STUDIES ON THE NUTRIENT CHEMISTRY OF MUDBANKS

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CERTIFICATE

This is to certify that the thesis bound herewith is an authentic record of the research carried out by SRI. S. MURALEEDHARAN NAIR, under my supervision and guidance in the Chemical Oceanography Division, School of Marine Sciences, Cochin University of Science and Technology, in partial fulfilment of the requirements for the Ph.D. degree of Cochin University of Science and Technology and no part thereof has been presented before for any other degree in any University.

Cochin - 16
April, 1990.

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PREFACE

Coastal environments exhibit varied characteristics influenced by a broad range of conditions. An extensive knowledge of these complex environments is essential in order to maximise the utility of these areas for shelter, transport, food and recreation. This study attempts to describe the unique annually occurring event namely "Mudbank" (Chakara) or better known as "Zones of Bio-Rhythm",confined to the southwest coast of India. A manifestation of coastal zone processes during the southwest monsoon season, this phenomenon has wide ranging implications on fisheries and allied aspects. Thus, the socio-economic status of fishermen and the fisheries resources of India are largely influenced by the presence of the rich aquatic life in these mudbanks. Further, the presence of mudbanks has varied effects on the shore stability and induces coastal accretion/ erosion processes in adjacent areas.

Studies relating to the physical and biological aspects of mudbanks are available but chemical features have not been explained. This thesis attempts to quantify the extent, rate and pattern of nutrient cycling in the mudbank region. The investigations, significant from the view point of both theoretical and practical aspects of nutrient sorption and fractionation processes, are supplemented by data sets on hydrochemical parameters. The study is believed to make a major contribution to the understanding of coastal processes highlighting various aspects of environmental chemistry.

Additionally, research work in mudbank regions have been substantially supported by investigations in nearshore waters and adjoining backwaters; the following papers incorporate the findings from the main study as well as spin-off(s) from subjacent works.

PAPERS PUBLISHED

1. Anirudhan, T.S., Balchand, A.N., Nair, S.M. & Nambisan, P.N.K. 1987 Distribution pattern of salinity and silicon and their inter-relationship in Cochin backwaters. Proceedings of the National Seminar on Estuarine Management, Trivandrum. 26-31.

2. Sathyanathan, B., Nair, S.M., Chacko, J. & Nambisan, P.N.K. 1988 Sublethal effects of copper and mercury on some biochemical constituents of the estuarine clam *Villorita cyprinoides* var. cochinensis (Hanley). Bulletin of Environmental Contamination and Toxicology. 40, 510-516.

3. Nair, S.M., Balchand, A.N. & Nambisan, P.N.K. 1988 On the determination and distribution of hydroxylated aromatic compounds in estuarine waters. Toxicological and Environmental Chemistry. 22, 203-213.

4. Balchand, A.N., Nair, S.M. & Nambisan, P.N.K. 1990. A survey of the protein content in estuarine waters. Toxicological and Environmental Chemistry (in press).

SYMPOSIUM PRESENTATIONS

1. Nambisan, P.N.K., Balchand, A.N. & Nair, S.M. 1987 Chemical Oceanographic Aspects of Mud Banks - A unique coastal phenomenon along southwest coast of India. XIX IUGG Symposia, Vancouver, Canada. Proceedings - IAPSO OPS9A-P7.

2. Balchand, A.N., Nair, S.M. & Nambisan, P.N.K. 1987 Occurrence of unique seasonal phenomenon along western south coast of India - Theories and perspectives of Mud Banks. XIX IUGG Symposia, Vancouver, Canada. Proceedings - IAPSO OPS7-P18.

3. Nair, S.M., Balchand, A.N. & Nambisan, P.N.K. 1987 Transport of sediment - associated nutrients in a tropical fluvial system. XIX IUGG Symposia, Vancouver, Canada. Proceedings-IAHS HW 6d - P5.

4. Nambisan, P.N.K., Balchand, A.N. & Nair, S.M. 1988 Particulate related processes controlling trace metal distribution in tropical estuaries. Presented in the Symposium "Fate and effects of toxic chemicals in large rivers and estuaries", Quebec City, Canada.

5. Nair, S.M., Balchand, A.N. & Nambisan, P.N.K. 1988 Metal levels in recently deposited sediments of Cochin backwaters. Presented in the Symposium "Fate and effects of toxic chemicals in large rivers and estuaries", Quebec City, Canada (under publication in Science of the Total Environment).

CONTENTS

CHAPTER - 1

INTRODUCTION

The coasts, the confluence of land, sea and atmosphere are most susceptible to environmental changes on the earth. This region is generally reckoned as a strip of land of variable width that extends from the low-tide line on land to the first major change in landform features.

King (1979) on the basis of tectonics, classified coasts into three main types, viz, the trailing margin (eg: the coasts of western Europe and Africa), the marginal sea coast (eg: coast of eastern Asia) and collision margin (eg: coast of western South America). While Inman & Nordstrom (1971) based on morphology, classified them as mountain coasts, narrow shelves coasts and wide shelves coasts, Davies (1964) classified them into storm wave coasts, west and east coast swell wave coasts and low energy coasts. However, the most widely known and accepted classification is that of Shepard (1963) who classified them into two principal categories, namely primary coasts and secondary coasts.

West coast of India

The west coast of India is believed to have been evolved during the Mesozoic era. However, the sub-continent seems to have acquired its outline only the end of the Cretaceous period. The Quilon Beds indicate that a marked marine transgression seems to have taken place in the southwest coast of India during Burdigalian time (upper part of Lower Miocene). The elevation of the Tertiary sequence of formations known as the Quilon Beds & Warkalli Beds and their forming cliff sections as at Varkala, Cannanore etc. point out that the Kerala coast line took its present shape during post - Pliocene (Quaternary) times.

The present day south west coast of India (Figure 1) is characterised by broad strand plains intercoupled with cliffed shorelines with or without beaches. It is highly irregular, cliffed and wave eroded. Nearly 360 km out of 560 km of Kerala coast is vulnerable to

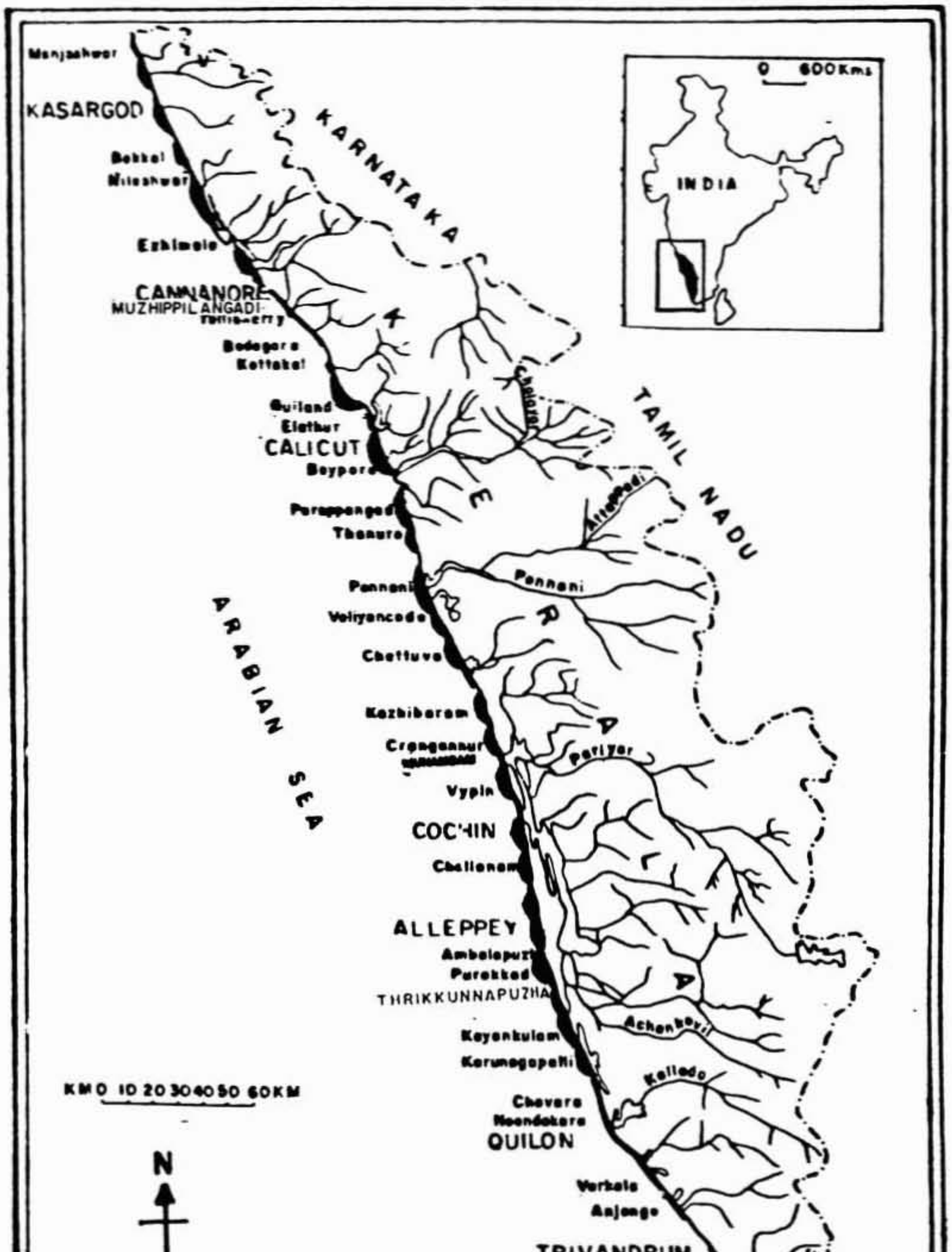

Figure 1. Southwest coast of India(Kerala coast) showing location of mudbanks

erosion during southwest monsoon. A number of known factors like seasonally reversing oceanic circulation currents, wave climate and presence/absence of mudbanks, influence the shoreline features. The generally straight coastline, trending NNW-SSE has a number of fault lineaments - some of them neotectonically active. A number of fluvial terraces along the banks of west flowing rivers, submerged shore flatforms at headland portions, formations of lagoons across the bounding bars and truncation of beach ridges are suggestive of neotectonic movements (Nair, 1987). Secondary control on shoreline development is exercised by the erosional/depositional factors. Straight line coasts are sandy permeable stretches while the crystalline shores assume irregular outline. The west coast shoreline is considered to be fluctuating which reportedly lost 600 m wide belt of coastal area during this century (KERI, 1971). The coast is described as "a submergent coast belonging to the category of terrigeneous coast of primary morphologic disequilibrium" (Garner, 1974). Hence towards attaining equilibrium, the long term tendency may be to increase the linear extent of erosional segments compensated by intervening depositional areas.

Coast of Kerala

The Kerala State has an area of 38, 860 km^2 ($8^o15'$ - $12^o45'$N; $75^o52'$ - $77^o08'$E) with a coast line of length 560 km. More than 20 rivers, cut the land surface of this coastal land. This coast falls under the category of "trailing edge" (Inman & Nordstorm, 1971) indicating relatively high sediment yields during the monsoonal climate. The features identified include beaches, beach cliffs, stacks, islands, shore platforms, spits, bars, beach ridges, estuaries, lagoons, mudflats, tidal flats and deltaic plains (Nair, 1987). A peculiar feature of the Kerala coast is the formation of mudbanks during monsoon; disturbing the equilibrium conditions of the coast adjacent to them (Srinivasan et al., 1980). Thrivikramji (1979) classified the shorelines of Kerala state as: strand plain shoreline, cliffed shoreline without a beach and cliffed shoreline with a beach. The wave and beach characteristics show that the direction of littoral drift is towards south in June and July months and towards north during other months (KERI, 1978).

General characteristics of mudbanks (Zones of Bio-Rhythm)

The formation of mudbanks triggers an active fishery season in the coastal environments of Kerala. The mudbanks generally occur on the alluvial belt of the coast extending from Thrikkunnapuzha to Cannanore over a distance of 270 km which is more significantly characterised by backwaters of Kerala: the coastal land between these regions is low and sandy with promontories and stacks (Nair, 1983). The mudbanks appear most often a week or so after the onset of the southwest monsoon. The phenomena brings about suspension of sediments in a semicircular region, affording calm and turbid waters. A seaward extent of 5 to 6 km and alongshore extent of 4 to 6 km have been recorded. The banks are laden with heavy suspension of fine clay (90% of <6 μ) at surface and highly viscous bottom sediments of unconsolidated ooze-like liquid mud (80% of $\angle 10$ μ). The suspended load content varies from 1000 to 1800 mgl^{-1}. The fine clay is characterised by soft, plastic touch, dark greyish green in colour with an oily appearance.

As many as 27 locations (Figure 1) were identified where the mudbanks had appeared sometime or other along the Kerala coast; this has been classified into three regions, viz. the southern strip (Thrikkunnapuzha - Alleppey), the Central strip (Chellanam - Munambam) and the northern strip (Calicut north pier - Muzhappilangadi) (Nair, 1983). The lagoon barrier complex is backed on the shoreside of the first two strips whereas the third is backed by lateritic terrain surrounded within Korapuzha and Kallai river systems (Nair, 1983).

Historical account of mudbank studies

The occurrence of mudbanks, centuries old, is evidenced from the reports of mariners, as these regions provide safe and smooth anchorage even in the gales of the southwest monsoon. Alternatively, various terms have been used in regional languages to denote this phenomena viz. Chakara or Santhakara (quite shores) or Ketta Vellam (stinking water). Navigators often consider the area as calm water anchorage.

Mudbanks along the southwest Indian coast was first mentioned as far back as 1678 in Pinkerton's "Collections of Voyages and Travels" appearing in the "Administrative Report of 1860 of Travancore" (India). The term "Mud Bay" has been applied by Captain Cope (1755) to denote Alleppey mudbanks in his book, "A new history of the East India". Crawford (1860) first gave an explanation that the bank of mud is created by the hydraulic pressure caused by the level of water in the vast backwaters, during monsoon, some 4 feet higher than the sea level. Crawford & Logan (1882) noticed the "mud volcanoes" or "mud cones" bursting up in the sea during the rainy season. Later, Philip Lake (1889) and Davey (1903) too observed mud cones at Alleppey. King (1884) in his report "considerations on the smooth - water anchorages of mudbanks of Narakkal and Alleppey on the Travancore Coast (1881)", discussed the migration and formation of the mudbanks between Alleppey and Purakad and between Cochin and Narakkal. John Rhode (1886) confirms the earlier observation of Crawford (1860) on mud volcanoes bursting up in the sea during the rainy season, which appeared "as if a barrel of oil had suddenly been started below the surface".

R.C. Bristow, founder of the Cochin Harbour, made an organized attempt to study the mudbanks in his book "History of Malabar Mudbanks" (1938), published in two volumes (Volumes I and II). He also details his exhaustive observation on the origin, formation and other features of the mudbanks in this book.

Theories on Mudbank formation

Various theories stated by different workers from time to time are briefly summarised hereunder. More details on the theories are available elsewhere (Kurup, 1977; Murthy *et al*., 1984)

1. Subterranean channel flow

Crawford (1860) explained the formation of mudbanks as due to the flow of accumulating water with vast quantities of soft mud from the inland rivers and backwaters through the subterranean channels into the sea. King (1881), in his report, made a suggestion that the position of banks within certain ranges of the coast, is entirely due to the discharge of mud from under the lands of Alleppey-Purakad and Narrakkal, this being effected by the percolation or underground passage of lagoon water into the sea. John Rhode (1886) explained the flow of mud and water as due to the hydraulic pressure developing in the backwaters during heavy rains in the southwest monsoon period. Captain Drury (1903) supports the above views on subterranean channel flow.

Ducane *et al.* (1938) is of the view that since the narrow strip of land separating the backwaters from the sea is a low-lying area, the increase in pressure is restricted to a maximum value of 21 lbs/sq inch for a maximum possible rise of water-level of 5 feet in the lake; above this level water will overflow. This pressure may not be sufficient to overcome the frictional resistance set-up by solids in suspension.

2. Water bearing stratum

Bristow (1938) opined that the theory as to the existance of an "underground river" which is made operative by a rise in the backwater level and is of sufficient stability to convey and discharge backwater mud or silt, roots of trees etc. into the ocean, appears to be highly doubtful. He proposed that a water bearing stratum exists at a good depth below the surface which brings down water from the hills and crops out under the sea at varying distance from the shore, thereby lifting the mud above it.

3. River deposition

Ducane *et al.* (1938) proposed that the mudbanks were formed by the churning up of clay and silt near the coast which were deposited gradually by the discharges of rivers during the monsoon period.

But this theory could not hold good for the formation of mudbank near Alleppey where there is no river or backwater emptying into the nearby coastal area.

4. The upwelling phenomena

Banse (1959) suggested that the southwest coast of India is a region of upwelling during monsoon season. Ramasastry & Myrland (1959) suggested that the formation of mudbank can be accounted as due to the upwelling during the southwest monsoon, which produces vertical acceleration with resultant lifting of bottom water/mud. According to them, the presence of upwelling is restricted to 20-30 m bathymetric lines of the coastal lines.

However, the presence of upwelling at such depths, does not help to explain the formation of mudbank from shore to 10 m depth, unless there is some other mechanism in the region of the bathymetric difference of the locations of the two processes (Murthy et al., 1984). Further the upwelling should commence from the bottom, so that the mechanism can operate and lift the bottom mud. Ramamirtham & Rao (1973), pointed out that the upwelling is all along the southwest coast, while mudbanks are limited to only certain regions.

5. Phase phenomena

Recently Murthy et al. (1984) proposed a hypothesis based on the relative fraction of the mud entering into three stages, namely, the thixotropic phase, the solphase and the gravity-influenced suspended stage. The theory also explains other characteristics of the mudbank region, such as longevity, intensity of calmness and stability of mudbank. Accordingly, the higher grade of calmness observed at the Alleppey mudbank is due to the richness in the first two fractions of the mud. They also suggested that towards the end of monsoon, in the absence of fresh supply of mud into the water column, the already available mud fraction which increases viscosity, gradually diminishes and thus, the mudbank dissipates.

Mud(Re-) suspension and the calmness in mudbanks

Different hypotheses were put forward in order to explain the two peculiar characteristics, viz. the mud(re-) suspension and calmness, observed in the mudbank areas. They may be summarised briefly as follows (Kurup, 1977; Murthy *et al.*, 1984 have reviewed these aspects in detail).

1. Oil as a calming agent

King (1881) pointed out the presence of oily matter in the Alleppey mud, derived, perhaps, in part from the decomposition of organisms, but principally from the distillation of oil in subjacent lignitiferous deposit belonging to the Varkala strata. He attributed the damping of waves in the mudbank region as due to the presence of oil in the mud. But Keen & Russel (1938) later ruled out the possibility of any such oily matter in the muds at Alleppey.

2. Elastic nature of mud as calming agent

The elastic or springy nature of the mud absorbs the wave energy, as waves pass over it by alternative contractions and expansions, so as to bring them to rest (re-emphasized by Murthy *et al.*, 1984). Keen & Russel (1938) had discarded this theory as the primary characteristic of any mud is plastic and not elastic.

3. The deflocculation processes

Keen & Russel (1938) found that the mud of the mudbank remains suspended (deflocculated) at lower salinity. This hypothesis was adopted by Kurup (1969) and Padmanabhan & Eswara Pillai (1971) in order to explain the high load of suspended solids.

4. Thixotropic effect

Keen & Russel (1938) have suggested that the wave damping effect (calming effect) of waves on the banks was due to the thixotropic properties of the mudbank mud. One of the condition, i.e. the loss of an electrolyte mentioned in the definition of thixotropy by Kerr *et al.* (1970) is well accounted by the decrease in the salinity during mudbank period and the other condition, i.e. a sudden shock, may be the decrease in temperature and change in features of monsoonal waves and coastal currents.

5. Rip current formation

Varma & Kurup (1969) said the rip flow, carrying fine offshore sediments, prevents the onshore transport of sediments by waves. Hence localisation of suspended sediments take place at the rip head. They also suggested that the rip currents carry low salinity nearshore water towards offshore, thereby dilutes the water of the mudbank and this will help the deflocculation of sediments in suspension. Reddy & Varadachari (1972) have also reported the presence of converging littoral currents at several points along the Kerala coast during the southwest monsoon season which result in rip currents.

