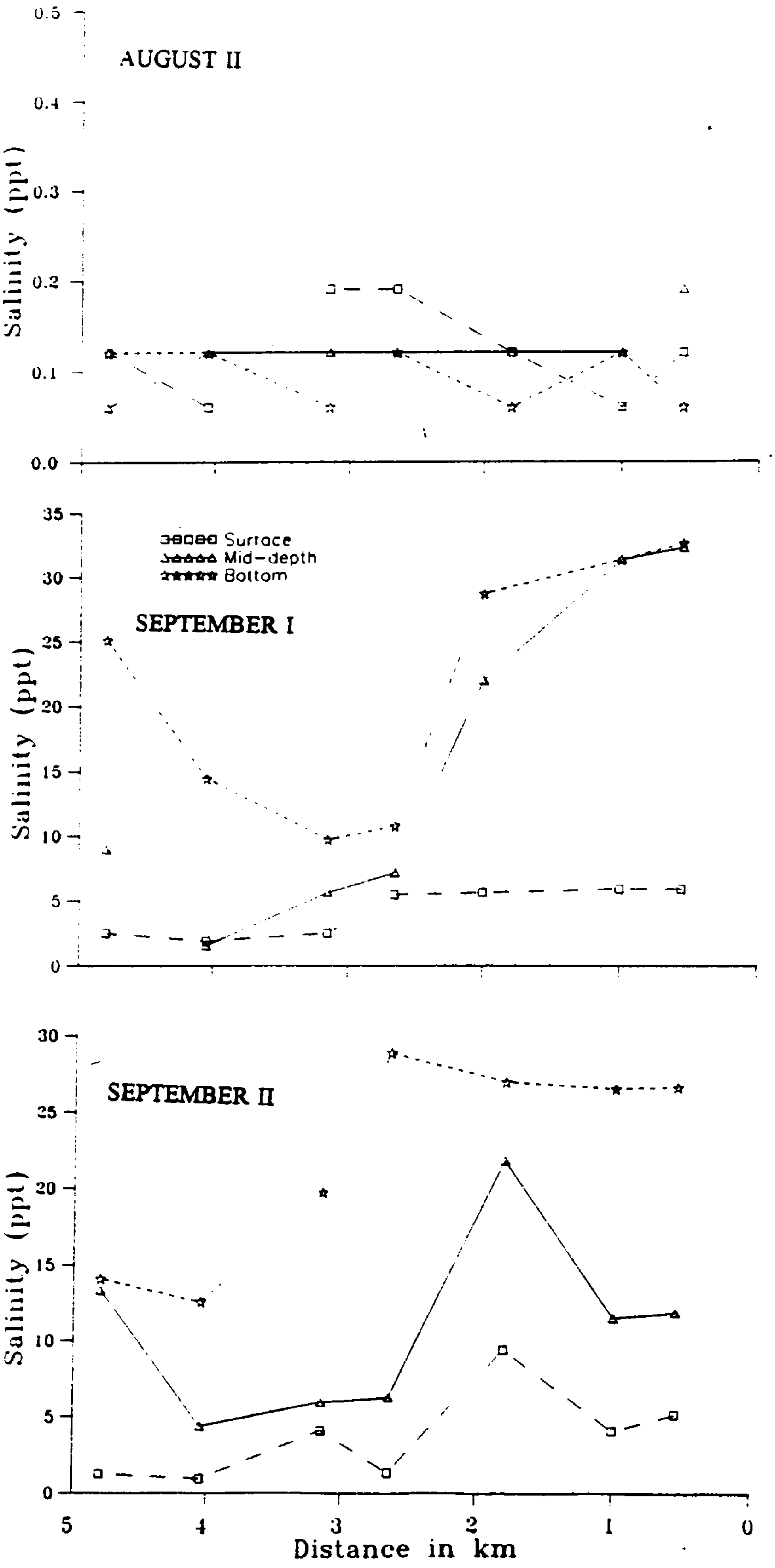


Fig. 2.5 Continued......

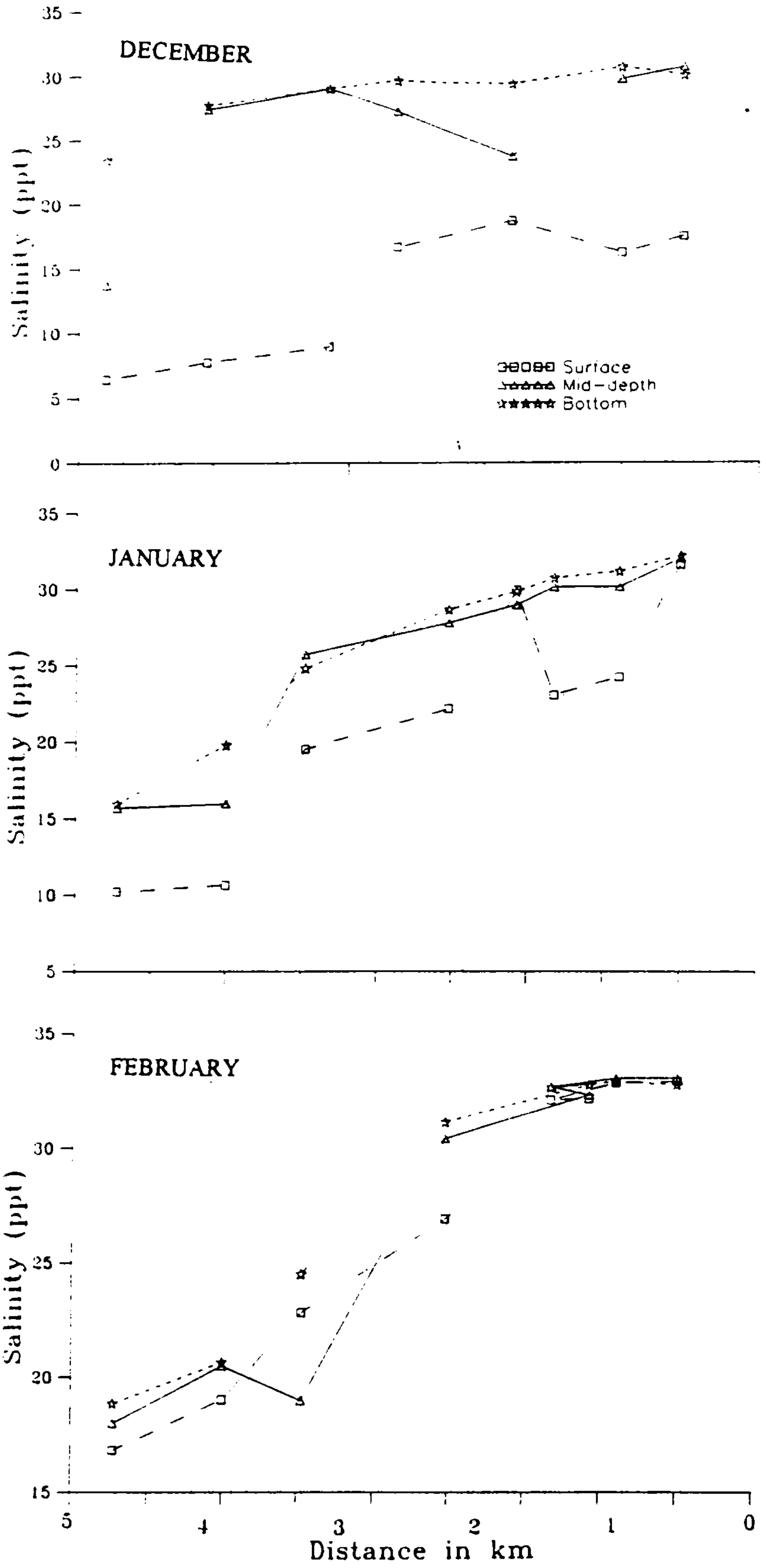


Fig. 2.5 Continued......

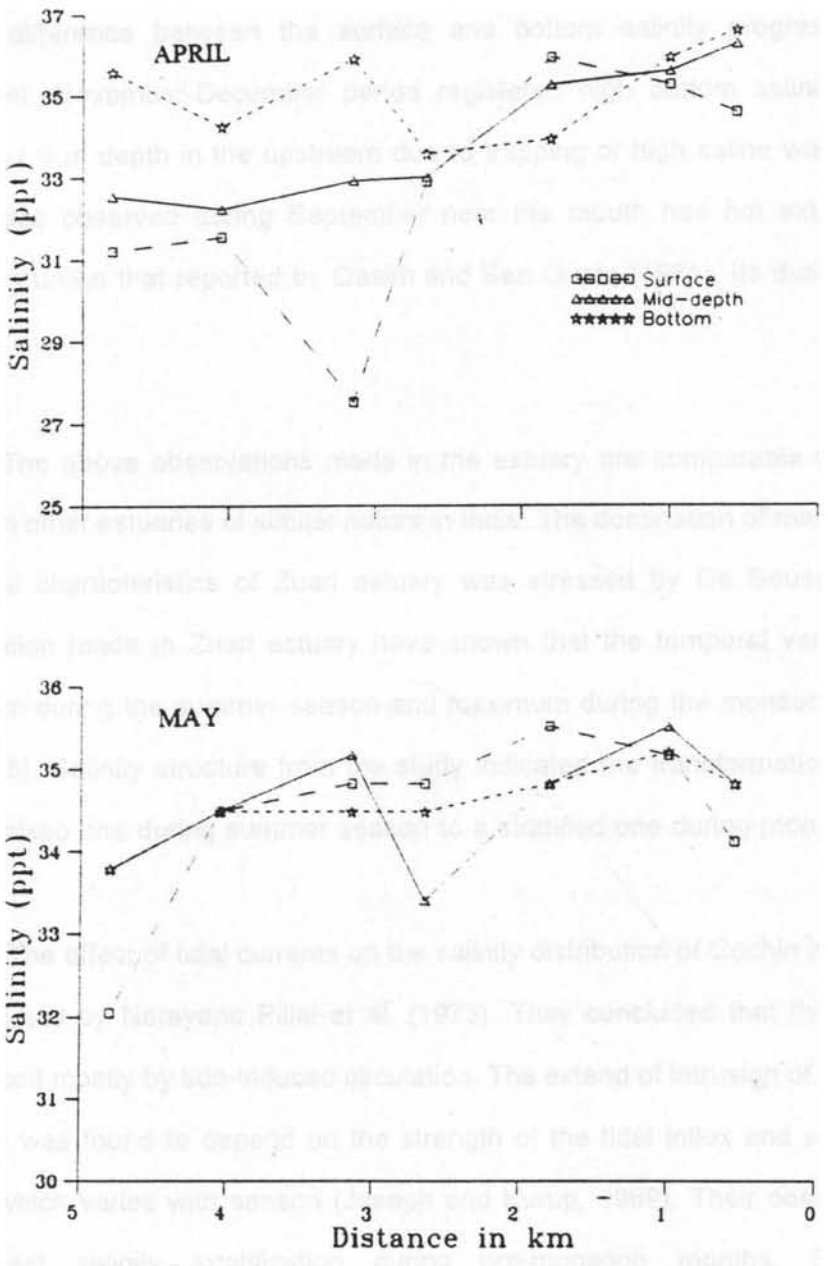


Fig. 2.5 Continued......

Stratified nature of the estuary continued in a more distinctive manner during the 1st survey in September. Vertical salinity gradient near to the bar mouth was 23%. During September second survey, stratification was observed up to station near the green island. Stratification extended further upstream during October. After October with the decrease in fresh water discharge the estuary become slowly marine dominated with well mixed conditions as the difference between the surface and bottom salinity progressively became less prominent. November-December period registered high bottom salinity at stations which exceeded 9 m depth in the upstream due to trapping of high saline waters in pockets . The salt wedge observed during September near the mouth has not extended beyond 1 km upstream unlike that reported by Qasim and Sen Gupta (1981). Its duration was limited to a month.

The above observations made in the estuary are comparable with the observations made on other estuaries of similar nature in India. The domination of monsoon on the physico-chemical characteristics of Zuari estuary was stressed by De Sousa (1977). Tidal cycle observation made in Zuari estuary have shown that the temporal variations in salinity are minimum during the summer season and maximum during the monsoon season (Cherian et al., 1975). Salinity structure from the study indicated the transformation of the estuary from a well mixed one during summer season to a stratified one during monsoon.

The effect of tidal currents on the salinity distribution of Cochin backwater system was investigated by Narayana Pillai et al. (1973). They concluded that the salinity values were influenced mostly by tide-induced circulation. The extend of intrusion of saline water in Cochin estuary was found to depend on the strength of the tidal influx and strength of fresh water efflux which varies with season (Joseph and Kurup, 1989). Their observation also supports the least salinity stratification during pre-monsoon months. Studies reported by Sankaranarayanan et al. (1986) also support the information presented above. Onset of monsoon manifests sudden changes in the hydrological parameters. A saline wedge was developed during monsoon with near freshening of the surface waters. Salinity increase during northeast monsoon and winter were due to reduced fresh water influx. Diurnal variations in salinity were found to be in tune with tides, exhibiting increase during flood tide and decrease during ebb tide. The phase lag observed between the peak flood tide and salinity can be attributed to the nature of flushing, especially due to the resistance encountered by the inflow of freshwater down the estuary. Considerable mixing was noticed at the final stages of flood tides and the mixed water flows out during ebb tides. This could be one of the reasons for sustenance of salinity at different levels even after considerable lapse of time during ebb tide.

Observation of Singbal (1976) in the Mandovi estuary could also establish the relation between temperature and salinity and concluded that they are influenced by tides in all seasons. Apart from the tides and routine efflux of river water, the salinity regime in Vasishta-Godavari estuary was found to depended on various factors such as annual flood, shallowness of stations and turbulent mixing (Saisastry and Chandramohan, 1990). Even in Beypore estuary, certain deeper parts are found to trap high salinity waters.

The salinity distribution in the Beypore estuary reveals that it behaves like many other tropical estuaries. The main factors controlling the salinity distribution are the tidal currents, and the fresh water brought in by the rivers. During the peak monsoon period the estuary virtually becomes fresh water dominated. Saline water intrusion is felt up to about 5 km during this period through the bottom. The estuary becomes well stratified during monsoon months with distinct salinity gradient. During summer months the effect of saline water intrusion was felt up to 22.5 km upstream. During post-and pre-monsoon periods, the estuary slowly transforms to a partially mixed one further to a well mixed one during pre monsoon months.

Dissolved oxygen:

Studies on dissolved gases, especially oxygen and carbon dioxide, help to understand the various physical, chemical and biological processes taking place in estuarine waters. Dissolved oxygen values are controlled mainly by the saline water intrusion, photosynthetic activity, fresh water influx and water temperature.

Dissolved oxygen (DO) values in the surface, mid-depth and bottom water samples are given in table 2.6. Time series graphs (Fig 2.6a-c) show spatial and temporal distribution of dissolved oxygen. During monsoon and post-monsoon months, the horizontal distribution of surface DO values exhibited more or less uniform longitudinal distribution and the values ranged between 4 to 7 mg/l (Fig. 2.7). However during the pre-monsoon period its distribution marked a decrease with an average value of 4.2 mg/l. Except for the month of May, an increase in dissolved oxygen content from bar mouth to upstream was noticed.

In the bottom waters, highest value of 6 mg/l was observed during January, February and April and June. The oxity values were of the order of 4-6 mg/l in February. DO registered minimum average values of 3.71 and 3.36 mg/l at mid-depth and bottom levels respectively during the month of August. The dissolved oxygen concentration is also influenced by the tidal incursion of saline water. Dissolved oxygen and salinity have inverse relation. Decreasing salinity increases the solubility of dissolved gases (Qasim and Sengupta, 1981). During August usually low concentration of dissolved oxygen was associated with high salinities all through the estuary. Coupled with this the bottom water temperature was low suggesting the intrusion of the upwelled water of shelf origin into the estuary. With the onset of south west monsoon, the wind reversal and associated circulation along the west coast of India are very conducive for upwelling. It has been mentioned while discussing the temperature profile in the estuary that upwelling plays an important role in the reduction of temperature during the August month. This is because the upwelled water brings in cold, nutrient-rich, high saline and low oxity waters into the surface layers (Smith, 1968). When the upwelled water come near the entrance of estuaries, due to gravity they spread into the interior of the estuaries (Duxbury, 1979). The cold and low oxity water present in the estuary during the monsoon period could be due to the intrusion of upwelled water.

The studies carried out by De Sousa (1977) on Zuari estuary revealed that dissolved oxygen registered high values during pre- and post-monsoon period compared to the monsoon period. Narayana Pillai et al. (1973) could observe substantial influence of tidal currents in the

Table 2.6 Longitudinal variation in dissolved oxygen mg ℓ^{-1}

Surface

Date				Stations			
	B.M	P.O	F.H	G.I	T.F	R.B	RDB
26.6.87	4.64	4.48	4.18	4.48	4.10	4.27	4.14
25.7.87	5.32	4.85	5.21	4.81	4.80	4.85	4.80
11.8.87	5.94	4.68	5.25	4.20	4.07	4.30	4.20
28.8.87	5.56	5.84	5.58	6.22	6.03	5.70	6.99
10.9.87	4.40	4.47	4.72	5.36	5.85	4.20	5.24
23.9.87	5.31	5.05	4.59	5.50	5.42	5.00	5.25
6.10.87	5.63	5.74	6.00	4.99	5.07	5.42	5.34
28.10.87	4.98	5.93	5.13	5.42	6.00	5.50	6.12
27.11.87	5.13	6.00	5.37	5.81	5.33	5.96	5.34
31.12.87	5.59	5.60	5.33	5.15	6.24	6.57	5.50
21.1.88 ..		5.93	5.89	5.71	5.33	6.76	7.36
24.2.88 ..		5.24	4.77	5.24	4.76	5.87	5.39
21.4.88	5.04	4.18	3.92	4.18	4.26	5.04	4.89
26.5.88	3.43	3.73	3.79	3.29	3.28	3.79	3.63
Average	5.11	5.12	3.98	5.03	5.03	5.23	5.28

Mid-depth

Date				Stations			
	B.M	P.O	F.H	G.I	T.F	R.B	RDB
26.6.87	4.39	4.23	4.31	4.31	4.61	4.80	4.38
25.7.87	4.64	3.97	4.28	4.00	4.40	4.10	4.20
11.8.87	4.40	3.85	3.21	3.80	3.79	3.96	2.98
28.8.87	6.39	5.97	5.75	5.65	5.97	6.08	5.67
10.9.87	2.70	1.93	2.84	5.19	5.48	4.48	3.94
23.9.87	4.79	4.20	4.93	4.98	4.35	5.75	5.30
6.10.87	4.93	4.94	4.83	4.41	4.75	5.42	5.92
28.10.87	5.08	5.18	5.07	6.03	5.44	5.19	5.46
27.11.87	5.53	6.50	5.62	5.78	5.67	6.21	6.30
31.12.87	5.22	5.75	5.67	5.26	4.69	6.04	5.38
21.1.88 ..		5.81	5.86	7.60	6.10	6.00	7.25
24.2.88 ..		4.72	4.73	5.11	4.81	4.93	5.66
21.4.88	5.38	4.70	4.14	4.60	4.70	4.59	3.70
26.5.88	3.70	3.89	3.80	3.70	3.56	3.90	3.76
Average	4.76	4.69	4.56	5.03	4.88	5.10	4.99

Bottom

Date				Stations			
	B.M	P.O	F.H	G.I	T.F	R.B	RDB
26.6.87	3.70	4.45	4.21	4.25	4.34	4.14	4.12
25.7.87	4.01	3.42	4.01	4.00	4.10	3.80	4.00
11.8.87	3.80	3.38	3.19	2.98	3.37	3.86	3.00
28.8.87	5.94	5.87	5.48	5.81	6.21	5.60	5.07
10.9.87	3.15	1.89	2.10	4.89	5.08	3.91	2.38
23.9.87	5.00	4.32	4.65	4.51	3.91	4.09	5.40
6.10.87	3.71	4.91	4.20	4.02	3.91	5.30	4.04
28.10.87	5.70	4.09	4.47	4.95	4.96	4.86	5.64
27.11.87	5.43	5.42	5.62	5.40	6.08	5.38	5.50
31.12.87	5.69	6.09	5.78	5.49	4.62	5.29	4.85
21.1.88 ..		5.28	5.00	5.81	5.26	5.55	6.10
24.2.88 ..		4.97	6.01	5.35	5.22	5.33	4.77
21.4.88	4.70	4.59	4.14	5.15	4.37	4.70	5.60
26.5.88	4.38	4.25	3.88	3.67	4.29	3.96	3.98
Average	4.60	4.46	4.49	4.71	4.69	4.56	4.60

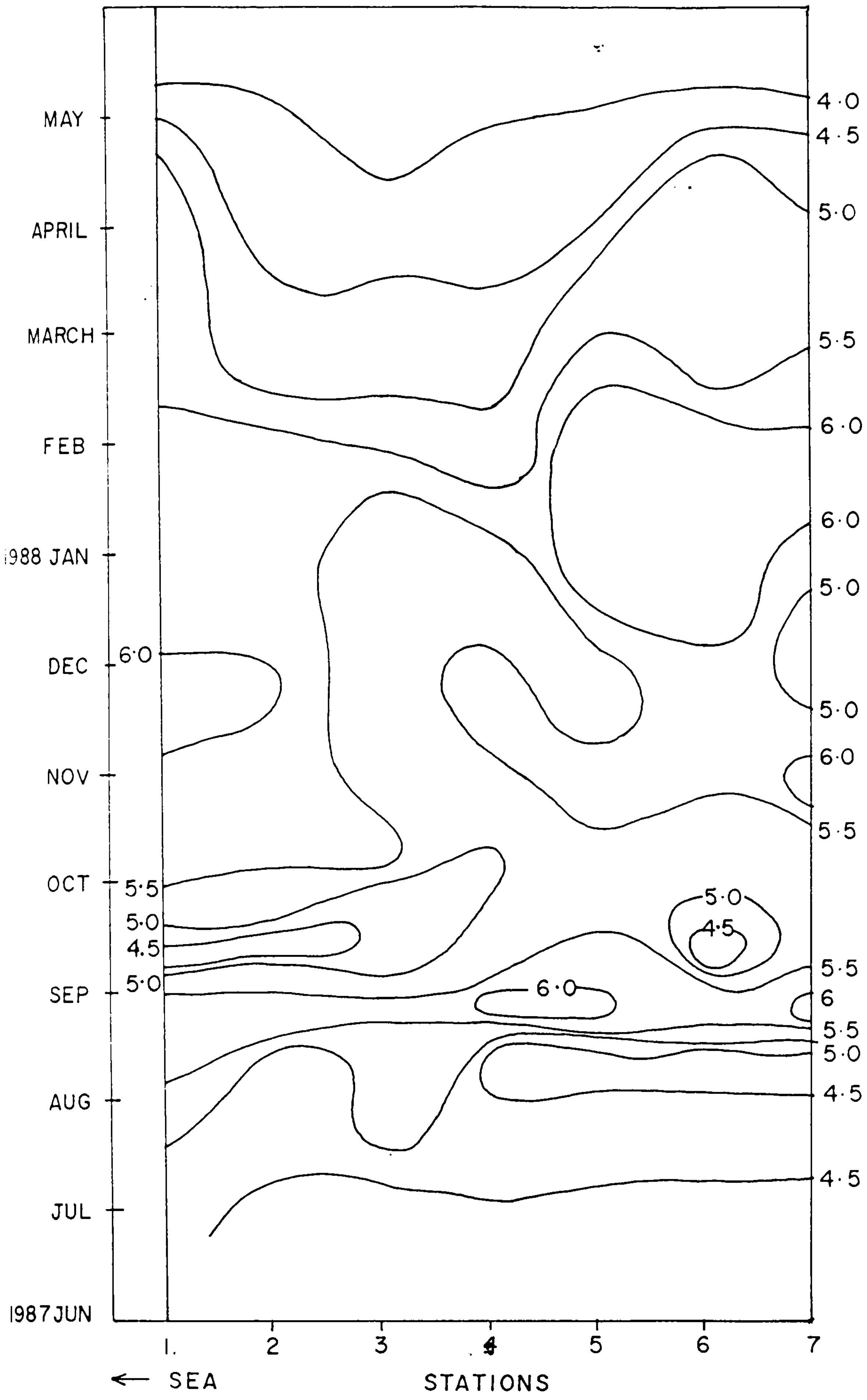


Fig. 2.6a Time series for dissolved oxygen at surface (mg l⁻¹)

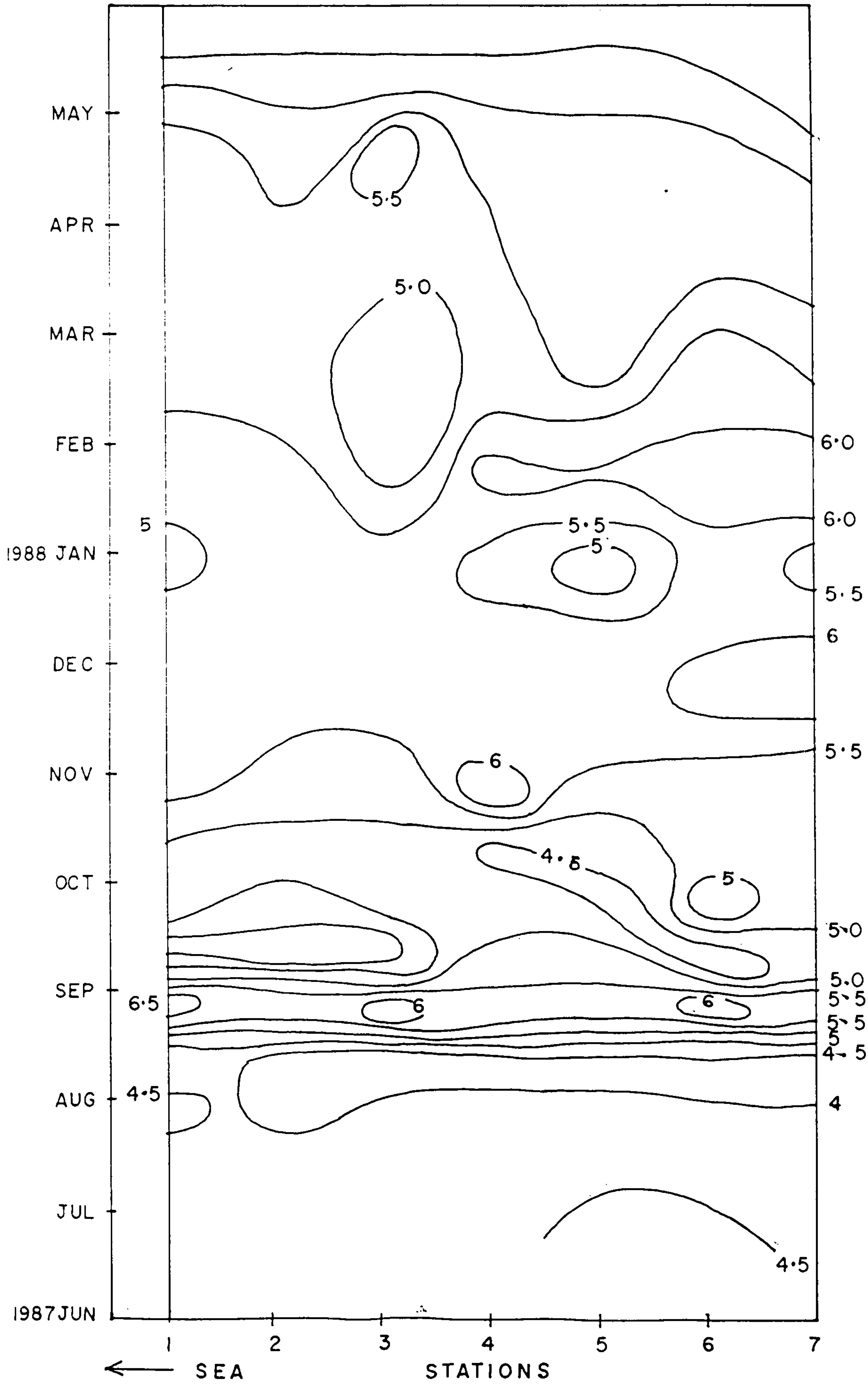


Fig. 2.6b Time series for dissolved oxygen at mid depth (mg l⁻¹)

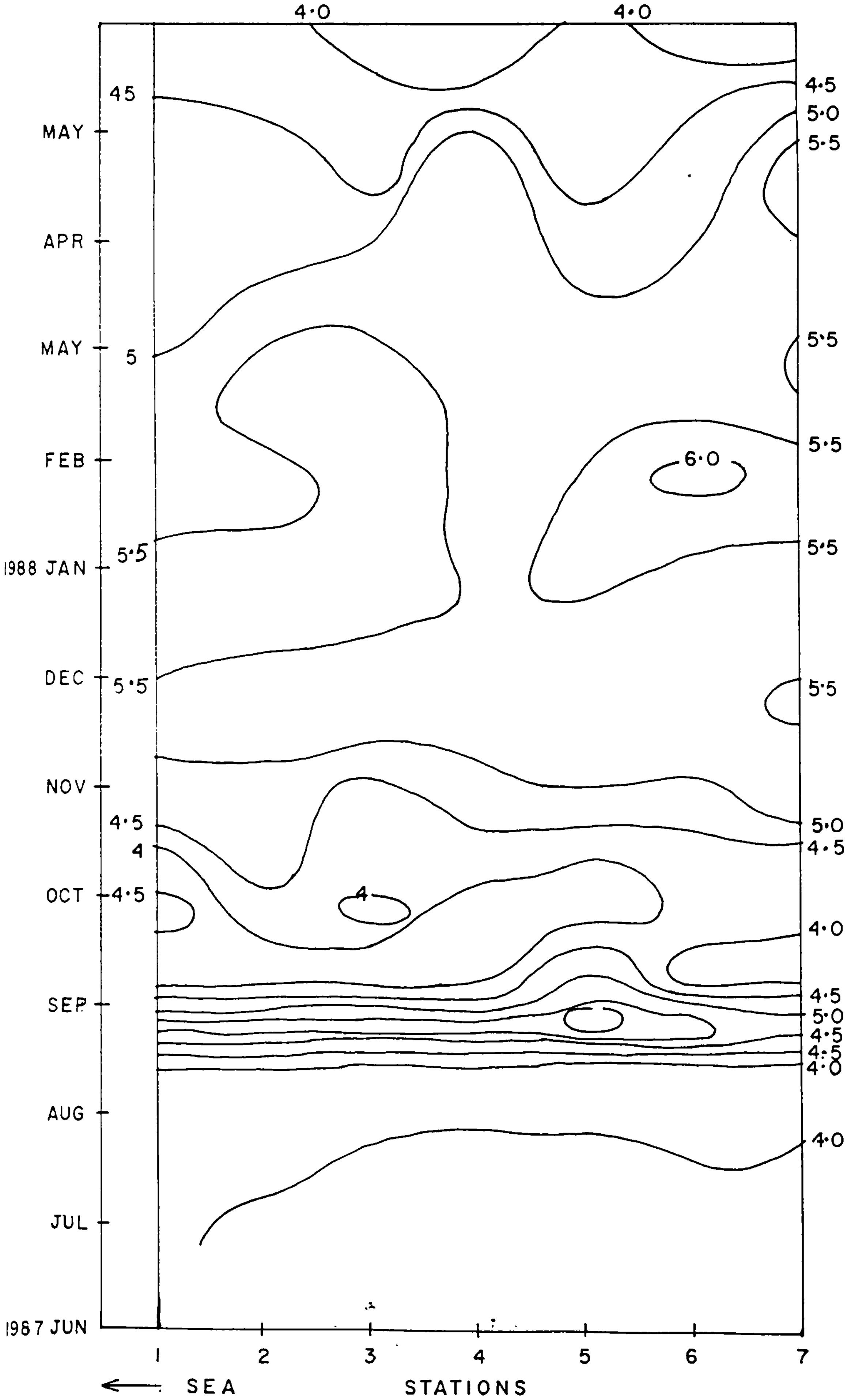


Fig. 2.6c Time series for dissolved oxygen at bottom (mg l^{-1}).