However, Gopinathan & Qasim (1974) observed no strong rip currents either before or after the mudbank becomes active, because the converging waves at the mudbank get some what dampened and the coastal currents in this region are always stronger than any rip current that might be produced as a result of wave breaking at an adjacent area.

Migration of mudbanks

A number of workers have noted the migratory behaviour of mudbanks (Ducane *et al.*, 1938; Ramasastry & Myrland, 1959; Varma & Kurup, 1969; Gopinathan & Qasim, 1974; Nair, 1983 etc). Murthy *et al.* (1984) suggest that in the case of mudbanks of Alleppey, it moved from the place of incidence by about 0.5 to 2 km, year by year southward and this was due to the gradual discharge of mud by the southerly flow of the water. This movement continued till the beginning of the northeast monsoon winds, and the subsequent reversal of the southerly drift, when conditions had already set in for the dissipation of the mudbanks. Kurup (1977) suggests that the movement of any mudbank is the result of changes in the location of rip flows which is determined by changes in the refraction pattern caused by changes in the bathymetry and in the spectrum of waves approaching the shoreline.

Implications of mudbanks

The formation of mudbanks have wide and varied environmental impacts. The socioeconomic life of fishermen and fisheries resources of the State of Kerala are largely dependent on the rich aquatic life in these mudbanks. Gopinathan & Qasim (1974) called the mudbanks as "God's gift given to Kerala fishermen". The mudbanks are considered to be a "boom" for fisherman, as the calm area, abound in prawns, sardines, mackerel, soles etc. provide a temporary fishing harbour in which it is possible to do fishing by indigenous crafts during the southwest monsoon period, when the sea is highly turbulent elsewhere. Gopinathan & Qasim (1974) suggested that the viscous stirring up of mud by the wave action probably forces the fish and prawns to move upwards. Further, the upwelling effects prevailing along the Kerala coast, force fish and prawn to move towards the shore to avoid the oxygen deficient waters (Sankaranarayanan & Qasim, 1969). This condition, in conjugation with the southerly surface drift, may bring shoals of fish and prawn more towards the shore, close to the mudbank (Gopinathan & Qasim, 1974). Biologically, the migration of fish and prawns towards the mudbank could also be for feeding purposes as the mudbanks provide a richer source of food than the adjoining sea.

The presence of mudbanks have varied effects on the shore stability and induces coastal accretion/erosion processes in adjacent areas. The effect of mudbanks on the coastal processes is summarised by Moni (1971): (1) traps the littoral material from the updrift side and thereby prevents its down coast movement (2) causes refraction and diffraction of waves on its sides and (3) causes accretion of the beach within the mudbank areas.

However, Padmanabhan & Easwara Pillai (1971) explained the influence of mudbanks in relation to erosion processes. The material trapped within the mudbank cannot reach the downdrift side owing to the absence of waves in this area, so that the shore immediately on the downdrift side gets eroded to make up the deficiency.

Gopinathan & Qasim (1974) are of the view that the presence of a mudbank along the coastline, may result in the erosion of beach on either side and the protrusion of the beach may be due to the gradual deposition of sediments from the eroded beach material.

Since the mudbanks are closely associated with the stability of the southwest coast of India, it is to be reckoned in any programme of coastal development or protection in this area (Moni, 1971). Murty et al. (1980) observed that at places where the deformation of the beach is primarily due to formation of a mudbank (which is of transient nature) the remedial measure should also be transient which could be removed after the purpose is served.

Recent studies (1953 - 1989)

The first document on mudbanks appeared as a book (Bristow, 1938); later followed by scientific studies, since 1953. Seshappa (1953) and Seshappa & Jayaraman (1956) first initiated the chemical studies of mudbanks reporting high phosphate contents. Ramasastry & Myrland (1959) made a hypothesis that mudbanks may be associated with upwelling and divergence near 20-30 m bottom layers. Some physico-chemical properties of sediments were studied and compared by Nair et al. (1966) and fisheries aspects, reviewed by Rao (1967). The role of estuarine output in mudbank formation was discussed by Varadachari (1966). The effect of flocculation to keep mud in suspension was postulated by Damodaran & Hridayanathan (1966). The textural studies conducted on Narakkal mudbank by Dora et al. (1968) noted predominantly fine clay fraction in mudbank sediments. Varma & Kurup (1969) explained the mudbank theory on the basis of role of waves and rip currentsand Kurup (1972) extended the hypothesis to converging littoral currents in the inshore waters of Kerala coast. Moni (1971) and Iyer & Moni (1972) explained the influence of mudbanks on the shore stability of the southwest coast of India. Reddy & Varadachari (1972) attempted to explain mudbank movement in the light of wave refraction studies. Some biological aspects of benthos were studied by Damodaran (1973). Gopinathan & Qasim (1974) studied the role of currents and waves in the formation, maintenance and dissipation of Alleppey mudbank in detail. Some chemical studies (high levels of phosphorus and organic carbon) on Alleppey mudbank was reported by Jacob & Qasim (1974). The seasonal and distributional variation of temperature and salinity was discussed by Kurup & Varadachari (1975) and in 1977, Kurup detailed the physical aspects of mudbanks evaluating the role of texture of sediments in mudbanks. Nair (1976) published a review paper on the mudbank of Kerala coast. Mathew _et al_. (1977) ascertained the diurnal variation of zooplankton related to currents and other ecological parameters. A mathematical model for the wave damping by viscous fluid mud at the bottom has been proposed by Mac Pherson & Kurup (1981). Kurup _et al_. (1981) have related the wave damping to viscosity. Nair (1983) reported some of the chemical and sedimentological aspects of Kerala coast. Studies on the physical, chemical and biological aspects of mudbanks were recently published in CMFRI bulletin No.31 (1984). More recently, the geochemical aspects of mudbanks, focussing more on the sedimentological characteristics were published by Mallik & Ramachandran (1984); Ramachandran & Mallik (1985); Mallik _et al_. (1988) and Ramachandran (1989). The paper by Shenoi & Murty (1986) explained the viscous damping of solitary waves in mudbank region.

The salient physical and chemical features of the mudbanks have been reviewed as part of this study (Nambisan _et al_., 1987; Balchand _et al_., 1987).

Parallel phenomena along coasts of other continents

The environmental features of mudbanks make it a typical phenomenon along Kerala coast. The shores of Peru and the Cordillens (the Pacific Islands) show some similarity in the formation of such local ecosystems, developed by the upwelling of waters from the deeper to the surface layers with vast amounts of nutrients, so that "patches of life" and intensive fishing is underway. The high rate of the evolution of plankton protozoa is very typical in the offshore waters of Peru.

There are reports on "mudbanks" in other parts of the world to describe the heavy load of suspended particles, but different from the Kerala mudbanks. The French Guiana coast extending over a distance of 350 km between Brazil and Suriname is characterised by migrating mudbanks. The sedimentological and hydrodynamic features of the Suriname mudbanks were reported by Nedeco (1968), Augustinus (1978), Wells & Coleman (1981) and Rine & Ginsburg (1985). The Guyana mudbanks have been investigated by the Delft Hydraulics Laboratory (1962), Eisma & Vander Marel (1971) and Barreto et al. (1975). Allersma (1971) and Froidefond et al. (1988) stated that the mudbank migrated along French Guiana coast. The propagation of fluid muds along the coast of south America was pointed out by Wells (1977). In 1962, 21 mudbanks were counted between Cayenne in French Guiane and Waini Rinn in Guyana (Delft Hydraulics Laboratory, 1962). In short, the "mudbanks" of the Kerala coast maintains its identity from that of other muddy coasts of the world in that they do not form regular relief forming features (Mallik et al., 1988).

Scope and scheme of the present work

Scope of the study

The aim of this study is to investigate the nutrient chemistry in the mudbank region under three periods, namely pre-mudbank, mudbank and post-mudbank. Distributional characteristics of nutrients in this region are compared to those of a non-mudbank area. Information on the physico-chemical processes in these zones are of much significance from the view point of both theoretical and practical aspects of studies on the role of nutrients in supporting the abundant biological life. The variations concurrently recorded in the hydrochemical parameters like temperature, pH, dissolved oxygen, dissolved organic carbon, sediment organic matter, salinity, chlorophyll a etc. form the supplementary data set to that of nutrients. Thus the overall study of nutrients in the dissolved and sedimented form would help in understanding the potential availability of life supporting elements in the mudbank area, since the concentration and distribution of nutrients have a conclusive role in the high productivity of the mudbank region.

In the quantitative studies on nutrients, phosphorus is known to behave as a growth limiting nutrient (Ishikawa & Nishimura, 1989). The capacity of sediments to act as "traps" or "buffers" for nutrient phosphorus will be largely determined by two factors viz. the chemical forms in which sedimental phosphorus reach the interface and the subsequent diagenesis of these forms. This part of the study involves the separation of different fractions of sedimental phosphorus by various sequential chemical extraction schemes. Since each specific reagent can preferentially remove a particular phosphate fraction, the extraction procedure would provide valuable information on the mobility of the sedimental phosphorus and the forms in which it is held in the sediments collected during the mudbank and non-mudbank periods.

Additionally, because the sediments have an important role in nutrient (phosphate) uptake and regeneration, fluctuations in phosphate concentrations associated with the chemical characteristics of surficial sediments will potentially influence the nutrient budget of this zone. Sediment surface again acts as a physical catalyst for releasing or trapping of phosphate depending on its concentration in overlying waters. This paves way to investigate the quasi-steady state phosphate-phosphorus equilibrium between the sediments and the overlying waters under various simulated laboratory conditions to quantify the sorption (adsorption/desorption) processes prevelant in these coastal environments.

Scheme of thesis

Briefly, the thesis deals with the distributional variability of hydrochemical parameters and nutrients. Trace metal concentrations in the sediments of mudbank are also incorporated in the study. The present study also examines the phosphate adsorption/desorption characteristics and the phosphate speciation of mudbank sediments.

The overall study is presented in 6 chapters. Chapter 1, Introduction, describes the status and implications of the mudbanks along with the aim and importance of the work. Chapter 2, Materials and Methods, includes the description of location, sampling procedure for water and sediment and the analytical methods employed. Chapter 3, presents the general hydrochemical characteristics viz. temperature, pH, salinity, dissolved oxygen, dissolved organic carbon and chlorophyll a. The parameters like organic matter, moisture content, grain size and trace metal concentration of sediments are also included in this chapter. Chapter 4, presents the change in the concentration levels of dissolved and sedimental forms of nutrients for three periods. Data on silicon is presented only in its dissolved form. The various forms of nitrogen in the water media include ammonia, urea, nitrite and inorganic and organic nitrate, whereas the sedimental phase contains urea and adsorbed and interstitial forms of nitrite and inorganic and organic nitrates. Results on the inorganic and organic forms of phosphates in the watermedia and the adsorbed and the interstitial forms of inorganic and organic phosphates in sediments are also reported and compared with values of those of non-mudbank area. The discussion part highlights the nutrient chemistry of mudbanks. Chapter 5 reports the speciation of phosphates in the sediments collected during the mudbank and non-mudbank seasons. By applying eight different sequential chemical extraction schemes, the major forms of phosphorus viz. exchangeable P, anion exchangeable P, carbonate bound P, labile and resistant organic P, Fe-and Al-bound P, calcium bound P, and hydrolysable surplus P have been determined, compared and the significant features related to mudbank phenomenon are explained. Chapter 6 deals with phosphate sorption (adsorption/ desorption) studies of mudbank sediments under various laboratory (simulated) conditions. The results are used in explaining some of the intrinsic processes taking place within the bank's active period. The study thus helps to distinguish and differentiate the various aspects of phosphate speciation during mudbank and non-mudbank periods and further delineate the sorption mechanisms during the mudbank period.

The list of references are included at the end followed by a chronological table on theories and related works on mudbanks (annexure-1). Tables on preparation of artificial seawater and values of various parameters presented as figures in the text are given in annexures 2, 3 and 4. Papers published are also appended.

CHAPTER - 2

MATERIALS AND METHODS

This chapter describes the location of study and the analytical methods employed in the estimation of various parameters.

Description of location

The location chosen for this study was Mararikulam ($9^{o}35'$-$9^{o}40'$ N; $76^{o}20$ - $76^{o}23$ E) near Alleppey; hereafter designated as mudbank area (Figure 2). The formation of a mudbank near the same location during the previous years had motivated this site selection. Another area considered was Nattika (near Trichur), but subsequently dropped as the mudbank did not develop during monsoon. The characteristic feature of most of the mudbanks to shift slightly (towards south) was observed here also in the course of investigation at Mararikulam in late August 1987. Other features observed were the semicircular shape with a red tinted border, a seaward extent of 3.5 to 4 km from the shore, along the shore extent of about 3 km and wave heights of only 10-20 cm. The sediment, characteristically was soft, plastic and dark greyish green clays with an oily appearance. The bank matured in July and dissipated in September sheltering a variety of fishes (sardines, prawns, catfish, mackerals etc).

The non-mudbank area selected for a comparative study was situated near the Cochin barmouth ($9^{o}57'$ N; $76^{o}11'$ - $76^{o}14'$ E). The tides of this region are of a mixed type, predominantly semidiurnal (Qasim & Gopinathan, 1969); waves are generally rough during June-August (monsoon) while calm conditions were observed during rest of the year. The predominant wind direction during the months July to September remains persistently northwest (Sundaresan Pillai, 1989). The turbidity in this region was below 75 mg l^{-1} in monsoon and the coastal bed was composed of clayey sand.

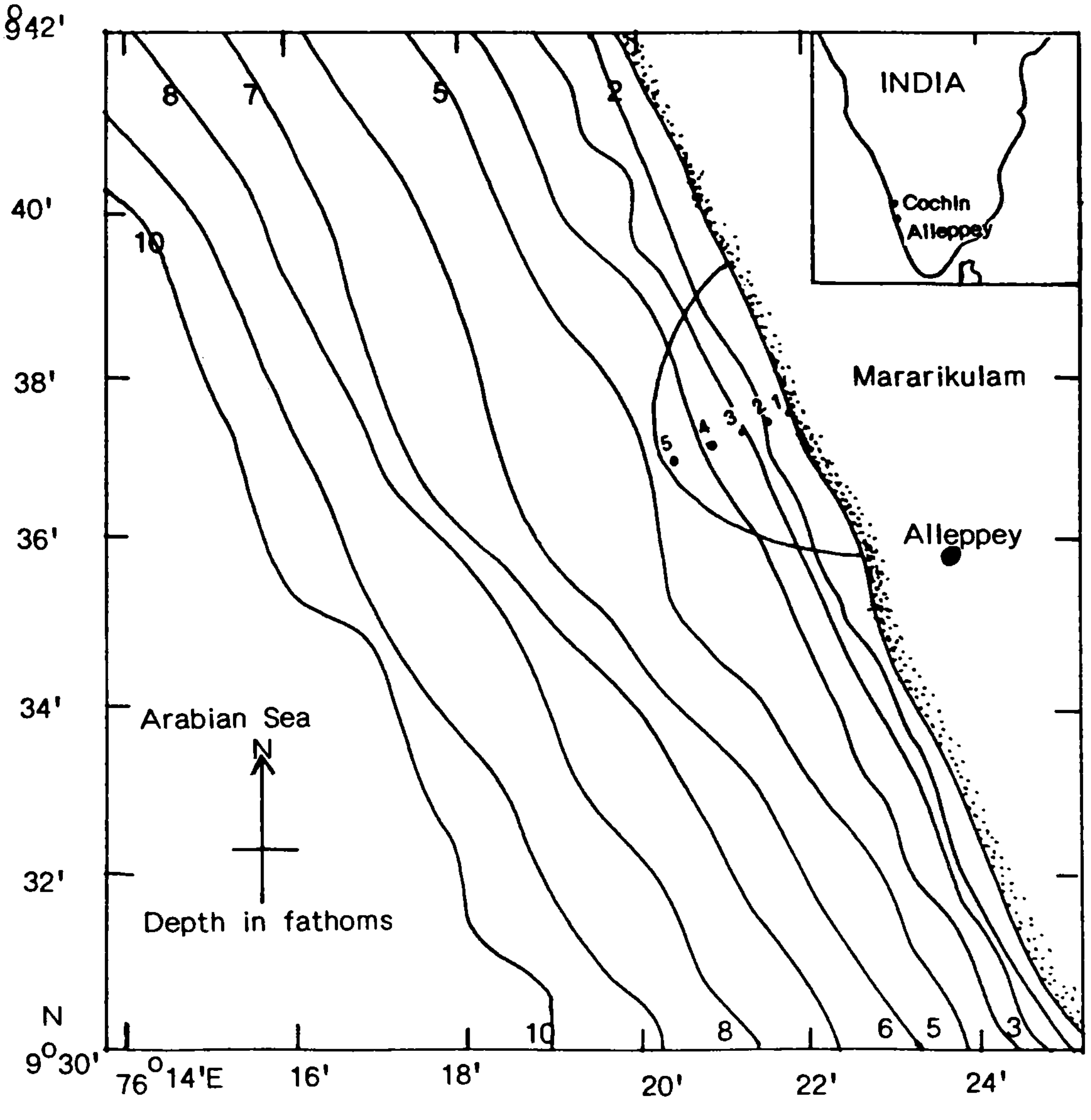

Figure 2. Location of stations (1-5) at Mararikulam near Alleppey on the south west coast of India.

Analytical techniques

Sampling procedure

Samples of water (surface and bottom) and sediment were collected from March 1987 to December 1987, at monthly intervals from the mudbank and non-mudbank areas. The nine months of collection falls into three distinct periods designated as pre-mudbank (March-May), mudbank (June-August) and post-mudbank (September-December). All the surveys were carried out using country boats.

The stations were fixed by taking bearings and cross checked on an echo sounded topography map. The distance of each of the five stations from the shore was:

Station 1 - 25 m
2 - 500 m
3 - 1000 m
4 - 2000 m
5 - 3000 m

Surface samples were collected using a clean plastic bucket and bottom samples at depths of 1,3,5,7 and 9 m from stations 1-5 respectively using a pre-cleaned teflon Hytech water sampler. Filtered samples for nutrient analysis which could not be completed within a day were stored deep frozen in plastic containers and were analysed within a week. A stainless steel plastic lined van-Veen grab was used to collect sediments and aliquots were carefully skimmed (excluding shells) to ice-box storage in closed polythene containers for transport to laboratory; these were stored at -5^{o}C till analysis was performed.

Analytical methods

The analytical methods employed are summarized in the tables given below:

a) Hydrochemical characteristics - General

No.	Parameter	Methodology	Reference
1.	Temperature	Mercury-in-glass thermometer (1/10°C)	
2.	pH	Electrometrically determined using a pH meter (Systronics - Digital No.333)	
3.	~~pH~~ Eh	Portable Philips ~~Eh~~ pH meter - pp 9046.	
4.	Salinity	Argentometrically, by the modified Mohr's method, developed by Knudsen.	Grasshoff (1983 a)
5.	Dissolved Oxygen	Modified Winkler method	Grasshoff (1983 b)
6.	Chlorophyll a	Samples filtered through GF/C glass filter paper, dispersed and disintegrated the paper in 90% acetone - absorbance determined on a spectrophotometer (Hitachi 150-20) according to UNESCO formula.	Strickland & Parsons (1977a)
7.	Dissolved* organic carbon	Dichromate reflux method	APHA (1980)
8.	Sediment organic matter	Chromic acid oxidation method	El Wakeel & Riley (1957)
9.	Textural analysis	Dried in hot air oven (90°C) for 6 hours - subsequent mechanical sieving and pipette analysis.	Krumbein & Pettijohn (1938)
10.	Sedimental trace metal analysis	Digestion using concentrated HNO_3 and HCl (1:3) metal concentration readout on atomic absorption spectrophotometer (Perkin Elmer-2380).	Johansson (1975)

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*it is expressed in terms of chemical oxygen demand (COD) - mg l^{-1}

No.	Parameter	Methodology	Reference
11.	Moisture content	Difference in the weight of sediment in its wet and dried form.	

b) Hydrochemical characteristics - Nutrients

No.	Parameter	Methodology	Reference
1.	Silicate	Formation of silico-molybdate complex using ascorbic acid as the reductant.	Koroleff (1983a)
2.	Ammonia	Indophenol blue method using citrate buffer.	Koroleff (1983b)
3.	Urea	Diacetyl monoxime spectrophotometric method.	Koroleff (1983c)
4.	Nitrite	Formation of a azo dye with sulphanilamide and N - (1 - naphthyl ethylene diamine dihydrochloride)	Grasshoff (1983c)
5.	Nitrate	Reduction using copper coated cadmium column and determined as nitrite	Grasshoff (1983d)
6.	*Organic Nitrate	UV-irradiation (250 nm) method	Strickland & Parsons (1977b)
7.	Phosphate	Formation of Phospho-molybdate complex - using ascorbic acid as reductant.	Koroleff (1983d)

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* The organic nitrate refers to the nitrogen bound to readily oxidizable organic matter.

No.	Parameter	Methodology	Reference
8.	Organic Phosphate	Destruction of the C-O-P bonds using UV-irradiation (250 nm) and estimate as vide 7 above.	Hansen & Grasshoff (1983)
9.	Sediment urea	Diacetyl monoxime thiosemicarbazide method	Nakas & Litchfield (1977)
10.	Interstitial and adsorbed forms of nitrite, nitrate and phosphate.	Separation of interstitial and adsorbed forms using the extractants NaCl and NaOH respectively - Analytical technique for each nutrient as above.	Rochford (1951)

c) Speciation studies

In speciation studies, the sediments were classified into two types - one which was collected during the mudbank season (June-August 1987) and another of non-mudbank season (March to May and September to December 1987) from mudbank region. The eight different extraction schemes applied in this study are summarised hereunder.

Scheme	Extractant	Solid - to-extractant ratio (mg:ml)	Experimental conditions	Forms of Phosphate	Reference(s)
I.	a) 1M NH_4Cl	25 : 25	pH 7- 30 minutes	Exchangeable and carbonate bound	Hieltjes & Lijklema (1980)
	b) 0.1M NaOH	25 : 25	16 hours	Fe-and Al-bound	
	c) 0.5M HCl	25 : 25	24 hours	Ca-bound	

Scheme	Extractant	Solid - to-extractant ratio (mg : ml)	Experimental conditions	Forms of Phosphate	Reference(s)
II.	a) 1M NH_4OAc	300 : 10	pH 7 1 hour	Exchangeable	
	b) 0.01M HNO_3 + 0.1M $NH_2OH.HCl$	300 : 10	1 hour	Carbonate bound	Engler <u>et al.</u> (1977)
	c) 30% H_2O_2 + 1M NH_4OAc	300 : 10	pH 2.5 1 hour	Organic bound	
	d) Dithionate + Na. Citrate	300 : 10	1 hour	Fe-and Al-bound	
III.	a) 0.5M NaCl	300 : 25	30 minute	Exchangeable	
	b) 0.1M NaOH+ 1.0M NaCl	300 : 25	16 hours	Fe-and Al-bound	Williams <u>et al.</u> (1971)
	c) 0.27M Na.Citrate +0.11M $NaHCO_3$	300 : 25	85^oC 15 minute	Ca-bound	modified by Li (1973)
IV.	a) 0.1M HCl	50 : 25	6 days	Exchangeable, organic bound, carbonate bound, Fe-and Al-bound	Duinker <u>et al.</u> (1974)
	b) 0.1M HCl	50 : 25	1 minute	Exchangeable, organic bound, carbonate bound, Fe-and Al-bound	Sörensen <u>et al.</u> (1971)

Scheme	Extractant	Solid - to-extractant ratio (mg : ml)	Experimental conditions	Forms of Phosphate	Reference(s)
V.	a) 0.2M Oxalic acid + 0.4M Ammonium oxalate.	300 : 20	2 hours	Exchangeable, carbonate bound, Fe- and Al - bound	Shukla (1973)
	b) 0.27M Na. citrate + 0.11M Bicarbonate + Dithionate	300 : 15	80°C 20 minutes	Exchangeable, carbonate bound, Fe- and Al- bound	
VI.	a) 0.215M H_2SO_4 + 0.87M HCl	100 : 10	15 minutes	Exchangeable, organic bound, carbonate bound, Fe- and Al- bound	
	b) 0.2M HCl + 0.03M NH_4F	100 : 10	5 minutes	Exchangeable, organic bound, carbonate bound, Fe- and Al- bound.	Spear (1970)
	c) 0.5M $NaHCO_3$	100 : 10	pH 8.5 30 minutes	Exchangeable, carbonate bound, organic bound	
VII.	a) 0.058M HCl+ 0.0125M H_2SO_4	60 : 20	10 minutes	Exchangeable, carbonate bound, organic bound, Fe- and Al- bound	
	b) 0.1M NaOH + 0.1M NaCl	60 : 40	16 hours	Exchangeable, carbonate bound, organic bound, Fe- and Al- bound	Cowen (1974)
	c) Anion Exchange resin (20-50 mesh Dowex 1-x 8)	100 mg: 250 mg	24 hours	Exchangeable	

Scheme	Extractant	Solid - to-extractant ratio (mg : ml)	Experimental conditions	Forms of Phosphate	Reference(s)
VIII.	a) Ca-NTA + ascorbic acid	1000 : 25	pH 6 6 hours	Fe- bound	
	b) Na-NTA + ascorbic acid	1000 : 25	pH 6 6 hours	Ca-bound	Golterman (1982)

d) Sorption studies

The studies were conducted on sediments collected from the mid-mudbank region (station 3) during mudbank period. The method described in APHA (1980) was used for the preparation of synthetic seawater (Annexure-2).

The sorption experiments were classified into three categories.

1. Desorption characteristics of mudbank sediments at different salinities (with constant initial phosphate concentration)

i) Mudbank water

A constant weight of sediment (5 gm) was allowed to desorb phosphate at different salinities of 500 ml of mudbank water (5,10,15,20 and 25 x 10^{-3}) diluted with double distilled water. (pH 7.8 ± 0.3). 1 ml of the supernatent solution at a depth of 2 cm from the surface was withdrawn at different intervals of time to estimate the amount of phosphate desorbed.

ii) Synthetic seawater

The above experiment was repeated replacing mudbank water with synthetic seawater of salinities 5,10,15,20,25,30 and 32 x 10^{-3} .

2. Sorption characteristics at different concentrations of phosphate in mudbank water

In this study, separate aliquots of leached sediment, unleached sediment and Kaolin (2 g) was allowed to undergo sorption at different phosphate concentrations in mudbank water (200 ml). Leached sediment was prepared by treating a bulk amount (100 g) of sediment in NaCl, NaOH, HCl, H_2SO_4 and finally washing in distilled water. The initial concentration of phosphate solutions were 0.005, 0.05, 0.01 and 0.10 µg at ml^{-1}. Aliquots were withdrawn for phosphate estimation at different time intervals.

3. Adsorption characteristics at different sediment concentrations

The mudbank sediment was leached subsequently with NaCl, NaOH, HCl, H_2SO_4 and distilled water and varying quantities (2,5,10,25,50 and 100 g) were dispersed in 200 ml each of distilled water having a concentration of 0.02 µg at ml^{-1} phosphate and sampled at pre-fixed time intervals.

In all sets of experiments the phosphate was determined spectrophotometrically by the method of Koroleff (1983 d).

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CHAPTER - 3

HYDROCHEMICAL CHARACTERISTICS - GENERAL

Introduction

The study of the chemical and physical aspects of the nearshore environment provides background information necessary for the understanding of the coastal processes. Compared to open ocean systems, where the composition are temporally invarient and chemical processes are in rather steady state, the coastal region exhibits environmental gradients occuring spatially and temporally on micro or macro-scale. The in-situ environmental fluctuations develop a multidimensional heterogeneous area (multidimensional dynamic equillibrium) showing variations in the physical and chemical parameters. There is greater potential in applying the tools of modern oceanography and chemistry to unravel the geological, biological and anthropogenic coastal processes.

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

The coastal areas of the tropics are productive except turbid river mouths, where light penetration is poor. In the shallow areas, the high productivity is accounted by the increased regeneration rate of nutrients due to high temperatures accelerating all bacterial processes at the bottom (Nair et al., 1968). One of the major findings of the International Indian Ocean Expedition (IIOE; 1966) was the extremely high rates of primary production and large standing crops of phytoplankton and zooplankton along the western regions of the Arabian Sea. The values of primary production and standing crops in the central Arabian Sea were higher than the average values encountered in the world oceans (Wooster et al., 1967). The maximum production was reported nearer to the coasts, within 50 m depths and gradually decreasing seaward (Nair et al., 1968). High rate of production was noted also in the shallow waters of the coastal regions of Laccadive and Minicoy islands (Prasad & Nair, 1960).

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

A qualitative and quantitative survey of the hydrographical characteristics of mudbanks was carried out under three different periods viz. premudbank, mudbank and postmudbank. Such a survey provides important background information necessary for the study of the littoral processes. The monsoonal effect on the hydrography of the western coast is more visible in nearshore regions, especially in mudbanks, as reported hereunder.

Materials and methods

The details of the collection of samples and analysis are given in Chapter 2.

Results and discussion

The results of the survey on various hydrochemical parameters (temperature, salinity, dissolved oxygen, pH, dissolved organic carbon and chlorophyll *a*) of samples collected during the three periods in the mudbank area are represented in figures 3 and 4. Figures indicating stations on x-axis are not to scale. These results are compared with those of non-mudbank area; the range of values (surface only) are depicted on the same figures in the order of pre-mudbank, mudbank and postmudbank periods respectively. Figures 5 and 6 show the monthly variations in some of the hydrochemical parameters in the mid-mudbank region (data for the month of October 1987 not fully incorporated). The corresponding values of non-mudbank area are also represented in the graph. The sediment analyses also incorporate determination of sediment organic matter (SOM), moisture content, grain size and trace metal concentration; the salient features of their distribution are discussed hereunder.

Temperature

The surface water temperature is depicted in figure 3(a). The average values and the range were higher during pre-mudbank period (32.0^{o} - 33.5^{o}C). The lowest values (29.4^{o} and 30.0^{o}C) were observed during mudbank period at the two stations adjacent to the beach.

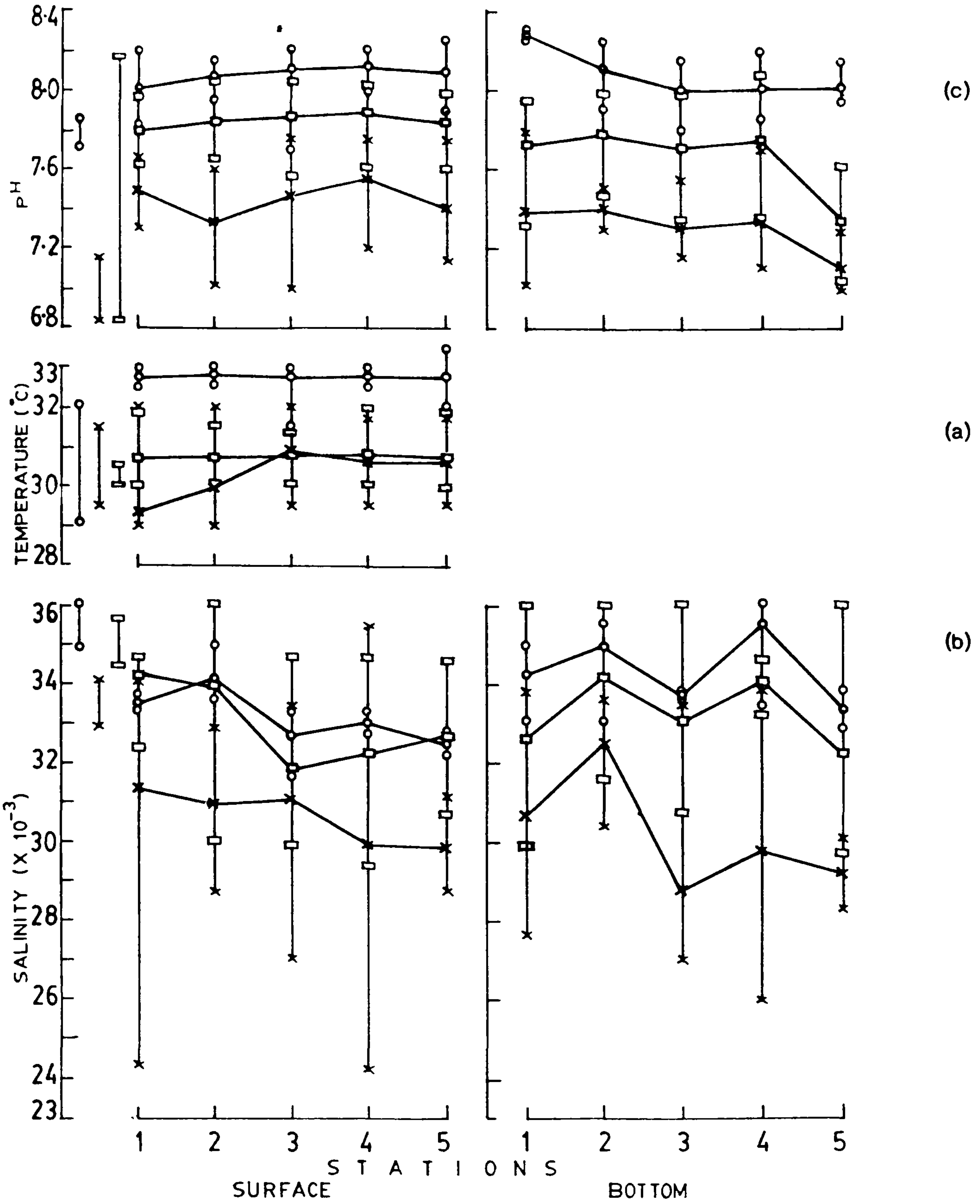

Figure 3. Mean and range of values of salinity (b) temperature (a) and pH (c) during pre-mudbank (O——O), mudbank (x——x) and post-mudbank (□——□) periods at stations 1-5; range of surface values of non-mudbank area are given on ordinate.

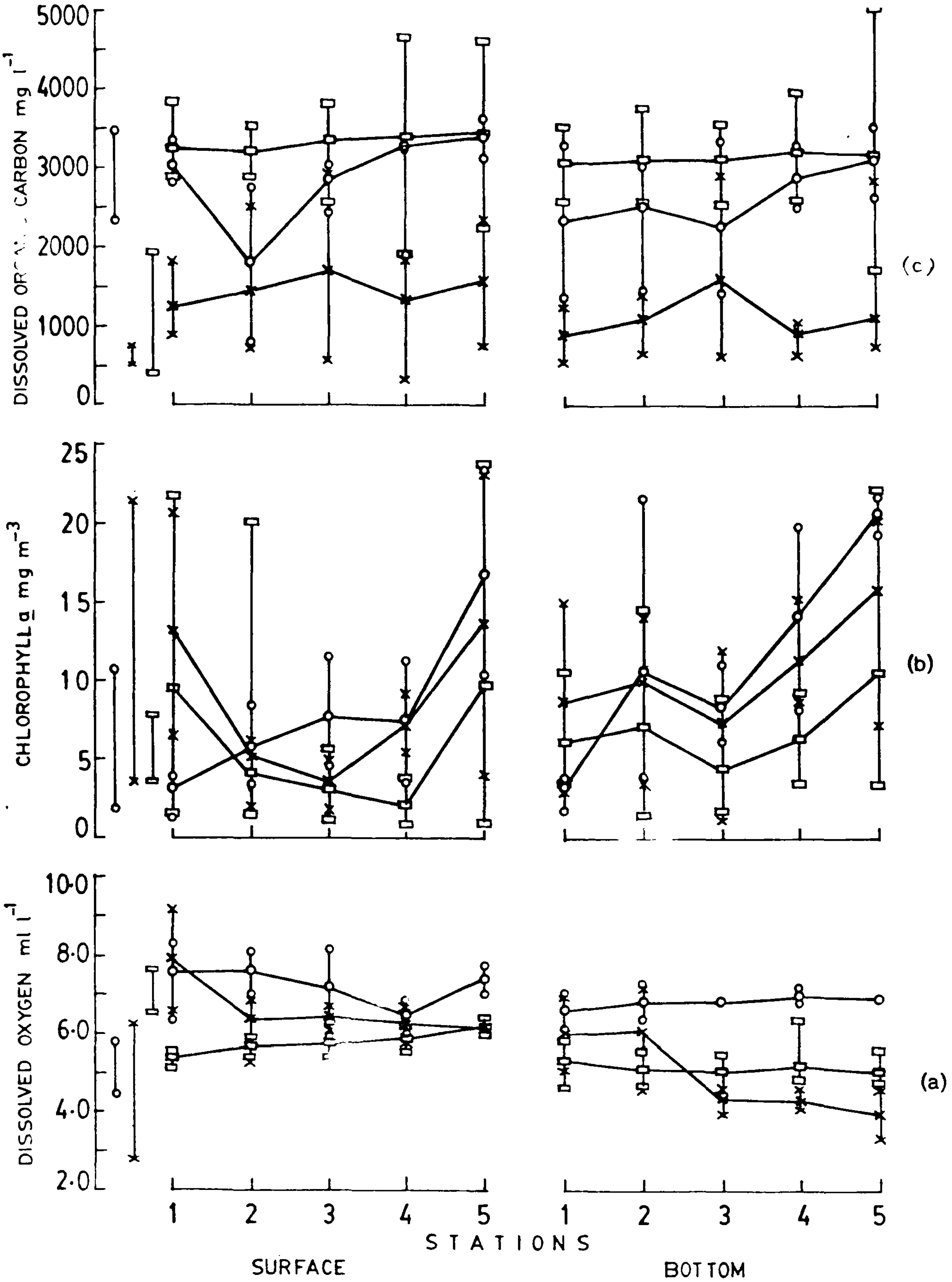

Figure 4. Mean and range of values of dissolved oxygen (a) chlorophyll a (b) and dissolved organic carbon (c) during pre-mudbank (O——O), mudbank (x——x) and post-mudbank (□—□) periods at stations 1-5; range of surface values of non-mudbank area are given on ordinate.

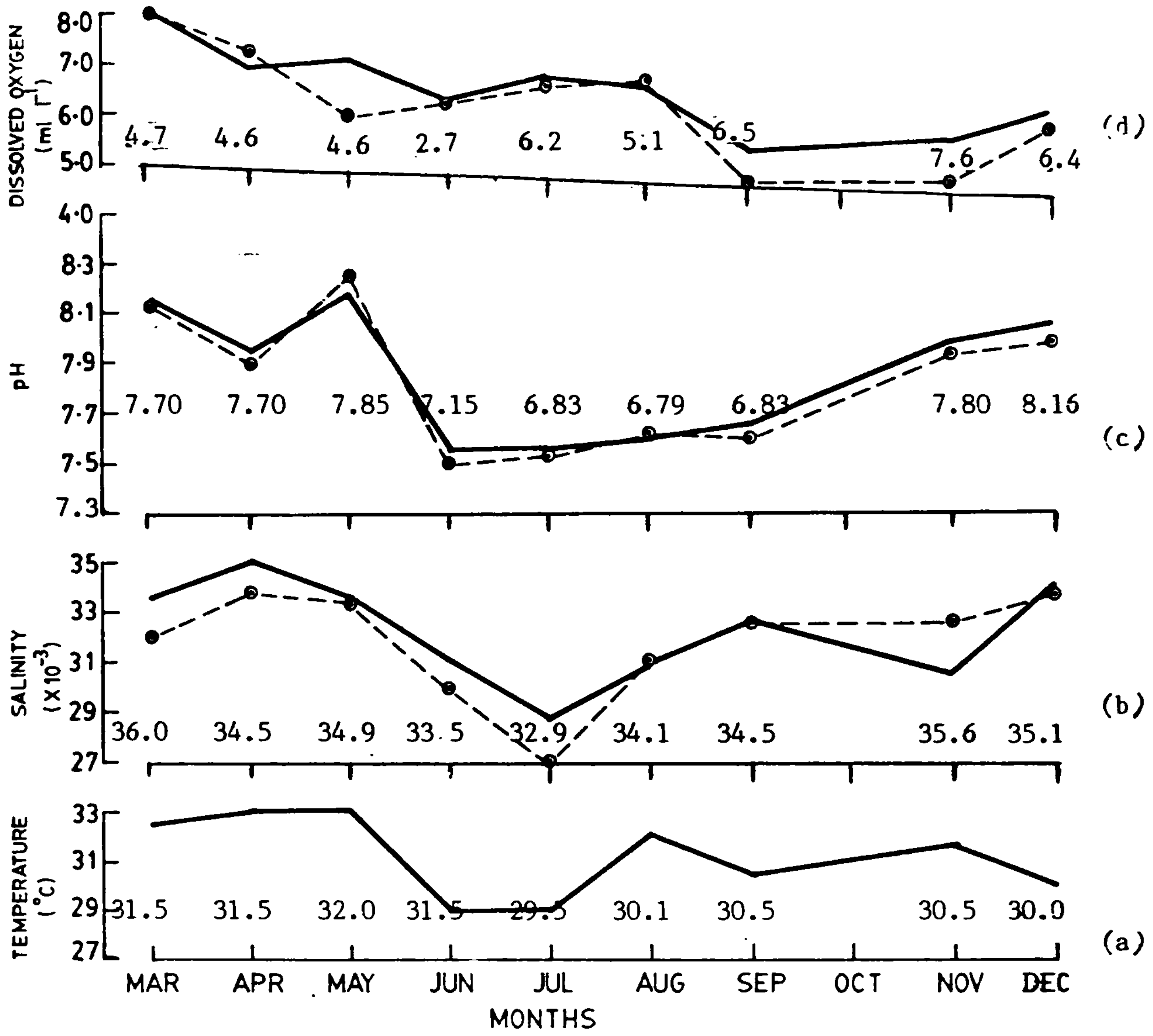

Figure 5. Monthly variation of temperature (a), salinity (b), pH (c) and dissolved oxygen (d) at mid-mudbank area (—— surface, ⊖---⊖ subsurface). The numerical values indicate surface data from non-mudbank area.