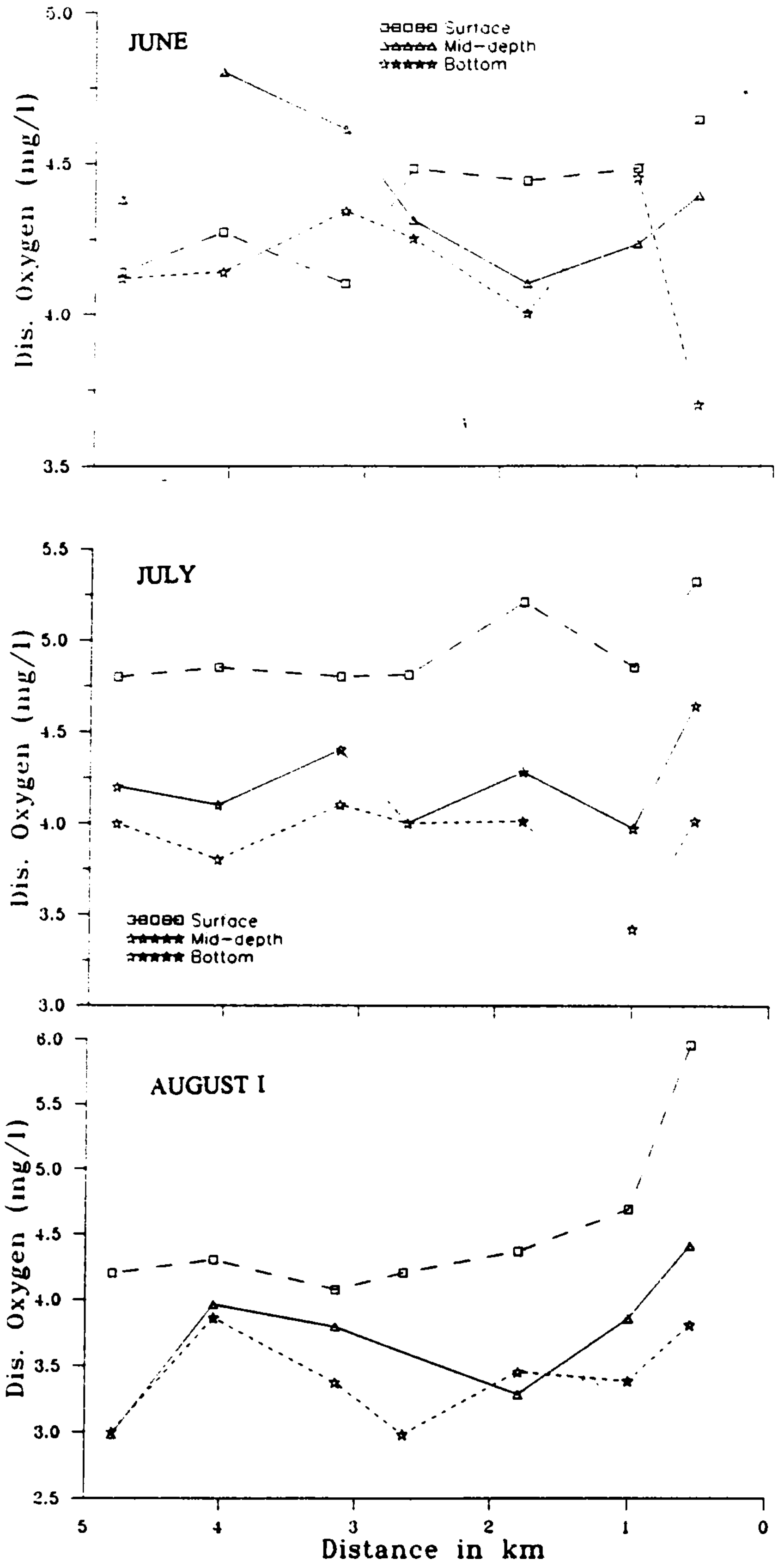


Fig. 2.7 Longitudinal variation of dissolved oxygen during different months

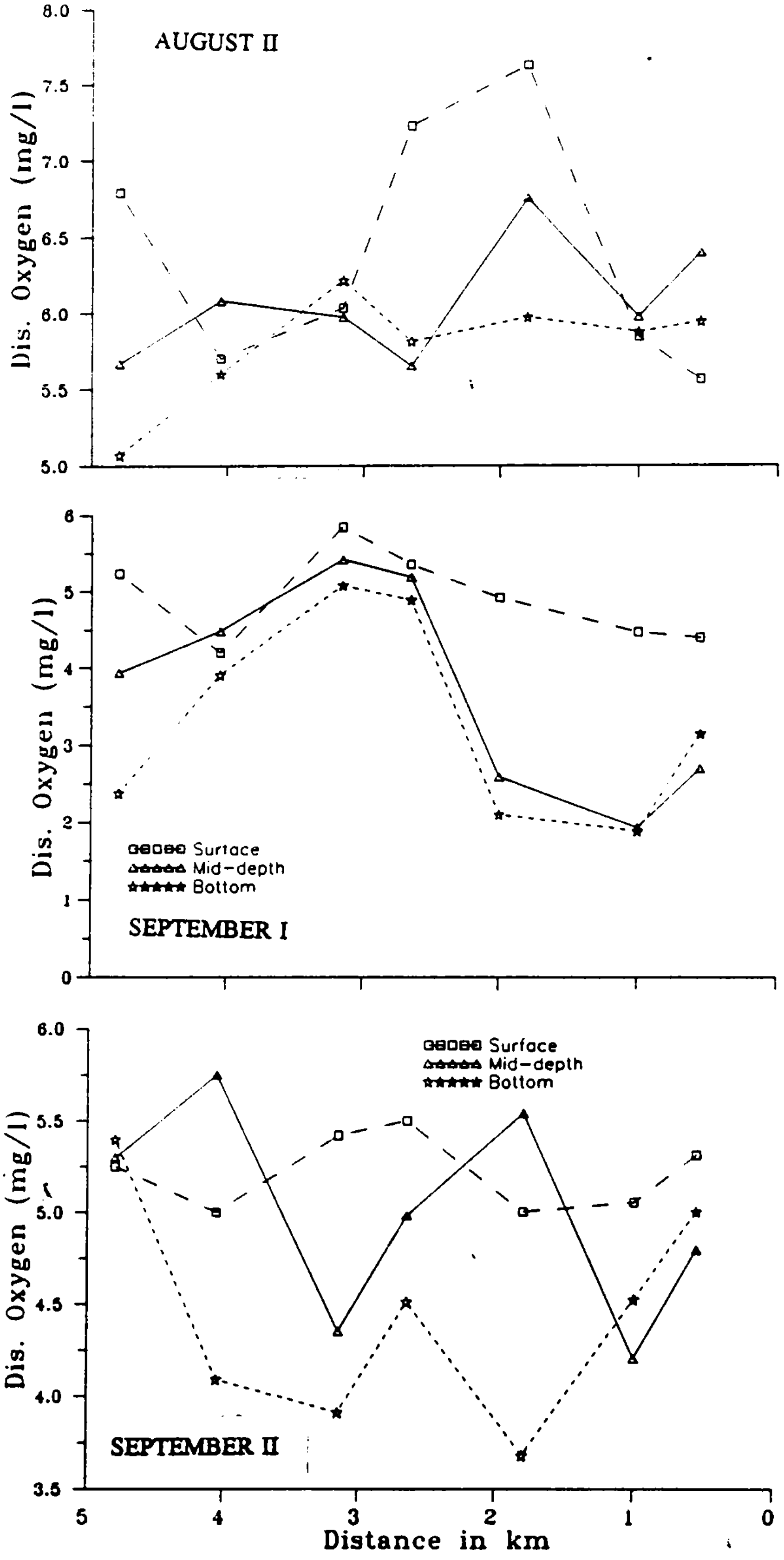
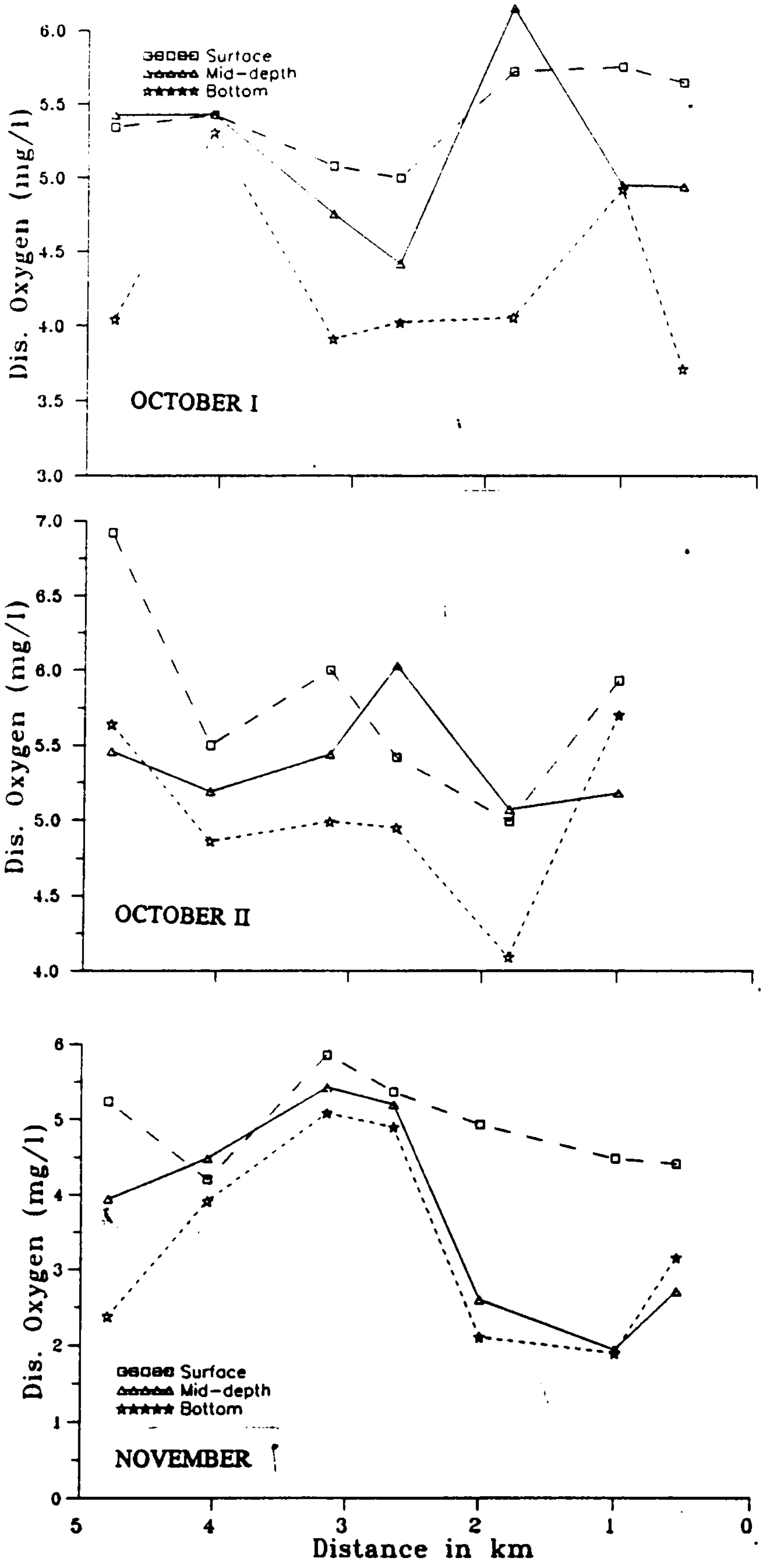


Fig. 2.7 Continued......



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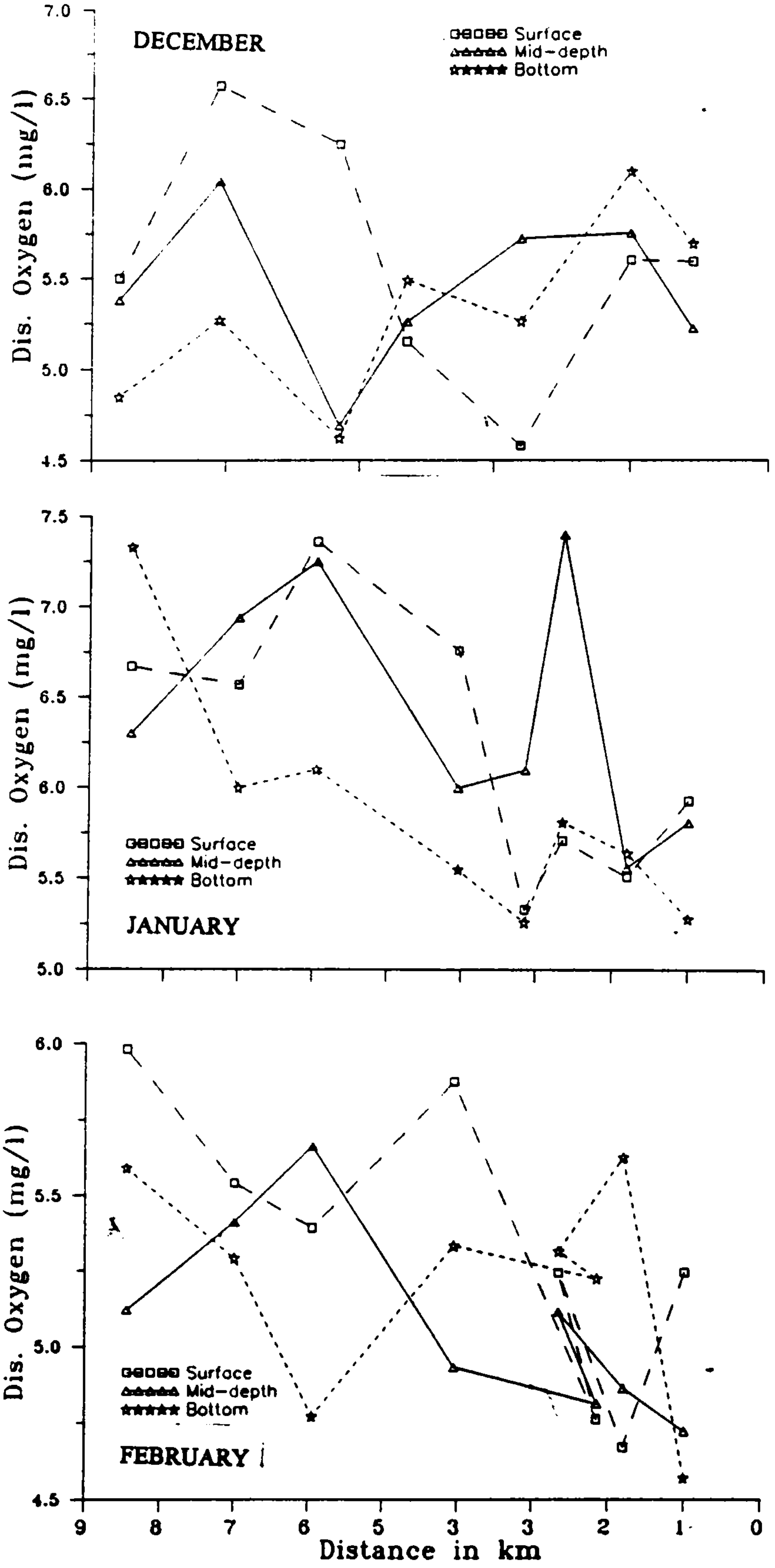

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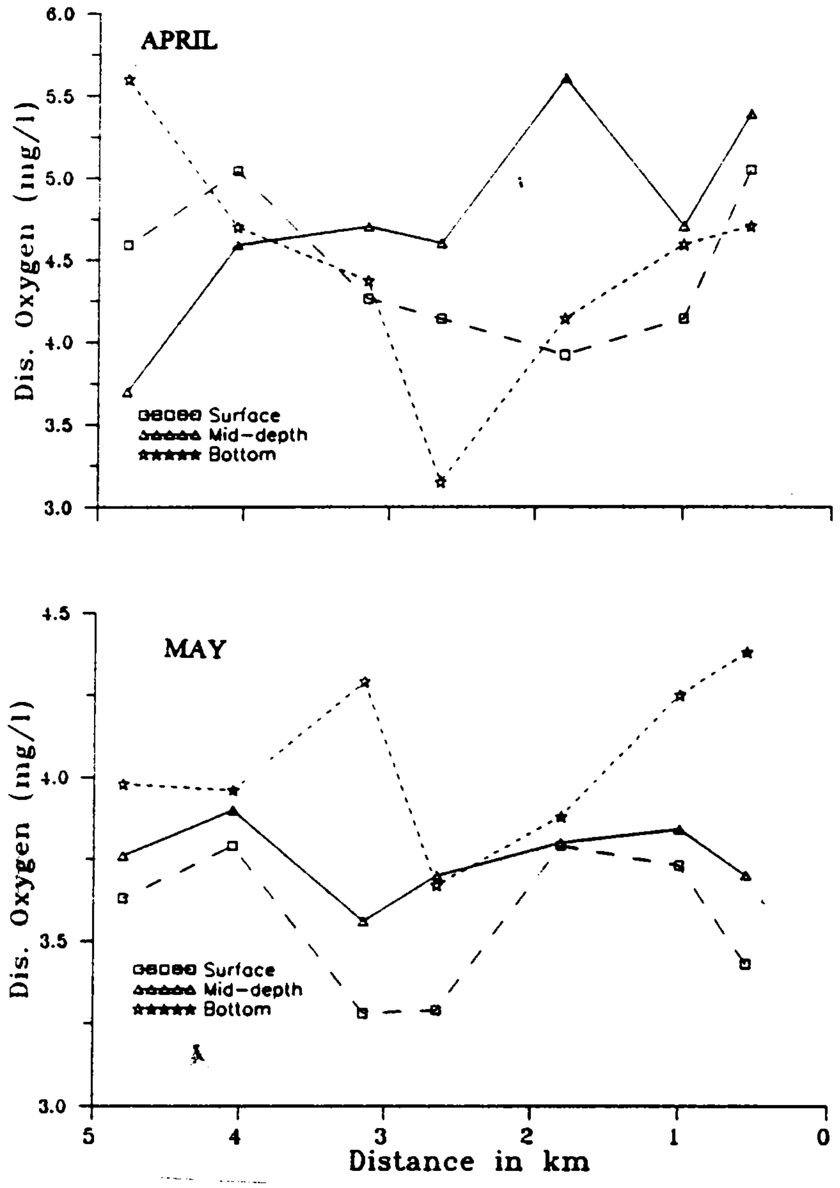


Fig. 2.7 Continued......

distribution of dissolved oxygen in Cochin estuary and a clear relation was obtained between flood and ebb tides both at surface and sub surface levels. A contradicting conclusion came from Singbal (1976), after making observations on hydrographic features in Mandovi estuary, that dissolved oxygen content in the estuary was independent of tidal effects. However, the subsequent studies by De Sousa et al. (1986) confirmed the salinity dependence on oxygen solubility in estuarine waters of Mandovi estuary. They concluded that, the low oxygen concentration of the bottom waters during monsoon at the mouth of estuary was due to the inverse relation of oxygen solubility with salinity. Another factor for low oxygen concentration observed at high saline values during monsoon periods at bottom waters is attributable to the entry of sea water into the estuary while fresh water flows out into the sea at surface leading to the formation of a salt wedge (Sankaranarayanan and Jayaraman, 1972). The sub-surface sea water has low oxygen content than the surface sea water and fresh water from river. The third important factor which is responsible for low oxygen content at the mouth of the estuary could be the formation of sand bar, which leads to trapping of high saline water at the bottom due to its shallow still resulting in very little vertical mixing and stagnant condition inside the bar mouth.

Salinity dependence on oxygen solubility was explored in Zuari and Mandovi estuaries by De Sousa and Sen Gupta (1986) and reported that plots of oxygen against salinity showed peaks at extreme ends (fresh water and sea water). Another peak at an intermediate salinity (18-24 ppt) was also observed. The upper reaches of Mandovi showed super saturation with respect to DO while the lower reaches showed under saturation. A similar nature for DO distribution was observed in the Beypore estuary.

Saisastry and Chandramohan (1990) noticed that the concentration of dissolved oxygen in the Vasishta-Godavari estuary is highly variable and dependent on a multitude of factors. The variations were primarily due to greater depth of water column, frequent drainage of farm water, turbulence due to wind, and production and decomposition of phytoplankton in abundance. They could not find any anoxic conditions. Low dissolved oxygen content arising out of eutrophication was reported by Raman and Ganapathy (1986). Nair, et al. (1984) studied the seasonal changes in Dissolved oxygen in Kadinamkulam estuary. During May to October at least in two stations anoxic conditions prevailed and low dissolved oxygen content was noticed. The reason for the depletion of dissolved oxygen content was attributed to the retting activity going on in the numerous enclosures along the banks of this backwater systems. A similar situation with retting activities were also noticed in the lower part of the Beypore estuary.

Sasamal et al. (1986) observed high dissolved oxygen content during March-April period in the waters along Orissa coast due to the high primary productivity. High dissolved oxygen content observed during June-July period was attributed to the high influx of fresh water having higher dissolved oxygen content. Similarly, high dissolved oxygen content due to primary production was reported by Nair et al. (1984) at Neendakara, Kadapuzha and Kayamkulam estuaries along the Kerala coast. De Sousa and Sengupta (1986) observed high dissolved oxygen content in the upper reaches of Mandovi due to high photosynthetic activity, coupled with discharge of fresh water having high dissolved oxygen content through various streams joining the estuary. Under-saturation at the lower reaches of the estuary was explained by the turbid nature of water which reduces photosynthetic activity. Due to intense fishing activity using mechanised boat and other human activities, the water in the barmouth region up to the fisheries jetty (1.8 km upstream) was turbid, thus impairing the primary production leading to low oxity content compared to the upper reaches of the Beypore estuary.

Currents:

The magnitude and direction of current occurring in the estuary during June 87, July, August, November, December and January 88 are depicted in figure. 2.8. Maximum surface values were observed during peak monsoon period. Maximum outward flow of 100 cm/sec was noticed during July near the bar mouth. During fair weather season, current varied from 5-50 cm/sec. The peak values were registered coinciding with the peak flood and ebb tides, reversing the direction. In June, the observations were made at flood tide, during which the

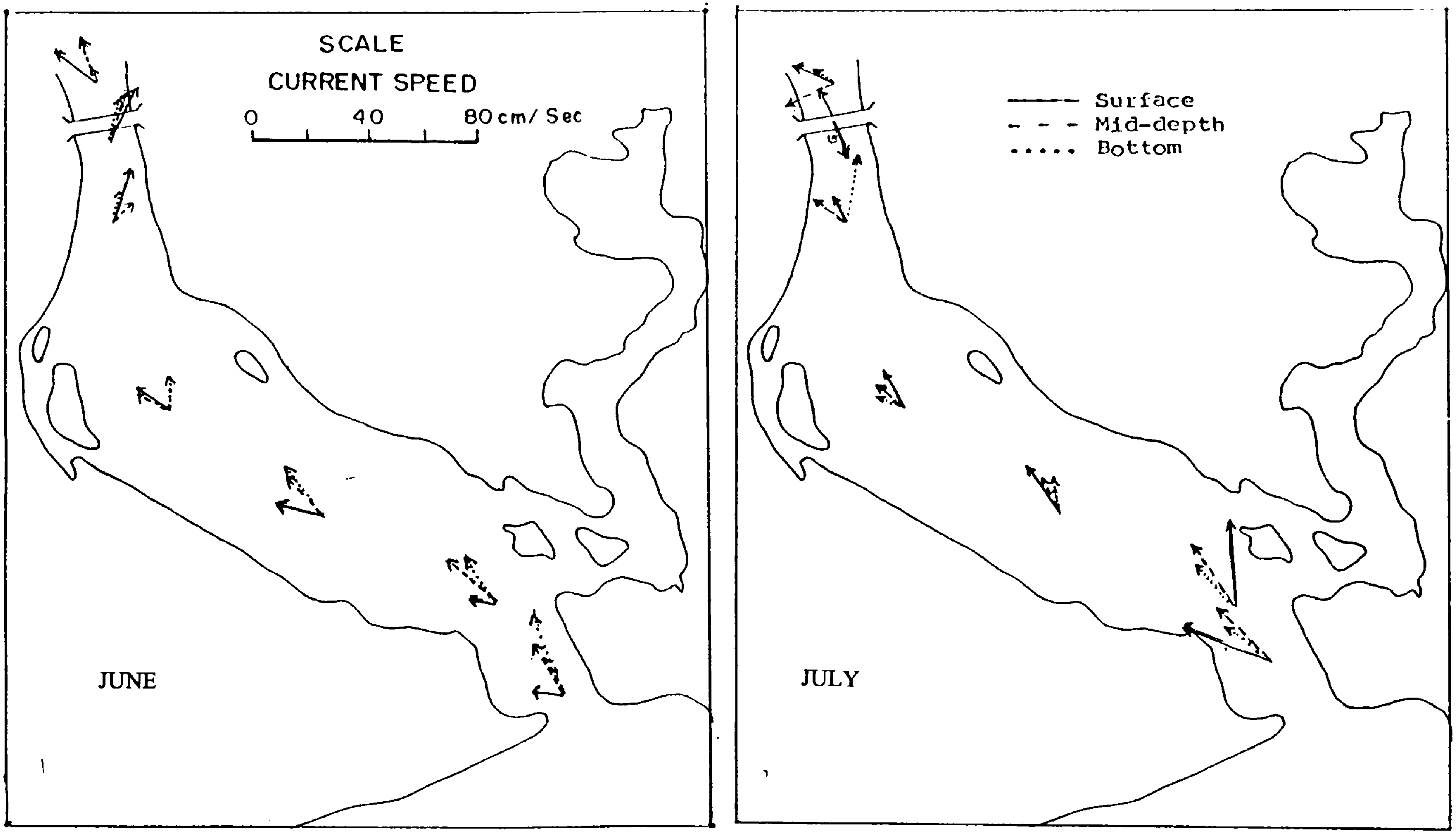


Fig. 2.8 Direction and magnitude of currents at different levels over the months

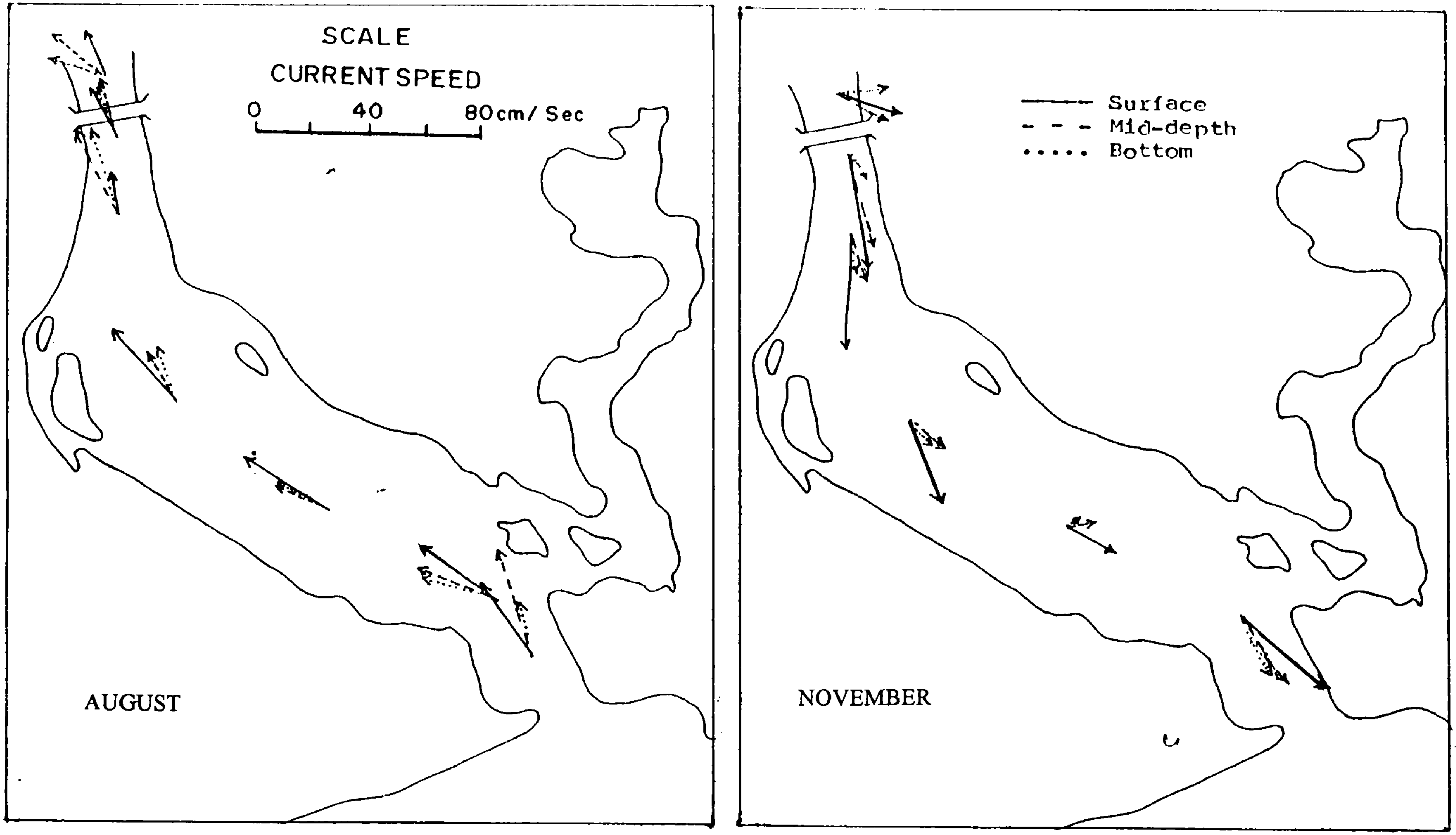


Fig. 2.8 Continued......

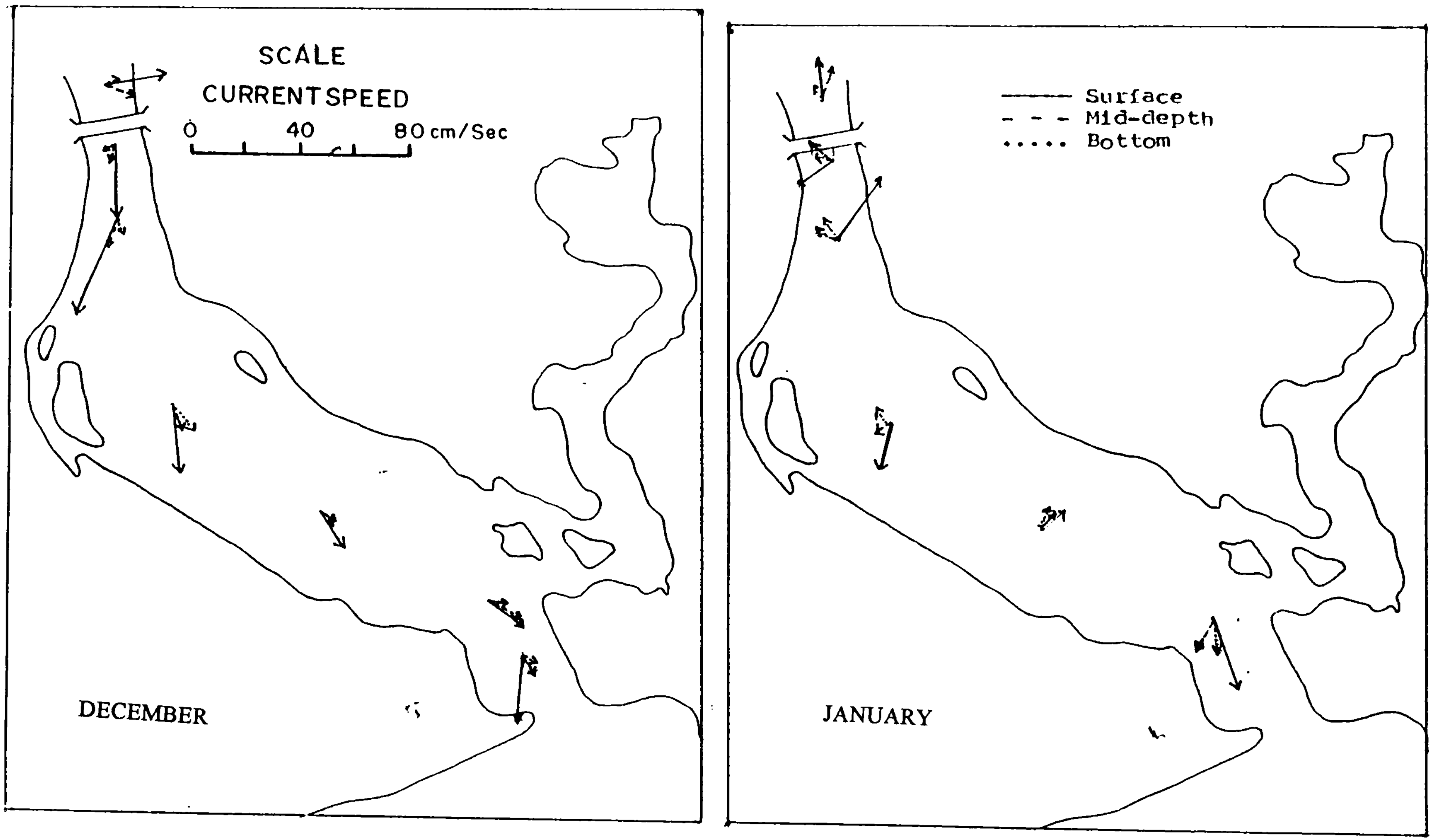


Fig. 2.8 Continued......

surface water flow picks up intensity towards upstream. Corresponding reduction in speed was noticed in sub-surface layers with gradual clock-wise shift in direction. Current pattern scenario changed in July with varied intensities and directions at different levels, only making obvious of a flood tide signal. August data was also collected at flood tide, demarcating a more intense surface inflow than the sub-surface layers. November, December and January observations were made at ebb tide, clearly illustrating a seaward flow. Irrespective of the months, surface layers recorded stronger currents than sub-surface layers. Especially during November, surface currents were the most intense. This was found to be not only due to ebbing, but also due to the higher fluvial discharge owing to moderate precipitation. Certain local effects due to orientation of the bank, nature of bottom profile and hurdles such as bridges and islands were found to affect the general direction and magnitude of flow. During March the residual current was 9 cm/sec at surface and was directed towards the head of the estuary. At the near bottom level the speed was 6 cm/sec. During peak monsoon season, the residual currents were always directed outward and the estuary is found to be fresh water dominated.

CHAPTER III

SUSPENDED MATTER AND DISSOLVED TRACE METALS

3.1 Introduction

Suspended sediments in rivers and estuaries play a vital role in the transfer of materials from land to sea. The main contributors of suspended sediments to rivers and estuaries are weathering of rocks, industrial effluent, agricultural land, etc. Particulate matter generated by biological productivity may also be important in the supply of suspended sediments in the lower portion of the estuaries (Biggs, 1970). Infrequent catastrophic storms augment abnormal fluvial load (Schubel, 1974). The suspended matter present in the fresh water after coming into contact with sea water flocculate and creates zones of turbidity maxima. Primary production is inhibited by such turbidity and sedimentation destroys spawning ground of fish. High concentration of suspended material can clog the respiratory system of river fish and are detrimental. Suspended material discharged by rivers into estuaries also transport many pollutants into the ocean. From the biologic and health point of view, suspended materials form natural food for the filter feeding organisms and hence the pollutants scavenged by the suspended material can adversely affect many varieties of sea food. This is one reason why information on the nature of suspended sediments brought in by the river and discharged into an estuary becomes important. Knowledge about the mechanism of transport of the suspended material can be used to estimate the fate of many pollutants in estuaries and oceans and can help to adopt methods to divert or decrease the detrimental turbidity in regions of sea food harvesting.

The study of particulate suspended matter is important in understanding (1) genesis of sediments, (2) transport and dispersal of suspended matter into a basin and (3) relative contribution of terrigenous, volcanic, biogenous and chemogenous material to suspended matter. The study is also important in forecasting the fishery resources of a particular region as the particulate matter forms part of food material for a large variety of marine life.

Suspended sediments could be used as a natural tracer to determine the surface circulation in estuarine and coastal regions (Klemas, et al., 1977). Since the distribution of suspended solids in an estuary is influenced by the tides, it can also be used as a natural tracer for understanding tidal currents (Muralikrishna, 1985). The distribution pattern of suspended solids would also reveal information on pollutant concentration and dispersion. Sedimentation in harbours and bays is a problem for navigation at several places along the west coast of India. An understanding of the sources and sinks of suspended solids is very important for the rational management of the estuaries.

Geochemical behaviour of particulate material in estuaries is complex owing to the numerous possibilities for metal transport into this environment, where it may be unstable in relation to the prevailing hydrographic conditions. Trace metals are transported by rivers in dissolved, colloidal and particulate forms to the coastal and estuarine regions. The suspended solids are considered to be the scavengers of trace metals. The dominant factor in sediment transport is the motion of water. Depending on the turbulent motion of the current and the nature of transportation, deposition of the eroded material vary. The processes of erosion, transportation and deposition are closely related. The particles are moved by running water either by sliding, rolling, saltation or suspension. Coarser particles are deposited upstream. Finer particles are seen towards the lower part of the estuarine region. Part of the sediment transported by the rivers settle in the estuarine zone and the rest passes to the open sea.

Depending on the prevailing conditions of salinity, the particulate material brought in by rivers may be unstable and are subjected to various changes.The coarser material entering the estuary generally retain their individual sizes and the depositional characters are chiefly controlled by the hydrodynamic factors. Particle sizes in the clay (<4 μm) and colloidal ranges (<0.25 μm) are subjected to various estuarine processes. Depending on the electro-kinetic charges associated with the suspended particles, which is greatly influenced by salinity, flocculation or deflocculation takes place to effect formation of new solid phases, uptake of dissolved materials in the solid phases and release of material into solution from particulate phase.