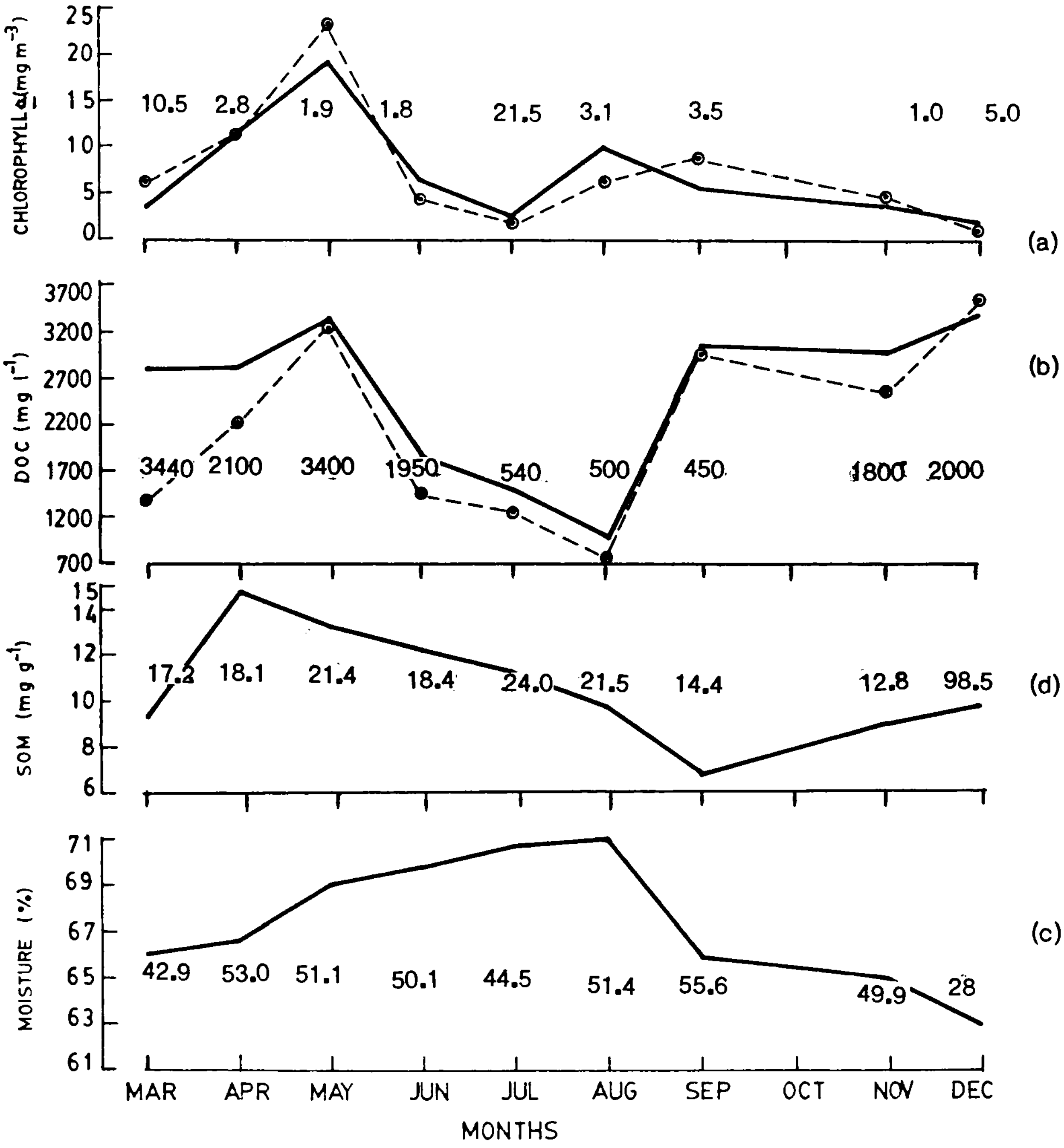

Figure 6. Monthly variation of moisture (c), sediment organic matter (d), dissolved organic carbon (b) and chlorophyll a (a) at mid-mudbank area (——— surface, ⊖———⊖ subsurface). The numerical values indicate surface data from non-mudbank area.

The range of values further seaward fluctuated widely, whereas in the pre- and post- periods the mean values were almost constant; 32.7° to 32.8°C and 30.7° to 30.8°C respectively and in a narrower range of variability. The seasonal variability in the non-mudbank area indicated more fluctuating values, though the general trend was more or less the same as that observed in the mudbank area.

The monthly variation of temperature (Figure 5(a)) in the mid-mudbank region recorded the lowest values in June and July (29°C) and the highest values in April and May (33°C). The non-mudbank area also showed a decrease in temperature in the monsoon months, but the variation is not so prominent.

Nair (1983) observed the temperature variation of the surface waters to be between 29.1°C to 30.8°C which is comparable to that observed in this study. Rao _et al_. (1984) have reported a slight lowering of surface water temperature from 29° to 26°C; Damodaran (1973) recorded that the temperature reaches a minimum of $\approx$27°C in July - August months from a maximum of 30°C in April. The low values observed during the mudbank period may be strongly related to the upwelling in the region. This feature had also been reported by Sastry & D'souza (1972). Further, the combined effect of large influx of land run-off and monsoonal rains account for the lowering in surface temperature values.

Salinity

Figure 3(b) indicates the variability of salinity at both surface and bottom waters and Figure 5(b) shows the monthly distribution of salinity in the mid-mudbank region along with values of non-mudbank area. In general, the bottom salinity was found to be slightly higher than the surface salinity. The salinity in a broader range of minimum and maximum values were observed during mudbank period both at surface and bottom of the mudbank region. (24.3 to 35.5 x 10^{-3} and 26 to 33.9 x 10^{-3} respectively). The surface salinity varied from 31.6 to 35.0 x 10^{-3} and 29.4 to

36.1 x 10^{-3} for pre- and post-mudbank periods respectively, whereas bottom salinities varied from 32.9 to 36.2 x 10^{-3} and 29.8 to 36.1 x 10^{-3} respectively for pre- and post-mudbank periods. The salinity values recorded in the non-mudbank area show distinctly less variability compared to the mudbank region. However, the pre-mudbank values were higher than the mudbank period; the subsequent values recorded during the post-mudbank show moderate values.

In the mid-mudbank region, the highest salinity was observed in April (35 x 10^{-3}) and the lowest in July (27 x 10^{-3}); in the non-mudbank area the highest is in March (36 x 10^{-3}) and the lowest, in July (32.9 x 10^{-3}).

The minimum values in July and maximum values in April was also observed by Nair (1976). The comparatively low salinities of the waters of the mudbank area during the southwest monsoon period indicate the possibility of a flow directed offshore in the mudbank region (Kurup & Varadachari, 1975).

A number of earlier workers have reported varying values of lower salinities in the mudbanks. The lowest surface salinity (24.3 x 10^{-3}) observed in this study was found to be higher than that reported by Kurup (1972) as 8 x 10^{-3} and Kurup & Varadachari (1975) as 19 x 10^{-3} in the surface waters of the nearshore zone during the southwest monsoon period. Varma & Kurup (1969) and Kurup & Varadachari (1975) explained the low salinity values obtained in their study as due to the influx of freshwater or very dilute seawater carried by the rip currents.

Nair (1983) reported the salinity of surface mudbank area waters to range from 20.6 x 10^{-3} to 30.5 x 10^{-3} and that of bottom waters between 22 x 10^{-3} to 32.8 x 10^{-3} during mudbank period. This is in contrast to the results of the present study which show that during the mudbank period the bottom salinity was slightly lower than post- and pre-mudbank periods. This may be a case of instable stratification of short-time scale, produced by turbulance induced mixing. The subterranean channel flow during the southwest monsoon, one of the causes for mudbank formation near Alleppey, (Murthy *et al.*, 1984) may be attributed as a reason for the lower bottom salinities observed during the mudbank period. Rao *et al.* (1984) also observed a similar trend in subsurface waters (lower salinities) during the mudbank season. Since the mudbanks are observed during the period of upwelling on the southwest coast, the reason for low salinity during mudbank period may be associated with the upwelling phenomena which bring about changes in water circulation.

pH

The results of the survey on the pH at surface and bottom waters are given in figure 3(c). It is noted from the figure that generally the mean surface pH was slightly higher than bottom pH. During the pre- and post-mudbank period the mean surface pH values remain constant at offshore survey stations. Fluctuations in the pH values were recorded during mudbank period (7.00 to 7.74 and 7.00 to 7.78 at surface and bottom respectively). Higher values in pH were observed during pre-mudbank period ranging from 7.80 to 8.26 and 7.80 to 8.30 at surface and bottom waters respectively. In the post-mudbank period, the values lie between pre-mudbank and mudbank period values. In the non-mudbank region the pre-mudbank, mudbank and post-mudbank period pH ranged from 7.70 to 7.86, 6.82 to 7.16 and 6.82 to 8.16 respectively. From the figure (5(c)) on monthly variation of surface and bottom pH, in the mid-mudbank region, the lowest values were recorded in June and July ($\approx$ 7.50 to 7.56) and the highest in May (8.26). Correspondingly in the non-mudbank region, August recorded the lowest pH (6.79) and the highest (8.16) was in December. Comparatively, a wider range in the minimum and maximum values were observed during the post-monsoon period in the non-mudbank area (Figure 5(c)).

No earlier work dealing with the seasonal or temporal variations of pH in mudbank regions is available. The pH is an important hydrological feature indicating the level of dissolved carbon dioxide in the water which may in turn reflect the activity of phytoplankton and the level of dissolved oxygen in the sea (Skirrow, 1975). Nair et al. (1984) have recorded high phytoplankton production during the pre-mudbank period in mudbank area. So the excess photosynthetic activity of algae during the pre-mudbank period will result in depletion of the amount of carbon dioxide and hence increase of pH value.

The low pH during the mudbank period may be due to the large influx of run-off associated with monsoon, since the rain/river water has generally a lower pH. Further the biochemical decomposition of organic matter brought to the coastal waters by monsoonal land run-off may increase the carbon dioxide content and subsequently lower the pH.

Though the non-mudbank area retained the same trend in the seasonal variation of pH as in the mudbank regions, considerable reduction in the magnitude of non-mudbank area values were observed. Various factors like high primary production, respiration rate, mineralization processes etc. can alter the pH of the coastal systems interlinked to the changes in oxygen and carbonate concentrations. Natural turbulence with concomitant aeration can also influence the pH, though to a limited extent (Zingde & Desai, 1987).

Dissolved Oxygen

Dissolved oxygen (DO) content at both surface and bottom waters are plotted in Figure 4(a). The dissolved oxygen content of bottom waters were found to be slightly lower than that of surface waters. Pre-mudbank periods recorded the highest values ranging from 6.1 to 8.3 ml l^{-1} and 6.1 to 7.3 ml l^{-1} for surface and bottom waters of mudbank region respectively. In the surface waters, the mean mudbank values at the collection sites were always greater than post-mudbank values. But in bottom water, the post-mudbank values exceeded the mudbank values beyond a distance of 500 m from the shore. Also the dissolved oxygen of bottom waters in pre- and post-mudbank periods showed almost a steady value upto a distance of 3 km offshore. During the mudbank period, both surface and bottom waters exhibit decreasing dissolved oxygen with increasing distances offshore. The seasonal variability in the distribution pattern of dissolved oxygen, during the entire period of study, in the non-mudbank area, was found to be in contrast to that of the mudbank area described above; the post-mudbank period recorded the highest values and the fluctuations between minimum and maximum values of the mudbank period were largely magnified alongwith significantly lower values in the pre-mudbank period in the non-mudbank regions.

Monthly variability of dissolved oxygen in the mid-mudbank region (Figure 5(d)) exhibited minimum and maximum values during November and March respectively, whereas, in the non-mudbank area, the highest values occurred in November and the lowest, in May-June.

The surface replenishment by atmospheric exchange and photosynthetic activity and the sub-surface consumption of oxygen for the oxidation of organic matter make the dissolved oxygen content of surface waters to be slightly greater than that of sub-surface waters. The wind induced surface turbulence may also favour the high oxygen content in surface waters. The southwest coast of India was characterised by the phenomenon of upwelling, the influence of which is more felt in the nearshore and estuarine region by the intrusion of upwelling waters, poor in oxygen content (Banse, 1959; Sankaranarayanan & Qasim, 1969). This upwelling phenomenon during the mudbank period was responsible for the observed depletion of dissolved oxygen in bottom waters. The oxidation of organic compounds in the mudbank region may further reduce the oxygen content of subsurface waters of the mudbank period. The effect appears to be more magnified beyond the mid-mudbank region.

Rao et al.(1984) reported that the mean mudbank region values of the dissolved oxygen at the surface and at the bottom were around 4 ml l^{-1} during pre-mudbank period and decreased to about 3.2 ml l^{-1} during the mudbank season. Rapid reduction in the dissolved oxygen content of the water during post-mudbank period commencing from the mudbank period was attributed to the heavy bloom of the organism, Noctiluca miliaris (Rao et al., 1984). Mathew et al. (1984) observed that the dissolved oxygen of mudbank waters fluctuated from about 0.5 ml l^{-1} to 3.0 ml l^{-1} with a mean value of about 2 ml l^{-1}, indicating the processes of mixing in the mudbanks.

Phytoplankton acts as an important source of oxygen in the sea as a photosynthetic product (Chan, 1965) and thus the dissolved oxygen values may provide a general indication of primary productivity (Mountford, 1969). The high level of dissolved oxygen observed during the pre-mudbank period corresponds to a high degree of photosynthetic activity. Nair et al. (1984) reported the presence of a large population of phytoplankton in the pre-mudbank period. Inspite of the slightly higher temperature and salinity during the pre-mudbank period, the dissolved oxygen content was found to be higher. This may be explained as due to the high rate of primary production, which is inferred from the high chlorophyll a levels observed during this period.

The observed low oxygen content of post-mudbank period may be the net result of low primary production and higher utilization of oxygen for the decay of organic matter in the mudbank areas.

The non-mudbank area exhibited seasonal variability in accordance with the general trend that the solubility of oxygen is inversely proportional to the temperature, of course with slight fluctuations. Unlike the mudbank area, this pattern did not deviate much, since the primary production in the pre-mudbank period and grazing of phytoplankton by zooplankton during the mudbank period were limited.

Chlorophyll *a*

The variations of chlorophyll *a* in the three periods, at both surface and bottom waters are depicted in figure 4(b). The distribution pattern of chlorophyll *a* in the surface waters was very similar to that in the bottom waters; in general, the bottom waters were more enriched with the pigment than the surface waters. It has been noted that there was an appreciable increase in the concentration of chlorophyll *a* offshore of the mid-mudbank region (station 3). The mean mudbank period values (3.0 to 15.7 mg m^{-3}) were greater than post-mudbank period ones but were lower than the pre-mudbank period values except near the shore station, where the values during the mudbank period were the highest. The mean values observed during pre-mudbank period ranged from 2.4 to 20.7 mg m^{-3}. The range between the minimum and maximum values were more pronounced in the post-mudbank period ie. from 1.0 to 23.7 mg m^{-3}. Nearly identical distribution pattern was observed in the non-mudbank area but the fluctuations between the minimum and maximum values were more amplified in the monsoon season.

The monthly variation of chlorophyll *a* (Figure 6(a)) in the mid-mudbank area showed the highest value in May (19.0 surface & 22.5 subsurface mg m^{-3}), and the lowest in December (1.5 mg m^{-3}) whereas in the non-mudbank area, July recorded the maximum value (21.5 mg m^{-3}). and November exhibited the minimum value (1.0 mg m^{-3}).

Jacob & Qasim (1974) discerned that the chlorophyll *a* content in the mudbank period was extremely low, whereas in this study the bottom waters were distinguishable with appreciable amounts of chlorophyll *a*. This indicates the active regeneration of surficial sedimental chlorophyll *a* to the watermedia.

Nair *et al*. (1984) reported two to three fold increase in the values of chlorophyll *a* in regions of mudbank formation during the mudbank period than non-mudbank period and the values observed were ranging from 10 to 33 mg m^{-3} during the mudbank period. This is in contrast to the present observation in which the pre-mudbank period showed the highest values. This observation gives the first indication of the mudbank phytoplankton outburst.

Dissolved Organic Carbon

Dissolved organic carbon (DOC) (figure 4(c)) in the bottom waters were found to be slightly lower than in surface waters, but to be identically distributed at both surface and bottom in mudbank regions. Significant station-wise variability was not observed. Post-mudbank period indicated the highest values (mean values ranging from 3060 to 3400 mg l^{-1}) compared to other periods; the lowest values were recorded during the mudbank period, ranging from 910 to 1720 mg l^{-1}. One of the characteristic features found in the distribution of DOC during mudbank season was the rise in its content in the mid-mudbank region.

In the non-mudbank area, the high DOC values in the pre-mudbank season were followed by comparatively more fluctuating lower post-mudbank values. The monsoonal values, (540 to 770 mg l^{-1}) were lower than the values obtained in the mudbank region at any period.

In the mid-mudbank region (Figure 6(b)), the maximum value (3600 mg l^{-1}) was observed in December 1987 and the minimum (750 mg l^{-1}) in August 1987; the non-mudbank area recorded the highest amount of DOC (3400 mg l^{-1}) in May. August and September values of DOC (450 to 500 mg l^{-1}) were the lowest in the seasonal variability of DOC observed in the non-mudbank area.

Earlier works dealing with dissolved organic carbon studies in mudbank area are scanty, though some reports on sedimental and particulate organic carbon are available. The slightly lower values of DOC observed in the bottom waters may be partially attributed to the phenomenon of upwelling recognised by other workers too

(Banse, 1959; Sastry & D'souza, 1972). In the mudbank regions the suspended materials increase from surface to bottom (Kurup, 1977). Kurup (1977) reported the maximum concentration of suspended solids at the surface as 1200 mg l^{-1} and at the bottom as 1500 mg l^{-1}. The suspended particles act as a good scavenger of the dissolved organic matter and this is partially responsible for the subsurface reduction in values of DOC.

During the mudbank period, the mudbanks are laden with heavy suspension of fine clay (90%) of less than 6 μ size (Jacob & Qasim, 1974). Presence of very fine clay fraction largely increases the available surface area which in turn, increases appreciably the number of adsorption sites. This factor may also account for the lower DOC values obtained during the mudbank period.

The actual concentration of DOC at any instant will depend on the balance between the rate at which dissolved organic carbon is formed by decay, excretion etc. and the rate at which it is removed by decomposition or utilization (Riley & Chester, 1971b). The biologically active mudbank period enhances the removal process, whereas the decay of the organic detritus matter during the post-mudbank period may produce significantly higher amounts of dissolved organic carbon. Eventhough the primary production is higher during the pre-mudbank period, the role of phytoplankton to remove the dissolved organic matter is probably quantitatively far less important than that by bacteria (Wright & Hobbie, 1966).

In the grain size analysis, the percentage of sand in the pre-mudbank period was found to be two to three fold greater than post-mudbank period (Table 1). This largely reduces the retaining (adsorption) capacity of the sediment, further explaining the observed features. The high value of DOC in the mid-bank region is found complemental to the depleted values of sediment organic carbon (discussed hereafter) in the mid-mudbank region during monsoon periods. For the entire west coast and connected backwaters, fairly high production rates during the post-monsoon period were linked to the proportionate availability and replenishment of nutrients (Gupta & Pylee, 1964).

Moisture

Results on water content of sediments is characteristic of mudbank areas (Figure 7(a)). Though the periodic variability was specific (63.6 to 71.7%) at no period the values fall below the content in the non-mudbank area (27.0 to 55.0%). The mudbank area is characterised by the presence of loose and non-rigid surficial sediments showing comparatively more moisture content. In the pre-mudbank period the values upto a distance of 1 km from shore showed lower content than the post-mudbank period, in which the mean value ranges from 62.9 to 71.3%. Further it was noticed that in the stationwise variability figure of moisture content in the pre-mudbank season, comparatively high values were obtained around the mid-mudbank region. In the non-mudbank area, seasonally the moisture content was more randomly distributed. Wider fluctuations in the minimum and maximum values were observed during post-mudbank period.

The monthly variation of moisture content at the mid-mudbank area (Figure 6(c)) showed distinct feature - intermediate values in pre-mudbank period (66.0 to 69.6%), maximized values in mudbank period (69.2 to 71.0%) and marginally reduced values in post-mudbank period (63.0 to 65.6%). Minimum (63%) and maximum (71%) values were recorded during December and August respectively. However in the non-mudbank area, the monthly variation was randomly distributed with high values of $\simeq$55% in September and the low values of around 28% in December, 1987.

Nair (1976) recorded that the water content of mudbank region was unusually high and ranged from 60 to 80%. Damodaran (1973) and Jacob & Qasim (1974) reported similar sediment characteristics from

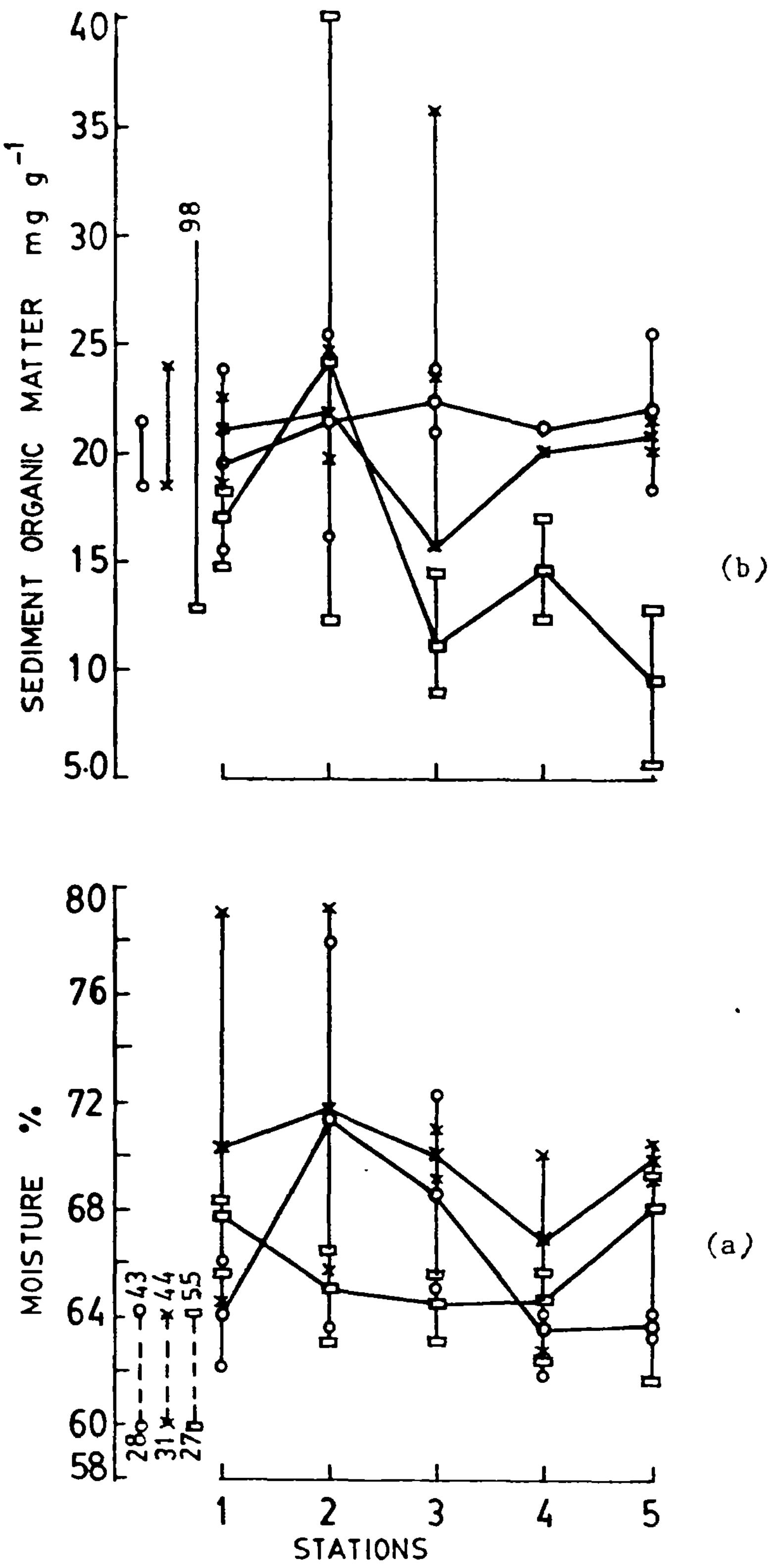

Figure 7. Mean and range of values of moisture (a) and sediment organic matter (b) during pre-mudbank (o——o), mudbank (x——x) and post-mudbank (□——□) periods at stations 1-5; range of surface values of non-mudbank area are given on ordinate.

different banks. Mallik et al. (1988) also suggested the thickening of the upper water clay layer resulting from the mass transport of sediments by southwest or northwest - approaching waves along the coast over shallow depths (1-9 m). According to Varma & Kurup, (1969) when the salinity of the water column increases during the post-mudbank season, the flocculated settlement of mud occurs resulting in the disappearance of mudbank. This settlement of mud flocculates will leave a soft muddy bottom of high moisture content in mudbank area as compared to the non-mudbank area. The spatial complexity better known as "turbidity processes" is largely responsible for the mobile characteristics of the mud and supports prolonged sediment - water interactions during the entire mudbank season; it is suggested that the mudbank formation is due to the stirring up of the already existing bottom sediment in the nearshore region by the action of high waves generated by the pre-monsoon winds (Ducane et al., 1938; Jacob & Qasim, 1974).

Sediment Organic Matter

Sediment organic matter (SOM) has a crucial role as far as a region of "bio-rhythm" like mudbank is concerned. Sediment organic matter potentially influences the biological productivity of the mudbank area.

Seasonal variability of sediment organic matter (SOM) in the mudbank region (Figure 7(b)) shows close resemblance with that of chlorophyll a and dissolved oxygen fluctuations. The highest values observed during pre-mudbank period showed least fluctuations (19.6 to 22.5 mg g^{-1}). In the mudbank period, the values ranged from 16.0 to 21.9 mg g^{-1} with a marginal reduction around the mid-mudbank region. The lowest values observed during the post-mudbank season showed characteristic or significant decrease offshore (16.9 to 8.9 mg g^{-1}). This pattern of seasonal variation was more or less reversed in the non-mudbank area. The post-mudbank values shot up to 98.6 mg g^{-1} with its lowest value of 12.3 mg g^{-1}, compared to the range of the pre-mudbank and the mudbank values of 18.2 to 21.4 and 18.5 to 24.0 mg g^{-1} respectively.

From the monthly variation graph (Figure 6(d)) of sediment organic matter in the mid-mudbank area, April-May values (15.0 mg g^{-1}) occupied the height of a peak decending to low values (7.0 mg g^{-1}) in September, 1987. In the non-mudbank area the lowest (12.8 mg g^{-1}) and highest (98.5 mg g^{-1}) values were observed during November and December, 1987 respectively. Further, the monthly distribution of sediment organic matter showed more fluctuations. The high values observed in the non-mudbank area, of the post-mudbank period is linked to the coastal productivity and the subsequent enhancement in the organic detritus in sediments.

It was illustrated in the discussion of chlorophyll a and dissolved oxygen that high values of these parameters observed were complementary to the high primary productivity reported by many workers in the pre-mudbank period. Jacob & Qasim, (1974) also reported high organic content of the mudbank muds. The observed seasonal variability in the distribution of sediment organic carbon may signal the variability in bioproductivity. Thus there is a close resemblance in the seasonal distribution pattern of chlorophyll a, SOM and dissolved oxygen in the mudbank region and their high values during pre-mudbank period reflecting in higher production.

Since the sediments during the mudbank period is largely composed of very fine clay particles (Table 1), the retaining capacity for organic matter is fairly enhanced evenafter the utilization of an appreciable amount during the pre-mudbank period, a time when the primary production was the highest. As stated in the discussion of dissolved organic carbon, the depletion in the value of sediment organic matter around the mid-mudbank region is counter balanced by the corresponding enrichment of dissolved organic carbon in the mudbank period. Since the central region is an active part of a mudbank - being more productive - the regeneration processes may be enhanced.

From the point of view of finer grain size, the high values of sediment organic matter during the pre-mudbank period is noteworthy. It can be seen from Table 1, that eventhough the sediment of the pre-mudbank period contained an appreciable amount of sand, it was also enriched in (16 to 20%) finer particles having diameter of $<$ 0.001 mm. This may be one of the characteristic features responsible for the prime build up of a biological chain of life in the phenomenon of "mudbank".

Textural characteristics of sediments

Table 1 illustrates the textural characteristics of sediments of the mudbank and the non-mudbank region, collected monthly. The grain size studies were restricted to only few selected months to furnish supplementary data to the hydrochemical parameters discussed earlier.

The sand content gradually decreased from a high of 49.62% in March to a low of $<$1% in July in mudbank region. During the active phase of the mudbank, ie. in June-July the sediments were constituted by a large percentage of particles of diameter $<$0.001 mm (32.31 to 68.65%). In the month of September particles having a diameter of 0.032 mm constituted a major proportion (36.37%) of the sediment which is greater than the amount of sand (12%). In the non-mudbank area the month of March recorded fairly high percentage of particles of smaller diameters.

The grain size distribution observed in this study was found to be well comparable with results of earlier workers. Nair *et al*. (1966) and Dora *et al*. (1968) reported that the dominant component was always clay (45 to 65%) with marginal amounts of silt and very small amounts of sand fraction.

Mallik *et al*. (1988) reported higher values of clay and silt content as 92.6% and 46.5% respectively and that sand was present only in meagre amounts. Nair (1983), Dora *et al*. (1968)

Table 1. Percentage grain size distribution of mudbank sediments

Size fraction	Sand	Silt			Clay		
Month	>0.032 mm	0.032 mm	0.016 mm	0.008 mm	0.004 mm	0.002 mm	<0.001 mm
March 1987	49.62	12.02	9.29	0.98	4.36	6.82	16.91
May 1987	33.73	29.16	2.16	1.87	2.98	9.76	20.34
	35.60	27.36	3.88	0.16	0.32	13.63	19.05
June 1987	2.01	4.22	16.82	5.15	12.36	23.05	36.35
	1.97	8.99	14.30	3.42	15.52	23.49	32.31
July 1987	0.25	3.35	9.46	5.48	2.46	10.35	68.65
	0.73	2.92	10.51	5.79	2.61	11.57	65.87
September 1987	12.67	36.37	6.72	12.35	5.18	3.66	23.05

Contd...2.

Table 1 (Contd...) Percentage grain size distribution of non-mudbank area sediments

Size fraction	Sand	Silt			Clay		
Month	>0.032 mm	0.032 mm	0.016 mm	0.008 mm	0.004 mm	0.002 mm	<0.001 mm
March 1987	5.09	2.51	5.34	8.41	6.05	35.36	37.24
July 1987	57.07	2.24	1.76	1.49	9.78	9.98	17.68
October 1987	9.93	2.54	20.52	3.53	13.38	27.26	22.84

and Shepard (1954) also reported a higher phi median and phi mean (i.e. small grain size) in the mudbank sediments. The mudbank sediments are composed largely of kaolinite with secondary amounts of montmorillonite and illite (Nair, 1976).

Trace metals in the sediments

The concentration of a number of metals (Cd, Zn, Pb, Cu, Cr, Co, Mn, Ni & Fe) have been determined in the sediments collected during selected months from the mudbank and non mudbank area (Table 2).

Concentration of trace metals in the sediments collected at different months do not exhibit any significant features. Nair (1983) also pointed out that the trace element chemistry of the sediments of the mudbank and non-mudbank areas doesn't show much variations.

The observed values of Zn, (20.59 to 119.62 ppm), Co (4.92 to 8.07 ppm) and Ni (17.54 to 49.34) were found to be more or less the same as that reported by Nair (1983) but the values of copper (5.48 to 20.67 ppm) and Cr (16.68 to 55.44 ppm) were found to be lower.

The concentration of Cd, Cr, Co, Mn, Fe and Pb observed in July i.e. during the active phase of the mudbank was found to be slightly greater than those found in other months. Slightly higher values for Zn were reported during March and April (i.e. pre-mudbank period). A notable observation made in the trace metal analysis is the comparatively lower values obtained for all metals, except Fe, in the month of September, i.e. in the post-mudbank period.

In many cases of sediment - metal studies, generally a correlation always exist between metal concentration and particle size (Mehrotra, 1986). From Table 1, it may be noted that the sediments collected during July from mudbank area contained about 65 to 68% of particles of 0.001 mm; this could be an explanation for the higher concentration of Cd, Cr, Co, Mn, Fe and Pb observed in the sediments of that month.

Month	Cd	Zn	Pb	Cu	Cr	Co	Mn	Ni	Fe
March 1987	0.25	93.94	7.45	19.81	22.22	6.19	18.30	49.34	1662.7
May 1987	0.30	119.41	11.70	15.49	19.77	6.23	20.44	43.71	2099.6
	0.32	119.62	12.64	20.62	22.32	5.13	20.79	39.49	2103.3
June 1987	0.32	20.59	11.58	20.67	20.76	5.33	18.32	17.05	1999.9
	0.30	24.15	10.33	15.01	20.21	5.12	18.28	19.49	2099.6
July 1987	0.41	32.00	14.71	6.83	43.17	7.83	21.36	22.90	2130.6
	0.43	49.47	15.76	7.67	48.92	8.07	21.42	32.81	2163.0
	0.42	47.64	15.69	8.73	55.44	7.40	21.50	34.66	2137.9
September 1987	0.30	21.59	10.40	5.48	16.68	4.92	17.41	17.54	2103.0
Non-mudbank (Range: March-September 1987)	0.22-0.41	30-80	5-9	5-8	-	4-7	17-21	15-22	-

Eh

The redox potential may be defined as the level of oxidation or reduction of a reversible system, or as the oxidising or reducing capacity of a given system when compared to a standard potential; it fluctuates between positive and fairly negative values (Plante *et al.*, 1989).

The redox potential values are presented here, taken from the data of the cognate study conducted in the mudbank area during August 1989. The Eh values (mv) are recorded for the mudbank and non-mudbank region, double transects being held in the mudbank region.

Station	Mudbank region		Non-mudbank region
	Transect I	Transect II	
1.	+ 99	+ 103	+ 239
2.	+ 59	+ 99	+ 259
3.	+ 93	+ 110	+ 299
4.	+ 104	+ 98	+ 249
5.	+ 102	+ 101	+ 285

The characteristic features of the Eh values in mudbank region is the significantly lower values as compared to non-mudbank area. The observed Eh values in mudbank region, ranged from +59 to +103 mv, whereas in non-mudbank area it ranged from +239 to +299 mv.

An increase in the input of organic material to the marine environment results in a corresponding decrease in the redox values (Pearson & Stanley, 1979; Plante, 1989). This may explain the feature observed in the data collected from mudbank area and compared with that of non-mudbank area. No definite conclusions are drawn from the above (limited) data set.

Conclusion

The qualitative and quantitative studies on the hydrographical characteristics of mudbanks, under three periods and compared with non-mudbank area highlight many salient features associated with this unique coastal phenomenon; these are concluded hereunder.

Periodwise, the mudbank period indicated lower temperatures than others. The lower values were related to the drop in atmospheric temperature. Generally, the bottom salinity values were slightly higher than that of surface for this coastal region; but in mudbanks, the reverse was observed, indicating instable stratification of short-time scales, produced by turbulence induced mixing. Periodic changes of salinity showed lower values both at surface and bottom during mudbank period, alike to temperature changes in mudbank areas. The salinity values may also be influenced by upwelling processes. Terrestrial run-off is most likely another factor bring about the above changes in addition to precipitation.

Higher values of pH were recorded during the pre-mudbank period, whereas in the post-mudbank period, the pH was between pre-mudbank and mudbank values. The excessive photosynthetic activity observed in the mudbank region during the pre-mudbank period, increases the pH values and the low values of pH during the mudbank period may be due to influx of run-off associated with monsoon, since the rain/ river water has generally a lower pH; also the bio-chemical decomposition of organic matter brought to the coast in monsoonal run-off would influence pH changes.

The surface replenishment from atmospheric transfer accompanied by photosynthetic activity result in the dissolved oxygen content of surface waters to be slightly greater than that of sub-surface waters during all periods in the mudbank area. The oxygen content of sub-surface layers may be regulated more by processes of the oxidation of organic matter. Further, the wind induced surface turbulence favour the occurrence of higher oxygen content in surface waters. Aligned to pH changes, the high level of dissolved oxygen observed during the pre-mudbank period corresponds to a time of higher degree of photosynthetic activity. The upwelling phenomena causing the uplift of oxygen deficient sub-surface waters to upper layers along with the oxidation of organic matter decreased the oxygen content of bottom waters during the mudbank period.

The mudbank period chlorophyll a values were higher than the post-mudbank period values but were lower than the pre-mudbank period in mudbanks. The higher values of chlorophyll a in the pre-mudbank period is associated with higher primary production giving rise to indications of pre-mudbank phytoplankton bloom, more evidently noted in later months. Post-mudbank period contained the highest values of dissolved organic carbon compared to other two periods; the lowest values being recorded during the mudbank period. The concentration of dissolved organic carbon depends on the balance between the rate at which dissolved organic carbon is formed by decay, excretion etc. and the rate at which it is removed by decomposition or utilization (Riley & Chester, 1971b). The biologically active mudbank period enhances the removal processes of dissolved organic matter, whereas the decay of the organic detritus matter during the post-mudbank period significantly increases its amount.

The mudbank area characterized by the presence of loose and non-rigid surficial sediments, shows comparatively more moisture content. The turbidity processes are largely responsible for the turbulent characteristics of the mud and supports prolonged sediment-water interaction during the entire mudbank period. The high percentage of moisture during the mudbank period is also associated with enormous quantities of freshwater, laden with fine suspended load added to nearshore waters during this period as runoff.

The sediment organic matter has a crucial role as far as a region of "bio-rhythm" like mudbank is concerned, since it could potentially influence the biological productivity. Periodic variation of sediment organic matter shows close resemblance with changes of chlorophyll a and dissolved oxygen content—higher values in pre-mudbank period and lower values in post-mudbank period. The higher content of sediment organic matter during the pre-mudbank period is a characteristic feature of the area, an important influencing factor for triggering biological activity in the mudbanks. It follows that finer the clay suspension, higher the retaining capacity for organic material in sediments of mudbanks.

The studies on textural analysis reveal dominant clay composition of sediments in mudbank period with marginal amounts of silt and a very small fraction of sand. The concentration of trace metals in these sediments, seasonally, do not exhibit any significant features or variations. As a general rule, good correlation existed between metal concentration levels and the particle size of sediments.

The above salient features on the hydrographical characteristics of mudbanks reported under three periods viz., pre-mudbank, mudbank and post-mudbank, provide important background information necessary for understanding the biogeochemical cycling of nutrients in mudbanks.