The role of suspended particulates in an estuary is very important in controlling the trace metals content in the system. Metals get associated with the particulates through mechanisms such as adsorption, chelation, co-precipitation etc. The metals associated with the suspended sediments get destabilised when they reach the estuarine water. The suspended sediments in saline water flocculates and settle to the bottom to form the estuarine sediments. The metals associated with the bottom sediments become readily available to the over lying waters depending upon the changes in Eh/pH conditions. Many toxic substances are rapidly adsorbed by the sediments during river discharge and the transport of such substances from the land surface to rivers is frequently in association with particulate material. Thus, particulates are dominant pathway for many toxic contaminants (Walling and Webb, 1985).

The need for regular monitoring of water quality parameters in estuaries of Kerala was emphasised by Sankaranarayanan and Stephen (1978). Concentration of dissolved trace metals in the estuarine waters is of pivotal importance, since these are the easily available form for uptake by biota. Most metals in traces are needed for various metabolic activities of estuarine organisms. However, when exceeds the tolerance limit, they are toxic to the biota. Thus, study of dissolved trace metals is imperative as the back waters of Kerala in general are highly productive and form nursery ground for a variety of fish and shell fish in addition to their rich brackish water fishery. Besides this, the brackish waters provide considerable potential for the development of aquaculture. The ecological conditions in the back water system and the adjacent rivers and seas influence the resources in the estuarine environment. Hazards arising out of discharge of pollutant, especially high concentration of heavy metals in the environments, necessitates a regular monitoring of the levels of the heavy metals in the waters, bottom mud and organisms.

Dissolved trace metals are present in the marine zone in different chemical forms and their behaviour in the marine environment depends on their physico-chemical entity. The toxicity of metals and their availability to organisms are related to the type of metal species rather than to total metal concentration. The adsorption/desorption processes and the rate of chemical process in which a particular metal is involved depends on its form of existence of that metal.

3.2 **Review of Literature**

Extensive studies on suspended sediment distribution in the estuaries were carried out elsewhere (Biggs, 1970; Gibbs, 1976; Allen et al., 1976; Schubel and Carter, 1976). Only a few studies have been carried out on the suspended sediment concentration in the Indian estuaries (Cherian et al., 1975; Varma et al., 1975; Balachand, 1983; and Kurian, 1987).

Trace metals associated with suspended matter and their re-mobilisation under different conditions were studied by a number of workers. The role of organic matter association with suspended matter was explored by Salim (1983). Variations in chemical forms of iron, manganese and zinc in the suspended sediment were investigated by Schoer et al. (1983). Several attempts have already been made to know the trace metal enrichment in suspended sediments [Spencer and Sachs, 1970; Piper, 1971]. Gibbs (1977) carried out extensive studies to elucidate transport mechanisms of trace metals. Krank (1974) reported that effluent from paper and pulp industries discharged into an estuarine system can contribute substantially to the suspended sediment load. Cherian et al.(1975) made investigations on the relation between various hydrographic parameters and suspended sediment load near Marmugao harbour area which is dominated by periodic tidal exchanges of nearshore and estuarine waters. The comparative study on the suspended sediment load of the sea water with an adjoining estuary was carried out by Kurian (1987) .

Studies undertaken on the lower reaches of the Bow and Oldman rivers in Alberta, Canada by Blachford and Ongly (1984) revealed that for all metals, suspended matter is the major carrier phase. Similar findings were reported earlier for Rhine (de Groot and Allersma, 1975), Amazon and Yukon rivers by Gibbs (1977). In a generalised review on heavy metal transport by particulates, Golterman et al. (1983) indicated that the average ratio between dissolved and particulate associated transport in rivers is between 0.5:1 and 0.25:1 for copper, mercury, chromium and lead. They also reported that, under normal pH and Eh conditions, iron, aluminium and manganese are almost totally transported by suspended solids. Heavy metal concentrations in the particulate matter of the Cochin back water from the marine zone to the fresh water zone were reported by Sankaranarayanan and Stephen (1978). Variation in chemical forms of iron, manganese and zinc in the suspended sediments of the Elbe and Weser rivers during estuarine mixing were studied by Schoer et al. (1983). George et al. (1984) conducted studies on Mandovi waters on dissolved cadmium, lead, and copper found that the Mandovi estuarine waters contain a higher concentration of dissolved metals. This was attributed to the run off from the mines situated in near by area and from the barge traffic.

Marine invertebrates accumulate trace metals to varying degrees and it was reported that body concentration may reach very high levels (Bryan, 1979; Prosi, 1979). Rainbow et al. (1980) found that certain marine organisms have the ability to regulate toxic metals in their body to certain extent. The high respiratory process and very efficient tidal current system which brings in oxygen-rich waters in contact with anoxic sediments play an important role in heavy metal remobilisation. Blachford and Ongly (1984) reported transport of organochlorine residues and found that the majority of the detectable substances were associated primarily with organic matter. Investigations carried out by Devassy et al. (1987) revealed that the industrial effluent in the Mangalore coast has influenced the primary productivity in that area.

3.3 **Methodology:**

3.3.1 *Estimation of suspended matter*

Surface water samples were collected from 10 stations during June, July, August, September, October 1987 and January, February and March 1988 from Beypore estuary and Chaliyar river. Figure (3.1) shows the locations of the sampling stations. Samples were

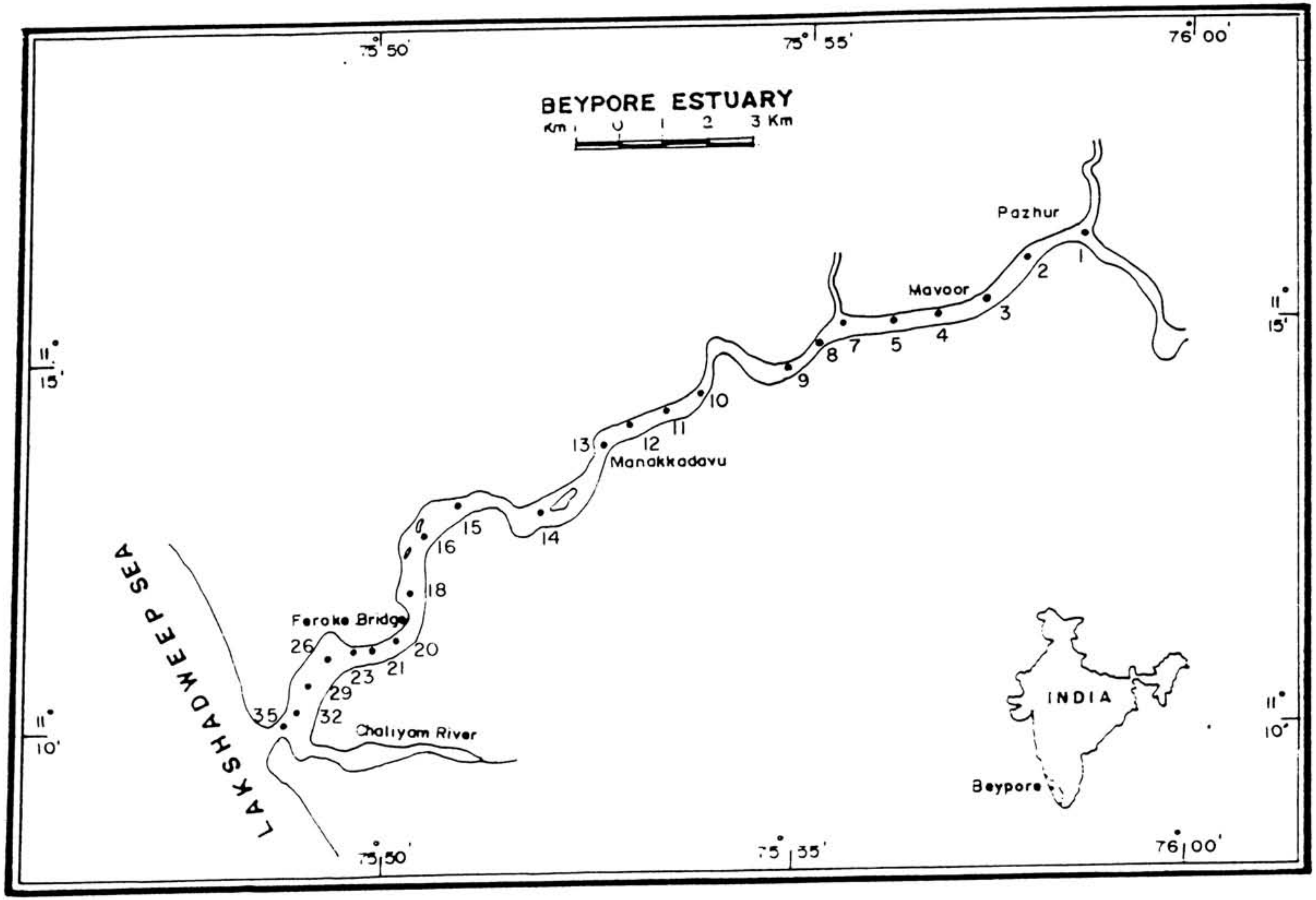


Fig. 3.1 Location map of samples taken for suspended and dissolved metal analysis

collected once in every month and during August, September and October surveys were carried out fortnightly. For monitoring variations over a tidal cycle, a station near the Fisheries Harbour (1.8 km upstream) was occupied and water samples were collected every hour from surface, mid-depth and near bottom. The water samples were filtered through pre weighed filter paper of 0.45 µm pore size and a diameter of 47 mm. The filtering was carried out at 25 cm mercury vacuum and the volume of samples filtered varied from 500 to 1000 ml. After filtration, the filters were rinsed with distilled water and dried at 60°C,cooled in desiccator and weighed. The difference in the initial and final weights gave the suspended sediment load.

3.3.2 *Determination of particulate trace metals*

In October, surface water samples were collected from 17 stations in the Beypore estuary and Chaliyar river. Surface water samples were collected from 30 stations in December, while in January samples were collected from only 13 stations. Surface, mid-depth and near bottom water samples collected from 5 stations in January were analysed for particulate trace metals to understand the vertical distribution of particulate trace metals. The dried filters containing the suspended sediments (after suspended matter estimation) were used for estimation of particulate trace metals. Each filter paper was transferred to a conical flask containing 1 ml of perchloric acid. After evaporation, the residue was digested with dil. HNO_3 and dried. The dried residue was treated with 1 drop of concentrated HCl and dissolved in 0.1 normal HCl and the volume is made up to 10 ml (FAO, 1975). Blank filter papers were also treated similarly. Trace metals were analysed using Flame Atomic Absorption Spectrophotometer (Perkin Elmer model 4000).

3.3.3 *Dissolved trace metals*

The surface and sub-surface water samples from Beypore estuary and Chaliyar river collected from selected locations in clean plastic bottles during the months of May, September, October and December 1987 and January, February and March 1988 were filtered through millipore filter paper (0.45µm pore size and 47 mm dia.) under vacuum of 25 cm mercury in clean laboratory conditions. Surface water samples were collected from nearshore waters during the month of March and similarly processed. The filtered samples were stored in clean plastic bottles and analysed by AAS method detailed by Brooks et al.,(1976). 500 ml of the sample was poured into a separating funnel and pH was adjusted to 3.6-3.9 by the addition of acetic acid. After addition of 1 ml 4% APDC (W/V), the sample was extracted twice with 20 and10 ml of MIBK respectively. The combined extracts were evaporated to dryness in a silica Erlenmeyer flask and oxidised with 0.5 ml concentrated HNO_3. After dilution the oxidised extract was transferred to a polyethylene vial and metal concentrations in the extract were determined with AAS using standard addition technique. Extraction efficiencies (92-105%) are determined by re-extraction of previously extracted sea water samples after the addition of spikes.

3.4 **Results and discussion**

3.4.1 *Suspended matter concentration*

Longitudinal distributions of suspended matter are given in table 3.1 and figure 3.2. Suspended sediment concentration obtained in the month of June ranged from 3 to 14 mg/l. Highest concentration was observed at station near fisheries harbour. A decreasing trend was observed towards the bar mouth. A similar trend was observed in July. Maximum concentration of 25 mg/l was noted at station near fisheries harbour. Input from river discharge was not pronounced during June and July and the high concentration of suspended matter observed at station near fisheries harbour could be due to the resuspension of bottom mud by the disturbances caused due to the fishing activity concentrated in the area.

High suspended sediment concentration (SSC) was noticed during the months of August and September. This could be attributed to the high influx of river water with heavy load of eroded material. During 1st survey in August, SSC ranged between 23 and 85 mg/l with an average value of 62 mg/l, while during the second survey the range was 40 and 115 mg/l with an average value of 84 mg/l. During September a maximum value of 137 mg/l was obtained at station near Road Bridge while a minimum value of 38 mg/l was registered at the barmouth station. During the post monsoon period the contribution by the rivers receded and

Table 3.1 Longitudinal variation of suspended matter at 1m below surface $mg\ \ell^{-1}$

Stations	June	July	Aug I	Aug II	Sept.	Oct.	Jan.	Feb.	March
L.H.	8	6	23	40	38	4	3	6	8
P.O.	12	12	40	85	60	7	4	7	6
F.H.	14	25	38	95	114	10	9	9	12
G.I.	7	17	83	110	90	3	12	4	10
T.F.	12	19	85	115	74	12	6	5	6
R.B.	4	10	50	85	137	8	4	4	5
Rd.B.	4	12	65	90	143	6	10	4	9
LTF	10	17	70	94	115	10	12	5	7
IHT	3	18	85	88	80	5	2	3	6
II HT	3	16	85	60	84	9	4	4	5
Avg.	7.7	15.2	62.4	84.2	93.5	7.4	6.6	5.1	7.7
Min.	3	6	23	40	38	4	2	3	5
Max.	14	25	85	115	137	12	12	9	12

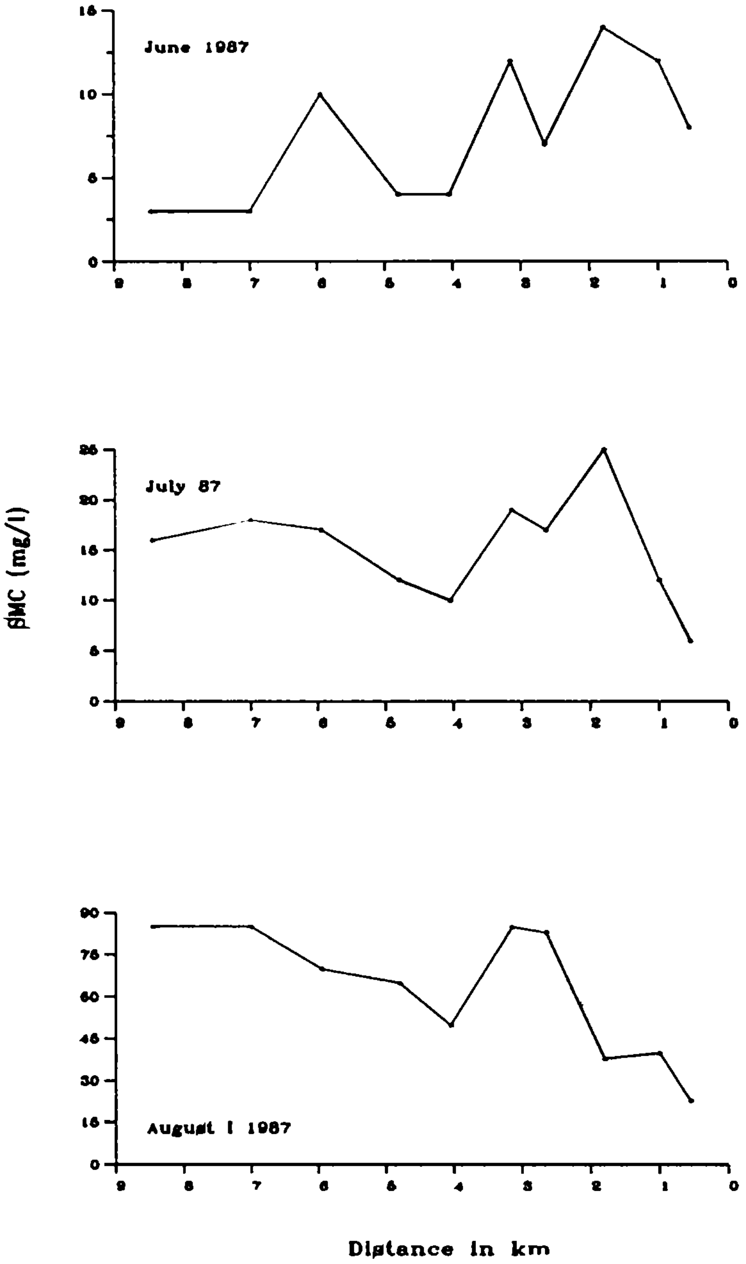


Fig. 3.2 Longitudinal variation of suspended matter during different months

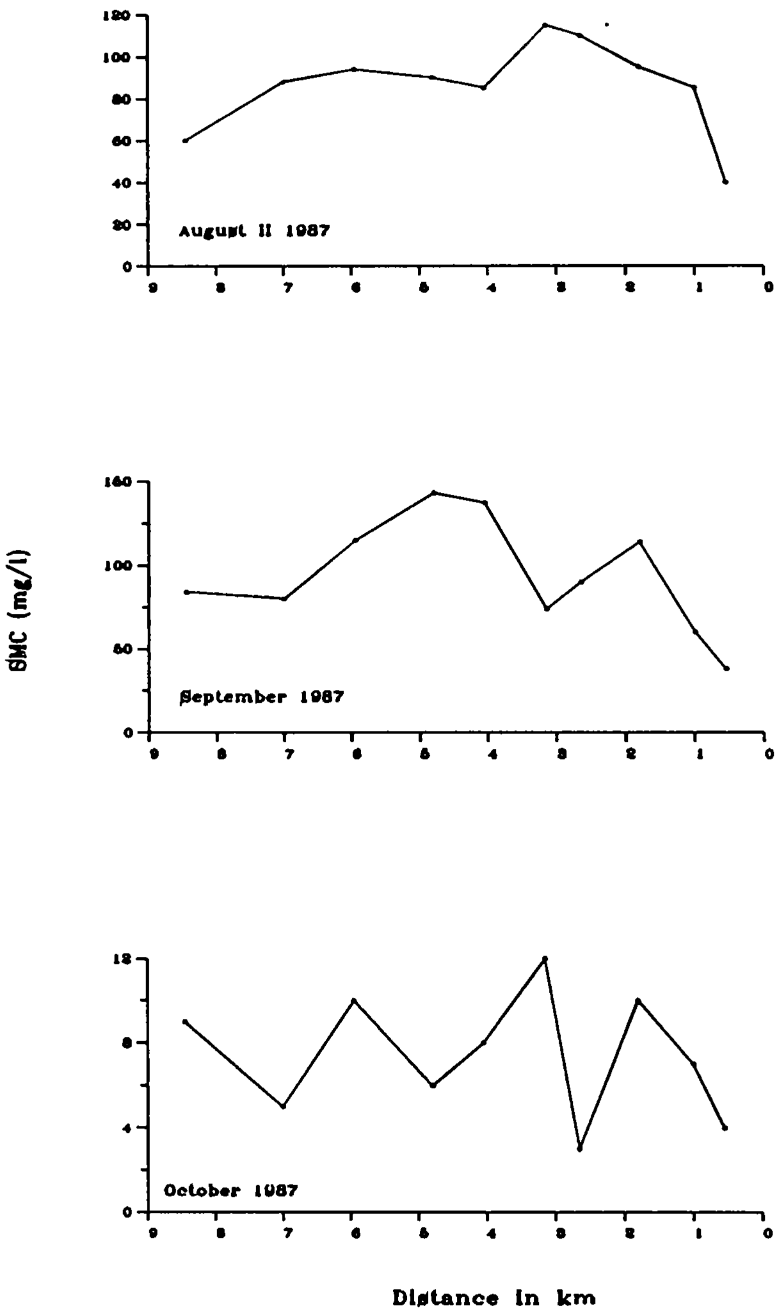


Fig. 3.2 Continued......

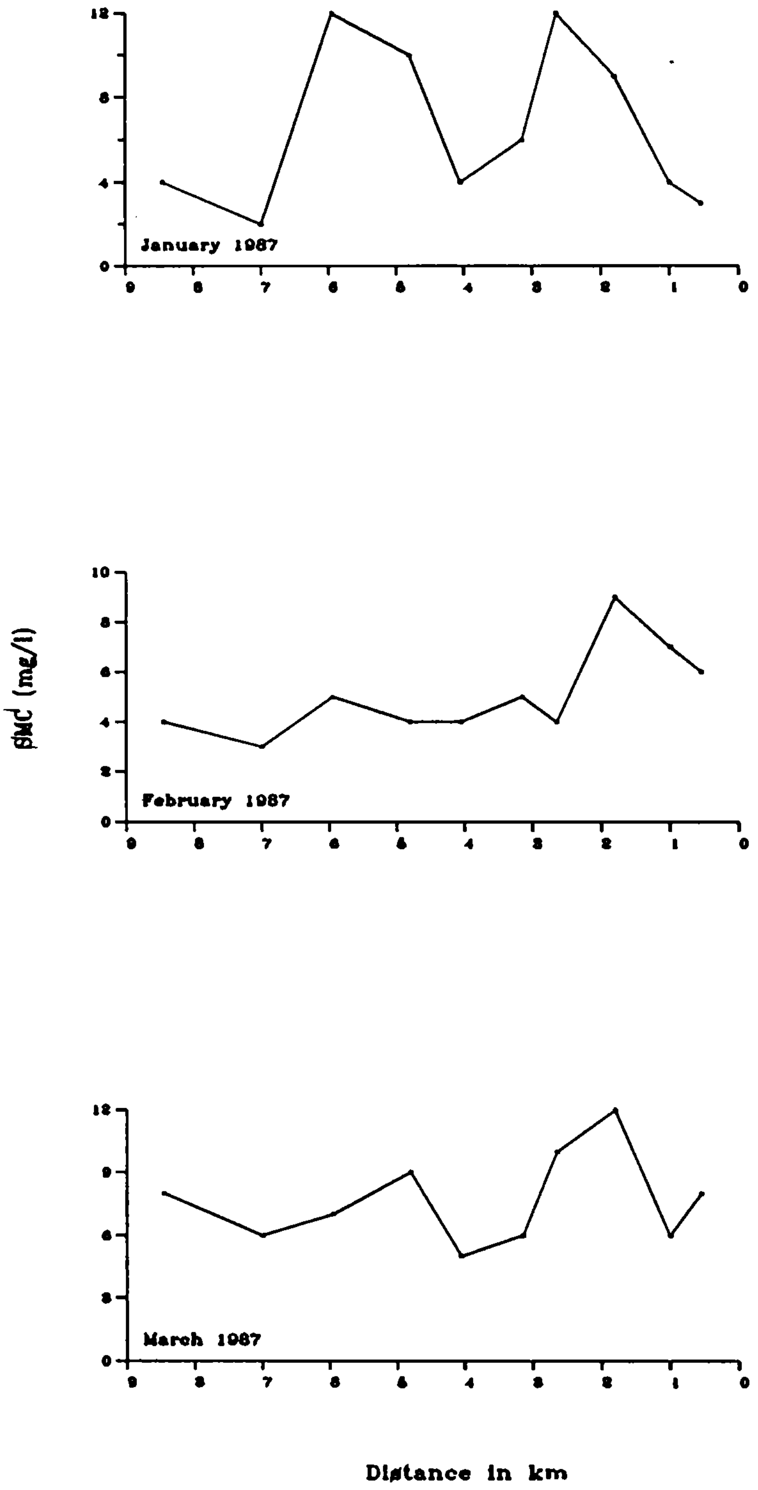


Fig. 3.2 Continued......

a low SSC was noticed. In the month of October the range of concentration was 4 and 12 mg/l with an average value of 7 mg/l. Similar pattern was followed for the month of January, February and March and the average suspended sediment concentration observed were 12, 9 and 12 mg/l respectively.

Summary of SSC variation over a tidal cycle in the months of June, July, August, September, October '87, January, February and March '88 are given in table 3.2 and illustrated in figure 3.3. It was observed that the bottom waters always registered higher values of SSC obviously due to the resuspension of bottom mud owing to scouring effect of tidal currents. The net sediment content over tidal cycle varied considerably over months. The average value of 26.1 mg/l during February increased to 32.8 mg/l in March. Increase in net sediment content was found to co-vary with the increase in salinity during March.

The observations carried out by Nair et al. (1987) revealed that, the contribution of SSC by the two tributaries joining the Chaliyar river was not so significant during the premonsoon months. Only during monsoon months, higher concentrations were observed in both estuary and river. Relative higher concentrations of suspended load obtained during summer months might not have been derived from the river as the river discharge was very low during that time compared to the monsoon months. The higher SSC during summer months might have come along with the intrusion of sea water during flood tide. Moreover, intense wave action can feel the shallow bottom of the estuary resulting in resuspension of bottom mud. Compared to the Muvattupuzha river (where suspended sediment load was reported by Balachand, 1983), the concentration in Beypore and Chaliyar were found to be low. In Vembanad lake, suspended sediment load varied from 0 to 25 mg/l during March with 10 mg/l concentration in the near coastal waters (Sankaranarayanan and Stephen, 1978), and this information agrees well with the satellite derived data (Kurian, 1987). Balachand (1983) observed 30-40 mg/l values in the Muvattupuzha river. Substantial contribution by rivers to the estuarine suspended sediment load was reported by Biggs (1970) and Schubel et al. (1976). The influx of water having high sediment load creates zones of turbidity (Allen et al., 1976).

Table 3.2 Suspended matter concentration over tidal cycles at surface (S), mid-depth (M), and bottom (B) levels

Jun-87

Time	Suspended Sediments(mg/l)		
	S	M	B
645	3.48	3.38	2.65
740	5.58	9.22	20.02
840	4.9	10.32	195.94
940	4.36	24.88	161.48
1040	5.6	96.08	75.66
1140	4.28	62.49	59.34
1240	4.82	30.7	31.88
1340	5.74	16.92	32.94
1440	3.28	15.1	21
1540	2.04	10.78	18.7
1640	2.66	9.58	17.14
1740	1.53	7.3	8.02
1840	4.34	5.14	5.56
1940	2.28	5.44	5.98

Jul-87

Time	Suspended Sediments(mg/l)		
	S	M	B
630	6.08	2.38	26.8
730	9.64	9.1	22
830	1022	16.1	14.72
930	6.1	8.8	12.02
1030	1.06	7.94	19.02
1130	7.6	6.56	4.78
1230	5.4	7.1	3.63
1330	4.48	7.96	7.02
1430	6.22	6.8	15.24
1530	8.92	9.04	5.92
1630	5.96	6.92	5.26
1730	3.2	2.98	5.64
1830	2.44	11.64	3.56

Aug-I-87

Time	Suspended Sediments(mg/l)		
	S	M	B
630	0.62	4.06	5.7
730	3.12	7.84	8.22
830	4.62	7.5	21.82
930	5.2	3.22	15.14
1030	8.74	44.9	69.8
1130	7.72	27.12	33.16
1230	6.42	17.5	18.72
1330	2.5	3.56	8.28
1430	4.1	4.32	14
1530	3.7	8.54	12.7
1630	3.94	8.24	9.34
1730	5.2	9.56	17.78
1830	5.6	4.9	19.62
1930	7.8	19.58	2.84

Aug II-87

Time	Suspended Sediments(mg/l)		
	S	M	B
600	87.52	34.38	120.56
700	58.72	44.94	83.26
800	36.78	46.21	119.7
900	44.2	63.8	67.42
1000	22.06	59.22	123
1100	11.96	72.08	86.6
1200	4.2	4.14	34.48
1300	28.86	47.52	59.6
1400	59.9	57.82	74
1500	21.06	49.86	52.94
1600	52.1	69.9	14.5
1700	123	113.18	124.92
1800	89.4	137.88	169.46

Sep I-87

Time	Suspended Sediments(mg/l)		
	S	M	B
900	12.34	23.32	19.62
1000	6.5	15.8	15.46
1100	7.32	12.58	17.74
1200	6.32	25.94	26.1
1300	14.56	20.16	25.52
1400	14.08	26.72	32.34
1500	12.64	32.84	62.44
1600	5.94	25.3	73.66
1700	14.62	90.82	237.86
1800	43.56	124.46	186.36
1900	39.8	111.26	409.54
2000	35	166.66	482.82
2100	39.48	112	181.1
2200	26.9	143.48	148.04
2300	86.94	89.2	98.14
2400	10.94	9.08	74.66
100	7.84	129.36	141.02
200	6.68	148.28	304.58
300	116.98	326.44	363.34
400	140.12	233.74	343.08
500	30.98	224.96	265.44
600	59.84	185.36	208.6
700	54	130.82	175.08
800	11.78	176.56	488.22
900	23.62	58.16	362

Table 3.2 Continued.....

Sep II-87

Time	Suspended Sediments(mg/l)		
	S	M	B
900	10.48	10.54	16.6
1000	12.94	15.24	18.96
1100	8.96	11.42	32.36
1200	2.96	13.43	19.68
1300	3.52	3.88	48.74
1400	1.08	13.46	21.32
1500	18.08	17.74	33.02
1600	4.28	54.52	79.24
1700	47.18	61.86	137.88
1900	45.7	53	115
2000	15.38	345	202.76
2100	19.57	17.24	170.88
2200	16.66	94.3	132.14
2300	6.48	69.59	116.82
2400	32.92	82.28	157.08
100	4.16	..	141.12
200	83	116.82	134.24
300	13.86	109.22	123.18
400	17.24	102.06	187.78
500	117.1	136.54	137.42
600	..	129.06	112.76
700	100.58	170.18	119.24
800	21.9	..	134.78
900	..		

Oct-87

Time	Suspended Sediments(mg/l)		
	S	M	B
730	11.24	37.36	38
830	2.62	21.18	33.2
930	13.66	15.5	23.08
1030	14.22	13.6	23.02
1130	13.88	18.54	29.76
1230	3.46	12.22	39
1330	7.14	17.12	40.68
1430	0.98	11.48	50.22
1530	0.54	7.94	29.04
1630	4.58	28.04	43.82
1730	13.32	43.52	92.52
1830	33	67.26	115.78
1930	29.92	40.4	81.42

Jan-88

Time	Suspended Sediments(mg/l)		
	S	M	B
915	7.92	7.2	7.96
10	4.6	4.7	4.8
1055	7.45	7.1	7.98
1155	8.34	11.16	17.18
1250	4.98	6.74	8.46
1355	4.64	7.76	9.06
1455	7.86	8.38	11.1
1550	6.5	0.24	12.94
1650	8.8	10.14	11.2
1745	8.2	10.76	15.5
1850	8.98	14.72	17
1950	10.36	11.84	18.38
2035	9.94	11.24	13.4

Feb-88

Time	Suspended Sediments(mg/l)		
	S	M	B
800	14.2	17.36	21.52
900	16.64	16.62	25.32
1000	10.54	12.74	14.06
1100	9.92	15.76	12.16
1200	7.48	11.14	15.04
1300	11.44	12.34	20.08
1400	13.08	23.18	32.84
1500	40.54	43.56	54.92
1600	11.1	13.66	17.7
1700	11.84	17.26	26.64
1800	6.74	10.44	15.64
1900	2.76	7.7	9.74
2000	3.8	6.62	7.14

Mar-88

Time	Suspended Sediments(mg/l)		
	S	M	B
815	4.78	9.26	11.4
915	4.92	15.24	21.54
1015	8.78	9.92	11.72
1115	6.44	9.62	12.04
1215	11.78	23	44.52
1315	13.78	32.96	57.08
1415	34.84	49.8	68.78
1515	11.02	19.58	42.56
1615	16.58	17.78	41.32
1715	5.14	12.76	31.84
1815	11.78	27.08	30.7
19.15	6.76	14.28	24.22

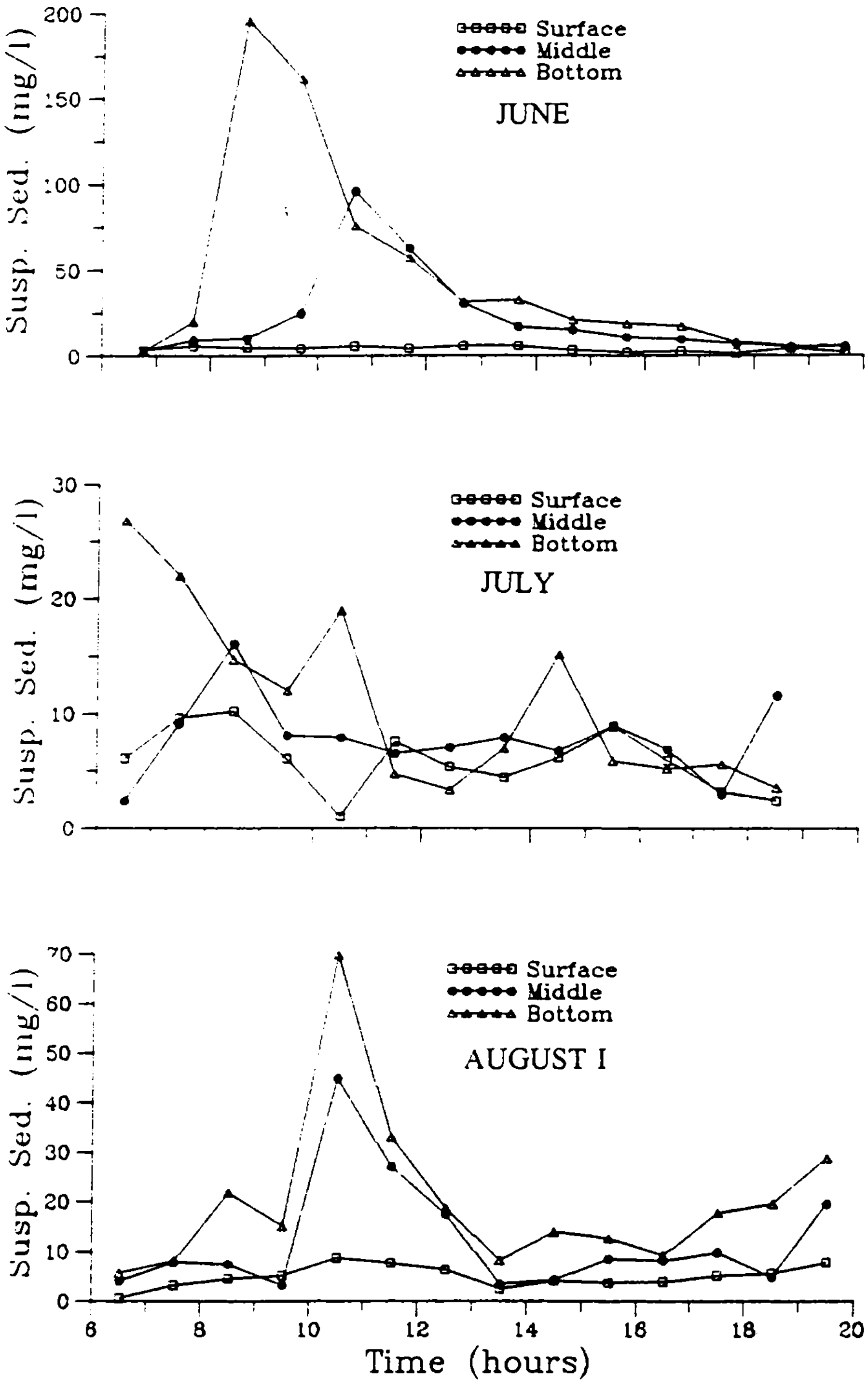


Fig. 3.3 Suspended matter variation over tidal cycle

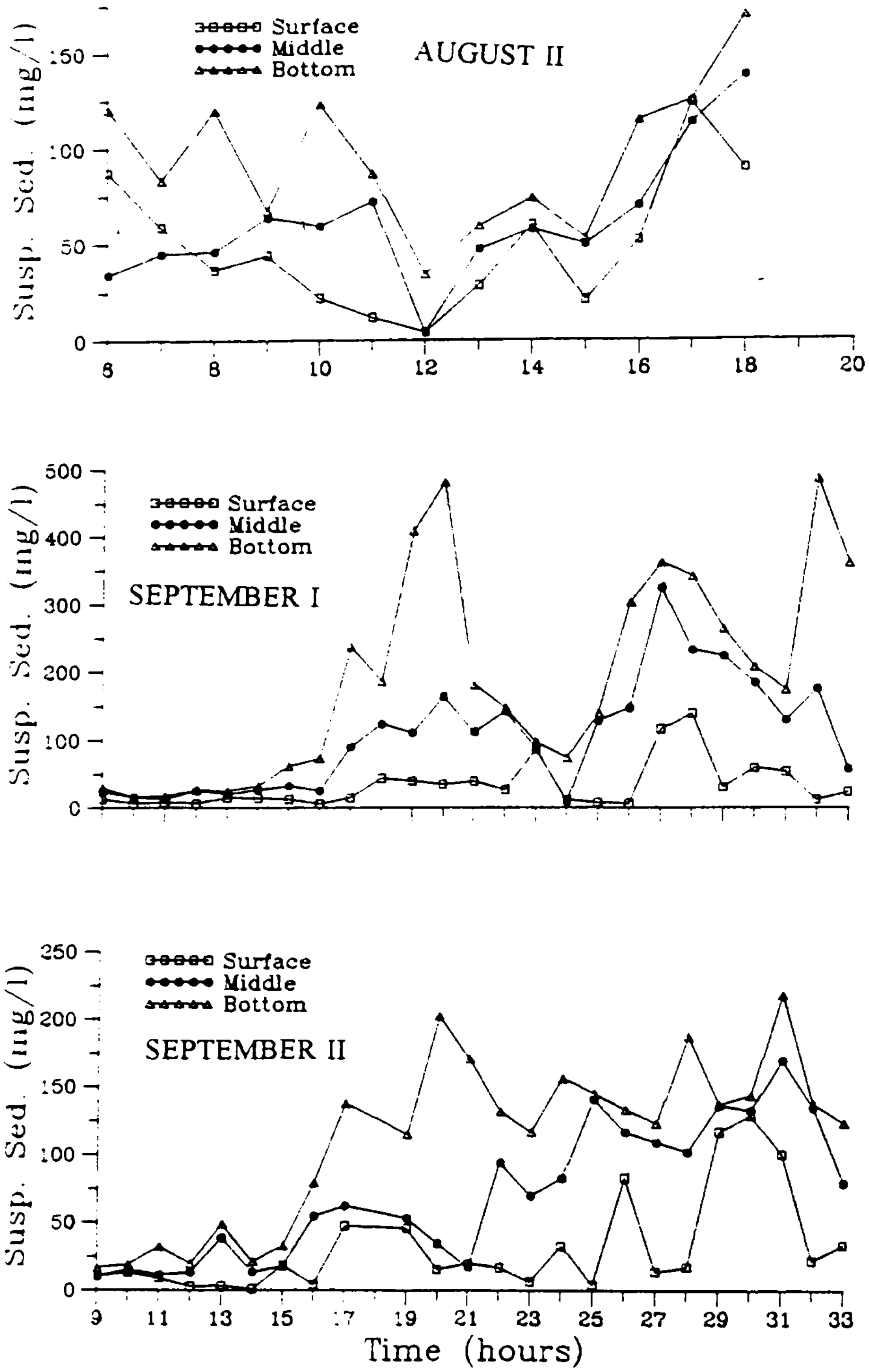


Fig. 3.3 Continued......

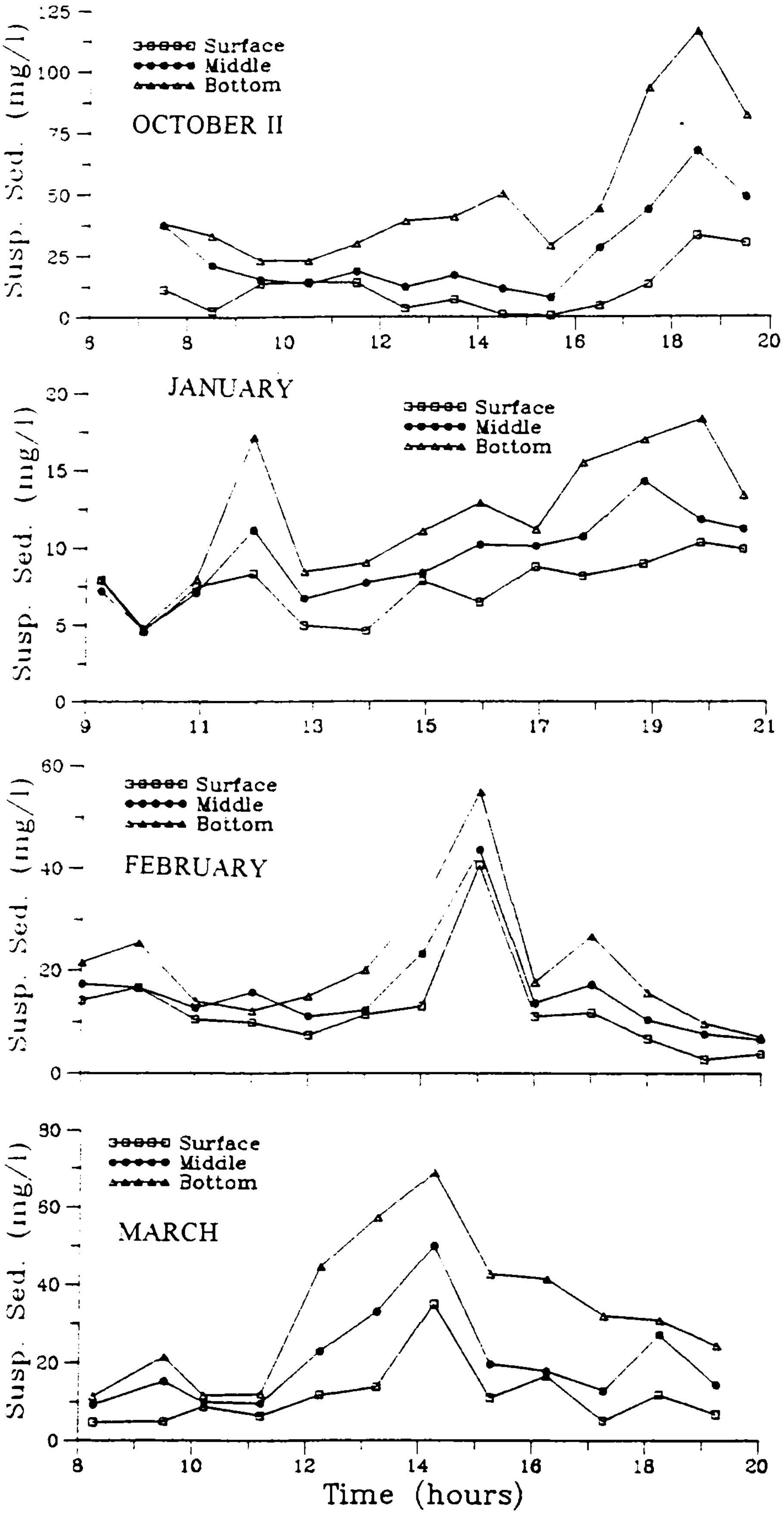


Fig. 3.3 Continued......

Estuaries with large upstream drainage basins, such as Chesapeake Bay, receive sediment mainly from river run off (Meade, 1969). It is quite possible that due to small drainage area, the contributions of suspended sediment load by the rivers joining the Beypore estuary might be far less, except during its full spate in monsoon.

The effect of tidal flows create more suspension in the near bottom zones of the estuary. With the increasing currents, scouring up of bottom sediments takes place and the sediments are kept in suspension. Investigations made on the suspended sediments in the Miramichi Estuary by Willey (1976) showed that the suspended particulate matter get settled on to the bottom sediments in February when currents are at minimum. The texture of the bottom sediments and its rheological behaviour matter a lot in deciding the nature of the resuspension process in estuaries. Dyer (1978) has pointed out that hysterisis between maximum current velocity and the suspended sediment is an important factor in determining the turbidity maxima. Certain temporal increase in suspended sediment concentration in estuaries was attributed to the increased wave action and shallowness of the estuary (Postma, 1967; Varma, et al, 1975). Vertical advective flux of sediment associated with tidal and non-tidal currents taking place in estuaries can also contribute to the SSC (Schubel, 1976). The higher concentration of suspended sediments observed occasionally at the entrance of Beypore estuary could be due to the entrainment from the deeper layers owing to one or several physical factors such as waves and currents operative in that area.

3.4.2 *Particulate Trace Metals*

Results of 3 surveys during October '87, December '87 and January '88 are presented in table 3.3. Lead had an average concentration of 1.5 mg/g and ranged between 0.9 and 3.8 mg/g in October. During December and January the average was 0.8 mg/g and the range of concentration was from 0.4 to 1.9 mg/g in December and 0.6 and 1.1 mg/g in January. In general the values showed a decreasing trend from upstream to bar mouth stations. Subsurface suspended particulates were found to contain more lead than in surface water and sediments.

Table 3.3 Trace metal concentration in suspended particulate matter

Oct-87

Station No	Lead	Chromium	Nickel	Copper	Cadmium	Zinc
3	2.3	4.5	0.7	0.7	0.3	6.2
4	3.8	0.6	0.8	3.1	0.4	2
7	1.6	0.5	0.7	0.8	0.1	6.4
8	1.5	0.3	0.6	2	0.1	7
9	2.2	0.8	0.8	1.4	0.1	10.5
10	0.9	0.3	0.3	0.4	0.2	5.3
13	1.5	1.2	0.7	0.8	0.2	7.5
16	1.9	0.6	0.8	1	0.2	7.4
18	0.9	0.1	0.3	0.4	0.1	5.6
20	1.7	0.2	0.3	0.6	0.1	9.4
21	0.9	0.4	0.5	0.1	0.1	5.9
23	1.1	0.3	0.8	0.1	0.1	7.5
26	1.2	0.8	1.1	0.3	0.2	9.1
29	1	0.8	0.8	0.2	0.2	8.3
32	1	1.1	0.8	0.5	0.1	6.7
35	1.3	1.1	1.1	0.2	0.1	6.4
38	1	1.3	1.4	0.5	0.2	7.3

Dec-87

Station No	Lead	Chromium	Nickel	Copper	Cadmium	Zinc
1	0.7	0.7	0.8	0.1	0.1	4.5
2	1.9	1.2	1.1	1.1	0.1	7.5
3	1.0	0.6	0.9	0.4	0.1	5.3
4	1.0	1.3	0.9	0.5	0.1	5.3
5	0.7	0.4	0.9	0.1	0.1	4.5
7	0.9	1.0	0.8	0.2	0.1	4.3
8	0.9	0.7	0.9	0.2	0.3	5.9
9	0.8	0.8	0.9	0.2	0.3	4.9
10	1.0	1.2	1.0	0.2	0.3	6.4
11	0.7	0.6	0.8	0.2	0.3	5.0
12	0.8	0.6	0.8	0.5	0.3	5.3
13	0.6	0.5	0.4	0.2	0.3	5.1
14	0.6	0.4	0.3	0.3	0.3	4.1
15	0.8	0.6	0.5	0.3	0.2	5.3
16	1.1	1.3	0.5	0.2	0.3	5.7
17	0.7	1.0	0.6	0.4	0.3	4.9
18	0.7	0.8	0.5	0.4	0.3	6.0
19	0.4	0.4	0.4	0.3	0.2	4.6
20	0.7	1.1	0.5	0.1	0.2	5.0
21	0.8	0.8	0.5	0.4	0.3	5.6
22	0.9	1.2	0.6	0.4	0.3	5.8
23	0.6	0.9	0.5	0.2	0.3	5.5
24	0.7	1.0	0.5	0.2	0.3	5.6
25	0.8	1.1	0.4	0.6	0.3	6.3
26	0.5	0.6	0.3	0.3	0.3	6.5
27	0.7	0.8	0.7	0.3	0.3	6.1
29	0.8	0.8	0.4	0.4	0.3	6.1
32	0.7	1.1	0.5	0.1	0.3	6.8
35	0.8	0.9	0.4	0.1	0.3	7.1
38	0.6	0.7	0.5	0.4	0.3	5.8

Table 3.3 Continued.....

Trace metals concentration in particulate matter (mg\g)

Jan-88

Station No	Lead	Chromium	Nickel	Copper	Cadmium	Zinc
6	0.7	1.4	0.5	0.2	0.2	7.7
7	0.7	1.0	0.5	0.2	0.1	9.4
8	0.5	1.4	0.3	0.3	0.1	7.9
10	0.6	1.1	0.5	0.2	0.2	7.7
11	1.0	1.1	0.4	0.8	0.2	7.8
12	0.8	1.3	0.4	0.4	0.1	6.9
13	0.7	1.2	0.2	0.1	0.1	7.0
14	0.7	1.4	0.5	0.5	0.1	7.1
15s	0.8	1.4	0.4	1.1	0.1	7.1
15m	1.1	1.6	0.3	0.8	0.1	8.1
15b	0.9	1.7	0.2	0.4	0.2	7.8
16s	0.7	2.1	0.2	1.4	0.1	7.2
16m	0.8	1.6	0.8	0.2	0.1	7.3
16b	0.8	1.6	0.4	0.6	0.1	8.2
18s	0.8	1.5	0.4	0.5	0.1	7.1
18m	1.1	1.8	0.4	0.3	0.1	11.1
18b	0.9	1.7	0.2	0.3	0.1	7.6
20s	0.9	1.6	0.4	0.4	0.1	7.5
20m	0.8	1.6	0.4	0.4	0.1	7.3
20b	1.1	2.2	0.4	0.2	0.1	9.8
29s	0.6	1.7	0.5	0.5	0.1	7.2
29m	1.0	1.6	0.8	0.2	0.1	7.8
29b	1.0	1.7	0.5	0.2	0.1	7.8

Maximum average value of chromium in the particulates was found to be in January (1.5 mg/g) with a maximum of 2.2 mg/l obtained for station near Green Island (2.65 km upstream). The minimum Cr concentration of 1.0 mg/g were observed at several stations. During December survey, the average concentration of Cr were 0.8 mg/g and it ranged between 0.4 and 1.3 mg/g. The maximum Cr concentration observed was at station near the Tile factory (5.95 km upstream). October results showed Cr average of 0.9 mg/g with range between 0.1 and 4.5 mg/g. Maximum value was noticed at station near Bund.

The average nickel concentrations were 0.7, 0.6 and 0.4 mg/g during October, December and January respectively. The minimum Ni observed were 0.3, 0.3, and 0.2 with corresponding maxima of 1.4, 1.1 and 0.8 mg/g. The average values show a decreasing trend from October to January.

Copper content was high during October survey (average: 0.6 mg/g). December and January recorded average Cu concentation of 0.3 and 0.4 mg/g respectively. The range of Cu for October was between 0.1 and 3.1, for December 0.1 and 1.1 and for January 0.1 and 1.4 mg/g.

The Cd concentration range were between 0.1 and 0.3 mg/g during October and December survey, while in January Cd values obtained were 0.1-0.2 mg/g. The average values were 0.2 mg/g during October and December, while it was 0.1 mg/g in January.

Content of zinc in the particulate matter was high compared to other metals analysed. The average Zn concentration for October, December and January were 7.0, 5.6 and 7.5 mg/g respectively. It ranged between 2 and 10.5 mg/g in November, 4.1 and 7.1 in December and 6.9 and 7.5 in January.

The spatial distribution of the elements in the particulates of surface waters did not show any particular pattern. The metal concentration are comparable with those reported from

Cochin estuary (Sankaranarayanan and Stephen, 1978). However, copper and cadmium depicted higher concentrations in sub-surface layers than that of surface waters which could be due to entrainment from bottom waters. The concentrations of metals studied were many fold higher than that of the bottom mud confirming the fact that the particulates play an important role in the transportation of trace metals as in the case of any other polluted estuary. Gibbs (1979) carried out extensive studies to elucidate transport mechanisms of Cr, Mn, Fe, Co, Ni and Cu in the Amazon and Yukon river waters. In rivers, trace metals are transported (1) in solution, (2) by sorption (3) in solid organic materials (4) as metallic coatings of particles, and (5) in detrital crystalline material. He observed that the main transport phases of Cr, Mn, Fe, Co, Ni and Cu are crystalline particles and hydroxide coatings over suspended material and together these two transport mechanisms contribute to 65-92% of metal transport. The remaining mechanisms were by solid organic materials which accounted for 5-19% and in soluble form accounting for 0.6-8% of the total metallic transport.

In Beypore estuary, increased concentrations of trace metals were found during the month of November. The oxide coatings of the suspended sediments scavenge metals from the surrounding water. The low concentration of metals found during December is attributed to the removal of fine grained suspended sediments during this period. Enrichment of certain trace metals in suspended matter compared to the bottom sediments were reported for many other estuaries (Spencer and Sachs, 1970; Piper, 1971). An increase in Hg content in suspended sediments was noticed by Cranston and Buckley (1972). Rust and Waslenchuk (1974) found that Fe, Mn and Hg were more associated with the fine grained phase of the sediments in Ottawa river waters.

Laboratory studies carried out by Hunt (1979) has shown that dissolved Mn can be rapidly transferred to the particulate phase following a Skeletonia Costatum bloom. Flocculant organic particulate matter derived from the bloom is implicated in the transfer process. An increase in the content of particulate lead and copper are also found in the bloom. He suggested that the removal of manganese and other metals from the water column of the nearshore and open ocean was due to adsorption by the flocculant organic matter derived from phytoplankton. This implies that, in the coastal zone as well as in other regions, particulate organic floc can incorporate trace metals. Subsequent deposition of this floc results in removal of metals from the water column. Sedimentary processes strongly influence the particle flux in the nearshore water column. Higher removal rates of metals associated with organic flocs may result from aggregation with the denser sedimentary particles or from removal through activities of filter feeders. In either of these cases, organic floc appears to be active in the uptake and removal of metals from marine waters. Salim (1983) found that the organic matter associated with the suspended sediment plays an important role in retaining most of the lead adsorbed in them.

The particulate matter was analysed for various metal concentrations in Cochin backwater by Sankaranarayanan and Stephen (1978). The study showed that some of the metals in the Cochin back waters were at higher levels in particulate matter. The high content of iron was attributed to the river water which flows through the lateritic bed, harbour activity and sewage effluent. The soluble iron brought in by rivers undergo precipitation and flocculation in contact with saline water and suspended matter. High values of copper in suspended matter during lean periods when fresh water discharge through the river was minimum were attributed to pollution as well as to other external sources. They concluded that the higher concentration of heavy metals associated with the suspended matter was either derived from industrial effluent or due to the activity in the harbour area. Particulate matter in the Beypore estuary were enriched with Cr and Zn in January, during which period fresh water discharge was very low.

3.4.3 *Dissolved Trace Metals*

In the present study the concentrations of dissolved copper, cadmium, lead and zinc in the Beypore estuary were carried out. The dissolved concentrations of lead, copper, cadmium and zinc are given in table 3.4 and illustrated in Figure 3.4.

Table 3.4 Dissolved trace metal concentration µg/l

Month	Distance km	Lead	Copper	Cadmium	Zinc
May-87	13.80	2.1	0.2	1.1	8.9
	4.05	2.1	0.6	0.4	11.4
	1.80	2.2	0.3	0.5	4.5
	0.55	2.3	0.3	1.5	6.1
Sep-87	13.80	2.6	0.8	1.2	10.7
	4.05	2.5	0.2	2.6	10.1
	1.80	2.8	0.4	2.7	8.3
	0.55	3.3	0.4	2.4	7.1
Oct-87	13.80	3.2	0.3	2.5	10.3
	4.05	3.2	1.1	2.6	9.2
	1.80	2.8	0.3	2.2	10.1
	0.55	2.4	0.2	2.0	4.2
Dec.87	13.80	1.5	0.4	1.3	7.9
	4.05	1.3	0.5	0.7	4.6
	1.80	1.4	0.9	1.8	5.7
	0.55	1.6	0.1	1.4	5.7
Jan.88	13.80	1.1	0.4	1.9	10.2
	4.05	1.7	0.4	2.7	5.4
	1.80	1.9	0.3	0.6	0.9
	0.55	2.1	0.2	0.9	2.1
Feb.88	13.80	1.6	0.7	1.6	10.3
	4.05	2.2	0.7	2.5	6.1
	1.80	2.2	0.3	2.4	4.6
	0.55	3.4	0.3	2.8	10.4
Mar-88	13.80	2.9	1.8	2.0	6.2
	4.05	2.1	0.5	0.7	10.7
	1.80	2.3	0.7	0.7	5.4
	0.55	2.6	0.5	0.8	7.8

The longitudinal distribution of lead was almost uniform during all seasons. Seasonal concentration exhibited moderate fluctuations in their values which ranged between 1.65 and 2.82 µg/l. The overall average during the study period was 2.24 and with a range of 1.1-3.4 µg/l. The concentration in the nearshore waters was 2.24 µg/l during premonsoon period.

Spatial distribution in copper content did not show any noticeable trend. Seasonal fluctuation also found to be marginal as evidenced from the average content which had a range of 0.47 and 0.68 µg/l. The average value during the study period was 0.56 µg/l with a range of 0.1 and 1.8 µg/l. The copper content in the nearshore water during pre monsoon was 0.84 µg/l.

Moderate variations in cadmium content was noticed between sampling locations. However, its seasonal concentration did not show much deviation and the average content during different seasons ranged between 1.15 and 2.32 µg/l. The annual average value was 1.73 mg/l and the values registered a maximum content of 2.8 µg/l and a minimum of 0.4 µg/l. Cadmium in the nearshore water was 1.12 µg/l.

Considerable fluctuations were noticed in the spatial distribution of zinc during all the seasons. The average seasonal concentration ranged between 6.0 and 9.8 µg/l. The average values during the period of investigation was 6.79 µg/l, the range being 0.9 to 11.4 µg/l. Zn concentration in the nearshore waters was 6.96 µg/l.

Lead and Zinc content during the study period exhibited higher values. Location specific fluctuations found in the case of zinc manifests the release of the metal from sediments already contaminated with industrial effluent. In the case of copper and cadmium, the concentrations were within the range of background levels reported for fresh water (Forstner and Wittmann, 1979). The variation in dissolved form of all the elements studied are small, though their concentration in suspended sediment load was considerably high. Turekian (1977) proposed that suspended materials in aquatic system play an important role in the

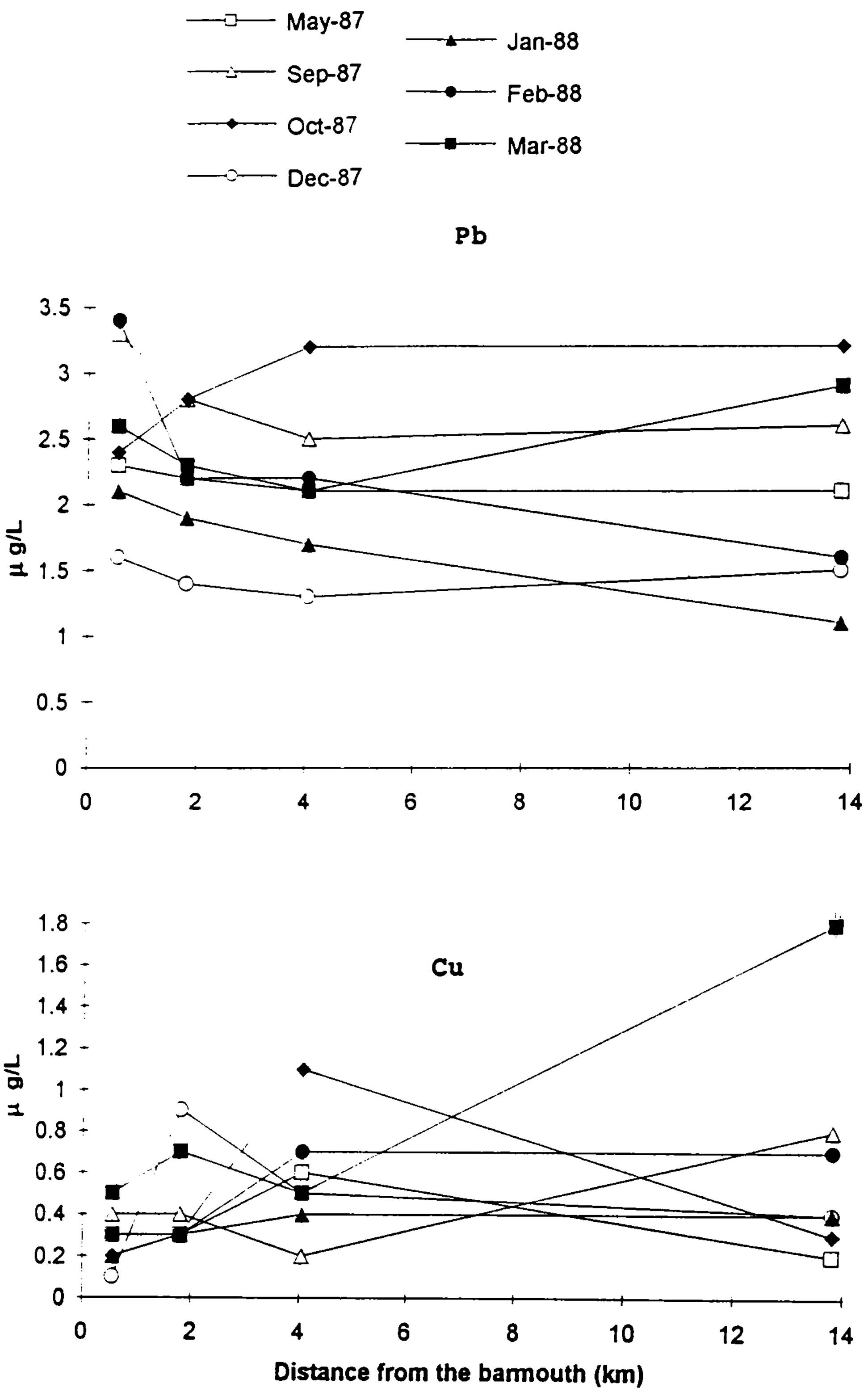


Fig. 3.4 Longitudinal distribution of trace metals during different months

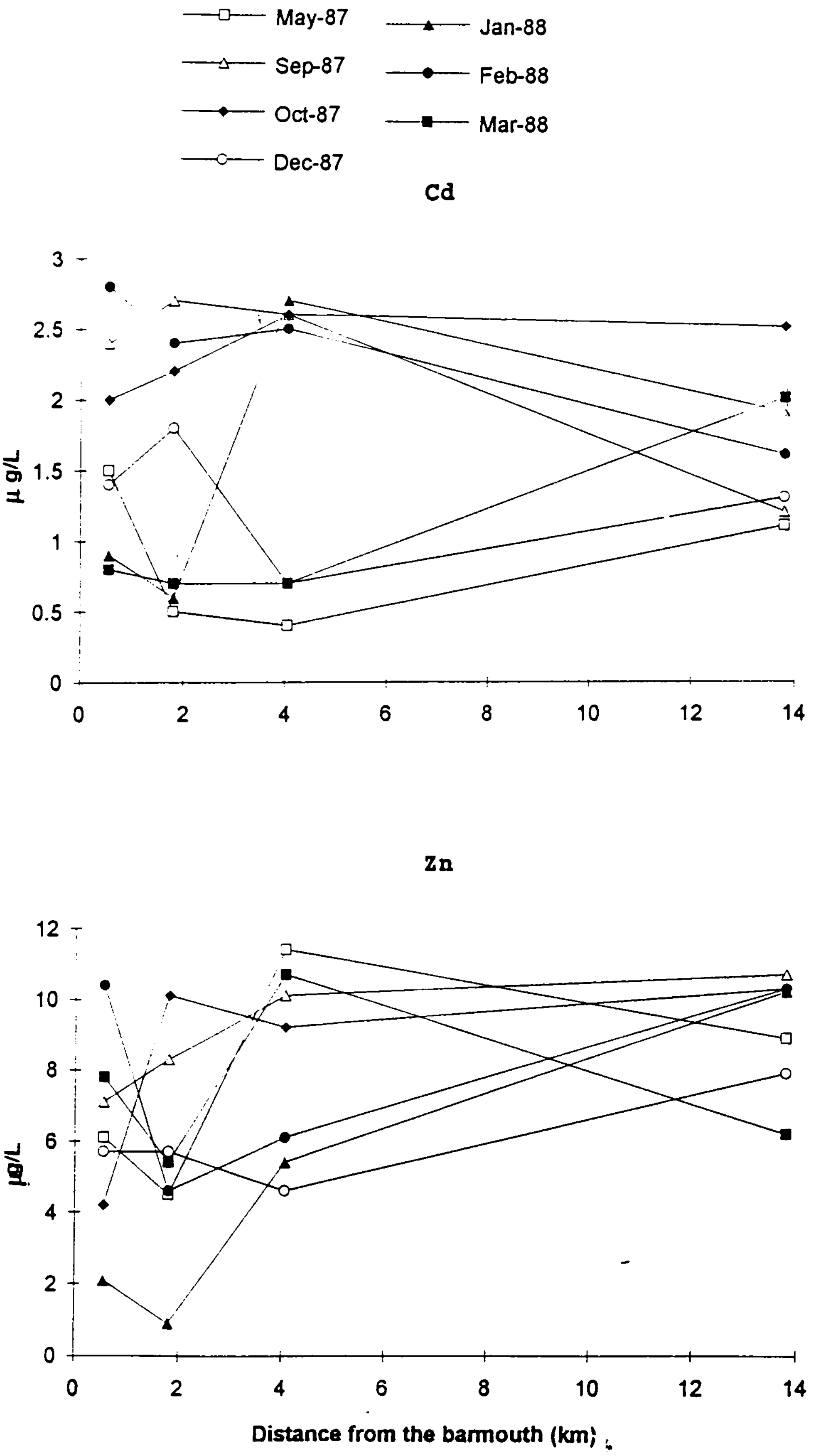


Fig. 3.4 Continued......

removal of dissolved metals from the water body. But the processes of removal of dissolved trace metals by suspended matter do not seem to be very effective in this estuary. Similar case was reported by Danielson et al. (1983) in the Gota river estuary. An increase in salinity is expected to cause a corresponding increase in cadmium content (Elbaz-Poulichet et al., 1984). However, in Beypore estuary, salinity is found to have little or very little influence on the metals studied. Concordant observations were made in Forth estuary in Scotland by Balls et al.(1994).

Sen Gupta et al. (1978) analysed the trace metals in Arabian Sea waters after pre-concentration by APDC/MIBK method. He observed that most of the heavy metals are present in ppb levels (in traces) and are closely knitted with the bio-geochemical cycle in the marine environment. Transition group of metals especially those with half filled d-shells have a tendency to attach to donor atoms to undergo bio-accumulation. Near the coast and river mouth, the chelating character of humus material can render many of the trace metals easily admissible to estuarine organisms. At shallow stations, quite frequently higher copper values were observed near the bottom indicating that the fraction of this metal concentrated at the surface has been released by the process of decomposition.

Copper is important as a biologically active element and is present in the chloroplast, haemocyanin and in several enzymes. Thus, presence of Cu is all the more important in controlling the productivity of water. The desired concentration of Cu is in traces and concentrations greater than 1 ppm is considered to be toxic to aquatic life. However, the average copper content in Beypore estuary was only 0.56 µg/l, which is much lower than the tolerance limit. Sankaranarayanan and Reddy (1973) made preliminary studies to understand the distribution of Cu in the inshore, estuarine and fluvial waters along the west coast of India. They observed that the concentration of copper in the bottom waters is invariably higher than those of surface in the inshore, estuarine and riverine waters. In the inshore surface waters its concentration ranged between 3 and 46 µg/l and at bottom 10-76 µg/l. During monsoon period, when fresh water discharge was more, the copper level were found to increased to 75 µg/l. Their studies could not establish significant relation between salinity and copper content either in inshore, estuarine or river waters. Trace metals content analysed in the Beypore estuary and the adjoining nearshore waters also did not show any mutual relationship.

CHAPTER IV

TRACE METAL CHEMISTRY OF BOTTOM SEDIMENTS

4.1 Introduction

Metals are natural constituents of sediments. Concentration of metals in river sediments reflect the abundance of certain rock types in the drainage area of the river. Since 1900, anthropogenic input of heavy metals to marine environment has became significant as revealed by studies on dated sediments (Chow et al., 1973; Young et al., 1973 and Bruland et al., 1974). Particulate matter in rivers and estuaries are the scavengers of most of the trace metals which forms part of the estuarine sediments after settling. Hence, analysis of sediment and water is an effective tool to assess the magnitude of pollution caused (Forstner and Wittmann, 1981; Allen, 1990).

Organic matter, mineralogy, texturally related qualities of sediments and the redox conditions of the environment control the concentration and reactivity of trace metals in estuarine sediments. For a long period, the concentration of trace metals in marine mud was reported as bulk sediment distribution. Later it has become necessary to distinguish the association of trace metals with various constituents of sediments. Usually, loosely bound trace metals in sediments are results of anthropogenic input, and are associated with organic carbon and oxide coatings of iron and manganese. They are easily available for uptake by marine organisms. Those metals associated with crystal lattices of minerals are not loosely bound and do not contribute to any metallic pollution. By adopting a selective leaching scheme and analysing the metals in each leachates, the bio-availability and extend of pollution caused by heavy metals could be assessed. Attempts were made by Tada et al. (1983) to classify Japanese rivers in terms of pollution status. They reported that 0.5 N HCl will be useful to extract the anthropogenic discharge of heavy metals from estuarine sediments. Various degrees of pollution in Japanese rivers were assessed after extracting the surficial sediments by 0.5 N HCl and analysing for heavy metals.Large percentages of heavy metals in non-polluted rivers are generally incorporated in the crystal lattices of minerals which make up the bottom mud. The heavy metals not found in the crystal lattices are distributed among the organic matter, the hydrous manganese and iron oxides. A chemical extraction technique was used by Filipek and Owen (1978, 1979) to separate the non-lattice held metals from lattice held metals. Investigations carried out by Suzuki et al. (1979) and Nariagun et al. (1981) concluded that a large percentage of heavy metals in bottom mud from the polluted rivers was held in the non-lattice positions.