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CHAPTER - 4

HYDROCHEMICAL CHARACTERISTICS - NUTRIENTS

Introduction

Nutrients regulate biological processes by limiting or enhancing organic production in almost all types of aquatic environments (Redfield et al., 1963). The study of nutrients in the dissolved and sedimented form would help in understanding the potential availability of life supporting elements in any particular region of the aquatic system (Klump & Martens, 1981). Nutrients taken up by phytoplankton in relatively large amount for their healthy growth are phosphorus, nitrogen and silicon; they are usually referred to as micronutrients in oceanographic terms because of their low concentration in sea water. The elements such as Fe, Mn, Cu, Zn, Co and Mo are also essential to the growth of phytoplankton, but it is unlikely that phytoplankton growth is ever limited by the "total" concentration of any of these nutrients (Riley & Chester, 1971a).

Since the coastal environment is a multi-dimensional system where the dynamic processes are rarely in equilibrium, the spatial and temporal variation of nutrients are of considerable significance. Quantitative and qualitative studies on nutrients are important for understanding the basic processes governing the distribution and biogeochemical cycling of nutrients. In general, the transformations of biologically essential nutrients depend on internal rates of organic production and subsequent decomposition (Bloesch et al., 1977; Priscu et al., 1986). There is however, an appreciable amount of experimental evidence to indicate that non-biological reactions can also contribute to the control of nutrient distribution (Pomeroy et al., 1965; Burns & Salomon, 1969; Liss & Spencer, 1970; Sholkovitz, 1976; Morris et al., 1981). It is to be noted however, that excessive amounts of nutrients in the aquatic environment may lead to eutrophication. The processes of over-enrichment of water by nutrients and the resultant enhancement in the growth and the decay of aquatic vegetation would lead to the depletion of oxygen. This is one of the most vexing environmental problems in the developed countries of the world (Ryther & Dunstan, 1971).

Studies on various aspects of nutrient chemistry of the marine environment have been reported by many workers. Detailed hydrological surveys of the coastal waters of Hong Kong (China) including nutrients were undertaken by Mok (1973), Watts (1973), Morton & Wu (1975). Sen Gupta & Koroleff (1973) studied the nutrient fractionation of the Baltic sea; more recent work in Baltic was reported by Nedwell et al. (1983). Nehring (1987) studied the temporal variations of phosphate and inorganic nitrogen compounds in Central Baltic waters. Wafar et al. (1983) investigated the nutrients and primary production in permanently well-mixed temperate coastal waters of Morlaix Bay (western English channel). Taft (1984) and Mc Carthy et al. (1984) discussed the nutrient dynamics of Chesapeake Bay and Pilson (1985) studied the annual cycling of nutrients and chlorophyll in Narragansett Bay. A budget of nitrogen recycling in Belgian coast was made by Billen (1978). Priscu & Downes (1985) and Chen et al. (1985) investigated some aspects of nutrient levels in the coastal waters of New Zealand. Diel changes in nitrite concentration in the Gulf of Mexico were recorded by French et al. (1983).

Christensen & Rowe (1984) and Kawase & Sarmiento (1985) have summarised the studies on nutrients in the Atlantic region. The nutrient regeneration studies on the Washington continental shelf was recently published by Christensen et al. (1987). Epifanio et al. (1983) reported the seasonal changes in nutrients and dissolved oxygen on the Pacific coast of Central America.

Dugdale (1972) critically examined the chemical oceanography and primary productivity in upwelling regions. Kokkinakis & Wheeler (1987) studied the nutrient status and phytoplankton growth in coastal upwelling regions of Washington and Oregon. Many investigators reported higher concentrations of nutrients and resultant higher productivity in upwelling areas off the coasts of Peru, Bengula, Oregon & Costa Rica Dome (Dugdale & Goering, 1967; Small & Menzies, 1981; Yoder et al., 1983; Minas et al., 1986; Kokkinakis & Wheeler, 1987). In comparison, the northwest Africa'- upwelling regions usually had high chlorophyll, but low nutrient concentration (Minas et al., 1986; Friederich & Codispoti, 1981; 1987). Codispoti & Christensen (1985) traced the effect of mixing and regeneration on the nutrient content of upwelling waters in eastern tropical south Pacific Ocean. Codispoti et al. (1982) made a comparison of the nutrient regimes off northwest Africa, Peru and Baja California. Eppley et al. (1979) explained the distribution and the role of ammonium in the growth of phytoplankton in southern California coastal waters. The general distribution pattern and concentration of nutrients differs from one ocean to another, since the circulation and exchange of deep water differs from ocean to ocean. Further, the concentration of the nutrients in coastal waters is often higher than in the water further off-shore.

International Indian Ocean Expedition (1962-65) recorded the nutrient data along with other parameters in the Arabian sea and Bay of Bengal (Wooster et al., 1967; Rao & Jayaraman, 1968; Sankaranarayanan & Reddy, 1968; Varadachari et al., 1968). The earlier reports on the nutrient characteristics of Bay of Bengal were made by Jayaraman (1951), LaFond (1957), Ganapati & Sarma (1958), Udayavarma & Reddy (1959), Sankaranarayanan & Reddy (1968), Sen Gupta et al. (1977), Rajendran et al. (1980), De Sousa et al. (1981) and Rao & Satyanarayana (1982). Satyanarayana et al. (1987) reported the nutrient distribution of Bay of Bengal with other oceanographic parameters: the concentration of nitrate, phosphate, and silicate varied in the range not detectable to 6.32, 0.06 to 0.83 and 0.66 to 10.17 µg at l^{-1} (in the surface mixed layer (0-50m)) respectively. The low concentration of nitrate and phosphate at the surface were reported as a result of high primary production. No regular trend with depth in the distribution of NH_3 was obtained in their study and its value ranged from not detectable to 0.72 µg at l^{-1} in the upper 50 m column.

Distribution of phosphates and silicates in the central western north Indian Ocean was reported by Reddy & Sankaranarayanan (1968).

Sen Gupta et al. (1976a) studied the relationship between dissolved oxygen and nutrients in the north-western Indian Ocean. The nutrient fractionation and stoichiometric relationships in the northern and the eastern basin were published by Sen Gupta et al. (1976b). De Sousa & Singbal (1986) presented the relationship of phosphorus and nitrogen compounds with the dissolved oxygen in the water masses of central Arabian sea.

Eventhough considerable work has been done on the distribution of nutrients in the marine waters around the Indian subcontinent there is a paucity of data on the nutrients distribution in the coastal waters which exhibit the phenomenon of mudbank. Earlier works do not present a complete picture of the mudbank nutrient distribution or its seasonal variation except compiling data projecting mostly the concentration of inorganic phosphates only. Seshappa (1953) and Seshappa & Jayaraman (1956) reported high concentration of phosphates in the sediments collected from the mudbank at Calicut. Jacob & Qasim (1974) reported the abnormal behaviour of mudbank sediments. Rao et al. (1984) gave a short account of reactive phosphate, nitrite, nitrate and reactive silicate of the mudbank waters. Nair (1983) and Mallik et al. (1988) also reported the phosphate concentration in mudbank sediments.

The fluvial and sedimentary phases contribute towards the nutrient dynamics of the mudbanks formed in the shallow coastal waters and an integrated study of both the phases can be more informative than the study of these phases in isolation. Moreover, the mudbank is a seasonal phenomenon and studies on seasonal variations in the nutrients are of great importance in their absolute concentration as well as compared seasonally. In the present study reported here, all these aspects had been given due consideration.

Materials and methods

Procedures have been detailed in Chapter 2.

Results and discussion

Surface and bottom waters and sediment samples collected at monthly intervals were analysed for different forms of nitrogen and phosphorus. Silicate was studied only in its dissolved form. The various forms of the nitrogen studied in the aqueous phase were ammonia, urea, nitrite, inorganic and organic nitrate; whereas the forms studied in the sedimental phase included urea and the adsorbed and interstitial forms of nitrite and inorganic and organic nitrate. The amounts of the inorganic and organic forms of phosphates in the watermedia and the adsorbed and interstitial forms of inorganic and organic phosphates in the sediments are also reported as figures and tables respectively. The data obtained were compared with similar observations on samples collected simultaneously from a non-mudbank area, (excluding bottom water samples) plotted as range values on ordinates of respective figures. Figures indicating stations on x-axis are not to scale. The monthly variation graph depicts lines for mudbank area and values for non-mudbank data.

Dissolved silicates

Organisms like diatoms, radiolaria, sponges, flagellates etc. use silicates for their growth and skeletal formation. The flux of particulate silica from surface waters and the subsequent transformations were reported to play important roles in the cycling of other elements such as Ra, Ba and Ge in the marine environment (Li et al., 1973; Froelich & Andreae, 1980). The major features which are responsible for the enrichment of silicate in the marine environment include river transport (Livingstone, 1963), submarine hydrothermal emanations (Wolery & Sleep, 1976; Edmond et al., 1979) and glacial weathering (Warnke, 1970; Hurd, 1973). DeMaster (1981) reported the total flux of dissolved silicate in the marine environment as $6.1 \pm 1.8 \times 10^{14}$g SiO_2 Yr^{-1}. Boyle et al. (1974) suggested that most estuaries and coastal environments however, do not remove a large percentage of the riverine silicate flux. Studies in Cochin estuary indicated that silicon behaves as a conservative element, and its value decreases with increase in salinity (Anirudhan, 1988).

Dissolved concentration of silicate at surface and bottom are shown in figure 8. Generally, the bottom silicate concentration was observed to be slightly greater than the surface concentration observed at off-shore stations 1 to 5. The highest values were recorded during the mudbank period in which the mean values ranged from 31.8 to 57.8 µg at l^{-1}. The range of values during the mudbank period rose to an upper limit of 78.2 µg at l^{-1}. The lowest values observed during the pre-mudbank period showed minimal fluctuations in mean values (16.2 to 23.4 µg at l^{-1}) or in other words, to state that the silicate concentration of the mudbank area during the pre-mudbank period was more or less uniform. The same seasonal trend was also reflected in the non-mudbank area, showing monsoonal high and pre-monsoonal low values.

The seasonal variation in dissolved silicate could be more easily understood from Figure 9(a) in which monthly data from the mid-mudbank station is depicted. The pre-monsoonal months (March and April) were characterised by the lowest concentration. A sharp rise was observed in the silicate concentration as the mudbank period commences (May to June). Rao <u>et al</u>. (1984) also reported high silicate concentration (≈ 35 to 50 µg at l^{-1}) during the mudbank period. The non-mudbank site also exhibited similar trends, though to a lesser extent.

The extensive turbidity during the mudbank period may increase the supply of dissolved silicate by diffusion processes and mixing of bottom water enriched in dissolved silicate. Further, this turbidity processes result in the transfer of previously accumulated nutrients in the sediments as in the case of phosphates (Chapter 5).

Comparatively, higher values of silicate in the bottom layers indicate that the zone of rapid silicate dissolution should occur at the top of the sediment column (DeMaster, 1981; Hurd, 1973; Schink <u>et al</u>., 1974). Yet another source of dissolved silicate could be the pore waters of marine sediment as suggested by Fanning & Pilson

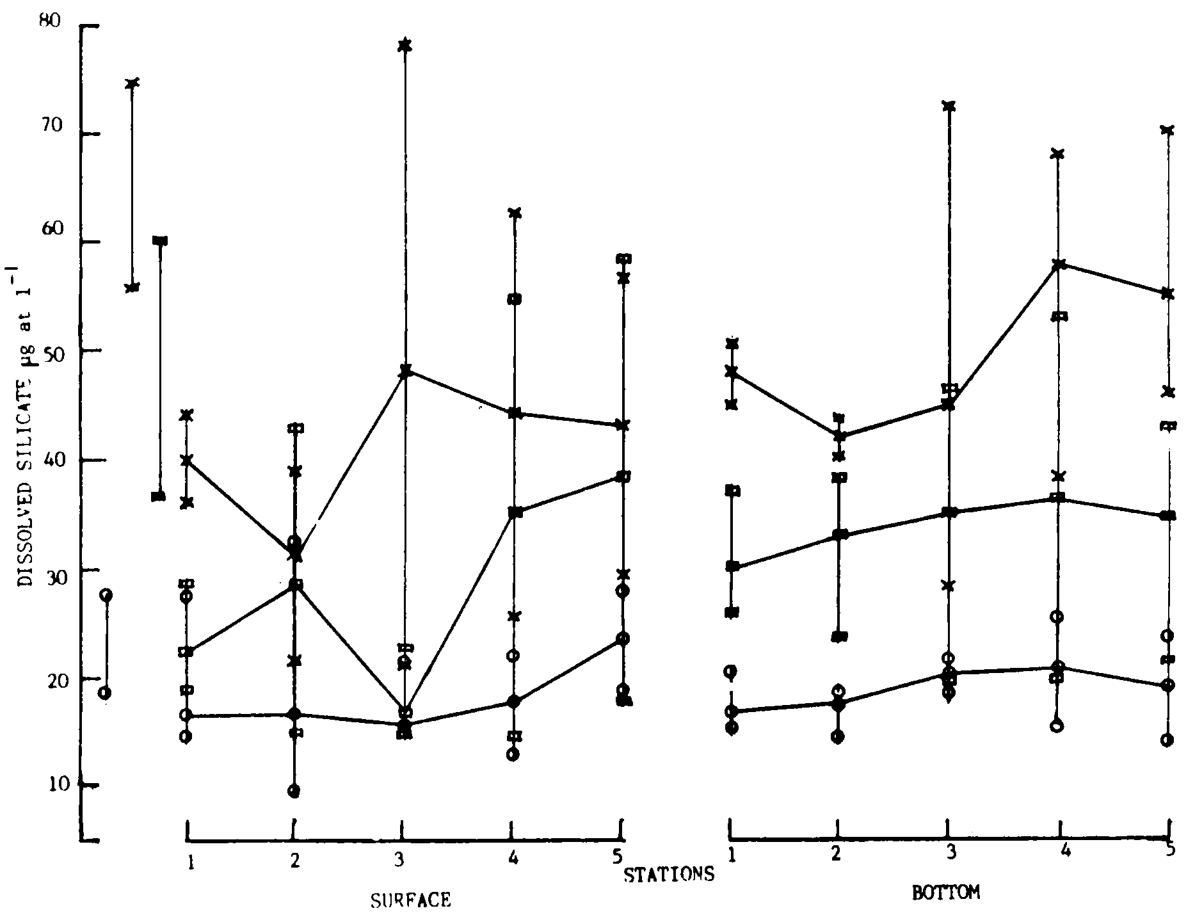

Figure 8. Mean and range values of dissolved silicate during pre-mudbank (O——O), mudbank (x——x) and post-mudbank (□——□) periods at stations 1-5; range of surface values of non-mudbank area are given on ordinate.

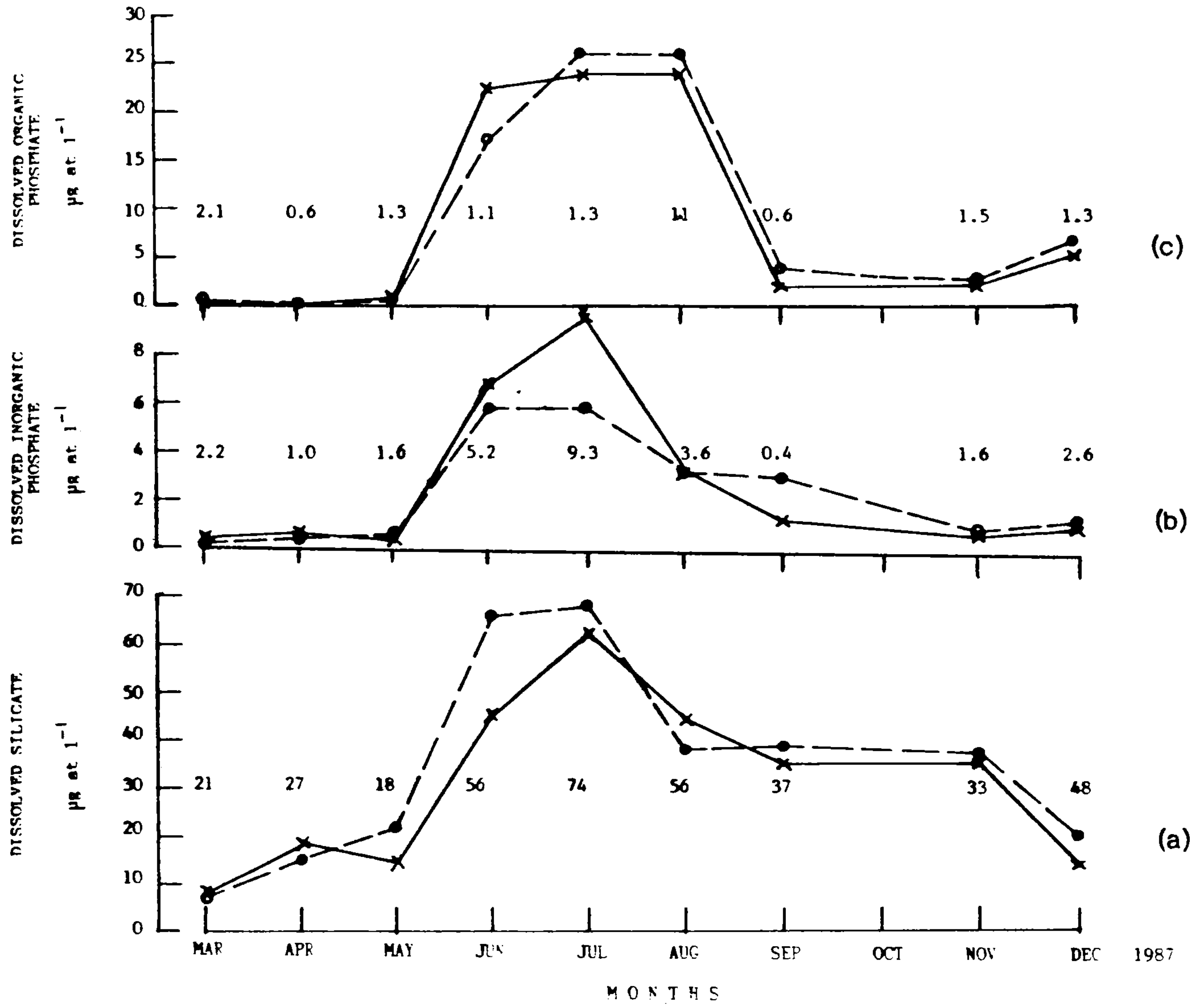

Figure 9. Monthly variation of dissolved silicate (a) and dissolved inorganic (b) and organic (c) phosphate at mid-mudbank area (x——x surface, ●- - -● subsurface). The numerical values indicate surface data for non-mudbank area.

(1973). This possibility is not ruled out, though it was beyond the scope of the present study. The dissolution of silicate from the siliceous organisms may be continuing rapidly during post-mudbank period, which explains the slightly higher dissolved silicate concentration.

This study recorded lowest salinities and highest content of dissolved silicon concentrations during mudbank period. Jones & Folkard (1971) also shows that low salinity coastal waters is related with relatively high silicon values in the eastern Irish sea. DeSousa *et al*. (1981) also reported the loss of silicon during the pre-mudbank period and suggested that biological utilization and abiological removal by adsorption onto suspended sediments may probably be the mechanism of removal.

Nitrogen

The evolution of satisfactory analytical techniques for the determination of some of the forms of nitrogen have recently provided opportunities for the indepth study of the chemistry of these species in seawater (Thayer, 1974). The chemical forms in which nitrogen can exist in seawater are many fold (oxidation states -3 to +5), relative proportions of different forms of nitrogen depend upon the ambient environment and are governed by conditions of temperature, redox (Eh) , pH etc. All the species have significant role in the marine environment; nitrate and nitrite accounts for about 65% of the soluble combined nitrogen (Martin, 1970; Ryther & Dunstan, 1971).

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

In addition to the regeneration and dissolution processes involved in the nutrient cycles of phosphorus and silicon, nitrification, denitrification and fixation processes are also involved in the nitrogen cycle. The biogeochemical cycling of nitrogen is of a complex nature because of varieties of chemical forms (species) in which the nitrogen is available for biological utilization. These aspects are comprehensively discussed in the frame work of the nitrogen cycle by Vaccaro & Ryther (1960).