4.2 **Literature review**

The geochemical association of trace metals in estuarine sediments were investigated by various workers world over. The adsorption/desorption of trace metals on clay minerals and oxide coatings of iron and manganese during estuarine mixing were carried out by Kharker et al. (1968), Cutshall et al.(1973), Rickard (1971) and Feick et al. (1972). Other important investigations are those by Reedes et al. (1972) in Meckenzie river, Trefrey and Priesly (1976) in Mississippi river, Duinker and Nolting (1976) in Rhine river, Gibbs (1977) in Amazon and Yukone rivers, Maybeck (1978) in Zaire river and Sarin and Krishnaswamy (1984) in Ganges-Brahmaputra rivers.

The variation in the heavy metal content in the Elbe estuary was well explained by Forstner and Muller et al. (1974) in terms of mixing up of marine and fluvial material. Estuarine sediments derived due to landward transport of marine sediments were reported by Meade (1969, 1972). and Solomons (1973). Various geochemical processes taking place in river basins were investigated by Gibbs (1967), Seetharamaswamy (1970), Sathyanarayana (1973), Seralathan (1979), Stallard and Edmond (1983) and Subramonian et al. (1985). Work has already been carried out in major rivers and estuaries to assess the degree of pollution due to various toxicants.

Pollution studies through metal surveys in South African estuaries were carried out by Watting and Watting (1983) by analysing surface sediments, water and core samples and found that the estuaries were devoid of any metal pollution. Abayachi and Douabul (1986) investigated trace element geochemical associations in the Arabian Gulf and a sequential extraction technique was adopted to monitor the geochemical fractionation of trace elements. It was observed that bio-availability and recycling of trace metals in aquatic environment depend very much upon the geochemical fraction with which metal is associated in the bottom sediments.

The cation exchange capacity (CEC) also plays an important role in metal exchanges. Experiments by Morgan and Stumm(1964) revealed that sediments having fresh coating of Fe and Mn oxides have high adsorption and cation exchange capacities and hence augment the retention of trace metals. The transport and fate of Mo in lacustrine environment was investigated by Sugawara et al.(1961), Bertine (1972) and Lahann (1977).

The role of organic carbon in the retention of trace metals was investigated by de Groot et al. (1976). They noticed striking parallelism between the concentrations of heavy metals and organic carbon. The chelating property of organic matter was investigated by Boxma (1974). Studies on the release of trace metals to the over-lying water column due to desorption processes were carried out by Turekian (1971) and Evans and Cutshall (1973). Grain size dependency of trace metals in aquatic sediments were investigated by de Groot et al. (1976) Mayor and Fink (1980).

Ackroyd et al. (1987) made investigations to assess the periodicity occurring in the trace metal content in the estuarine sediment and inferred that heterogeneous chemical reactivity was largely independent of the annual changes in the estuarine parameters and were controlled by the fluvial input of new material and the recycling of existing materials by river flow and tidal currents.

As per the estimations of Milliman and Meade (1983), the rivers in Indian subcontinent contribute to about 30% of sediments transported by the world rivers. Studies on mass transfer of geochemical constituents were carried out in Indian rivers by Subramonian (1980), Sarin and Krishnaswamy (1984), Sitasaward (1984), Seralathan and Seetharamaswamy

(1987) and Chakrapani and Subramonian (1990). Geochemical associations of metals in Krishna river sediments were reported by Seetharamaswamy (1970), Rao et al. (1988) and Ramesh et al. (1989, 1990).

Though major estuarine systems in Kerala are facing serious pollution threats, heavy metal studies in the estuarine sediments are sparse. Murthy and Veerayya (1972a, 1972b, 1981) analysed organic carbon, phosphorus and trace metals concentration in the bulk sediments of Cochin estuary. Paul and Pillai (1981) investigated the association of trace metals in various chemical phases in the sediments of Periyar river and Varapuzha estuary.

Few major and minor elements were analysed and reported in the sediments of Vembanad lake by Mallik and Suchindan (1984). Heavy metals in the Cochin estuary were studied by Ouseph (1987) from pollution point of view. Nair (1994) carried out studies on the mercury content in the Beypore estuarine sediments of sediments and obtained a striking parallelism between mercury content, organic carbon and clay fractions of the sediment. Granulometric control over the concentration of a few trace metals in Beypore estuarine sediments were carried out by Nair et al. (1995).

4.3 **Materials and method**

4.3.1 *Sample Collection*

Area of investigation and sampling locations are given in figure 4.1. Surveying method is as detailed in second chapter. Surficial sediment samples were collected using a Van Veen grab. A gravity corer was used for core sampling. Samples were collected during May '86, August '86, December '86 and May '87 to understand seasonal variation.

4.3.2 *Preliminary treatment*

The surficial sediment samples were homogenised and washed with distilled water to remove dissolved salts associated with it. The washed samples were oven dried at 60^0 C to constant weight. The core was cut open without disturbing the sediment column and sub-

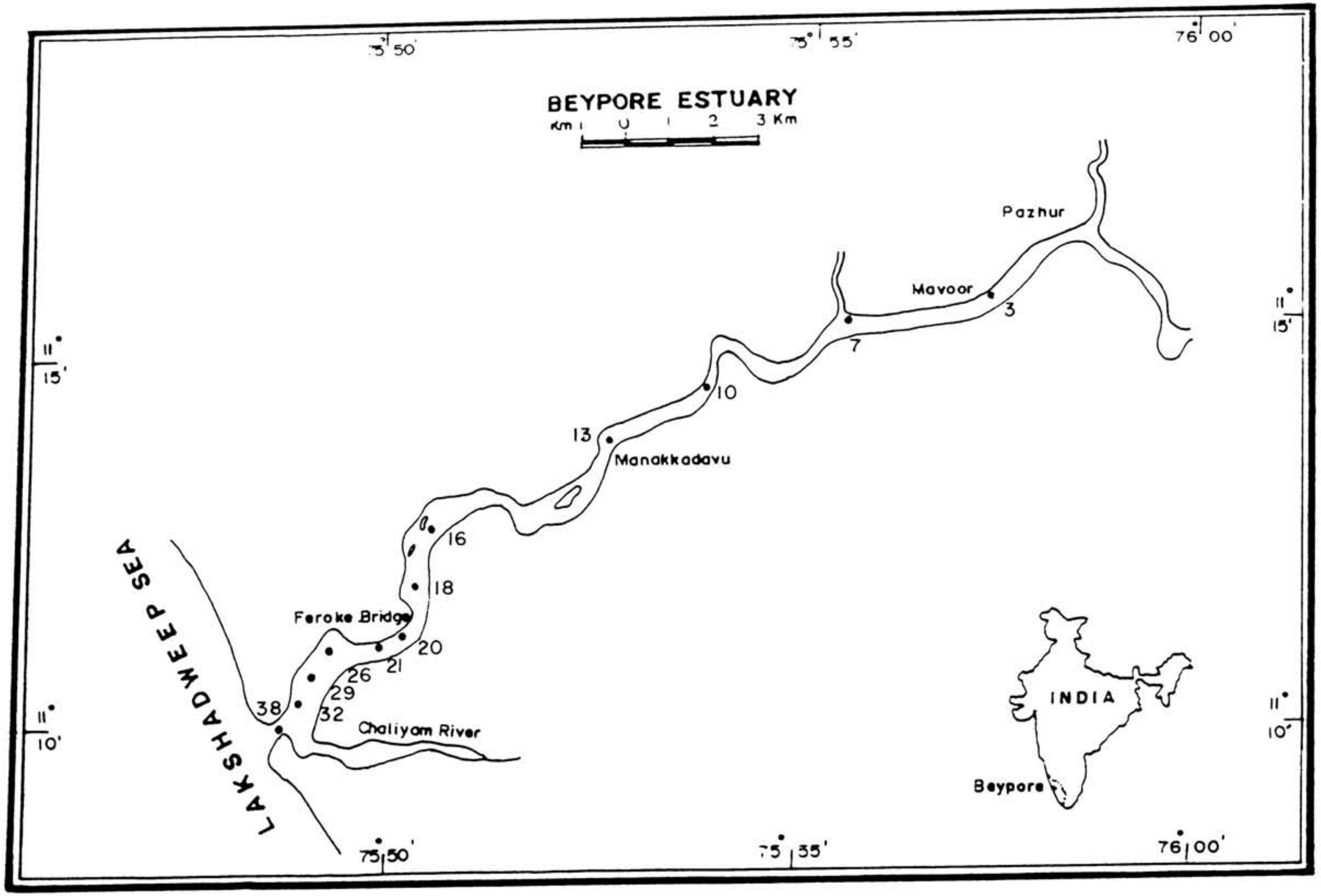


Fig. 4.1 Location map showing samples taken for textural and chemical analysis

sampled at 5 cm interval after marking top and bottom of the core. Each portion was properly labelled, desalted with distilled water and dried at 60°C to constant weight. The grab and core samples were processed and analysed for various parameters.

4.3.3 *Textural Analysis*

Wet sieving and pipette method were adopted to analyse the texture of the sediment samples (Lewis, 1984). Known weight of sediment sample was dispersed overnight in distilled water by adding 10 ml of 10% solution of sodium hexameta phosphate. Sediment fraction coarser than 63 µm was separated by wet sieving. The sieve retents were dried and weighed. The suspension passing through the sieve (#230) was transferred into a measuring jar of 1000 ml capacity and distilled water was added to bring the volume exactly to 1000 ml. The suspension was well stirred for about a minute to obtain a homogeneity and then left undisturbed. 20 ml aliquot was withdrawn from the suspension using a pipette from a specific depth after the lapse of time duration given for the desired fraction at the then room temperature. The aliquot was then transferred into a previously weighed 50 ml beaker. It was dried in an air oven at 60°C and weighed after cooling in desiccator. The dried aliquot weight was multiplied by a factor of 50 and the weight of sodium hexameta phosphate added was then subtracted. Weight of sand-silt-clay fractions were calculated from the above results and converted into percentages.

4.3.4 *Organic carbon determination*

The sediment organic carbon was determined by wet oxidation method of El Wakeel and Riley (1957). Organic matter was oxidised by a known quantity of chromic acid and the amount of chromic acid used was then determined by titration with standard ferrous ammonium sulphate solution. Diphenylamine was used as an indicator.

4.3.5 *Sediment digestion and analysis*

Major elements namely; Al_2O_3, Fe_2O_3, CaO and MgO were estimated by titrimetric method (Vogel, 1978) and trace metals using atomic absorption spectrophotometer

Sample preparation for major elements

Sodium carbonate fusion method as detailed by Maxwell (1968) was followed for sediment digestion. The silica was filtered off and the filtrate was used for subsequent analyses.

Determination of total iron:

25 ml of filtrate was pipetted in to a 250 ml beaker, diluted to 40 ml and added 10 ml concentrated HCl to oxidise all iron to Fe^{3+} state. The solution was boiled and stannous chloride solution was added till the solution became colourless. The solution is then rapidly cooled to about 20°C without air contact. Subsequently, 10 ml saturated mercuric chloride solution was added to remove the excess stannous chloride. The solution was allowed to stand for five minutes, added 20 ml 1:1 H_2SO_4, 5 ml orthophosphoric acid and a few drops of barium diphenylamine indicator. This was titrated against standard 0.01 N potassium dichromate solution until the pure green colour changed to grey-green. Then, dichromate was added drop-wise until the first tinge of blue-violet appeared, which remains permanent on shaking. From the titre values iron content was calculated.

Aluminium:

25 ml solution of the filtrate was pipetted out into a 250 ml beaker, added a few drops of phenolphthalein indicator and 20% NaOH solution till just alkaline, then 5 ml more was added and boiled for a few minutes. The solution was cooled and filtered through a Whatman filter paper (No. 40) and washed the filtrate with hot water. The filtrate and washings were collected in a 400 ml beaker. The filtrate was neutralised by adding 1:1 HCl till the solution became colourless. NaOH was added in drops to the solution to change it to just alkaline. 15 ml of ammonium acetate and 10 ml of 0.1 M EDTA were added and the beaker was covered and boiled for 30 minutes in a low flame. Cooled in ice and added 1 or 2 drops of xylanol orange indicator and titrated against 0.1 M zinc solution until the colour changed from Lemon-yellow to red. Al_2O_3 content was determined from the volume of Zn solution consumed.

CaO and MgO:

25 ml of the solution was pipetted out into a 250 ml beaker. 1 gm ammonium chloride and 10 to 15 ml NH_4OH were added. The solution was boiled for a few minutes and filtered through Whatman filter paper (No. 40) and the filtrate was collected in a 100 ml standard flask. Washed with hot water and the washings were collected in the same flask. The solution was made up to 100 ml. 25 ml of the made up solution was pipetted out into a 100 ml china dish and 2 ml ammonia buffer solution added followed by 1 or 2 drops Eriochrome black T indicator and titrated with standard 0.01 M EDTA until the colour changed from wine red to blue. The titre value corresponds to Ca and Mg content. Another portion of 25 ml solution was pipetted out into a 100 ml china dish and added 2 ml of 5% NaOH solution and 12 drops of muroxide indicator. The solution was titrated against 0.01M EDTA till the colour changed to violet. The titre value corresponds to Ca content. The difference in titre values corresponds to Mg content. From the titre values CaO and MgO content are calculated.

Sample preparation for Minor and Trace metals

0.5 gm of the powdered dry sample was taken in a platinum dish and added a few drops of H_2SO_4, 3 drops of $HClO_4$ and 25 ml HF. This was evaporated to dryness. Added 30 ml 1:1 HCl and heated to boil. The solution was transferred to a 100 ml standard flask after cooling and made upto the mark. Trace elements were then determined by Atomic Absorption Spectrophotometric method (Langmyhr and Paus, 1968). Rare earth elements were analysed using Inductively Coupled Plasma Emission Spectroscope - Mass Spectroscopic method.

4.4 **Results**

4.4.1 *Surficial Sediments*

Grain size variation:

Distribution of sand, silt and clay content in the sediments are given in table 4.1 and illustrated in figure 4.2. Textural spectrum of the sediments depict wide variation. Considerable spatial and seasonal variations were noticed in the sand percentage. The month-wise average

Table 4.1 Sand-silt-clay content of the sediments

	Sand %				*Silt %*				*Clay %*			
Distance from the Barmouth	May-86	Aug-86	Dec-86	May-87	May-86	Aug-86	Dec-86	May-87	May-86	Aug-86	Dec-86	May-87
0	83.68	88	15.53	15.2	9.19	5.44	44.4	45.5	6.93	5.66	39.57	39.29
1	43.79	96.54	82.44	74.83	22.21	0.55	0.18	17.87	34	2.91	17.38	7.3
1.8	89.86	98.01	4.94	81.2	4.42	0.07	49.98	14.23	5.72	2.7	45.08	4.57
2.65	95.66	96.88	85.6	90.87	0.74	0.44	4.46	5.82	3.6	3.61	10.2	3.31
4.05	5.86	98.41	9.24	18.61	33.41	0.17	51.32	53.8	60.73	1.42	39.44	28.31
4.8	4.43	17.41	15.14	7.19	35.23	48.07	74.29	61.8	60.34	34.5	10.57	33.63
5.95	89.23	67.45	97.53	85.85	6.15	23.2	0.62	9.05	4.62	9.35	1.85	5.09
7	54.65	37.56	5.77	68.62	21.07	45.05	48.29	2.01	24.28	17.39	40.01	11.27
12.1	88.5	15.47	17.12	97.72	6.23	56.65	40.52	0.3	5.27	27.88	42.36	1.98
16.5	86.22	87.3	19.08	96.49	9.13	10.19	43.61	1.47	4.65	2.33	37.31	2.04
20.55	49.92	79.4	18.85	94.5	28.58	15.64	45.28	5.43	21.5	4.96	35.87	0.64
25.5	53.89	99.32	19.08	95.52	23.24	0.26	43.71	3.12	22.87	0.42	37.21	1.36

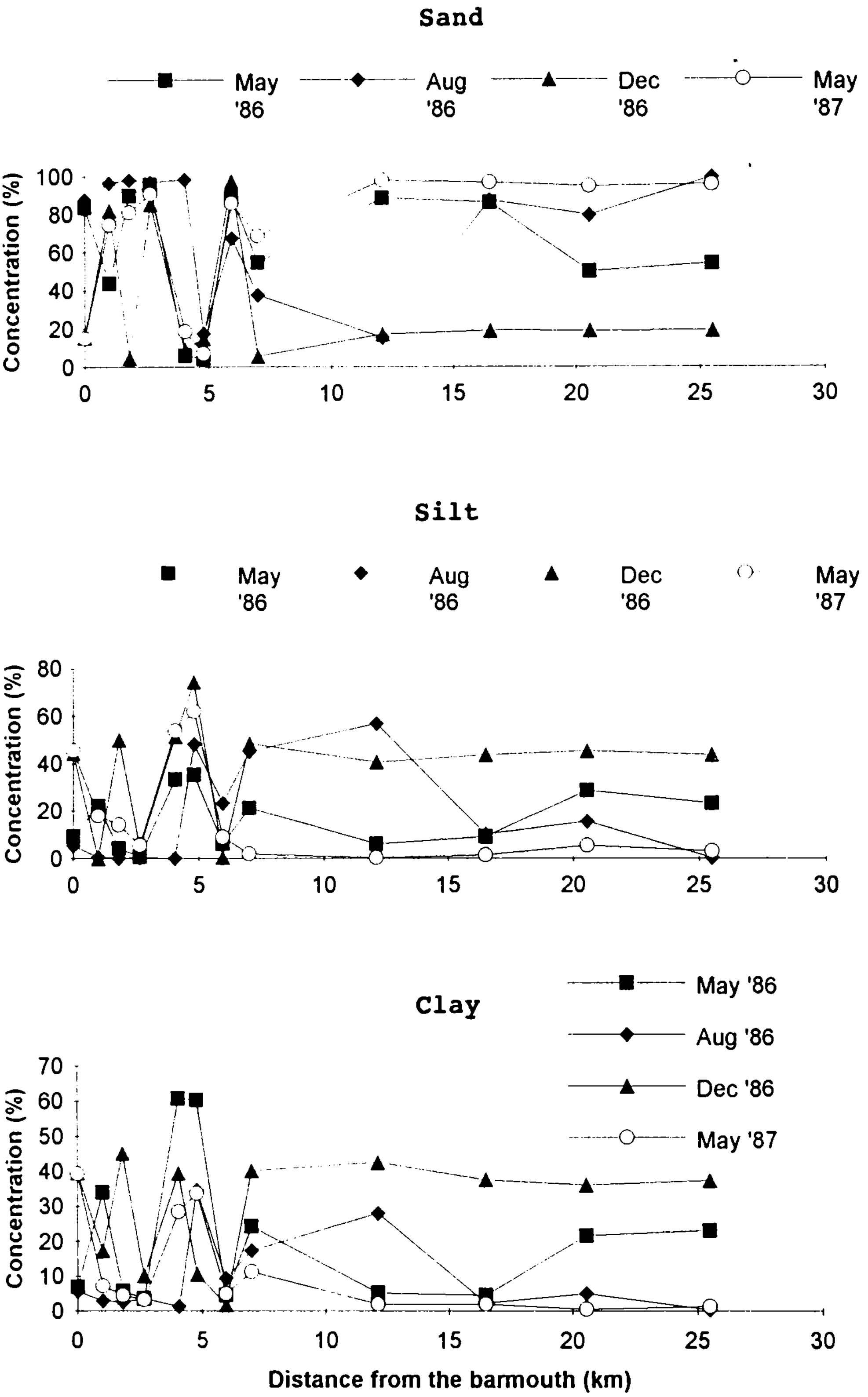


Fig. 4.2 Longitudinal distribution of sand, silt and clay percentages

of sand ranged between 32.53 and 68.88%. The annual variation in sand content was 4.43 and 99.32% with an annual average value of 59.25%.

Near uniform distribution of silt content was noticed in the upper estuarine and fluvial sediments. Fluctuations were noticed in the silt content at the lower part of the estuary. Substantial variation was noticed during different seasons and the average values ranged between 16.63 and 37.22%. Silt content during the study period registered a maximum of 74.29 and a minimum of 0.07%. The corresponding annual average was 18.18%.

Clay content followed a similar pattern of distribution as that of the silt content. An uniform distribution at the upper estuarine region was noticed while substantial fluctuation was found in the lower part. The seasonal distribution showed considerable variations. The average clay content during different seasons ranged between 9.43% and 29.74%. Clay content in the entire set of samples varied from 0.42 to 60.73% with a mean value of 18.06%.

Organic Carbon:

Fluctuations in the organic carbon content (OC) was observed in both river and estuarine sediments (Table 4.2: Fig. 4.3). Moderate seasonal variations were observed and the average OC content between stations varied between 1.07 and 2.30%. During the entire survey period, OC content ranged from 0.10 to 4.80 with an average of 1.48%.

Major elements:

Concentration of major elements (Al_2O_3, Fe_2O_3, CaO, MgO, Mn and Ti) are given in table 4.3. Spatial and temporal variations are depicted in figure 4.4. Individual pattern of distribution of elements are detailed below.

Spatial distribution of Al_2O_3 was marked with high fluctuations. Modest seasonal variations were indicated by the average seasonal values which range between 12.07 and

Table 4.2 Organic carbon content of the sediments

	Organic Carbon %			
Distance from the Barmouth	May-86	Aug-86	Dec-86	May-87
0	0.86	0.93	3.02	0.93
1	2.81	0.59	1.07	1.07
1.8	1.02	0.48	0.48	1.04
2.65	0.74	0.59	0.28	1.04
4.05	0.52	0.48	3.73	3
4.8	2.52	2.83	4.8	4.62
5.95	1.61	1.97	0.24	0.83
7	3.05	1.86	3.07	1.07
12.1	0.52	2.1	2.65	0.17
16.5	0.28	0.41	2.79	0.1
20.55	1.21	0.41	2.65	0.29
25.5	0.88	0.24	2.79	0.32

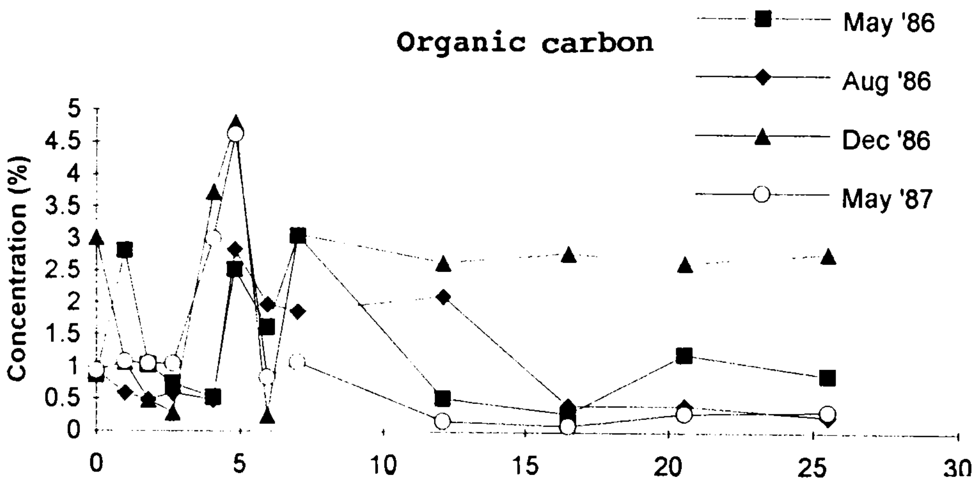


Fig 4.3 Longitudinal distribution of organic carbon in the sediments

Table 4.3 Major element concentration in the sediments

	Al2O3 %				Fe2O3 %				CaO %			
Distance from the Barmouth	May-86	Aug-86	Dec-86	May-87	May-86	Aug-86	Dec-86	May-87	May-86	Aug-86	Dec-86	May-87
0	12.75	1.28	25.5	17.85	7.99	5.99	23.95	20.33	4.2	2.45	3.85	2.8
1	17.85	12.75	15.3	10.2	10.38	4.39	13.57	14.77	2.8	1.75	2.8	2.8
1.8	10.2	10.2	12.75	10.2	7.19	5.18	11.18	11.58	2.45	2.45	3.15	3.15
2.65	12.75	10.2	5.1	10.2	4.79	7.98	9.58	13.97	1.75	2.1	2.8	3.85
4.05	10.2	12.15	7.65	17.85	7.98	3.59	27.94	27.54	2.8	2.1	2.1	2.45
4.8	20.4	20.4	20.4	20.4	10.78	13.57	7.94	20.55	2.45	2.1	3.75	1.4
5.95	12.75	12.75	5.1	12.75	7.58	11.18	11.98	14.37	2.45	2.45	3.15	2.8
7	17.85	7.65	25.5	12.75	9.98	14.77	14.37	13.17	2.1	2.1	1.4	2.48
12.1	20.4	22.95	22.2	10.2	6.39	13.57	11.97	8.78	2.8	2.45	2.8	2.1
16.5	12.75	15.3	25.5	10.2	7.58	12.77	14.37	7.98	2.45	3.15	2.1	2.1
20.55	17.85	28.95	23.2	5.1	14.37	9.18	13.15	11.58	2.8	3.15	2	2.45
25.5	12.15	10.65	22.2	7.15	10.72	8.78	14.26	8.74	2.85	3.15	2.1	2.25

	MgO %				Manganese (ppm)				Titanium (ppm)			
	May-86	Aug-86	Dec-86	May-87	May-86	Aug-86	Dec-86	May-87	May-86	Aug-86	Dec-86	May-87
0	2.25	1.25	2.25	2.25	435	300	335	380	4850	1850	8050	8150
1	2.52	1.25	2.25	2.5	380	260	350	405	8050	1050	4600	10600
1.8	1.51	1.75	1.75	2.5	300	330	395	390	6600	3550	2500	8650
2.65	1.26	1.25	1	2	210	225	200	420	2500	2550	3000	600
4.05	1.75	0.75	0.5	1.75	505	90	595	470	5800	4500	6850	10700
4.8	2.5	2.25	2.25	1.75	290	1015	360	845	6100	7150	9950	8450
5.95	1.51	1.5	1.25	1.25	460	700	340	320	7200	15100	3650	4450
7	1.01	0.75	2.25	0.75	450	395	1125	475	6800	17850	5350	6650
12.1	1.5	0.75	1.25	1.5	305	850	1235	240	1400	6500	6250	2200
16.5	2	2	1.5	1.25	610	1080	1155	220	7450	2250	6500	2750
20.55	2	1.75	1.5	1.25	705	690	1055	310	9100	9550	7000	1200
25.5	1.75	2	1.75	1.25	525	485	984	225	12850	7300	7800	2250

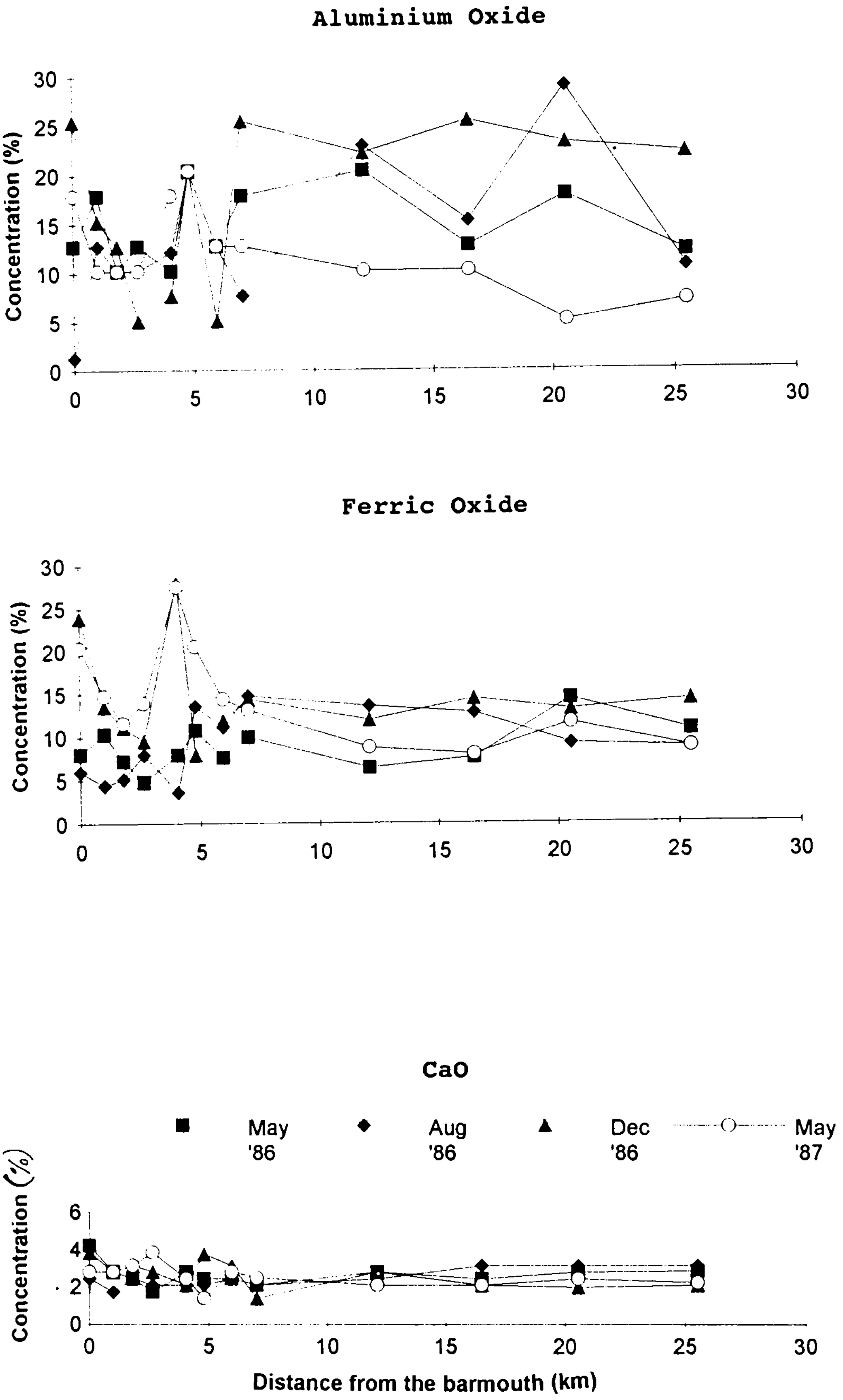
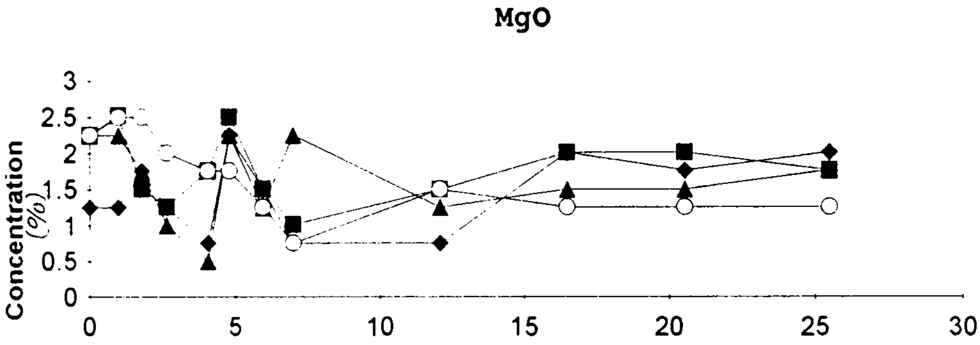
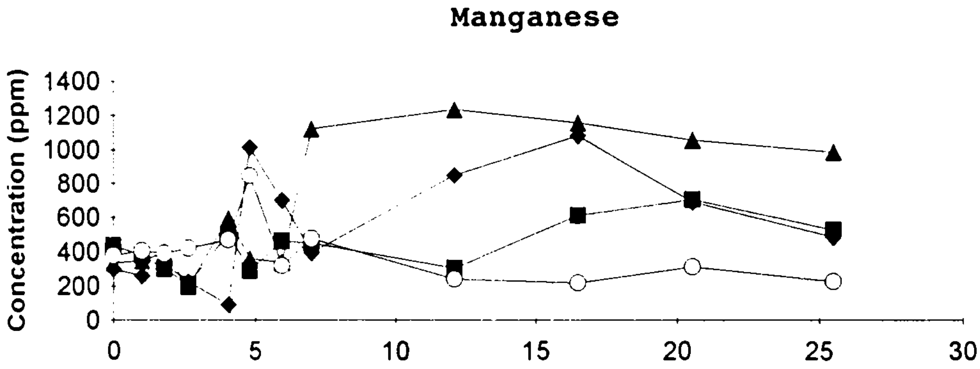


Fig. 4.4 Longitudinal distribution of major elements in the sediments





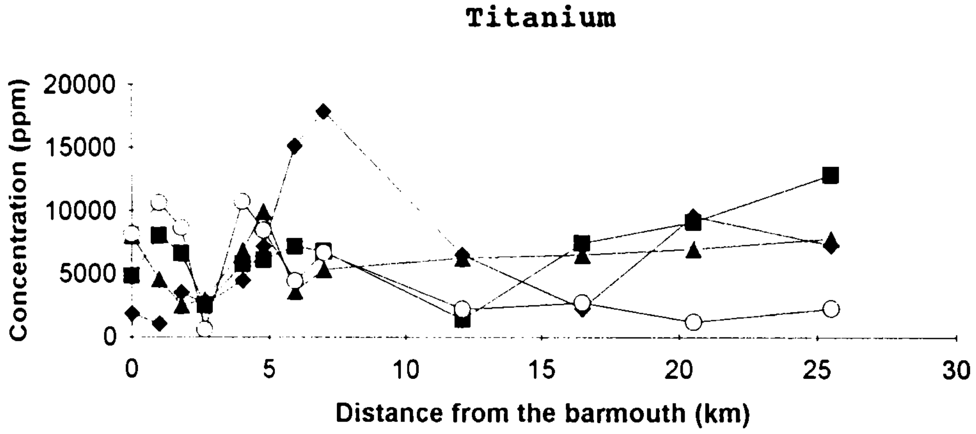


Fig. 4.4 Continued.....

17.53%. A maximum Al_2O_3 content of 28.95% and a minimum of 1.28% was noticed during the entire study period. The mean inter-seasonal value was 14.55%.

Iron content show significant variation in spatial distribution. The seasonal averages exhibited moderate fluctuation in iron content and average range of variation was 8.81-14.52%. Average iron content for the entire observation period was 11.76% and ranged between 3.59 and 27.94%.

An increasing downstream variation in CaO content was observed for the study period. CaO did not show much seasonal variations as evidenced by the average seasonal values which ranged between 2.45 and 2.68%. The average calcium content observed in the total set of samples was 2.58%, and the minimum-maximum variations were 1.40 and 4.20%.

Spatial distribution of magnesium was marked with a gradual increase in its contents towards the sea side. Seasonal variation in magnesium content was not so pronounced as seen from the average values which ranged between 1.44 and 1.80%. The average MgO content for the study period was 1.64% and it registered a minimum content of 0.5% and maximum of 2.52%.

Uniform spatial distribution pattern was noticed in the sediments of river and upper part of the estuary with a marked fluctuation in manganese concentration. Seasonal variations followed more or less uniform pattern and the season average ranged between 391 and 677 ppm. The sum total of variation in the entire set of samples varied from 90 to 1235 ppm with an overall average of 508 ppm.

Spatial distribution of titanium concentration was almost uniform with wide fluctuations in a few samples downstream. Moderate variations were observed during different seasons. Seasonal averages range between 5554 and 6600 ppm. Spectrum of variation among all samples collected irrespective of seasons was from 600 to 17850 ppm with a mean of 6158 ppm.

Trace metals

Trace metal data for different seasons are given in (Table 4.4). Longitudinal variation of Cu, Ni, Zn, Rb, Li, Cd, Ba, Bi, Be, Mo, Cr, Co and Sr are shown in figure 4.5.

Spatial distribution of copper content in Beypore estuarine sediments showed significant fluctuations. Station near tile factory (5.95 km upstream) registered very low concentration throughout the study period. Seasonal variations were not much pronounced in its levels. The differences in the average values range between 2.0 and 3.75 ppm. Cu variation ranged from 1 to 9 ppm. The annual average concentration of Cu in the estuary was found to be 2.86 ppm.

Nickel content was found to increase in the mid estuarine portion during the survey period. No significant variation was seen upstream. Downstream variation showed an increase in May 1987 period. The differences in the seasonal average attest this observation which ranged between 27 and 120 ppm. Ni variation for the study period ranged between 5 and 206 ppm with an average of 68 ppm.

Higher concentration of zinc was noticed in middle part of the estuary. Seasonal variations were significant and the average Zn content during different seasons varied between 68 and 114 ppm. The annual variation was from 10 to 187 ppm with an average value of 79 ppm.

Variation in rubidium content was not so pronounced in the upper estuarine region. Marginal increase in Rb concentration was noticed in the mid estuary. Higher concentration was found near bar mouth during August 1986 and May 1987 survey. Seasonal average

Table 4.4 Trace element concentration in the sediments $\mu g\ g^{-1}$.

Distance	Copper				Nickel				Zinc				Rubedium				lithium			
from barmouth	May-86	Aug-86	Dec-86	May-87	May-86	Aug-86	Dec-86	May-87	May-86	Aug-86	Dec-86	May-87	May-86	Aug-86	Dec-86	May-87	May-86	Aug-86	Dec-86	May-87
0	1	1	5	5	19	9	105	205	57	14	139	118	21	33	57	60	22	32	92	83
1	1	1	2	3	77	5	11	113	78	10	154	94	23	30	38	43	52	30	34	40
1.8	1	1	1	3	33	5	17	152	49	15	102	49	19	30	32	39	19	18	19	44
2.65	1	1	1	7	45	5	5	119	18	68	70	53	18	31	31	39	10	29	16	28
4.05	1	1	8	6	18	5	126	185	72	38	177	90	28	31	51	51	31	22	47	62
4.8	3	6	7	8	83	88	129	206	92	50	179	77	58	44	48	52	26	56	40	52
5.95	1	1	1	3	38	29	40	141	50	178	89	68	20	34	30	39	15	34	17	28
7	4	8	9	4	101	34	105	130	127	131	187	58	17	36	45	41	18	42	28	25
12.1	1	6	2	1	14	87	92	56	63	136	92	26	19	39	48	35	17	39	37	17
16.5	1	1	1	1	57	44	69	51	71	82	56	66	20	31	45	35	15	17	34	15
20.55	4	1	1	1	45	9	54	35	106	73	82	20	25	30	48	31	23	21	28	6
25.5	5	1	1	3	88	5	44	48	91	25	52	25	19	32	45	22	24	12	32	10

Distance	Cadmium				Barium				Bismuth				Beryllium				Molybdenum			
from barmouth	May-86	Aug-86	Dec-86	May-87	May-86	Aug-86	Dec-86	May-87	May-86	Aug-86	Dec-86	May-87	May-86	Aug-86	Dec-86	May-87	May-86	Aug-86	Dec-86	May-87
0	8	8	15	8	170	245	360	530	175	5	345	95	1	1	6	1	5	20	30	205
1	2	3	12	2	284	230	270	450	5	5	145	225	1	1	1	1	100	150	230	180
1.8	1	5	8	19	235	185	220	358	5	5	155	110	3	1	1	1	50	120	280	340
2.65	4	10	10	22	215	215	255	525	5	160	225	175	1	1	4	1	165	35	35	125
4.05	13	11	9	17	115	20	230	415	305	195	125	180	7	1	1	1	5	120	335	75
4.8	17	11	11	20	95	80	255	420	175	405	80	160	8	4	4	7	5	60	145	310
5.95	8	11	10	2	190	35	195	370	5	140	210	150	2	1	3	1	105	80	45	225
7	13	12	10	16	225	30	260	415	5	170	75	95	1	1	3	9	85	5	160	125
12.1	11	11	9	12	140	25	285	325	5	170	60	85	7	1	2	14	5	5	145	450
16.5	15	13	7	3	450	205	385	445	5	385	55	210	5	11	2	5	175	5	155	95
20.55	12	10	7	8	245	165	295	215	5	235	45	210	6	13	1	5	195	30	155	145
25.5	3	12	7	5	200	75	370	215	5	200	55	210	6	5	1	3	130	10	155	85

Distance	Chromium				Cobalt				Strontium			
from barmouth	May-86	Aug-86	Dec-86	May-87	May-86	Aug-86	Dec-86	May-87	May-86	Aug-86	Dec-86	May-87
0	95	120	90	125	25	45	20	25	210	140	160	140
1	120	55	15	180	30	20	95	25	100	195	170	215
1.8	95	55	25	205	15	25	50	15	175	180	160	190
2.65	55	65	35	120	15	30	40	15	150	155	125	275
4.05	210	85	105	230	20	35	80	35	235	165	90	145
4.8	245	235	125	220	35	85	80	30	135	140	100	85
5.95	145	105	35	160	25	35	35	5	125	225	50	130
7	170	215	175	195	25	50	80	20	115	150	65	115
12.1	70	205	125	80	10	70	85	5	165	145	90	125
16.5	205	155	200	135	25	35	80	10	125	235	100	130
20.55	225	140	175	40	45	50	50	5	130	270	90	60
25.5	175	155	135	95	35	45	85	7	140	175	120	95

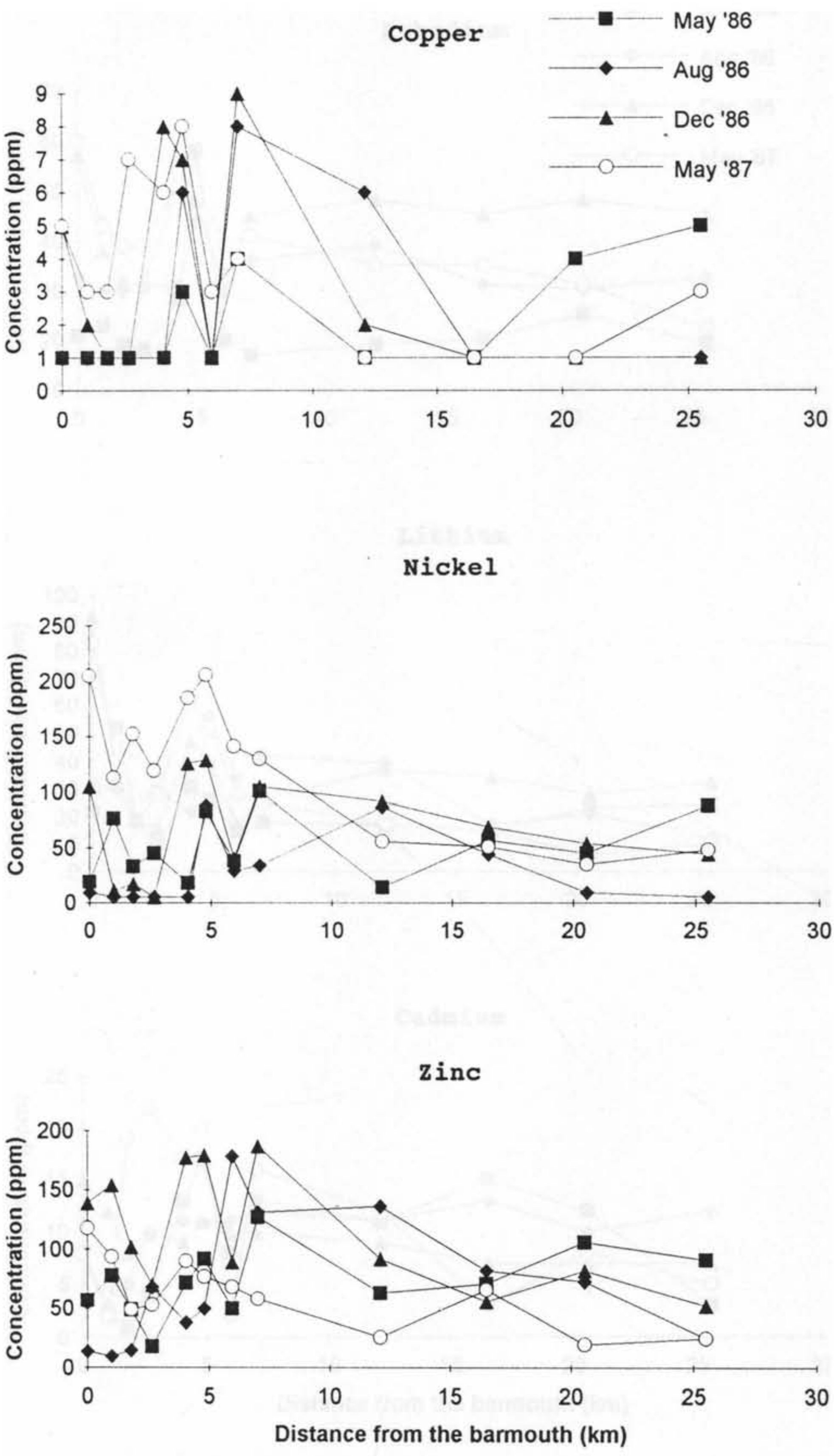


Fig. 4.5 Longitudinal distribution of trace elements in the sediments

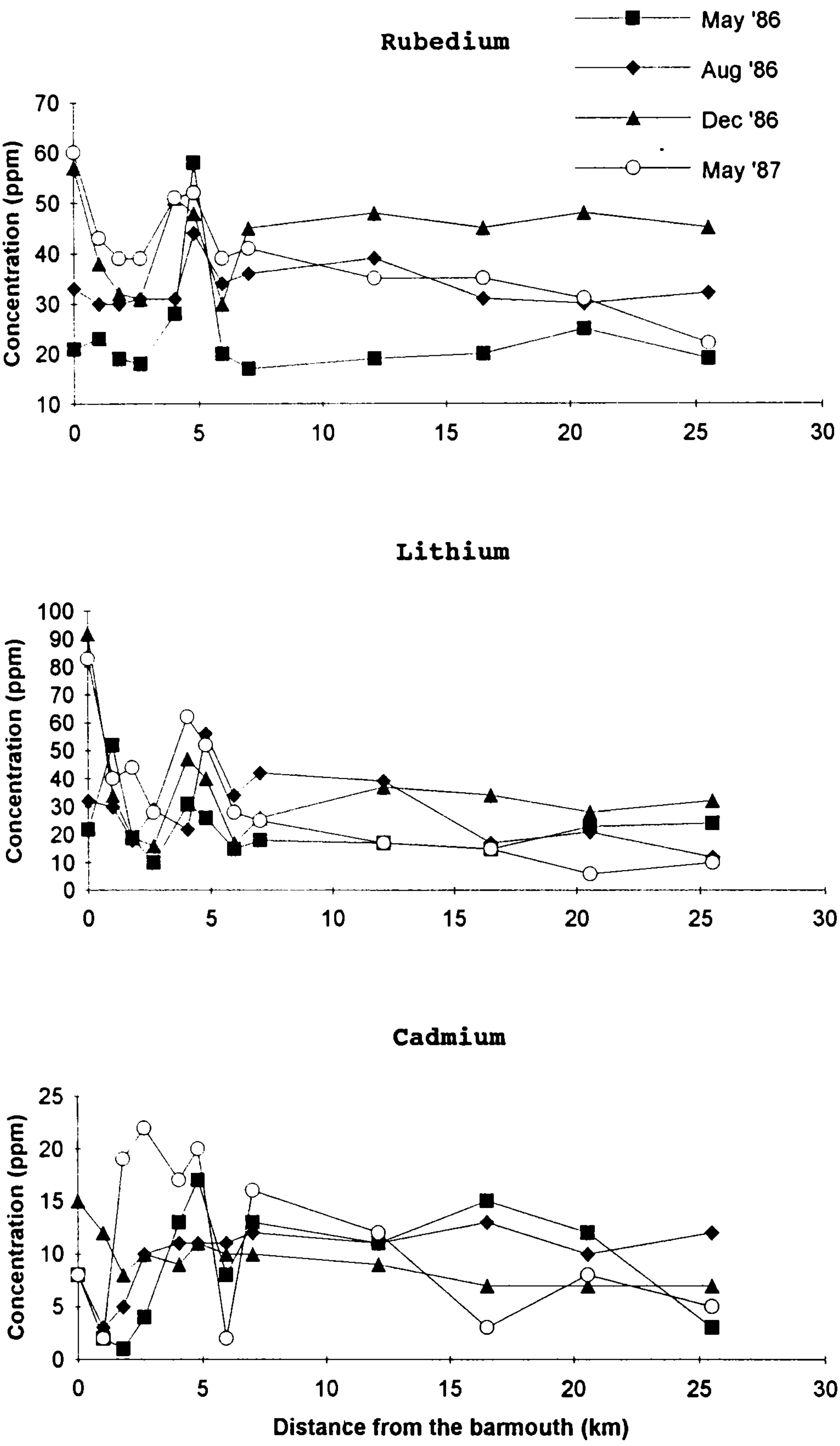
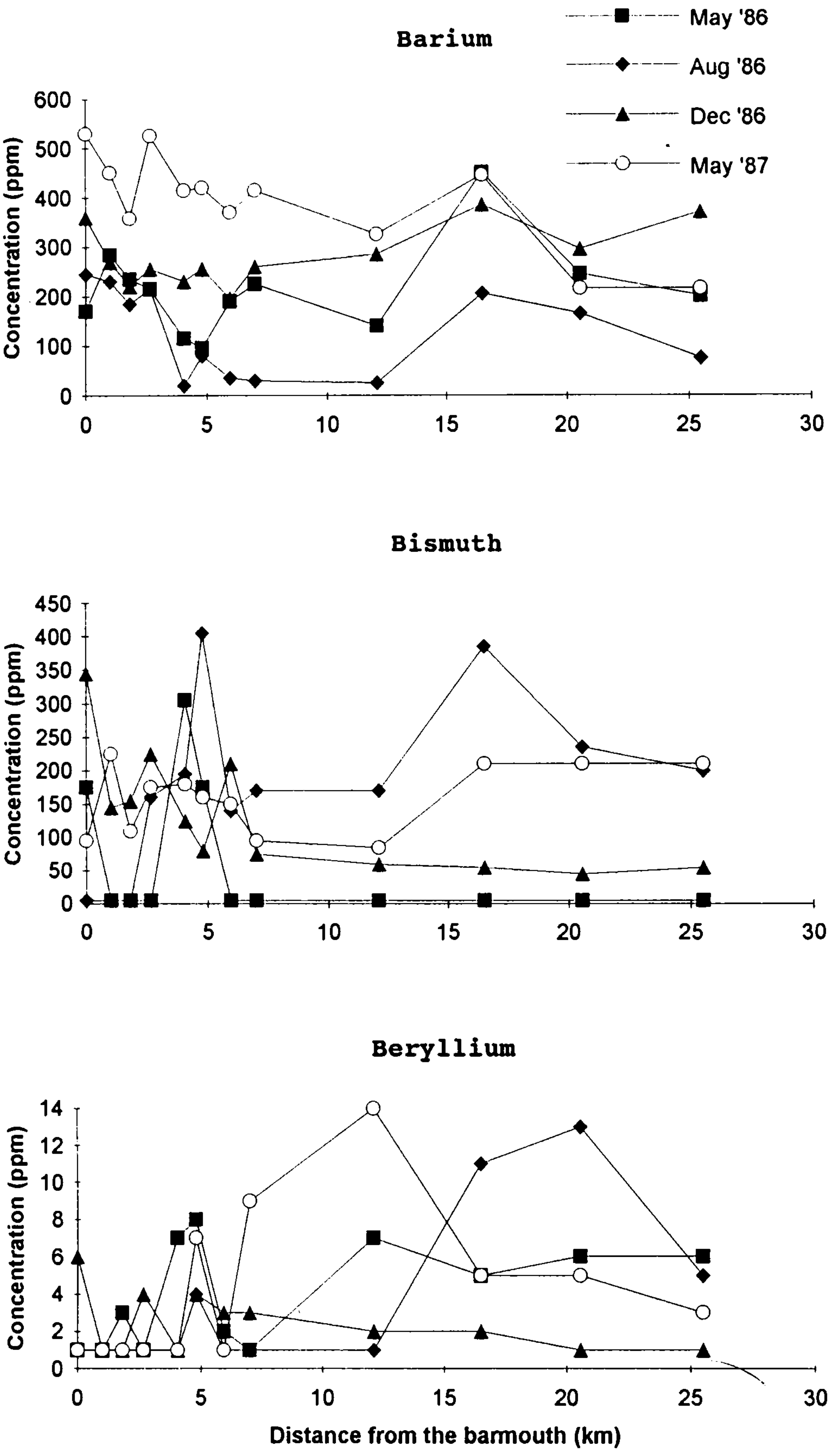


Fig. 4.5 Continued.....



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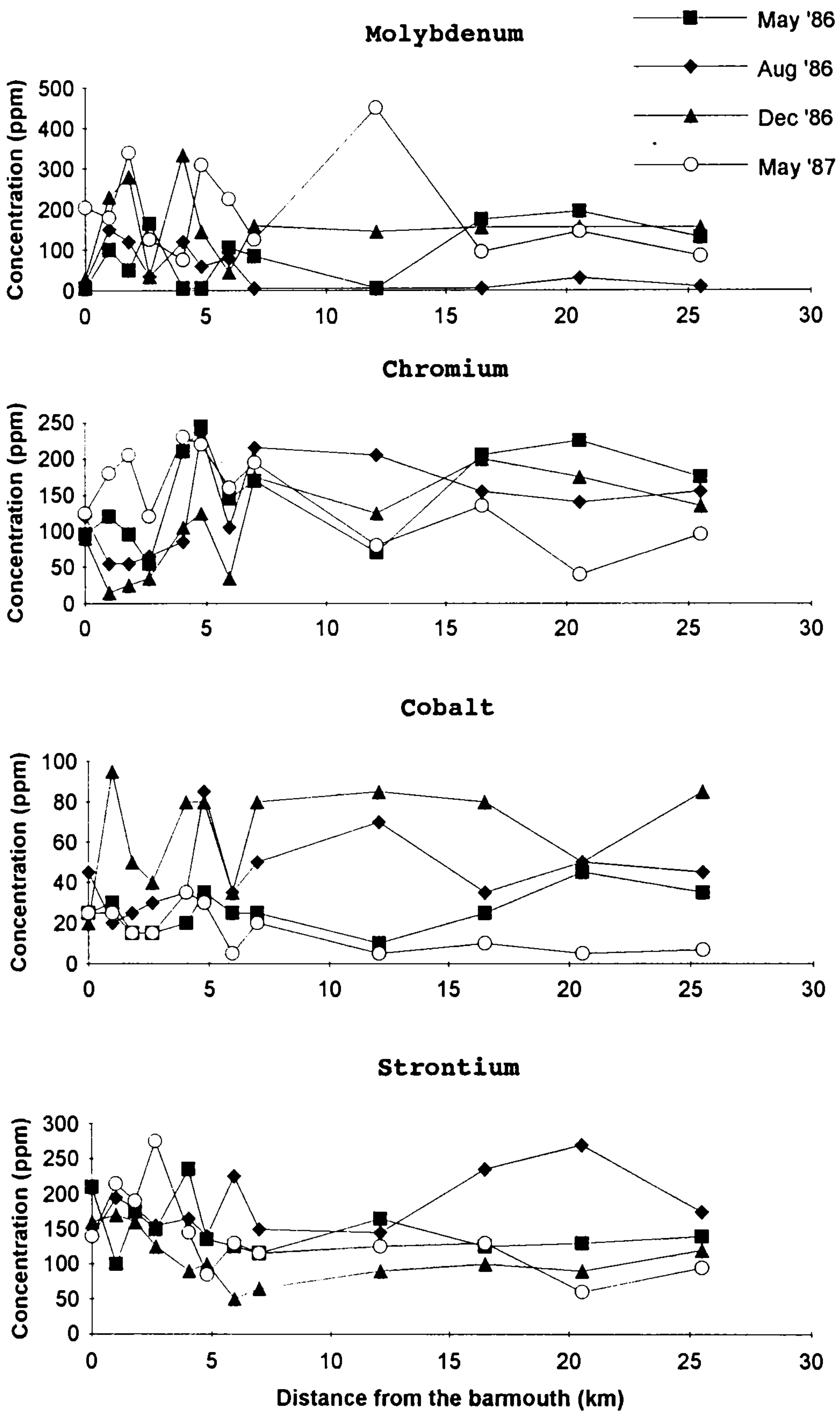

Fig. 4.5 Continued.....

variation (23-43 ppm) illustrates significant temporal fluctuations. The interseasonal range was between 17 and 60 ppm, the average being 35 ppm.

Lithium registered marked variations in longitudinal distribution. More or less uniform values were noticed in the upper estuary, whereas the sediments of lower part of the estuary was rich in LI. Seasonal changes are not so conspicuous (seasonal averages ranged between 22 and 34 ppm). In the complete set of samples, Li content ranged from 6 to 92 ppm with a mean of 30 ppm.

Considerable fluctuations were observed in the downstream distribution of cadmium both in river and estuarine sediments. The seasonal variations were marginal as testified by small range in the average Cd over months (8-11 ppm). The variation for the whole period showed a maximum of 22 and a minimum of 1 ppm with an average value of 9 ppm.

Barium distribution demonstrated a gradual increase from upstream to the lower part of the estuary and the same pattern was found during different survey periods. Considerable seasonality in Ba fluctuations was obvious as the monthly averages registered a maximum of 390 and a minimum of 125 ppm. The range of Ba during the study period was from 20 to 530 ppm, the annual average being 390 ppm.

Bismuth showed substantial difference in concentration along the course of the river and estuary. Seasonal averages exhibited considerable fluctuation (range between 58 and 172 ppm). Bi showed a mean concentration of 130 ppm and varied between 5 and 405 ppm.

Beryllium content depicted high fluctuation spatially. Seasonal data also substantiate high degree of dispersion in Be content. This is evidenced by its seasonal average which ranged between 2 and 4 ppm. The annual average value was 3 ppm with a range of 1 and 6 ppm.

Spatial distribution of molybdenum was marked by considerable scattering. Seasonal variations were also pronounced as seen from the average seasonal content which ranged between 53 and 196 ppm. The study period recorded a total variation of 5 and 450 ppm of Mo with a mean concentration of 122 ppm.

Significant fluctuations in chromium content was noticed in the river and estuarine region. Moderate seasonal variation was obvious from the average values (103 and 150 ppm). The annual average obtained was 133 ppm and among the whole set of samples Cr ranged between 15 and 245 ppm.

The spatial distribution of cobalt was not uniform. Seasonal fluctuation also demonstrated prominent dispersion (average content ranged between 16 and 65 ppm). The inter-seasonal concentration of Co ranged between 5 and 95 ppm with an average of 37 ppm.

An increased down stream variation of strontium was noticed. Seasonal fluctuation was marginal as indicated by the range of values (110-142 ppm). Among the complete set of samples analysed, Sr content varied between 50 and 275 ppm with a corresponding average value of 146 ppm.

4.4.2 *Core Samples*

The sediment textural composition in the core was mostly muddy with intercalations of sand fraction. Organic carbon registered a moderate increase towards the top of the core and had an average content of 2.44%. Range of OC values varied between 1.66 and 3.07% (Fig. 4.6).

The vertical distributions of iron, aluminium, calcium and magnesium content in the core sample are depicted in figure 4.6. An enrichment in iron content was observed towards the upper part of the core. The iron values ranged between 20.34 and 6.35% with an average of 24.41%. Aluminium distribution did not follow any pattern. The average content of the

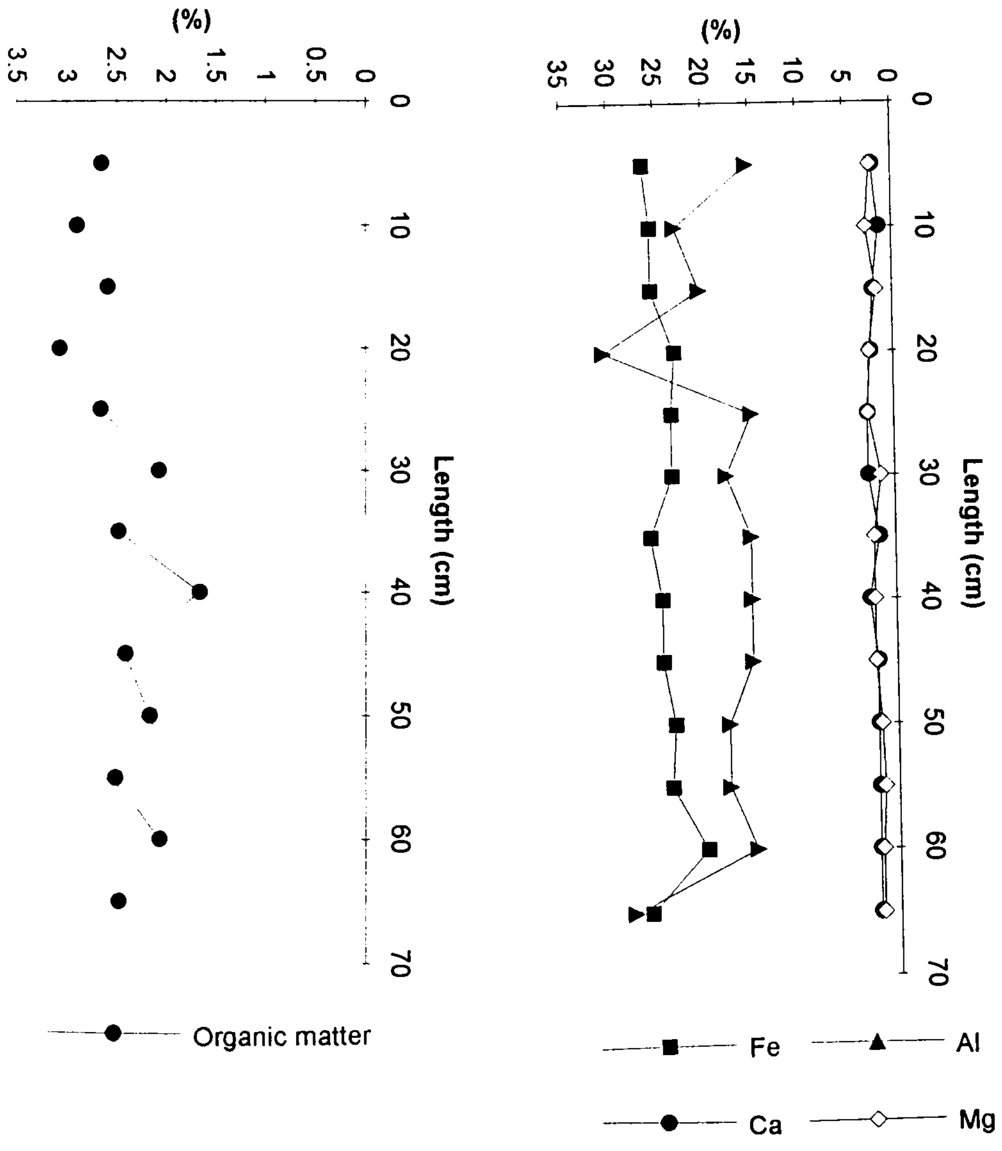

Fig. 4.6 Distribution of major elements in the core sample

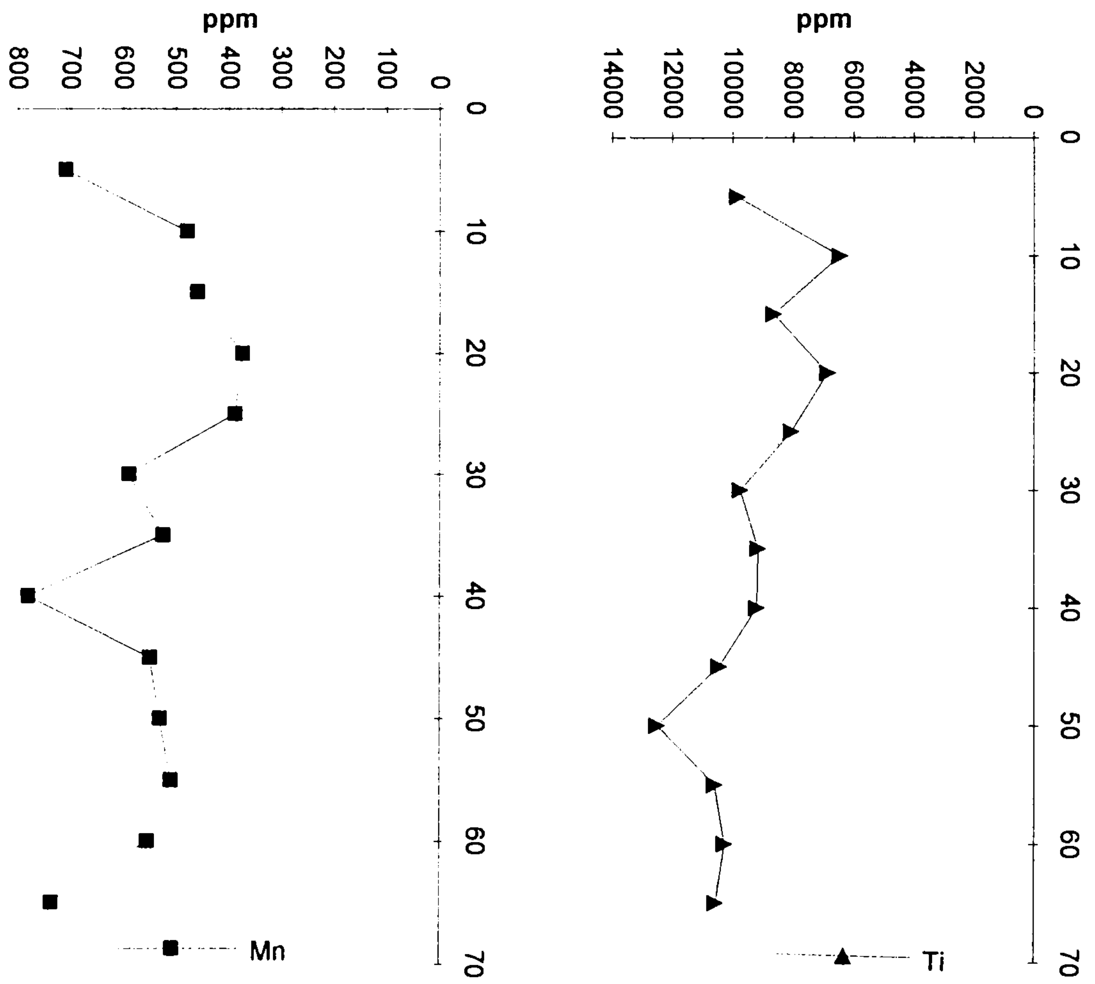

Fig. 4.6 Continued.....

element was 19% and the values ranged between 15.1 and 30.6%. Averages of calcium and magnesium were 2.21 and 2.08% respectively. Manganese distribution in the sediment core showed an increase towards the upper part. The average value obtained was 553 ppm with a maximum content of 780 and a minimum of 375 ppm. The vertical distribution of titanium is given in figure 4.6. A decreasing trend in titanium content was observed towards the top of the core. The titanium content ranged between 6450 and 12500 ppm and the average value was 9407 ppm.

The vertical variations in the concentration of copper, cadmium and beryllium are depicted in figure 4.7. Copper content showed an increase towards top of the core. From the middle portion, uniform distribution of Cu was noted. The average value of Cu for the core sample was 6.08 ppm with a range of 5 - 8 ppm. A slight increase in cadmium content was noticed at the middle portion of the core. An average value of 12 ppm was obtained for Cd with a range of 10-14 ppm in the core sample. Beryllium concentration was uniform at the lower part of the core. Considerable fluctuation was noticed in the upper part. Be content varied between 1 and 9 ppm and the average vale was 2.77 ppm.

Depth-wise distribution of rubidium, lithium and cobalt in the core sample are given in figure 4.7. Rubidium did not show much variation along the vertical profile. Average content of Rb was 49.85 ppm within a range of 147 and 55 ppm. Lithium content showed wide variations at the upper part of the core. A more or less uniform vertical distribution was obtained at the lower portion of the core. The average lithium content was 55.45 ppm and the values varied between 34 and 99 ppm. Cobalt concentration increased towards the upper portion and the distributions from the middle to lower portion were more or less uniform. Average Co obtained was 31.54 ppm and the range was between 20 and 45 ppm.