Ammonia

The surface and bottom distribution of ammonia in the mudbank area is depicted in Figure 10(a); corresponding values for the non-mudbank area are also given in the same figure. Both the mean and range of values of ammonia, during the pre-mudbank period were found to be significantly high except at station 1, near the shore line. The mean values at the stations 2 to 4 ranged from 15.5 to 32.5 µg at l^{-1} during the pre-mudbank period. During the pre-mudbank period the surface concentration is generally higher than bottom except at stations 2 and 4; a steady increase in the value from station 1 to 5 in surface waters during pre-mudbank period is also observed. A significant feature found in the seasonal distribution of ammonia was the almost constant values of both mean and range of ammonia observed during the post-mudbank period ($\lessapprox$5 µg at l^{-1}) along all stations. The increase in concentration of ammonia beyond a distance of 500 m in the pre-mudbank period is more or less reversed in the mudbank period; i.e. there was a decrease in concentration of ammonia after a distance of 500 m during the mudbank period. But from the non-mudbank area, it is not possible to draw such a pattern of seasonal distribution because the upper and lower limit of both pre- and post-mudbank values showed the same magnitude of variation and the monsoonal values ranged from 17.5 to 19.0 µg at l^{-1}.

In the mid-mudbank area (Figure 11(a)) the highest values were recorded during the pre-mudbank months (April and May). From September to December low values of small variation were observed. Thus, the

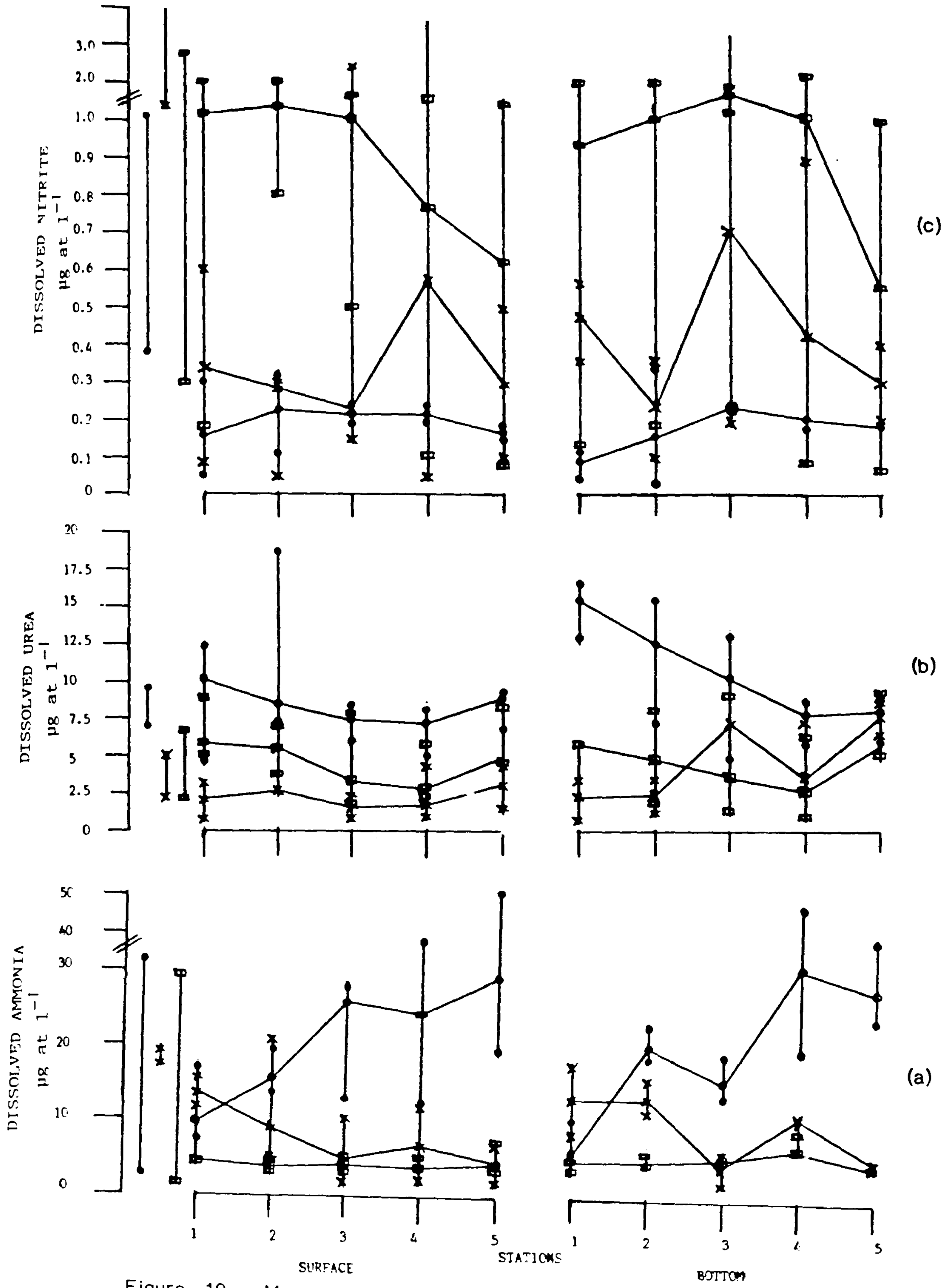

Figure 10. Mean and range of values of dissolved ammonia (a), urea (b) and nitrite (c) during pre-mudbank (●——●), mudbank (x——x) and post-mudbank (⊡——⊡) periods at stations 1-5; range of surface values of non-mudbank area are given

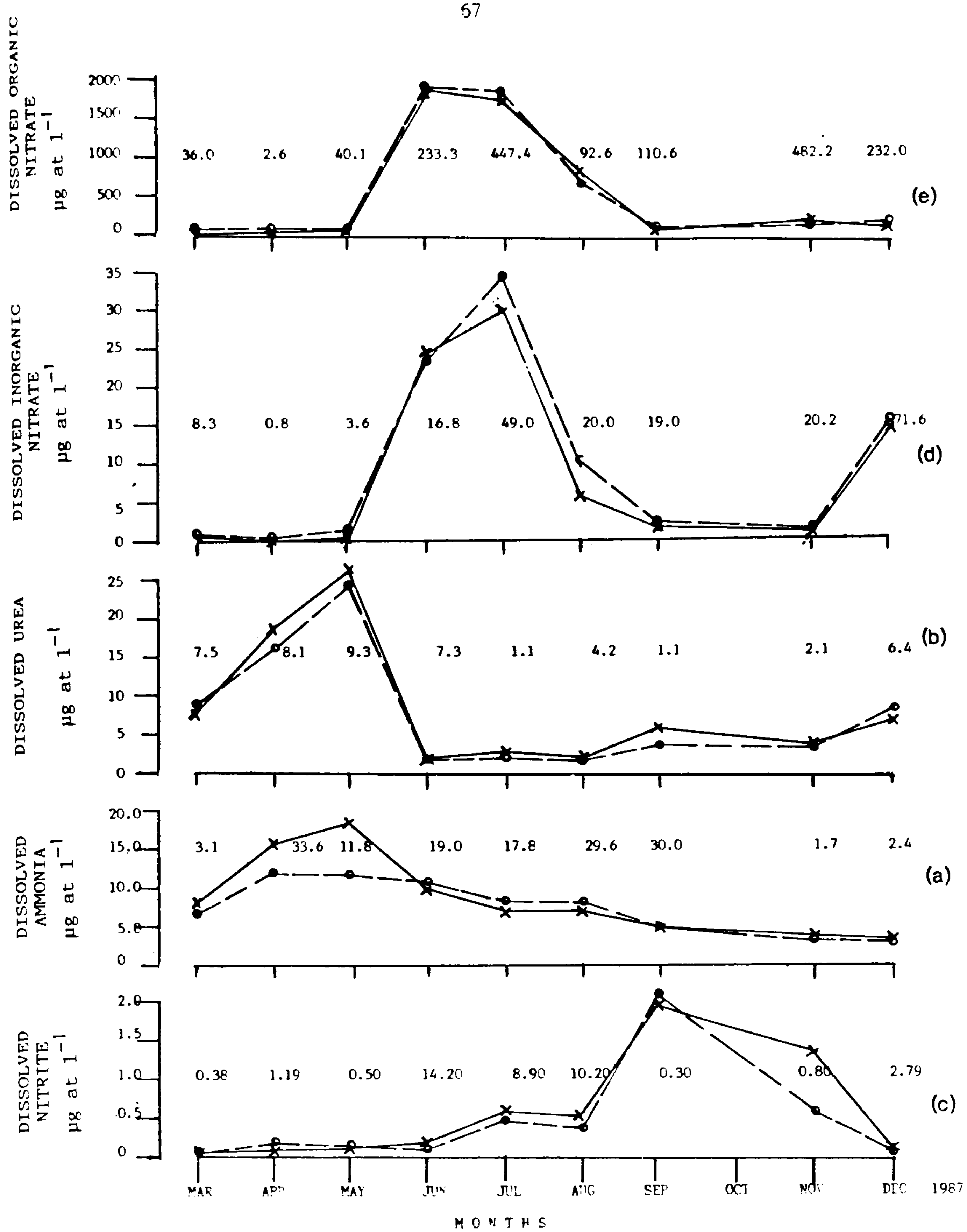

Figure 11. Monthly variation of dissolved nitrite (c) ammonia (a), urea (b) and inorganic (d) and organic (e) nitrate at mid-mudbank area (x——x surface, ●- - - -● subsurface) along with the corresponding non-mudbank area surface values

periodic variability of ammonia in the mud-bank area, there is a steady decrease in ammonia concentration from pre-mudbank period to post-mudbank period. But for the non-mudbank area, no seasonal distinguishable variations were noted.

Reports on the concentration of ammonia in mudbanks are lacking. Among the various forms of nitrogen, ammonia has been shown to exhibit preference for planktonic assimilation; in its presence the utilization of other forms are inhibited (Conway, 1977; Mc Carthy & Taylor, 1977). The higher concentration of ammonia observed during the pre-mudbank period exhibits the balance between the production and utilization, and these reserves might play a vital role for the propagation and growth of phytoplankton at a higher rate which may be the triggering mechanism for the so called "mudbank fishery" or "Chakara".

The higher rate of formation of ammonia may be from organic matter by a complex mechanism involving cell autolysis and microorganism, in the presence of high values of sediment organic carbon and dissolved oxygen during pre-mudbank period. Cline & Richards (1972) suggested microbial assimilation as the major sink for ammonia in the eastern tropical north pacific ocean. But Codispoti & Christensen (1985) and Friederich & Codispoti (1987) explained the ammonia flux in the waters off Peru as the reaction pathways in which ammonia produced during the breakdown of organic nitrogen is denitrified. The depletion of ammonia during post-mudbank period may be associated with the fact that the biological removal is not counter balanced by the ammonification processes.

Urea

Urea or carbamide ($CO(NH_2)_2$) is an organic nitrogen compound of low molecular weight. There is evidence that urea plays an important role as a potential source of nitrogen for primary production (Remsen, 1971). Mitamura & Saijo (1975) reported that urea decomposition associated with photosynthesis by phytoplankton, plays a significant role in the nitrogen supply for phytoplankton in coastal waters. Mc Carthy & Taylor (1977) and Kristiansen (1983) have opined that in coastal waters urea is often used in preference to some inorganic nitrogen forms (NO_2^-, NO_3^- etc), even when inorganic nitrogen concentrations are in excess. The urea assimilation and decomposition by natural phytoplankton have been studied using ^{15}N tracer technique (Eppley et al., 1970; Mc Carthy & Taylor, 1977) and ^{14}C tracer technique (Carpenter et al., 1972; Remsen et al., 1972; Mitamura & Saijo, 1980). These studies indicated that urea is a significant "nitrogen - source - nutrient" for phytoplankton.

Dissolved form

The surface and bottom distribution of urea in dissolved form is shown in Figure 10(b). The pre-mudbank values were the highest in the seasonal distribution of urea at surface and bottom (mean values ranged from 7.2 to 16.0 µg at l^{-1}). During the pre-mudbank period, the concentration of urea decreased steadily from the shore (16.0 µg at l^{-1}) up to the station 4 (8.0 µg at l^{-1}) in bottom waters; its range of values also showed the above characteristic distributional pattern. A similar trend was observed during post-mudbank period also. From the seasonal distribution of urea, the lowest values ($\simeq$ 1.5 µg at l^{-1}) were recorded during mudbank period, but in the bottom waters, the urea concentration increased above post-mudbank value after a distance of 500 m (3.7 - 7.5 µg at l^{-1}).

The monthly variation graph (Figure 11(b)) shows the highest and lowest values in the mid-mudbank area during May and August respectively. A nearly steady value (2.5 µg at l^{-1}) was observed during the mudbank period (June - August). The non-mudbank area did not show such a pattern of distributional characteristics of dissolved urea either of periodic nature (Figure 10(b)) or monthly variation (Figure 11(c)), except slightly higher values recorded during the pre-mudbank period.

Sediment associated form

The distribution of urea in the sediments are shown in the Table 3. The seasonal trend was found to be more or less the same as the dissolved urea variation; the highest values were again observed during the pre-mudbank period. The post-and mudbank period values were found to be in close proximity so that seasonal variation among these values could not be differentiated well. In contrast to the mudbank urea and also the distribution of dissolved urea in the non-mudbank area, the sedimental urea concentration in the non-mudbank area was found to be lower during pre-mudbank period.

From the monthly variation graph (Figure 12(a)), the highest values of sedimental urea in mudbank region were recorded during April and May, whereas the lowest values during September-November. In sediments, urea showed a steady low value (≈ 0.2 µg at g^{-1}) during the mudbank and the post-mudbank months. In the non-mudbank area the month of August recorded the highest value of sediment urea.

Similar to the variations in ammonia concentration, one of the characteristic features found in the distribution of urea is the pre-mudbank period high values. It was also observed that in the seasonal distribution of nitrite (NO_2^-) and nitrate (NO_3^-) (discussed later), the pre-mudbank values recorded were the lowest of all seasons. Sen Gupta & Koroleff (1973) suggested that in the absence of inorganic nitrogen, the organisms may satisfy their need by assimilating and regenerating, nitrogenous compounds from organic forms including urea nitrogen. This may be explained as the observed increase in urea concentration and the corresponding depletion in NO_2^- and NO_3^- during pre-mudbank period due to phytoplankton preferentially assimilating NO_2^- or NO_3^- instead of urea.

There is no earlier work dealing with the urea content in the mudbank area; Verlencar (1980) had reported the distribution of urea in the waters of the west coast of India, the values (0.3 to 7.76 µg at l^{-1}) are comparable to the results of this work. Remsen (1971) reported that in coastal marine areas, affected by pollution or upwelling,

Table 3. Stationwise variation of sediment nutrients (μg at g^{-1}) during three periods (NMA - non-mudbank area)

Sl. No.	Parameter	Station	Pre-mudbank period		Mudbank period		Post-mudbank period	
			Mean	Range	Mean	Range	Mean	Range
1.	UREA	1	0.22	0.16-0.58	0.28	0.21-0.59	0.23	0.03-0.43
		2	0.75	0.25-1.26	0.17	0.13-0.22	0.19	0.09-0.35
		3	0.31	0.18-0.35	0.25	0.12-0.51	0.23	0.07-0.39
		4	0.75	0.51-0.90	0.28	0.26-0.29	0.28	0.08-0.41
		5	0.55	0.40-0.70	0.15	0.11-0.16	0.15	0.11-0.22
		NMA		0.08-0.16		0.04-0.40		0.10-0.38
2.	NITRITE-ADSORBED	1	0.16	0.12-0.25	0.36	0.23-0.48	0.24	0.08-0.34
		2	0.15	0.10-0.25	0.30	0.25-0.37	0.25	0.16-0.43
		3	0.25	0.23-0.27	0.30	0.24-0.35	0.30	0.13-0.41
		4	0.30	0.25-0.38	0.41	0.36-0.43	0.32	0.23-0.33
		5	0.20	0.16-0.21	0.32	0.32-0.35	0.28	0.12-0.37
		NMA		0.05-0.41		0.19-0.38		0.20-0.31
3.	NITRITE-INTERSTITIAL	1	0.07	0.05-0.08	0.15	0.07-0.23	0.38	0.07-0.76
		2	0.05	0.03-0.09	0.12	0.05-0.14	0.30	0.16-0.58
		3	0.07	0.06-0.07	0.11	0.08-0.31	0.34	0.16-0.71
		4	0.11	0.07-0.11	0.12	0.12-0.13	0.28	0.07-0.52
		5	0.05	0.03-0.05	0.10	0.09-0.15	0.51	0.17-0.70
		NMA		0.02-0.11		0.01-0.04		0.05-0.40

Table 3 Contd...

Sl. No.	Parameter	Station	Pre-mudbank period		Mudbank period		Post-mudbank period	
			Mean	Range	Mean	Range	Mean	Range
4.	NITRATE-INORGANIC ADSORBED	1	0.20	0.16-0.38	77.8	7.15-167.40	2.22	0.16-6.25
		2	0.27	0.20-0.33	42.27	8.89-81.13	3.20	0.15-7.26
		3	0.35	0.25-0.44	26.31	7.53-62.79	2.75	2.00-7.46
		4	0.23	0.13-0.26	20.0	10.72-32.00	2.11	0.13-5.87
		5	0.27	0.10-0.30	22.0	6.55-38.00	0.40	0.11-11.63
		NMA		0.03-0.88		2.53-9.54		0.49-9.91
5.	NITRATE-INORGANIC INTERSTITIAL	1	0.25	0.10-0.34	24.05	3.84-47.27	7.31	2.14-19.70
		2	0.16	0.01-0.21	21.38	2.52-46.10	3.23	1.14-8.52
		3	0.22	0.04-0.29	18.09	6.46-45.89	6.77	2.06-18.24
		4	0.17	0.16-0.18	16.00	2.39-30.00	8.27	3.20-21.60
		5	0.27	0.24-0.27	16.50	13.45-16.90	6.83	2.35-18.13
		NMA		0.03-0.88		1.25-1.37		0.55-7.57
6.	NITRATE - ORGANIC ADSORBED	1	0.26	0.23-0.29	13.2	7.16-17.14	6.29	2.71-9.94
		2	0.37	0.22-0.49	10.1	9.17-11.04	7.17	1.12-11.61
		3	0.70	0.17-0.90	8.4	6.83-11.60	6.00	2.2-13.64
		4	0.52	0.24-0.78	6.0	5.00-8.00	3.87	1.83-7.11
		5	0.50	0.10-0.80	5.9	5.00-8.10	5.71	1.20-9.45
		NMA		0.09-0.50		9.10-11.57		8.47-17.00
7.	NITRATE - ORGANIC INTERSTITIAL	1	3.15	1.14-4.70	203.2	124.8-410.6	37.72	5.81-102.02
		2	2.95	1.21-3.95	200.0	123.8-439.8	35.99	4.61-93.31
		3	4.50	2.71-5.87	163.1	106.8-436.2	32.05	5.34-84.37
		4	4.23	4.10-4.34	185.0	130.1-450.0	37.88	5.96-100.75
		5	3.90	3.60-4.30	175.0	115.0-200.0	31.46	5.09-84.07
		NMA		0.09-6.17		13.63-98.47		5.81-218.60

Table 3 Contd...