Vertical distribution of nickel, zinc and barium are depicted in figure 4.7. Nickel concentration showed a more or less uniform distribution with slight increase towards upper part of the core sample. The average content of Ni in the core was 224.31 ppm and the

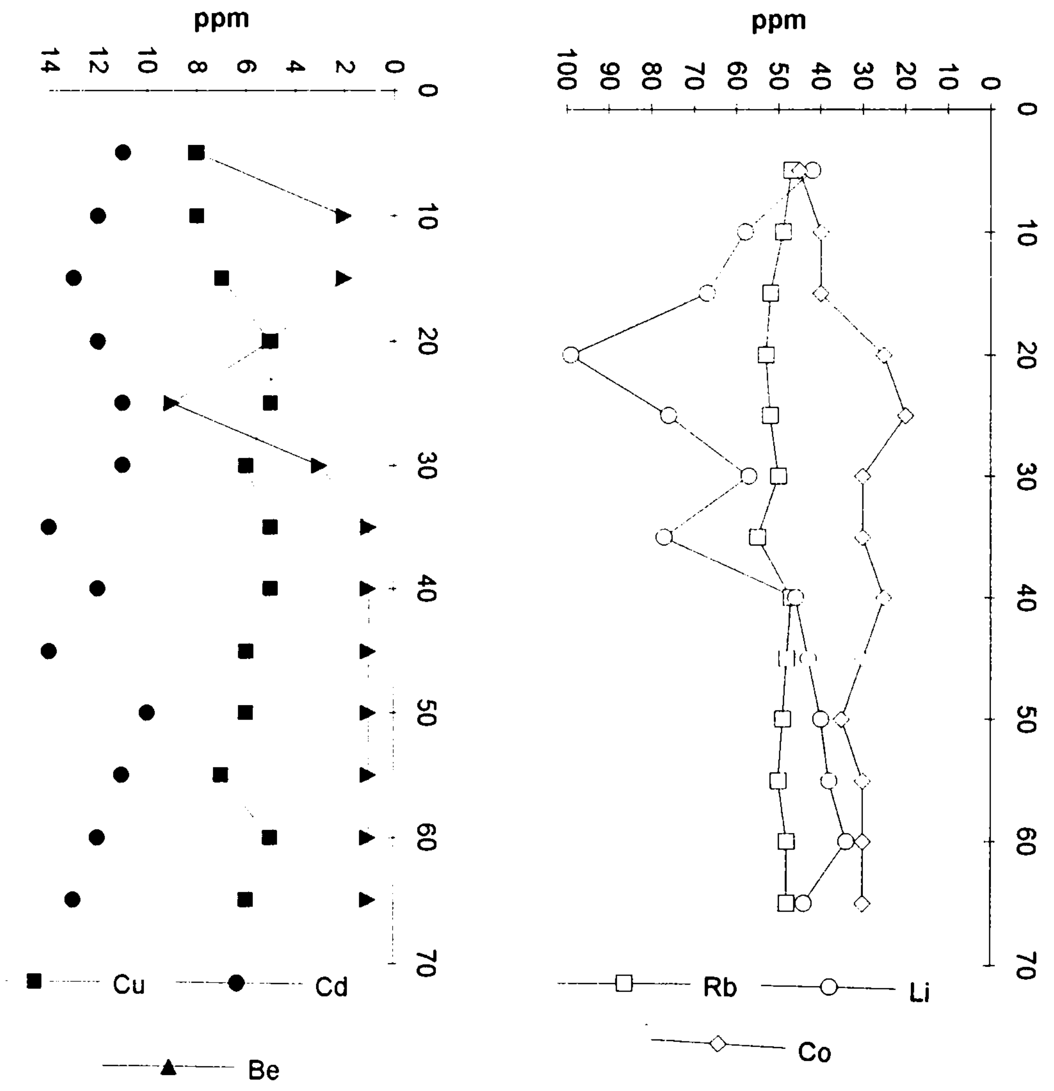

Fig. 4.7 Distribution of trace elements in the core sample

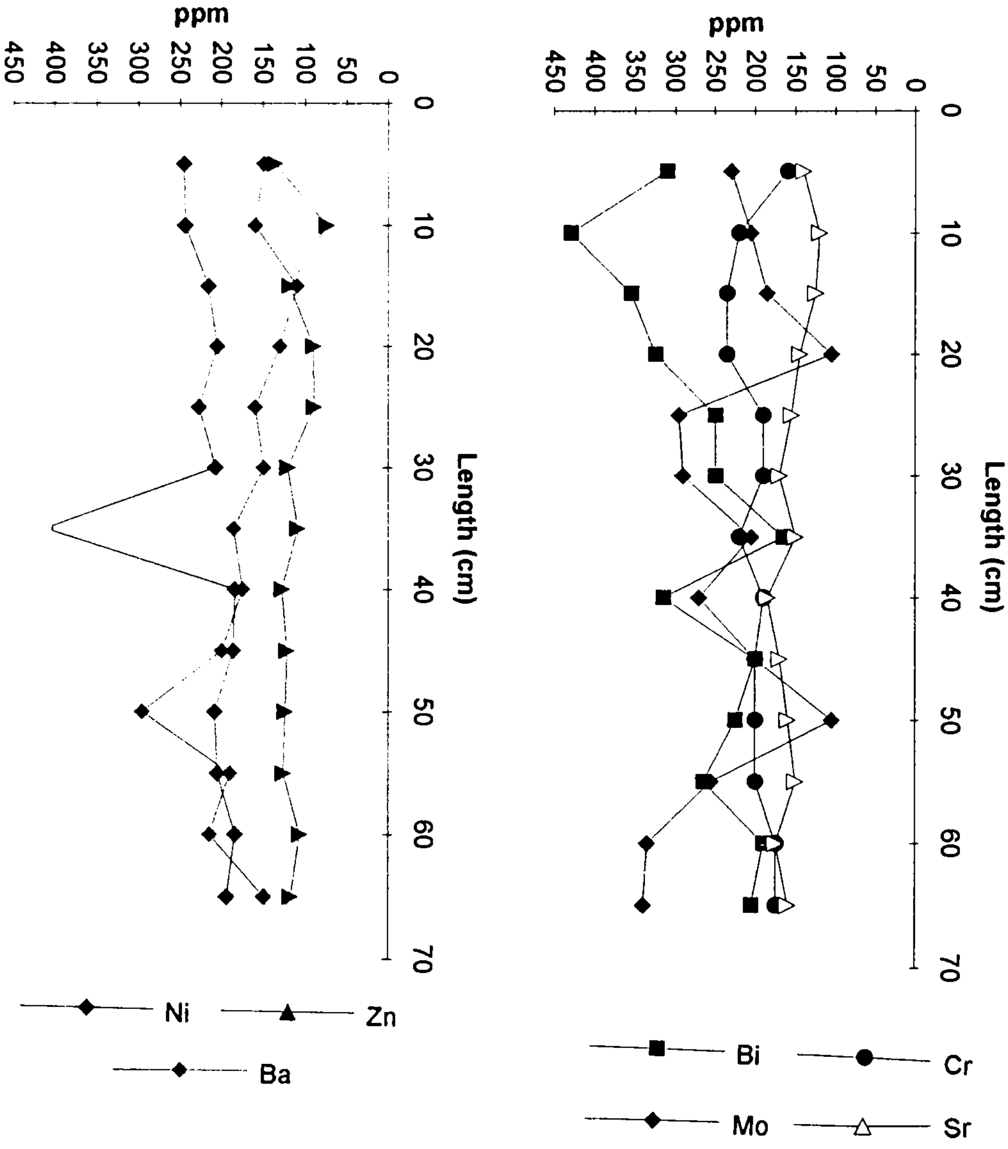

Fig. 4.7 Continued.....

values varied between 411 and 184 ppm. Variation of zinc in the core sample depicted a uniform presence with enrichment at the upper portion. An average Zn concentration was 112 ppm and the range is from 74 to 136 ppm. An increase in barium distribution was observed towards the upper part of the core. The average barium content was 174.62 ppm. The values ranged between 110 and 295 ppm.

The variation in the bismuth concentration was within 165-430 ppm with an average of 268 ppm (Fig. 4.7). Chromium and strontium contents showed similar variation in the middle and lower part of the core. Increased chromium values were seen at the top of the core, while strontium values exhibited more or less uniform pattern of distribution. Chromium values ranged between 160 and 235 ppm (Average = 199). Average strontium content was 154 ppm with a range of 120 to 180 ppm. Molybdenum values registered considerable fluctuation. An increase in concentration was observed at the upper part of the core. Average molybdenum content in the core was 232 ppm, ranging between 105 and 340 ppm.

4.5 **Discussion**

4.5.1 *Surficial Sediments*

Textural Composition:

Surficial sediments of the river bed from upstream to barmouth depict considerable inter mixing of textural grades viz. sand, silt and clay. Significantly, season-wise textural composition was found to be highly variable at most of the sampling stations. Sand, which was the most dominant of the textural grades, irrespective of the course of the river, showed its lowest prominence during December 1986 survey period (Fig. 4.2). Upto a point at 7 km from barmouth, sand content showed a gradual downstream reduction indicating textural maturity of alluvial streams. However, the proper estuarine portion is constrained to contain different proportions of sand, probably representing location specific hydro-mechanics operating in the system. The complementary pattern of distribution of other textural grades (Figs. 4.2) supplements the above view. Though it has been mentioned in earlier parts, that the tidal influence in the estuary extended up to 22.5 km upstream, velocity of flood flows may not carry the river bed sediments or affect the texture *in situ* at least in the upper part of the river. Nevertheless, the textural maturity exhibited in the upper part is a testimony to the differential transport of unidirectional flow, namely the fluvial discharge due to precipitation as observed by Seralathan, (1988).

Varied levels of mixing exhibited by sediments in the estuarine portion surmises *in situ* sorting processes owing to the ebb and flood tidal flows. During the flood tides, it is quite probable that due to scouring effect the finer population from the surficial sediments get resuspended and the same may get flushed onto the coastal zone during ebb tide. These fine sediments get flocculated upon contact with high saline sea water leading to its deposition. As observed at many other shallow tropical estuaries, in Beypore estuary as well the highly variant location specific textural distribution pattern was observed.

Organic Matter:

Input of organic matter in rivers and estuaries are mostly controlled by the rate of supply of terrestrial materials, rate of deposition of organic to inorganic constituents, organic productivity, rate of deposition of organic matter and the texture of sediment load carried by the system. Though not in very high concentration, Chaliyar river and Beypore estuary do contain appreciable amount of organic carbon in the surficial sediments. An interesting aspect of the sediments of fluvial realm was that they contain more organic carbon during December season, which is comparatively a lean period from the point of view of precipitation induced discharge. The inorganic load carried by river is least during December. General pattern of marginal improvement of organic carbon content was observed from upstream till the estuarine portion. In the estuarine portion organic carbon in sediments showed considerable fluctuation comparable with the textural grades. A correlation worked out between organic carbon and sand, silt and clay percentages of the sediments directly indicate control of textural grades over the concentration of organic carbon. It was found that the sand proportion have an inverse relation with that of organic carbon ($r = -0.753$). Conversely, silt content depict considerable co-variation with organic carbon ($r = +0.808$) followed by clay ($r = +0.578$). This kind of increase in organic carbon content with decrease in grain size has been reported by many previous workers. One of the main reasons attributed to this is the increase in surface area of fine particles to contain more dispersed organic particles (Sues and Muller, 1980). The size dependent scavenging of organic matter has been experimentally demonstrated to be due to adsorption of substantial amount of dissolved organic matter formed from the decomposition of phytoplankton by various clay minerals (Muller and Suess, 1979). A higher level of sympathetic relationship of organic carbon with that of silt could be due to the co-sedimentation of organic matter with silt sized particles as their settling velocities are similar. Organic matter plays an important role in modifying the ability of the sediment to fix trace metals and to control the Eh-pH stabilities of sedimentary minerals (Cline et al., 1973).

Major Elements:

Major elemental chemistry of the bulk sediments depends on the detrital and non-detrital factors of sediment composition. Hirst (1962) pointed out that most part of the major and minor elements are located within the lattices of detrital minerals. Exceptions are found for some of the elements which are abundant in non-detrital phases. Al_2O_3, Fe_2O_3, CaO, MgO, Mn and Ti are the major elements dealt here. Spatial variations of Al_2O_3 showed an increased level in the upper part of estuary compared to the lower part. However May 1987 data indicated a gradual increase in its composition from upstream to barmouth. Compared to Al_2O_3 variation, Fe_2O_3 presents a smooth pattern with very high values at certain locations within the lower estuarine part. CaO depict an independent picture as its concentration was nearly uniform in the upper estuary and with sudden variations in the lower estuary. Generally, the lower estuary contains more of CaO in the sediments. MgO also presents a near similar behaviour spatially and temporally with that of CaO. Maximum fluctuations both season-wise and location-wise were observed for Manganese. Especially, the lower estuarine part contain a depleted concentration of manganese. August to December data illustrate an enriched abundance of manganese in the upper part of the estuary. Variation of titanium is quite complex without any significant trend.

Table 4.5 Correlation matrix of texture, organic carbon, major and trace elements

	Cu	Ni	Zn	Rb	Li	Cd	Mn	Ba	Bi	Cr	Co	Ti	Be	Mo	Sr	OC	Sand	Silt	Clay	Fe2O3	Al2O3	CaO	MgO
Cu	1.000																						
Ni	0.690	1.000																					
Zn	0.567	0.337	1.000																				
Rb	0.498	0.609	0.388	1.000																			
Li	0.512	0.619	0.418	0.686	1.000																		
Cd	0.388	0.326	0.193	0.335	0.222	1.000																	
Mn	0.223	0.203	0.280	0.319	0.155	0.129	1.000																
Ba	0.143	0.587	-0.049	0.345	0.298	0.085	0.033	1.000															
Bi	0.125	0.025	0.086	0.301	0.220	0.292	0.054	-0.158	1.000														
Cr	0.449	0.495	0.156	0.299	0.269	0.355	0.480	0.088	0.085	1.000													
Co	0.300	0.008	0.495	0.399	0.230	0.047	0.623	-0.184	0.024	0.145	1.000												
Ti	0.399	0.316	0.508	0.219	0.433	0.103	0.261	-0.104	-0.026	0.546	0.268	1.000											
Be	-0.081	-0.054	-0.117	-0.030	-0.193	0.285	0.072	-0.029	0.279	0.167	-0.199	-0.066	1.000										
Mo	0.164	0.399	0.054	0.235	0.091	0.035	0.028	0.468	-0.288	-0.071	0.025	-0.042	-0.008	1.000									
Sr	-0.195	-0.250	-0.129	-0.185	-0.004	0.146	-0.140	-0.121	0.287	-0.016	-0.222	0.038	0.114	-0.258	1.000								
OC	0.622	0.566	0.551	0.563	0.555	0.233	0.472	0.094	-0.081	0.409	0.535	0.444	-0.182	0.133	-0.383	1.000							
Sand	-0.550	-0.492	-0.575	-0.640	-0.599	-0.217	-0.541	-0.049	-0.092	-0.482	-0.558	-0.422	0.070	-0.096	0.279	-0.753	1.000						
Silt	0.637	0.540	0.609	0.636	0.610	0.217	0.537	0.047	0.098	0.474	0.572	0.500	-0.109	0.123	-0.272	0.808	-0.942	1.000					
Clay	0.340	0.338	0.439	0.537	0.505	0.163	0.454	0.020	0.084	0.396	0.458	0.263	-0.045	0.051	-0.227	0.578	-0.921	0.747	1.000				
Fe2O3	0.636	0.691	0.514	0.687	0.696	0.326	0.326	0.388	0.281	0.323	0.271	0.372	-0.067	0.253	-0.201	0.542	-0.594	0.607	0.486	1.000			
Al2O3	0.237	0.289	0.360	0.395	0.377	0.154	0.612	0.069	-0.014	0.368	0.446	0.259	0.180	-0.038	-0.043	0.560	-0.590	0.579	0.512	0.276	1.000		
CaO	-0.088	-0.016	0.104	-0.038	0.123	0.177	-0.178	0.063	0.279	-0.165	-0.095	0.017	0.088	-0.235	0.427	-0.176	0.102	-0.066	-0.123	0.019	-0.033	1.000	
MgO	0.046	0.218	0.108	0.199	0.310	0.153	0.126	0.256	0.124	0.209	0.053	0.155	0.110	0.059	0.258	0.136	-0.190	0.170	0.215	0.087	0.332	0.416	1.000

Inter-elemental Variation:

The correlation matrix for the major, trace and textural parameters are given in table 4.5. Al_2O_3 show significant correlation only with manganese (r = 0.612). Though at a lower level, Al_2O_3 does show certain amount of positive affinity with MgO (r = 0.332), Fe_2O_3 (r=0.276), and Ti (r = 0.259). Fe_2O_3 on the other hand shows a marginal positive correlation with Ti (r = 0.372) and Mn (r = 0.326). MgO rather depicts a moderate positive loading only with CaO (r = 0.416). The correlation coefficient does not yield a clear picture of elemental association. However sympathetic behaviour of Al_2O_3 with Mn, CaO with MgO are some positive indications.

Grain size dependency of major elements:

Majority of major elements show a clear physical partitioning as their loadings are significant on sand, silt and clay (table 4.5). However, CaO and MgO do not show any correlation with any of the size grades. Al_2O_3, Fe_2O_3 and Mn show high negative loading with sand. Whereas, titanium shows a less significant negative loading with that of sand. All elements illustrate a sympathetic variations with silt and clay, except Ti.

From the spatial and temporal variations, inter-elemental variation, and grain size dependency, it can be seen that controlling factors for major elemental incorporation in sediments vary considerably. It can also be noted that organic matter depicts a positive relationship with Al_2O_3, Fe_2O_3, Mn and Ti. No deducible correlation is found between CaO and MgO with organic carbon. In the case of major elements the range of chemical composition are dominantly influenced by different proportions of major minerals in the sediments such as quartz, feldspar, montmorillonite, kaolinite and illite. No significant relation exist between Al_2O_3 and Fe_2O_3, though both show enrichment in finer fractions of sediment. This is an interesting aspect to be noted here. Al_2O_3, which is derived principally from the alumino-silicate minerals, is detrital in origin, though some of them could also be derived from authigenic process

(Cronan, 1980). Association of manganese more with Al_2O_3 and also their association in turn with silt and clay suggests similar partitioning of these metals. Like Al_2O_3, Mn is also transported from the continents in particulate form both in association with weathered minerals (clay minerals, feldspars, etc.). Geochemically Mn in sediments is very important as the sorption processes of many other mono- and divalent cations are controlled by MnO phases.

Unlike the other two, Fe_2O_3 probably represents the metalliferous fraction of sediments, though iron is also present in clay mineral lattices and in adsorbed state on the surfaces of other minerals. Probably the fine fraction enrichment of iron could be due to its incorporation in the sediments in the form of ferric oxide hydrosol stabilised by organic colloids. The spike in iron concentration observed in the lower part of the estuary could be due to flocculation and settling of iron in the increased saline water near the barmouth region (Casteno and Garrels, 1950). Microcrystalline framboidal concretions of pyrite normally observed in estuarine sediments also increases the Fe content. A moderate positive loading of TiO_2 on Fe_2O_3 ($r = 0.372$) also suggests contribution of iron in Fe bearing heavy minerals such as ilmenite.

TiO_2 on the other hand is mostly present in the silt fraction as fine grained Ti bearing minerals such as ilmenite and rutile. CaO and MgO form a dissimilar group of elements. Chemical analysis was performed on bulk sediment samples without removing the shell debris. So the CaO content in the sediment not only represent non-carbonate CaO held in alumino silicates, but also CaO concentration in carbonate shells.

Lack of textural control over the concentration of CaO is obviously due to this factor of non-carbonate vs. carbonate form of CaO. Almost similar type of association is indicated for MgO content in the sediments. MgO can be present as high Mg calcite or dolomite in shell debris. However slight positive correlation of MgO with Al_2O_3 ($r = 0.332$) also signifies incorporation of Mg in clay minerals. It was established that montmorillonite can fix higher amount of Mg^{++} ions from the over lying water column.

Trace metals in estuarine sediments:

Temporal and spatial variability of trace metals in estuarine sediments result from cyclic changes in the fresh and sea water conditions of temperature, pH, salinity, suspended solids and oxygen concentration. Their non-conservative interaction during mixing exert a major influence on heterogeneous chemical reactions in estuaries (Morris et al., 1981). Added to this, in recent years the fluxes of many trace metals from terrestrial and atmospheric sources to the aquatic environment have increased (Forstner and Wittmann, 1981). Determination of concentration of various trace metals in estuarine environment is of great significance. Especially biological significance of particulate trace metal contamination in aquatic environments is a complicated problem gaining attention from researchers in recent times.

Spatially many trace metals show considerable fluctuations in their concentrations from upstream to barmouth. In many cases their spatial relationships are complicated. This is especially true in the estuarine part as concentrations vary widely in adjacent locations. On the whole, Cu, Ni, Zn, Rb, Li, Cr and Co show uniform distribution in the upper part of the estuary. Considerable fluctuation observed in the trace metal concentration in lower part of the estuary could be due the variant level of mixing and the textural dissimilarity of sediments in this part. When the data was divided into four seasons, it showed wide variation for the different elements. These changes do reflect differences in the controlling factors of metallic association.

In the average order of absolute abundance of the trace metals, Ba > Sr > Cr > Mo > Bi > Zn > Ni> Co > Rb > Li > Cd > Cu >Be. Ba, Sr, Cr, Mo and Bi are concentrated in more than 100 ppm level and Zn, Ni, Co, Rb, and Li are more than 10 ppm, whereas Cd, Cu and Be are available in < 10 ppm level.

Inter-elemental variability:

A correlation matrix given in table 4.5 gives the interrelationship between various elements. Cu shows significant positive affinity with Ni, Zn, Li, Rb, Cr and Cd. This would probably indicate similar kind of association in different chemical phases of the sediments. However the positive affinity of Ni with that of Ba and Mo also suggests a relationship of Ni at variance with that of copper. Co though correlated at a low level with Cu, shows more semblance with Zn and Rb. This would also indicate a differential association between them. Bi, Be and Sr appears to be uncorrelated as their positive as well as negative loadings on other elements are very low.

Textural Dependence of Trace Metals:

Though a major part of elements come from terrestrial origin, considerable amount of these elements are introduced into the system by adsorption and other processes such as sulphide precipitation and organic relations in the nearshore sediments (Krauskopf, 1956). Total concentration and reactivity of metals in the sediments is a function of organic matter, mineralogy and textural related qualities of sediments (Willey and Fitzgerald, 1980). Rea and Pigula (1977) demonstrated the importance of texture on the authigenic precipitation of elements. This together with size aggregation of different minerals based on their density and entrainment during transport and deposition induce a major control of texture on geochemical partitioning. Further larger surface area of fine particles facilitate precipitation of metals onto them.

The correlation matrix exemplifies the above observations as both silt and clay show greater positive loading on elements such as Cu, Ni, Zn, Rb, Li, Cr and Co. A converse relationship holds true for all the elements listed above with that of sand, as deduced from the negative loadings. Cosma et al. (1979) earlier reported that a direct proportionality exists between Cu, Ni and Mn and finer fractions. In the preceding section it has been already mentioned that there exist a firm affinity between organic carbon and silt and clay fraction of the sediment. This association also found to dictate a similar sympathetic relation between organic carbon and the elements mentioned above. Singer (1977) showed great affinity of heavy metals in aquatic system for organic substances. This confirm that, apart from a surface area related enrichment of metals, cation exchange capacity (CEC) of sediment and affinity of metal ions for different types of clay surfaces also contribute substantially to the metal fine fraction proportionality of sediments. It has been established that CEC of sediments improve considerably with increasing organic carbon content and fining size (Hunt, 1981). Many researchers are unclear whether metal distributions result from the greater influence of grain size or organic matter content. However, Sholkovitz (1976) found significant metal association with organic matter. This is further supported by Hunt (1981) as he found that trace metal distribution are dictated more by organic carbon possibly through exchange reactions.

Clay minerals have ability to adsorb or release heavy metal ions (Farrah, et al., 1980). Electrostatic attraction between negative sites on the clays and the metal ions is certainly a major component of sorption process. Many variables control affinity of a cation for a particular clay surface (Eh, pH, nature of sites available, steric effects attributable to structure, nature of counter ions, etc.). Thus the ECE values of metal ion bonding vary with type of clay. Farrah et al. (1980) found that the efficiency sequence of clay type for a set of conditions is in the order of montmorillonite > illite > kaolinite. Though clay mineral studies have not been attempted in the present work, considering the peculiarity of the geological constrains of the drainage basin and based on available information on other estuarine systems, it is surmised that kaolinite is the most abundant clay mineral followed by montmorillonite and illite. Though, Farrah et al. (1980) presented a general pattern of clay affinity for metals, the sequence may

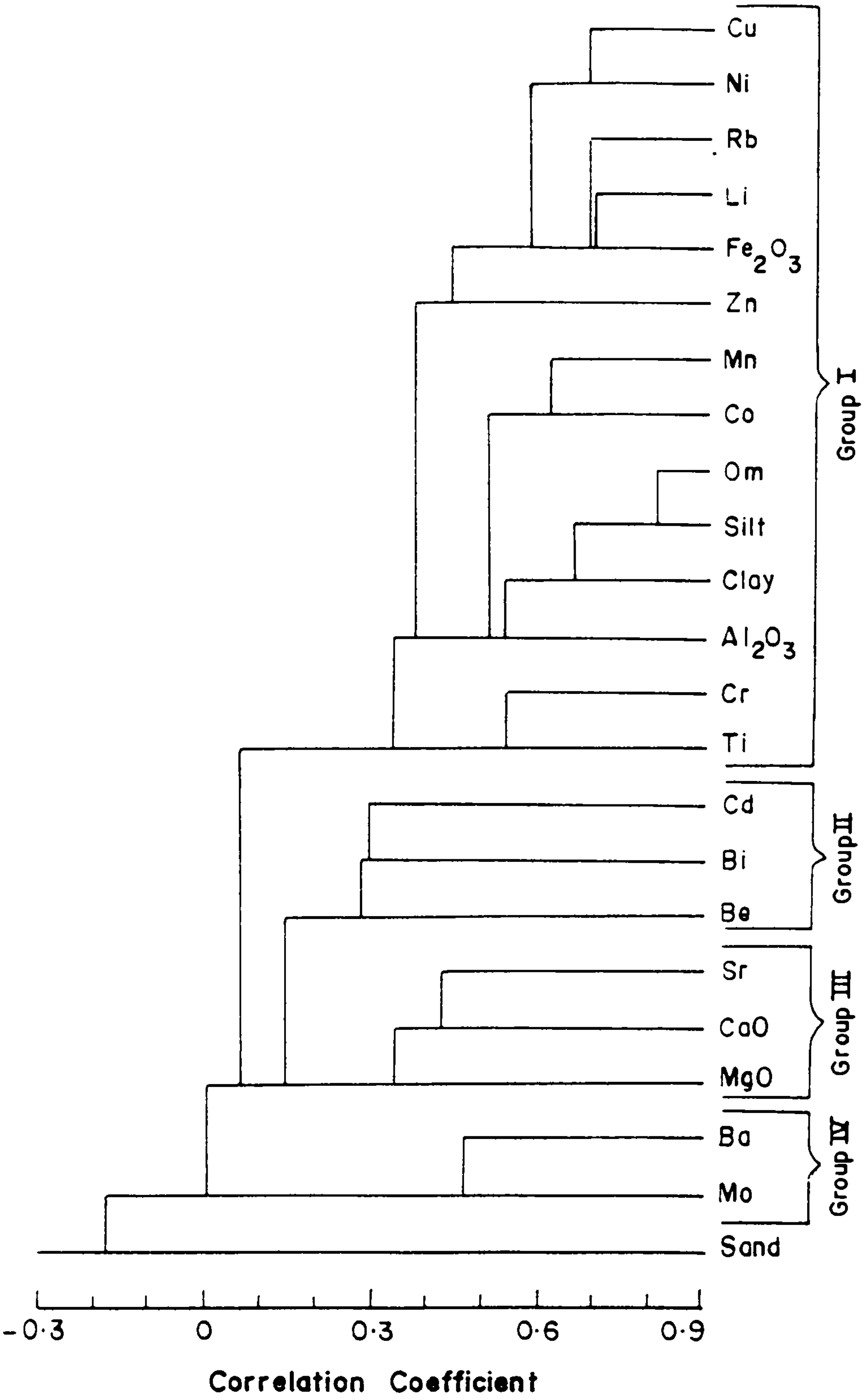

Fig. 4.8 Dendrogram depicting elemental grouping

be at variance for different metals. In the nearby marine sediments, absolute concentration of metals described above are found to be higher. Interestingly the nearshore sediments also registers an higher amount of montmorillonite compared to its estuarine counter part. Thus it is quite possible that clay mineral association, especially amount of montmorillonite in the sediments facilitates increased concentration of certain metals. The recent studies by Suraj et al. (1995) in Periyar river show that sediments abundant in kaolinite clay minerals selectively absorb more nickel.

Combined Cluster Analysis:

Based on the correlation matrix of the entire set of textural, organic matter, major and trace element data, cluster analysis is performed to obtain a dendrogram (Fig. 4.8). The dendrogram depicts 4 elemental groupings by considering 0.3 as the cut off averaged correlation coefficient. Group I consists of 3 interrelated sub-group of elements. Fe_2O_3, Cu, Ni, Rb, Li and Zn form a closely knitted sub-group. Organic matter, silt, clay, Al_2O_3, Co and Mn form another sub-group, Cr and Ti yet another sub-group.

Though essentially all the sub-groups are mainly associated with fine grained fraction of the sediment, Cr and Ti must be more bound in heavy minerals rich in silt fraction. The association of Al_2O_3 with Mn more in the finer fractions, in turn show co-variation with Co. The sub-group led by Fe_2O_3 probably represent their stronger association with metallic fraction more abundant in finer size grades and also in the non-lithogenous phase of the sediment.

The group II consists of Cd, Be and Bi that are un-correlated with any of the size grades and hence grouped together. This necessarily not imply uniform fractionation of them. Unlike Cu, Cd generally reacts slowly with organics. This is amply evidenced from the low correlation of Cd with organic carbon. It can either be bound with the soft parts of organisms or tightly bound in clays. Anthropogenic input is also considered as an important contribution of Cd as reported by Ouseph (1987) for Cochin estuary. Municipal waste is yet another enriching factor of Cd in the sediments.

Principal minerals in which Be is present are beryl and crysoberyl. Normally they are available in very traceable quantity. Be can be present in finely dispersed particles as it is easily fixed in them due to its small ionic size and high ionic potential. Thus, the grouping together of Bi, Cd and Be is just coincidental though their association in different phases of sediments are different.

CaO, MgO and Sr forms the group III. It has been already mentioned in above discussion that the presence of MgO is closely associated with CaO at least in the organic part. Normally in estuarine and nearshore sediments Sr closely flows the distribution of CaO available in shell fragments. Especially certain variety of molluscs contain good amount of Sr apart from planktonic and benthic foraminifera (Moore and Bostrom, 1978). However the positive loading of Sr on CaO ($r = 0.427$) can not be taken as highly significant. Hence, Sr can also be present in other forms such as trace elements in accessary minerals in diadochy with Ca and K, and also in different phases of clay fraction by adsorption and exchange reactions as they are held more tightly on clay minerals. Hence, such a grouping of CaO, MgO and Sr hold rational significance owing to an even history of metal incorporation.

The last group (group IV) consists only of Ba and Mo. Mo occurs naturally in oxidation states ranging from Mo^{+3} to Mo^{+6}, with the later the most stable under oxidising conditions. It is preferred for Ti^{+4} and Fe^{+3} sites in sphene, ilmenite, titanomagnetite and biotite. In many cases, it is found to be incorporated in fine grained sediment by uptake on Fe, Mn and Al oxides. Coprecipitation of Mo on ferric hydroxide achieve a maximum effectiveness at low pH (Seralathan and Hartmann, 1988). Ba can also be adsorbed by clays, hydroxides and organic matter, apart from it being present in mineral structures of feldspars, micas, appetite, calcite,

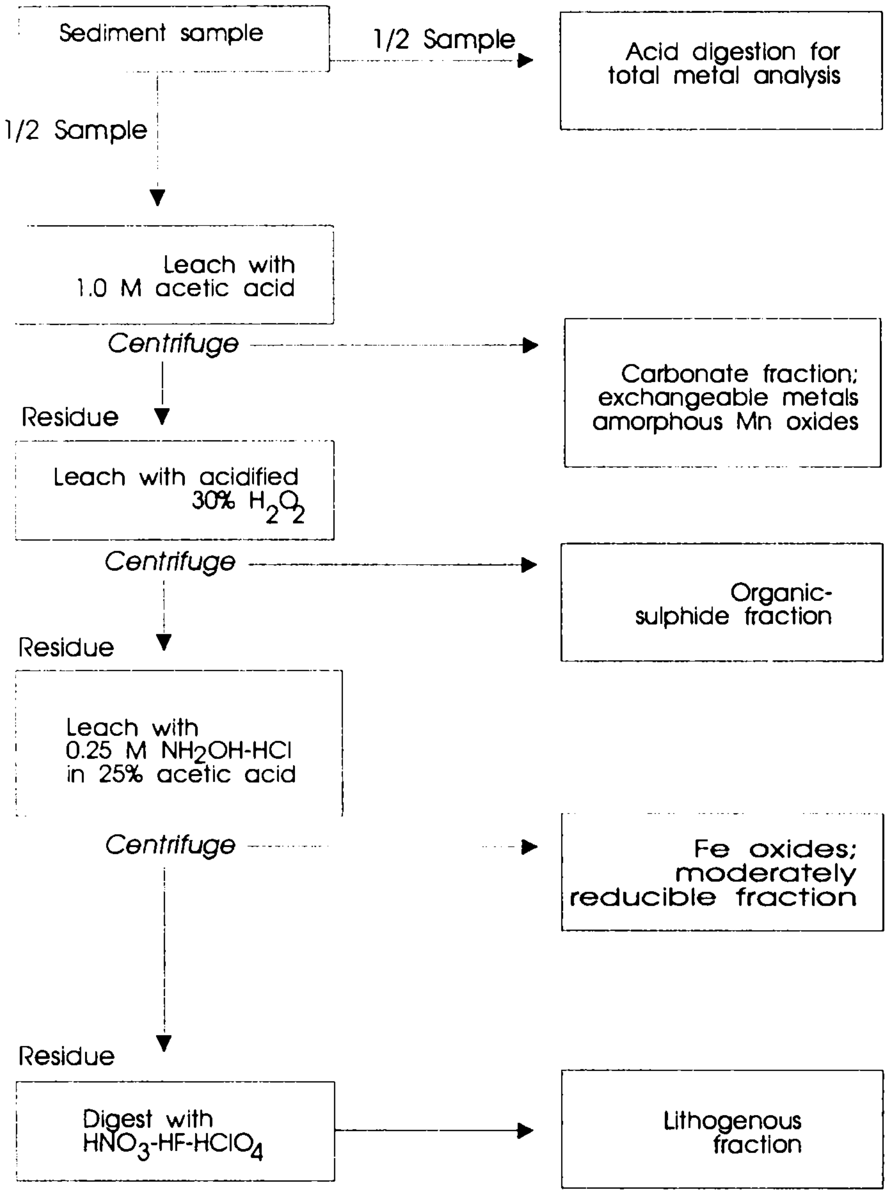

Fig. 4.9 Flow chart depicting sequential extraction technique (after Filipek and Owen, 1979)

Table 4.6 Sequential extraction results of trace elements and their percent contribution in each chemical fraction.

Sequential extraction

Lead ppm					Nickel ppm					Zinc ppm					Cadmium ppm				
Sample No	Acetic acid	H_2O_2	$NH_2OH.HCl$	HCl.Hf	Sample No	Acetic acid	H_2O_2	$NH_2OH.HCl$	HCl.Hf	Sample No	Acetic acid	H_2O_2	$NH_2OH.HCl$	HCl.Hf	Sample No	Acetic acid	H_2O_2	$NH_2OH.HCl$	HCl.Hf
1	0.261	ND	0.087	2.26	1	ND	0.026	0.129	0.67	1	0.24	0.32	0.54	2.23	1	0.009	ND	0.018	0.22
2	0.261	0.087	0.087	0.78	2	ND	ND	0.095	0.155	2	0.18	0.1	0.14	1.15	2	0.009	ND	0.009	0.1
3	0.436	ND	0.087	0.435	3	0.043	0.026	0.121	0.129	3	0.59	0.15	0.17	1.74	3	0.009	ND	0.009	0.018
4	ND	ND	ND	0.783	4	0.009	ND	0.067	0.198	4	0.21	0.13	0.26	1.46	4	0.009	0.009	0.009	0.028
5	ND	ND	ND	0.871	5	0.009	0.034	0.043	0.129	5	0.16	0.08	0.16	1.44	5	0.009	ND	0.018	0.018
6	0.174	ND	ND	0.61	6	0.026	ND	0.043	0.301	6	0.11	0.11	0.14	1.72	6	0.018	ND	ND	0.075
7	0.087	ND	ND	0.871	7	0.06	0.026	0.034	0.164	7	0.27	0.18	0.15	1.63	7	ND	ND	ND	0.028
8	0.348	ND	ND	1.045	8	ND	0.009	0.103	0.301	8	0.85	0.38	0.43	2.91	8	0.103	ND	0.028	0.047
9	0.174	0.348	ND	0.958	9	0.06	0.026	0.052	0.301	9	0.13	0.08	0.13	1.76	9	0.056	0.046	ND	0.085
10	ND	0.174	ND	0.61	10	0.017	ND	0.017	0.31	10	0.15	0.07	0.12	2.05	10	0.009	0.028	0.028	0.045

Percentage contribution

Lead					Nickel					Zinc					Cadmium				
Sample No	Acetic acid	H_2O_2	$NH_2OH.HCl$	HCl.HF	Sample No	Acetic acid	H_2O_2	$NH_2OH.HCl$	HCl.HF	Sample No	Acetic acid	H_2O_2	$NH_2OH.HCl$	HCl.HF	Sample No	Acetic acid	H_2O_2	$NH_2OH.HCl$	HCl.HF
1	10.01	0	3.33	86.66	1	0	3.15	15.64	81.21	1	7.2	9.6	16.21	66.97	1	3.69	0	7.29	89.06
2	21.48	7.16	7.16	64.2	2	0	0	38	62	2	11.46	6.36	8.92	73.24	2	7.62	0	7.62	84.75
3	45.51	0	9.08	45.41	3	13.48	8.15	37.93	40.44	3	22.26	5.66	6.42	65.66	3	25	0	25	50
4	0	0	0	100	4	3.28	0	24.45	72.26	4	10.19	6.31	12.62	70.87	4	16.36	16.36	16.36	50.91
5	0	0	0	100	5	4.18	15.61	20	60	5	8.69	4.34	8.69	78.26	5	20	0	40	40
6	22.19	0	0	77.8	6	7.03	0	11.62	81.35	6	5.28	5.28	6.73	82.69	6	19.35	0	0	80.65
7	9.08	0	0	90.92	7	21.12	9.15	11.97	57.75	7	12.1	8.07	6.72	73.09	7	0	0	0	100
8	24.98	0	0	75.01	8	0	2.18	24.94	72.88	8	18.59	8.31	9.41	63.68	8	57.86	0	15.73	26.4
9	11.75	23.51	0	64.73	9	13.67	5.92	11.85	68.56	9	6.19	3.81	6.91	83.81	9	29.95	24.06	0	45.45
10	0	22.19	0	77.81	10	4.94	0	4.94	90.12	10	6.28	2.93	5.02	85.77	10	8.19	25.48	25.48	40.95
Average	14.5	5.23	1.96	78.25	Average	6.77	4.44	20.13	68.66	Average	10.82	6.07	8.77	74.4	Average	18.8	6.59	13.75	60.81

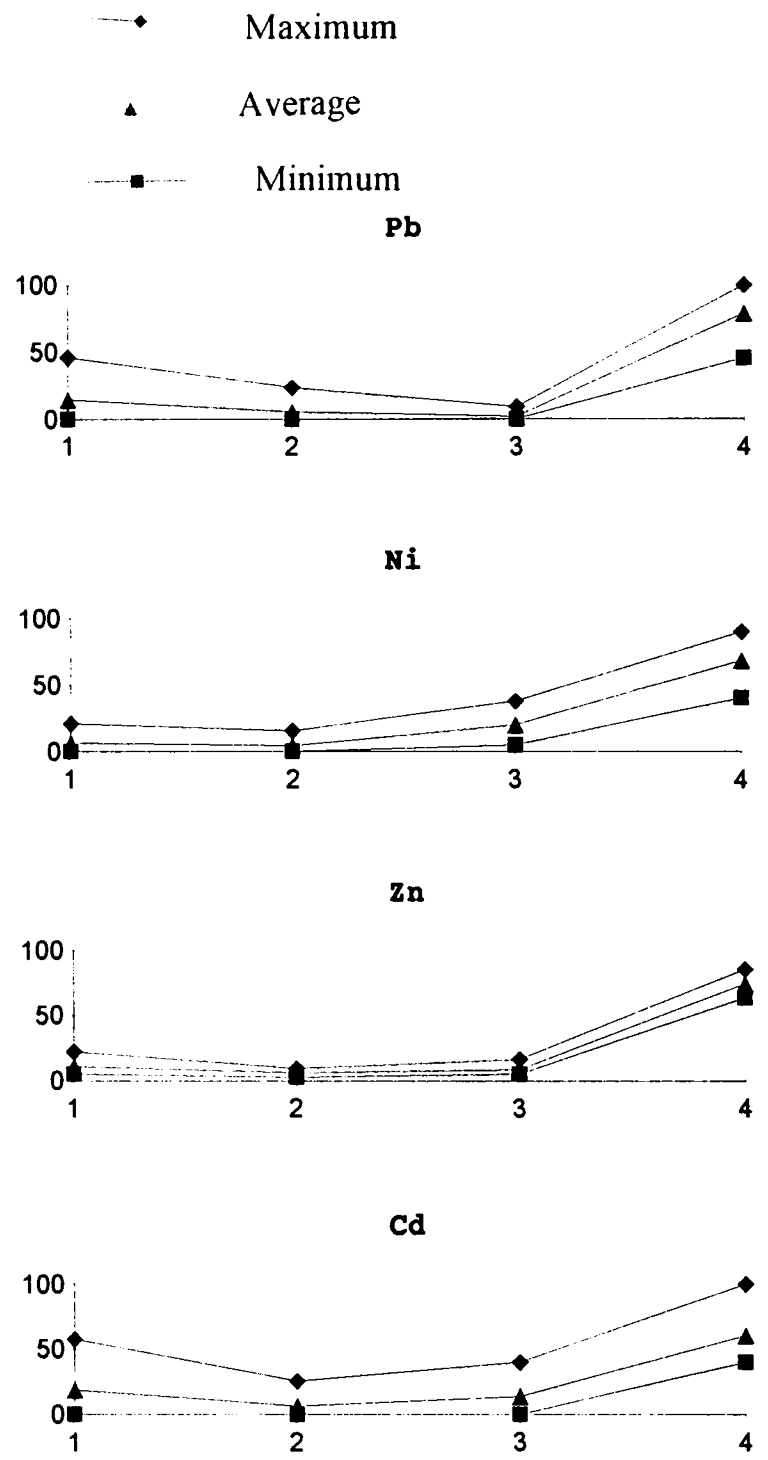

Fig. 4.10 Range and average plot of Pb, Ni, Zn and Cd in the (1) carbonate-exchangeable, (2) Organic-sulphide, (3) moderately reducible and (4) lithogenous fractions

etc. Its non association with CaO indicates a non biogenous precipitation. The grouping together of Ba with Mo could be due to the presence of both in adsorbed state in clays, hydroxides and in organic matter, despite both being geochemically different.

Sand is not grouped with any of the elemental groupings as it does not yield any positive correlation on any of the elements. However it do show negative correlation on many.

4.5.2 *Partition Geochemistry*

In order to have a direct comparison of metal concentrations in the various chemical extracts of sediments, sequential extraction method described by Filipek and Owen (1979) was adopted. The flow chart (Fig. 4.9) gives the details of step-wise extraction procedure. Metals Pb, Cd, Zn and Ni having high toxicity effects on biota were selected for partition geochemical analysis in Beypore estuarine sediments, to understand their bio-availability and nature of incorporation.In the bulk sediments, Zn is the most abundant (av: 79 ppm) followed by Ni (av: 68 ppm), Cd (av: 9 ppm) and Pb (av: 1 ppm).

Lithogenous fraction:

In the lithogenous fraction, Pb percent contribution varies between 45.41 (table 4.6) and 100 with an average of 78.25. Ni percent availability in the fraction range from 40.44 to 90.12 (averaging 68.66). Zn percent fluctuation is the minimum with a nominal variation from 63.68 to 85.78 (average 74.4). Maximum percent fluctuation is shown by Cd as it ranges between 40 and 100% with an average of 60.81. Thus the metal availability in the lithogenous fraction of the 4 elements are in the order of Pb > Zn > Ni > Cd(Fig. 4.10).

The concentration of heavy metals in the crystalline or lithogenous fraction of coastal sediment is controlled almost exclusively by the mineralogy of the land derived detrital fragments. Thus, this fraction is not affected by anthropogenic inputs (Gibbs, 1977). Except

Cd, the other 3 elements are closely found to be associated with fine fractions of sediments. Their greater abundance in the lithogenous fraction and grain size control are attributable to their predominant incorporation in the clay mineral lattices (Rea and Pigula, 1977). In other words, depletion of these metals in sand fraction could only be due to their poor availability in quartz and feldspars which dominate the sand fraction.

Non Lithogenous Fraction:

The non lithogenous fraction of the elements are the sum total of the first 3 phases, namely, 1) carbonates and exchangeable metals, (2) organics, sulphides and manganese oxides and (3) moderately reducible iron oxides and hydroxides. The average abundance of non-lithogenous fraction of the elements are just converse to their lithogenous fraction relation (Cd > Ni > Zn Pb).

(1) *Carbonate and exchangeable fraction*:

Metals in carbonate fraction may be either authigenic or detrital (Stumm and Morgan, 1970). But metals in exchangeable portion are generally authigenic. However heavy metals in both these phases are relatively mobile and readily available for biological uptake (Copeland and Ayers, 1972). This fraction accounts for (table 4.6) relatively good amount of Cd (range = 0 to 57.86%, av. = 18.8%), Pb (range = 0 to 45.51%; av. = 14.5%), Zn (range = 5.28 to 22.26%; av. = 10.82) and Ni (range = 0 to 21.12%, av. = 6.77%). None of these elements have shown any association with CaO in the bulk sediments. Thus majority of the metal concentration in this phase reflect their exchangeable phase that are generally authigenic.

(2) *Organic and sulphide fraction*:

Many heavy metals become associated with organic matter through biological uptake, and adsorption with subsequent incorporation into sediment organic degradation products such as humic substances. Diagenic processes in reducing layers of sediments or detrital incorporation constitute majority of metal sulphides. All the 4 metals studied yield a low level of availability in this fraction. In the order of average percent abundance, Cd (6.59) > Zn (6.07) > Pb (5.23) > Ni (4.44). However percent contributions of Cd, Pb and Ni are found to be relatively high. Since many of these metals show positive affinity with fine particles, it is quite possible that some of them are complexed with organics or sorbed in hydrous form on to sediment particles. A moderate concentration of metals in this fraction could be due to pollution input, but certainly not at an elevated level.

(3) *Moderately reducible fraction*:

Association of heavy metals with hydrous Fe oxides either by coprecipitation or by sorption onto the preexisting oxide coatings is a well recognised process. Lead is available in very low percentage in this fraction (1.96% av.). A greater amount of NLF Ni is found in this fraction (av. = 20.13%). Cd is also concentrated marginally (13.75%). Zn is present in relatively low values (av. = 8.77%). Ni and Zn affinity for finer fractions surmises their coprecipitation in the form of hydrous iron oxides. Though some of these metals are associated with organic and sulphide fraction, there can be a competition for coprecipitation of these metals between iron organic complexes and hydrous iron oxide complexes. This situation is complicated because hydrous iron oxides themselves can complex with organic, especially humic substances in sediments (Greenland, 1971).

Thus the differentiation between inorganic and organic iron species is not always definitive in natural aquatic systems. Further, the previous fraction with this fraction can combinedly pose a threat as potential pollutant phase of these metals. Especially this observation is significant as Ni and Cd to a greater extend and Zn to a lesser extend are incorporated in these two phases combinedly. However, during the sampling time the major polluting industry (a rayon factory situated upstream) was not functional and hence the low level of metal concentration in the NLF fraction.

4.5.3 *Core sample*

The surficial sediment analysis results are more meaningful provided the data on base line values of metals are available. Base line levels are needed to assess the extend of anthropogenic input in a particular estuary. If natural metal fluxes are altered by human activities, an increase in metallic content could be noticed near the surface in the most recently deposited sediments. By analysing core samples, the magnitude of metal enrichment could be assessed. However there are instances in which metal concentration at sub-surface may be higher due to diagenetic processes taking place within the sediment column. The core samples for the present study were collected from the mid estuarine portion, 4 km upstream from the bar mouth using a gravity corer. The texture of the sediments through out the core was mostly clayey. Chemical analysis was performed on core samples that were sub sampled at 5 cm intervals. Organic carbon content keeps almost a uniform pattern of variation as evident from the low standard deviation value (0.36) with an average value of 2.44 (fig 4.6). However, a close examination of the downward variation does indicate a decreasing tendency probably due to consumption of organic matter during diagenitic processes. Average amount of organic carbon present in surficial sediments tally with the average value obtained for core sample.

Abundance of major elements are in the order of Fe_2O_3 > Al_2O_3 > CaO > MgO > Ti > Mn. Vertical distribution of Fe_2O_3 is without much fluctuation (20.34 - 26.35%) averaging 24.41% (standard deviation = 1.6). Fe_2O_3 is available in more than two fold in core samples compared to the surficial sediment average. A marginal depletion of Fe_2O_3 concentration is noted towards the bottom layers of the core sample. Unlike in surficial samples, Al_2O_3 concentration is only next to Fe_2O_3 value. It shows considerable fluctuation from 15.1 - 30.6% (average = 19%, standard deviation = 4.99). Especially the top layers depict considerable variation and the trend of downward variation is not so significant. In the case of Al_2O_3, core abundance is little higher than their surficial sediment values. CaO availability is only very near to the values reported for the surficial sediments. It depicts a near uniform vertical concentration with an average of 2.21%. MgO also approximately follows the distribution pattern of CaO with an average concentration of 2.08. The MgO values are higher in core samples compared to its surficial counterparts (Fig 4.6).

Abundance of Ti showed a downward increasing tendency in the core sample. Its average concentration is 9407 ppm which is higher than the average for surficial sediments. Mn distribution is found to be nearly uniform throughout the sediment column with an average value of 553 ppm which is marginally higher than the amount reported for surficial sediments.

The inter-elemental correlation revealed that Al_2O_3 does not yield any significant loading on Fe_2O_3, CaO, MgO, Mn and Ti. However, its semblance with organic carbon is clear from the moderate positive loading (r = 0.554). Higher concentations of all the elements present in the core samples are mainly due to the abundance of clay in the sediments. Biogenous association of CaO and MgO is also indicated.

Trace elements also depict an enhanced level in core samples except for Ba. The order of abundance of trace metals is Bi > Ni > Cr > Ba > Mo > Sr > Zn > Li > Rb > Cu > Cd > Ni.

Mo shows considerable fluctuation towards the bottom, where as Bi decreases downward (Fig 4.7). Cr, Sr, Zn, Ni and Rb illustrate a uniform downward trend. Ni, Li, Be, Cd showed considerable fluctuation in the vertical profile.

The correlation matrix shows that Cu, Ni and Co have higher positive affinity than Cd with Fe_2O_3. Li and Cr depict semblance with Al_2O_3. This in itself shows a differential pattern of association of elements from that observed in the surficial sediments. The reason could be

(1) limited textural variation of the sediments in the core sub samples, and (2) the post depositional diagenetic alterations brought into the different layers of sediments.

4.5.4 *Rare earth elements*

Rare earths elements consist of 16 elements [Y (39) and La (57) to Lu (71)], out of which except Pr all are naturally occurring (Muller, 1965). Rare earth abundance in sediments have been an important geochemical tool. The rare earth elements comprise a uniquely coherent group because under most natural conditions all members share a common (3+) oxidation state with anomalous behaviour occurring under similar conditions for Ce (+4) and Eu (+2). Balashov et al. (1964) examined the chemical separation among the lanthanides brought about by weathering and sedimentary conditions. In most natural situation, chemical separation within the rare earth group occur as a smooth function of atomic number. This makes it possible to find genetic relationships among different materials and to determine the process led to their formation.

Table 4.7 gives the absolute concentration, and chondrite and North American Shale Complex (NASC) normalised values of sediment samples analysed by ICPMS method. Absolute concentration value ranges between 6.31 for Ce and 0.06 for Lu in upper estuarine sample and respective range is from 6.01 to 0.01 in the lower estuarine sample.

Texture, organic carbon and major element composition of the two samples are given below (Table 4.8). In general, the upper estuarine sample contain a higher amount of REE than the lower estuarine portion. It is also noticeable that the sand content and Fe_2O_3 content in the upper estuarine sample is higher than the lower estuarine portion.

For purpose of demonstrating elemental fractionation among lanthanides, it is a common practice in comparing the distribution of lanthanides in substances to that of another

Table 4.7 Absolute concentration, and Chondrite and NASC normalised values of rare earth elements (REE) in the bulk sediments

	Chondrite normalised values (ppm)		Bulk sediment (ppm)		NASC normalised	
Element	PR/70-14	PR/70-50	PR/70-14	PR/70-50	PR/70-14	PR/70-50
La	8.97	8.76	2.96	2.89	0.09	0.09
Ce	7.17	6.83	6.31	6.01	0.09	0.08
Pr	5.09	4.82	0.57	0.54	0.07	0.07
Nd	4.63	4.6	2.78	2.76	0.08	0.08
Sm	3.65	2.93	0.66	0.53	0.12	0.09
Eu	3.04	2.46	0.21	0.17	0.17	0.14
Gd	1.77	1.97	0.44	0.49	0.08	0.09
Tb	1.7	2.34	0.08	0.11	0.09	0.13
Dy	2.33	1.55	0.74	0.49	0.13	0.08
Ho	1.43	1.43	0.1	0.1	0.1	0.1
Er	1.85	1.75	0.37	0.35	0.11	0.1
Tm	2.67	2.67	0.08	0.08	0.16	0.16
Yb	1.35	1.4	0.27	0.28	0.09	0.09
Lu	1.76	2.06	0.06	0.07	0.13	0.15
Y	1.32	1.27	2.59	2.49	0.1	0.09

Table 4.8 Textural and major element composition of samples taken for REE determination (%)

Parameters	Estuary Lower	Upper
Sand	93.33	81.20
Silt	3.76	14.23
Clay	2.91	14.23
Org. C	0.28	1.04
$Fe2O_3$	13.17	11.58
Al_2O_3	7.65	10.20
CaO	2.10	3.15
MgO	1.50	2.50

to eliminate the zig-zag effect. This is normally done by dividing lanthanide distribution element by element by the lanthanide abundance in chondrites. The resulting ratios are plotted on a logarithmic co-ordinate against lanthanide atomic number. The chondrites normalised plot is given in figure 4.11. An abundance of LREE over HREE is indicated (La to Gd - LREE; Tb to Lu+Y - HREE). On comparing distribution found in several sedimentary rocks, Haskin and Gehl (1962) noted that the relative lanthanide abundance in sediments are clearly different from the presumed solar average. Composite of North American Shales (NASC) was reported to contain different pattern of lanthanide distribution from that of chondrite as sun's atmosphere. Studies carried out by Balashov et al. (1964) have shown that concentration and relative abundance of lanthanides and Y exceeded those in shales. However, with climatic change their differentiation can be variable. There is a tendency of higher lanthanides to mobilise and travel some what farther from their source region than the lighter lanthanides. Lanthanides concentrations are reported to decrease in the order shales < sands < carbonates. Relative abundance light to heavy lanthanides decrease in same order. The observed enrichment of lighter lanthanides is in agreement with the previous work (Haskin and Paster, 1979). This is due to two main effects: i) transformation of silicate minerals to clay due to weathering resulting in lathanide concentration mainly in clays, ii) relative abundance of LREEs in the source rock itself. The mixing of these two effects get slightly modified by mobilisation of lathanides for long distances. The near uniform pattern of lathanide distribution in the two sediment samples located at distal portion in the estuary indicate the thoroughness of mixing of lathanides during weathering and transportation, despite the sediment being texturally diverse.

If we presume that the shale is the representative of material brought in to the ocean by rivers, it has been a widely accepted practice to normalise the REE concentration in the sediments with the REE values of NASC. The resulting ratios plotted on a logarithmic ordinate is shown in Figure 4.11. The pattern of variation does not show any obfuscating zig-zag effect.

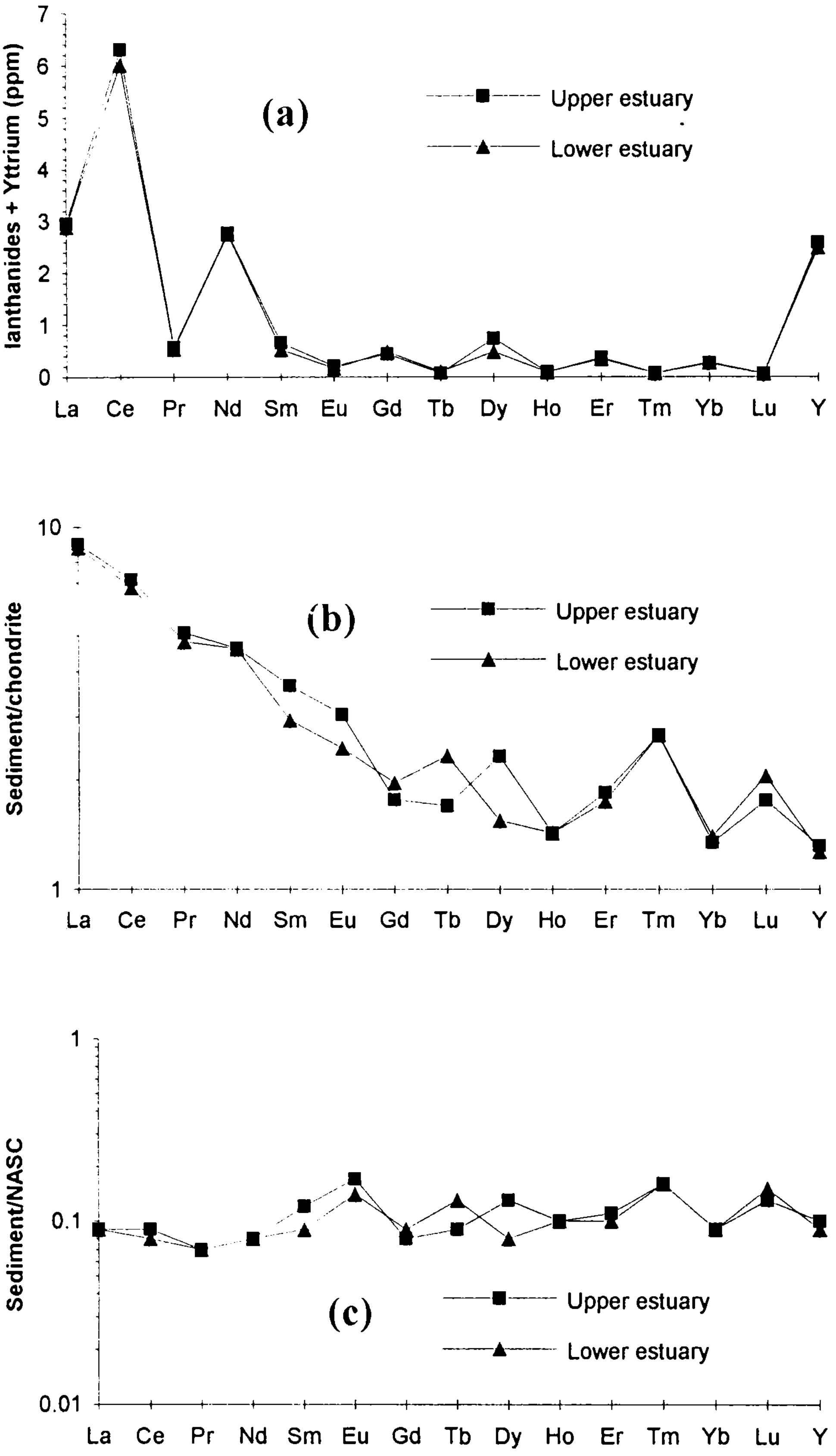

Fig. 4.11 Plot of (a) absolute concentration of REE, (b) chondrite normalised and (c) NASC normalised patterns

However, the ratio in itself indicates a one tenth reduction of lathanide concentration in the estuarine sediments of Beypore compared to the shales. One of the many reasons could be due to the poor REE fixation by the estuarine sediments.

CHAPTER V

SUMMARY AND CONCLUSIONS

The river Chaliyar, which is the third major river of Kerala, forms an estuary at Beypore and joins the Arabian Sea. Like the other rivers of Kerala, the Chaliyar is also swift flowing and exhibits stream like characteristics. This river within its 169 km course crosses varied physiographical units and forms a high flux and dynamic estuary. Major industrial houses such as Gwalior Rayons Factory, ship breaking yard etc. flush their effluent into this estuary. Even a casual visitor to this part of the river can witness the scars of pollution caused to the estuarine biosphere. Situated in a hydrographically and physiographically unique locale, pollution monitoring in this area provides ample scope to generate a base-line threshold database. The present study focuses attention on the trace metals distribution in the Beypore estuary. The investigation was planned and carried out to achieve the objectives of studying the sources of trace metals, their transporting pathways and various physical and chemical parameters which control their distribution within the estuary. Hydrological parameters were monitored and their inter-relationship assessed. Based on the results of investigation, the quality of the estuary is derived. The physical parameters monitored include tidal forcing, water temperature, currents, salinity and dissolved oxygen. Suspended sediment load, particulate and dissolved trace metals were estimated for the water column. In addition to the concentration of trace metals in surficial sediments and core sample, their dependence on sediment texture is established. Organic carbon content and the concentration of major elements in the sediments are also dealt in detail. Nature of metal incorporation was deduced through step-wise chemical extraction procedure. The rare earth elements in the upper and the lower estuarine sediment samples are analysed and reported for the first time.

The salient features of the investigation are summarised below:

The water temperature in the Beypore estuary was found to be dependent mainly on solar radiation. River discharge also sometimes influenced the temperature distribution. Temperature regime showed a seasonal cyclicity with increase in temperature during pre- and post-monsoon periods. Relatively lower temperatures were observed in the sub-surface layer near the mouth of the estuary during monsoon months attributable to the influx of upwelled water into the estuary. Pre- and post-monsoon months depicted negligible difference between surface and bottom layers.

Salinity varied widely in space and time. Main factors controlling the salinity distribution are the tidal pumping and the fresh water discharge from the river. Diurnal variations in salinity were found to be in tune with tides. During peak monsoon, the estuary becomes fresh water dominated. Saline water intrusion by tidal forcing was noticed upto 5 km upstream during monsoon months. Clear stratification was observed with well defined salinity gradients during monsoon. During post- and pre-monsoon periods the estuary transforms to a partially mixed and then to a well mixed one. Saline water intrusion was observed upto 22.5 km upstream during summer months when fresh water discharge was considerably low.

Dissolved oxygen content was higher when river discharge was maximum. The effect of upwelled water was manifested during August and September resulting in depletion of dissolved oxygen concentration especially in the bottom layers. Turbidity in water column due to disturbance by anthropogenic activities results in low photosynthesis at the lower portion of the estuary. This has resulted in low D.O content which could affect the biota adversely. Inverse relationship between D.O and salinity is established in the lower reaches of the estuary. The lower D.O. content noticed during pre- and post-monsoon months can also be attributed to the reduction in oxygen rich fresh water supply and to the oxygen consumption by various biodegradation processes.

Maximum surface current speed was observed during peak monsoon period. The strongest currents observed were found to coincide with the flood and ebb in respective directions. Irrespective of the seasons, sub-surface currents were less stronger than surface currents. Certain local effects, such as, bank orientation, bottom profile, bridges and islands were found to control the flow regime at different locations.

Land derived materials brought in by the rivers contribute maximum to the suspended sediment load in the Beypore estuary and Chaliyar river. Maximum concentration of suspended sediments was observed during monsoon period. Abnormal concentration of suspended sediments observed occasionally at the barmouth region and fisheries harbour area could be due to resuspension of bottom mud caused by the fishing activities using mechanised boats. Increased wave action coupled with shallowness of the estuary has resulted in the higher concentration of suspended sediments in the lower reaches. Resuspension of bottom mud due to scouring action of tidal forcing seem to contribute to high suspended sediment concentrations in the bottom layers.

Spatial distribution of trace metals in the particulates of surface waters were devoid any specific pattern. The metal concentration are comparable with those reported for Cochin estuary. Higher concentration of Cu and Cd in the sub-surface layers could be due to bottom entrainment. Particulate metal concentrations were found to be many fold higher than that of the bottom mud confirming the role of suspended particulates as carriers of lethal toxicants. During the lean period, enrichment of Cr and Zn in the particulate phase were noticed. Higher concentration of heavy metals associated with the suspended matter was either derived from industrial effluent or due to the activity in the harbour area.

Among the dissolved trace metals studied, Pb and Zn recorded higher concentration, probably due to the release of these metals from sediments already contaminated with industrial effluent. Dissolved copper content in the estuary was much lower than the tolerance limit reported for fresh water.

Almost all stations exhibited significant season-wise fluctuation in textural characteristics, indirectly indicating the discharge dependency. Considerable intermixing was noticed between different textural grades. A gradual downstream decrease in sand content indicates textural maturity of the sediments as observed in other alluvial streams. This is attributed to dominant unidirectional differential transport of sediment by fluvial dynamics.

Sand, which was the most dominant of the textural grades, seem to be diluted with fines during the post-monsoon season. Though the tidal effect was felt upto 22.5 km upstream, the bottom sediment distribution appears to be controlled by the tidal regime only upto 7 km. *In situ* sorting processes are observed in Beypore estuary due to the scouring effect of tides as the sediments get resuspended and flushed out during ebb flow to the open sea.

Bottom sediments of Chaliyar river and Beypore estuary have an average level of organic carbon comparable to other tropical estuaries. During periods when discharge was minimal, an enhanced level of organic carbon was noticed in the lower reaches of the estuary. Correlation studies indicate definite control of textural grades on organic content in sediments. Silt and clay fraction contained maximum organic carbon than sand. One of the important reasons attributed for the occurrence of higher organic carbon content in fines is their larger surface area that accommodate more dispersed organic particles.

Major elemental chemistry of the bulk sediments is found to be mainly dependent on the detrital and non-detrital fractions. MgO and CaO content were high in the lower estuarine sediments. The range of chemical composition are dominantly influenced by different proportions of major minerals in the sediments except for CaO and MgO. Dominant relationship existed between the major elements and textural composition. The fines contained higher concentration of Al_2O_3, Fe_2O_3 and Mn and hence indicate affinity to organic carbon as well. Lack of textural control exhibited by CaO could be attributed to the selective partitioning with the higher proportions of carbonate than non-carbonate phase of the sediments.

Tidal mixing appear to control the temporal and spatial variability of trace metals concentration in the estuarine sediments. Cu, Ni, Zn, Rb, Li, Cr and Co showed uniform distribution in the upper part of the estuary, whereas in the lower reaches their concentration found to be fluctuating considerably. This phenomenon seems to have a direct bearing on the sediment textural distribution and local hydrography. The average abundance of trace metals are in order of Ba > Sr > Cr > Mo > Bi > Zn > Ni > Co > Rb > Li > Cd > Cu > Be. Total trace metal concentration is found to have a combined influence of mineralogy, organic carbon content and texture. Cu, Ni, Zn, Rb, Li, Cr and Co affinity for finer fractions and organic carbon could be attributed to their higher cation exchange capacity. The clay minerals, especially montmorillonite in sediments is found to facilitate concentration of these metals. Thus, apart from land derived contribution from natural processes, trace metals enrichment by anthropogenic input is also found to be significant in the sediments of Beypore estuary. Cluster analysis indicated four distinctive groups consist of (1) silt, clay, Organic Carbon, Al_2O_3, Fe_2O_3, Co, Mn, Cu, Ni, Rb, Li, Zn, Cr and Ti, (2) Cu, Be and Bi, (3) CaO, MgO and Sr, and (4) Ba and Mo. Respective controlling factors for such groupings are inferred.

Among the four trace metals analysed by sequential extraction method, Pb was found to be mostly associated with lithogenous fraction (lattice-held) followed by Zn, Ni and Cd. In NLF (labile fraction) toxic elements were found to be concentrated more in (i) organic and sulphide phase and (ii) moderately reducible phase. Higher concentration of Ni and Cd in these two phases together could pose a threat to aquatic organisms.

The core sample showed predominance of clay throughout the length. A slight depletion of organic carbon towards the lower layer of the core could be due to its consumption during diagenetic processes. Considerable variation in trace metal content in the sediment column was noticed and only in the case of some elements a base line data could be generated. Higher metal concentration observed in the core sample is mainly due to the fineness of the sediments.

The concentration of rare earth elements (REE) in the upper estuarine sediments are found to be marginally higher than that in the lower reaches of the estuary. Chondrite normalised pattern indicated dominance of LREE over HREE. NASC normalised values signify one tenth reduction of lanthanide concentration in the estuarine sediments of Beypore compared to the shales.

With the exception of a few elements in the particulate and bottom sediments, the observed concentration of most of the trace metals were much below tolerance level. This does not necessarily indicate that the Beypore estuary is pollution-free. During the investigation period, one of the major sources of industrial pollution especially in the lower reaches of the estuary viz., The Mavoor Gwalior Rayons factory was under lock out. During the reconnaissance survey conducted prior to the field investigation in the estuary, information from the local populace indicated the very high pollution levels in the estuary, which had hampered river sand mining and exploitation of benthic bivalves used both for food and lime. Moreover, lignin coating on bottom sand near the effluent discharge point of the Mavoor Gwalior Rayons factory was observed even during the field survey.

The presence of higher concentration of some of the heavy metals could be due to the residuals of the earlier pollution load and indicates a high residence nature of these pollutants in the bottom sediments. Since 1990, the factory is back in operation discharging industrial effluent into the estuary. The Beypore estuary falls well within an area dominated by the monsoon, and is hence unique. Since, similar studies are meagre along the southwest coast of India, the present study provides ideal data set for the assessment and comparison of estuarine pollution derived from industrial sources. With the factory re-opened, a time series monitoring of various pollutant load in this estuarine system is imperative for its better understanding and sustainable use.

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