Sl. No.	Parameter	Station	Pre-mudbank period		Mudbank period		Post-mudbank period	
			Mean	Range	Mean	Range	Mean	Range
8.	PHOSPHATE-INORGANIC ADSORBED	1	1.09	0.68-1.47	14.83	1.97-47.68	1.35	0.67-1.54
		2	1.05	0.97-1.39	15.06	1.12-49.20	1.40	0.90-1.68
		3	0.75	0.42-0.88	16.20	1.99-41.25	1.38	0.81-1.88
		4	1.25	1.08-1.43	20.00	9.80-22.00	1.39	1.05-1.67
		5	1.10	0.68-1.32	13.00	8.20-15.00	1.60	0.60-1.95
		NMA		1.09-7.93		2.51-12.61		0.90-2.03
9.	PHOSPHATE-INORGANIC INTERSTITIAL	1	0.35	0.24-0.59	3.47	0.49-11.50	0.38	0.23-0.65
		2	0.33	0.11-0.69	2.72	0.41-8.21	0.30	0.22-0.37
		3	0.20	0.18-0.22	4.08	0.54-10.52	0.26	0.23-0.39
		4	0.22	0.20-0.24	5.70	1.95-8.00	0.35	0.30-0.39
		5	0.17	0.16-0.21	4.40	2.40-8.24	0.29	0.13-0.41
		NMA		0.21-0.39		0.12-0.37		0.007-0.366
10.	PHOSPHATE-ORGANIC ADSORBED	1	1.64	0.06-3.88	26.68	21.57-78.82	0.48	0.18-0.75
		2	2.91	2.87-2.96	62.36	59.36-65.36	0.66	0.20-1.52
		3	0.08	0.06-0.10	12.32	9.50-31.97	0.57	0.26-0.84
		4	0.99	0.22-1.77	24.00	22.10-24.60	0.22	0.20-0.55
		5	0.31	0.18-0.36	24.00	10.00-27.30	0.27	0.05-0.43
		NMA		0.49-7.33		0.93-2.53		0.4 -0.80
11.	PHOSPHATE-ORGANIC INTERSTITIAL	1	0.82	0.04-2.15	12.87	11.99-17.26	0.10	0.02-0.15
		2	1.42	1.30-2.56	11.15	8.10-12.92	0.22	0.15-0.24
		3	0.05	0.03-0.06	9.00	7.50-13.94	0.03	0.01-0.04
		4	0.06	0.05-0.08	12.50	11.00-12.90	0.03	0.02-0.05
		5	0.19	0.09-0.22	13.00	9.10-15.00	0.18	0.11-0.25
		NMA		0.01-1.73		0.08-0.19		0.03-0.28

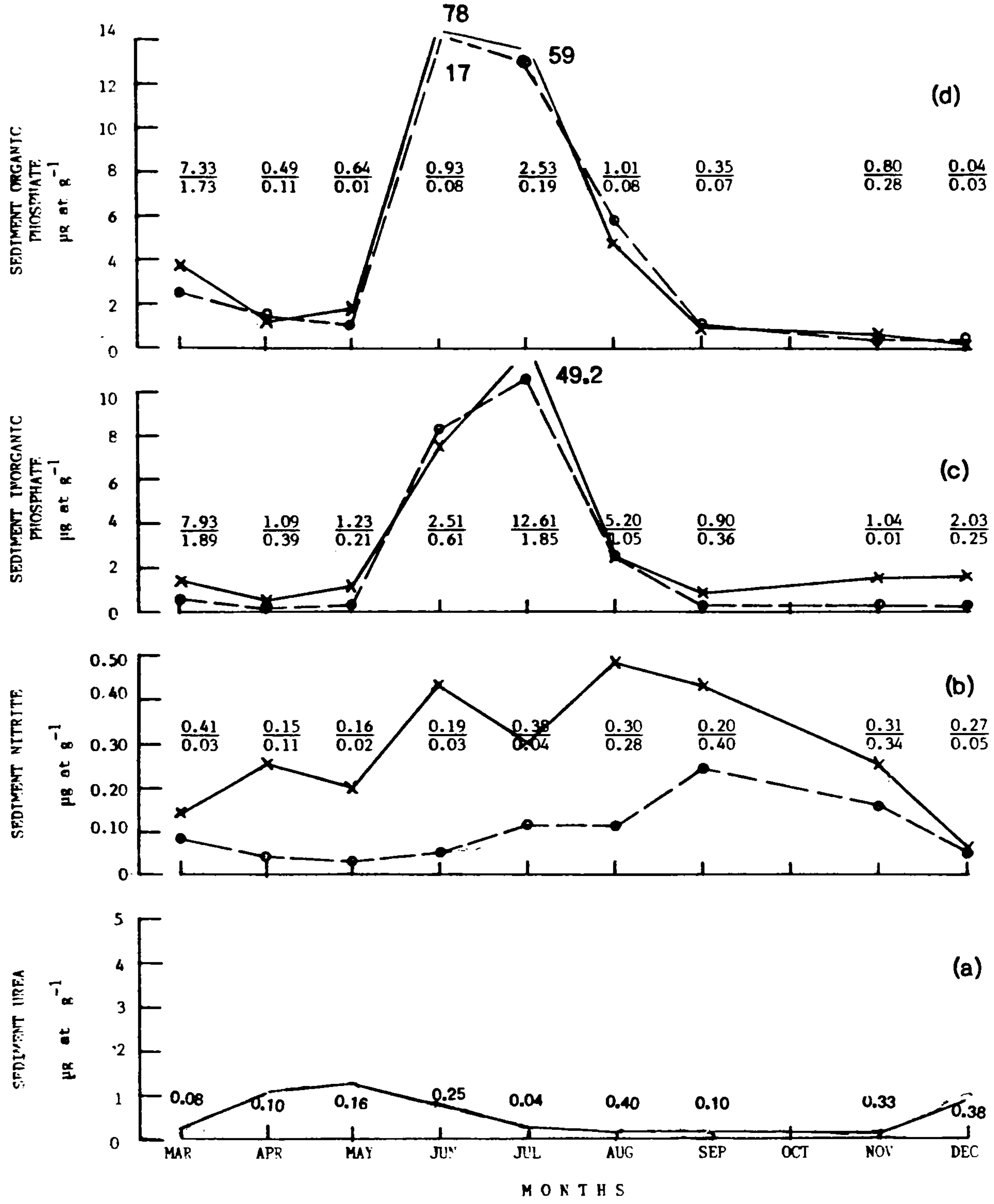

Figure 12. Monthly variation of sediment urea (a), nitrite (b) and inorganic(c) and organic(d) phosphates at mud-mudbank area (x——x adsorbed, ●- - -● interstitial) along with the corresponding non-mudbank area values (top - adsorbed, bottom - interstitial).

urea constitutes between 15 and 72% of the available nitrogen compounds and some species of phytoplankton can satisfy their need for nitrogen by assimilating it as urea. Since upwelling in the mudbank area has been already reported (Ramasastry & Myrland, 1959) the high values of urea during pre-mudbank period is substantiated from the above postulation; further investigations are required to ascertain the quantity of urea that would be assimilated by phytoplankton in the mudbank area.

The higher concentration of urea in the nearshore waters and its decrease in concentration in off-shore waters (especially dissolved form of urea) indicates that urea is recycled rapidly as suggested by Remsen (1971), Mc Carthy (1972), Kristiansen (1983) and Kaufman _et al_. (1983). They also found urea in significant quantities in the euphotic zone of most coastal regions of temperate and tropical oceans. Further, like ammonia which produce through regeneration processes, urea is also a product of the regeneration by heterotrophs (Remsen _et al_., 1972). The human pollution as a source of urea in natural coastal waters is not completely ruled out.

In general, the high concentration of urea observed just before the formation of mudbank signifies the availability of nutrient stored in different forms of nitrogen as a reservoir for later assimilation for the efficient growth of phytoplankton. The concentration of urea in the coastal upwelling regions of Oregon and Washington ($\approx$0.16 µg at l^{-1}) reported by Kokkinakis & Wheeler (1987) and off Peru (0.4 µg at l^{-1}) reported by Friederich & Codispoti (1987) is lower than those observed in the present study. The presence of urea in the waters off the continental shelf between Panama and Callo, Peru were studied and the data suggests that urea may be acting as available source of nitrogen for phytoplankton growth (Remsen, 1971).

Nitrite

Nitrite is formed as an intermediate in the oxidation of ammonia to nitrate or in the reduction of nitrate. The factors which influence the availability of various forms of nitrogen for biotic uptake is most important which inturn depends upon the concentration of the particular species of nitrogen. The nitrite is usually present in lower concentrations in the sea than the other forms of combined inorganic nitrogen.

Dissolved form

Figure 10(c) shows the surface and bottom distribution of nitrite. No significant difference in the concentration of NO_2^- was observed in the surface and bottom distribution of nitrite in the three periods. The high values odserved during the post-mudbank period decreased as the distance from the shore increased ($\approx$ 1.19 to 0.54 µg at l^{-1}). During the pre-mudbank period, nitrite values are more or less uniformly low throughout (0.09 to 0.23 µg at l^{-1}).

A nitrite maxima was observed during the mudbank period around the mid-mudbank region both in surface and bottom waters (0.57 and 0.70 µg at l^{-1} respectively). A wide fluctuation in the minimum and maximum values was observed during post-mudbank period; more specifically the upper limit of the range of values shows a steady decrease with increasing distance from the shore. One notable feature in the seasonal distribution of nitrite in the non-mudbank area is the significantly higher values observed during the mudbank period (1.40 to 8.90 µg at l^{-1}). The pre-and post-mudbank period values recorded were 0.38 to 1.19 and 0.30 to 2.79 µg at l^{-1} respectively.

September recorded the highest ($\approx$ 2.1 µg at l^{-1}) and March recorded the lowest (0.05 µg at l^{-1}) values in the mid-mudbank area, while in the non-mudbank area June (14.20 µg at l^{-1}) and September (0.30 µg at l^{-1}) marked the highest and lowest values respectively (Figure 11(c)). From March to June, almost steady low values were noted in mudbank area.

Sediment associated form

The distribution of adsorbed and interstitial forms of NO_2^- during the three periods are shown in Table 3. The values of absorbed nitrite during mudbank period (mean values ranged from 0.30 to 0.41 µg at g^{-1}) were noticeably higher than those of other periods. This is the only difference observed in the seasonal distribution of sedimental nitrite to that of dissolved. The two forms of nitrite show a maxima during all the three periods; of the two, adsorbed nitrite distribution feature is more clearly pictured. The adsorbed nitrite concentration during mudbank and pre-mudbank period were (0.30 to 0.41 and 0.15 to 0.30 µg at g^{-1} respectively) higher than those of interstitial nitrite (0.10 to 0.15 and 0.05 to 0.11 µg at g^{-1} respectively). Though the minimum and maximum values of interstitial nitrite varied in a wide range during post-mudbank period, the average values were found to be slightly greater than those of adsorbed nitrite. The upper limit of the range of values also indicated a nitrite maxima in most cases. For the non-mudbank area season-wise distinguishable variations were not clearly noted. However, the mudbank period values lie between those of post and pre-mudbank periods.

The monthly variation of adsorbed and interstitial form of nitrite are shown in Figure 12 (b). August and September indicated the maximum concentration of adsorbed and interstitial forms of nitrite respectively. The adsorbed form of NO_2^- was subjected to a greater degree of monthly fluctuations from May to August. A steady decrease in the concentration of both the forms of sedimental nitrite were noted from September to December. In non-mudbank area, March and September recorded the higher concentrations of the adsorbed and interstitial forms of nitrite respectively.

The values of dissolved NO_2^- reported by Mathew <u>et</u> <u>al</u>. (1984) were found in good agreement with the present values, though there are deviations in the seasonal trends. They observed higher concentration of nitrite in the water media during the mudbank period. But in this study both the dissolved and sedimented forms of nitrite recorded higher concentration during post-mudbank period except the adsorbed form of nitrite in sediment, which shows higher values in mudbank period.

The highest values of ammonia and urea and the lowest values of all forms of nitrite (dissolved/sedimented) during pre-mudbank period indicate that the oxidation of ammonia is taking place only to a limited extent. Naturally, the intermediate product of nitrite is low in concentration. The gradual increase in the nitrification processes during the succeeding seasons is reflected in the corresponding increase in NO_2^- and NO_3^- concentration. But the nitrification process appears to slacken the NO_2^- to NO_3^- conversion, so that the intermediate product (i.e., NO_2^-) has an appreciable concentration compared to NO_3^- . This explains the higher concentration of nitrite obtained during the post-mudbank period. In short the nitrification - denitrification processes account for the observed variability in nitrite concentrations. Codispoti & Christensen (1985) also suggested the nitrification - denitrification couple to explain the fluxes of various forms of nitrogen in the upwelling regions of south Pacific ocean; Friederich & Codispoti (1987) applied the above concept for regions off Peru.

During the active phase of the mudbank (i.e. in the mudbank period) the dissolved nitrite maxima obtained near the mid-mudbank region coincided with the corresponding depletion of ammonia indicating the process of nitrification to proceed at a higher rate. Occurrence of nitrite maxima in the ocean has been thought to result from either ammonia oxidation by chemoautotropic bacteria (Brandhorst, 1969; Olson, 1981; Ward et al., 1982) or zooplankton excretion during assimilation and reduction of nitrate (Vaccaro & Ryther, 1960). The dissolved oxygen concentration cannot be taken as a tool to explain the seasonal distribution pattern of nitrite, since the study was confined to coastal area; the water is highly oxygenated in all seasons, though it showed a seasonal distribution pattern of small magnitude of variation in its value. Under such a well oxygenated condition, nitrification may be more relevant than the reduction of nitrate. A slightly higher concentration of nitrite during the mudbank period in the non-mudbank area is an indication of varying bio-chemical processes and physical factors such as diffusion and advection (Wada & Hattori, 1971) taking place in the coastal area.

The close similarity in the distribution of nitrite in water and sediment indicated two simple processes in operation, either that the nitrite is being produced in the water column by bacterial oxidation of the ammonia or that the nitrite is being generated within the sediment and released concurrently with ammonia (Knox et al., 1986). The nitrite concentrations in the upwelling regions of Washington and Oregon (Kokkinakis & Wheeler, 1987) is more or less the same as observed in the present work. Barber & Huyer (1979) suggests that off Peru high nitrite concentrations occur in a static stability minimum. Similar results were also reported in the north eastern tropical Pacific by Garfield et al. (1983). Friederich & Codispoti (1987) reported a maximum nitrite concentration of 4.5 µg at l^{-1}. All these studies, including the present one, is an indication of the interplay of an appreciable amount of nitrites in coastal upwelling areas.

Nitrate

Nitrate is the most abundant and thermodynamically the most stable form of combined inorganic nitrogen in well oxygenated sea water. Further nitrate is the final oxidation product of nitrogen compounds in sea water. In sea water, nitrate is considered to be the micro-nutrient controlling primary production in the euphotic surface layers; concentration in these layers is governed by the advective transport of nitrate into the surface layer, the microbial oxidation of ammonia and the uptake by primary producers (Grasshoff, 1983d).

Dissolved form

The surface and bottom distribution of inorganic nitrate are shown in Figure 13(a) and that of organic nitrate in Figure 13(b).

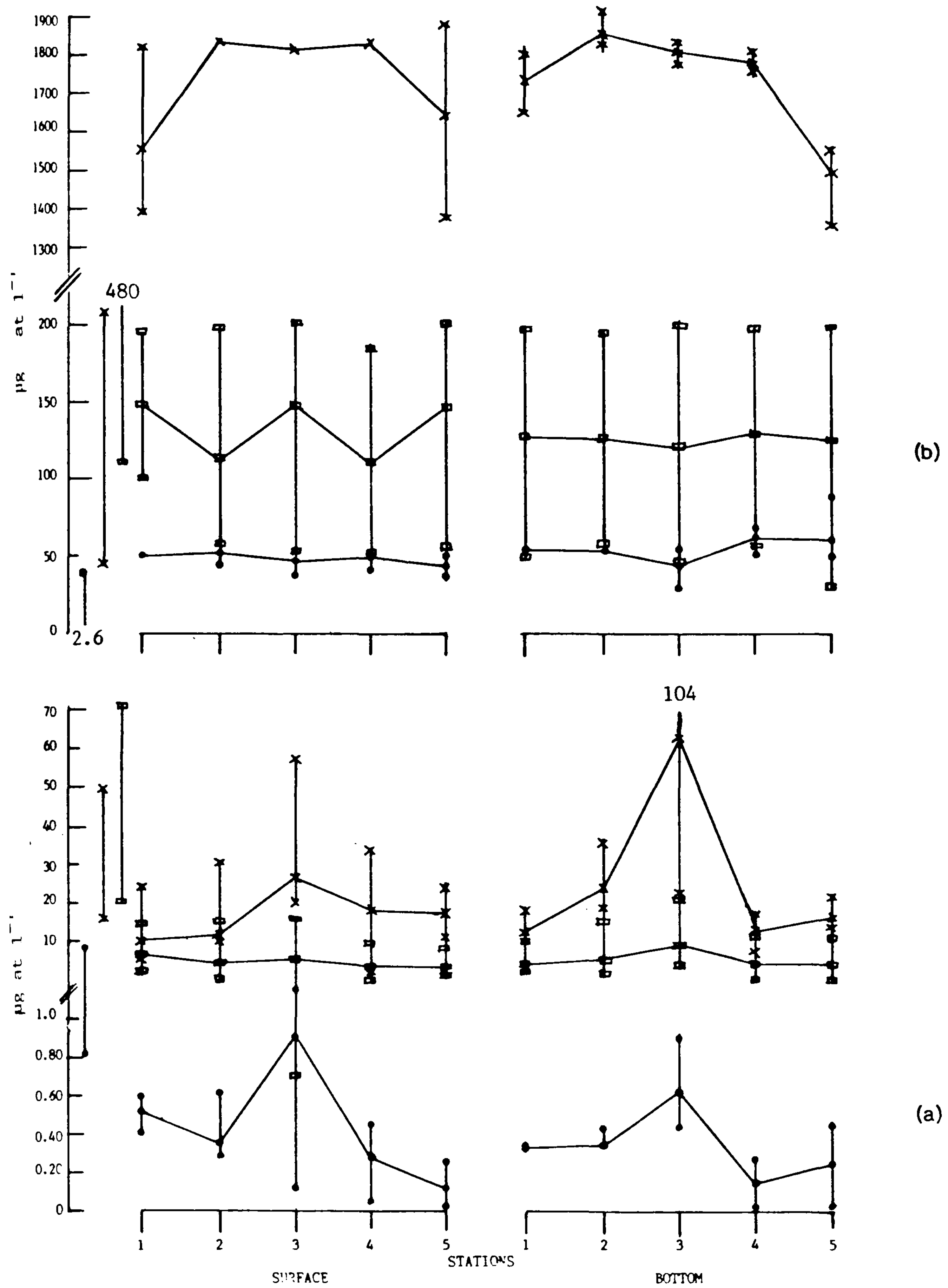

Figure 13. Mean and range of values of dissolved inorganic (a) and organic (b) nitrate during pre-mudbank (●——●), mudbank (×——×) and post-mudbank (▯——▯) periods at stations 1-5; range of surface values of non-mudbank area are given

The corresponding values of the surface waters of the non-mudbank area are also shown in the respective figures.

Similar patterns of seasonal distribution was observed for both inorganic and organic forms irrespective of surface or bottom values. The inorganic nitrate mean values ranged between 0.13 and 62.85 µg at l^{-1} in the three periods but the corresponding organic nitrate values were observed to be exceedingly high, ranging from 43 to 1860 µg at l^{-1}. In both cases, the high values were observed during mudbank period (10 to 62 µg at l^{-1} for inorganic NO_3^- and 1550 to 1840 µg at l^{-1} for organic NO_3^-) and the lowest during pre-mudbank period (0.13 to 0.91 µg at l^{-1} for inorganic NO_3^- and 43 to 63 µg at l^{-1} for organic NO_3^-).

A striking feature in the distribution of both inorganic and organic forms during the mudbank period was the nitrate maximum obtained in the mudbank region. Such a maximum was also found in the pre-mudbank period distribution of inorganic NO_3^-. During the pre-mudbank period the organic nitrate is more or less uniformly distributed ($\approx$ 50 µg at l^{-1}).

Post-mudbank period inorganic (3 to 9 µg at l^{-1}) nitrate also showed a similar distribution pattern. Even though the post-mudbank organic NO_3^- mean values ($\approx$ 120 µg at l^{-1}) along the stations indicate least variability, higher fluctuations were observed between the minimum and maximum values of inorganic and organic forms.

The only difference in the seasonal distribution pattern of both inorganic and organic forms of nitrate in the non-mudbank region was that the post-mudbank values were higher than those during the mudbank period. An important finding in the nitrate distribution of mudbank area is the very high concentration of dissolved organic nitrate in the mudbank period, which ranged from 1360-1910 µg at l^{-1} whereas in the non-mudbank area, the highest value observed was only 480 µg at l^{-1} which was in the post-mudbank period. The lower and upper limit of the range of values had also almost identical distribution pattern as mean values.

The monthwise distributional pattern of inorganic and organic nitrate in the water media are shown in Figures 11(d) and (e) respectively. The mudbank period months i.e., June and July, recorded the highest values of surface and bottom inorganic and organic dissolved nitrates while the lowest values were observed during March and April. Both inorganic and organic nitrates, at surface and bottom, recorded low steady values from March to May. In the case of non-mudbank area, November marked the highest values of organic and inorganic nitrates.

Sediment associated form

Table 3 illustrates the seasonal distribution of adsorbed and interstitial forms of inorganic and organic nitrate.

All the four forms of sedimental nitrates (i.e. adsorbed and interstitial forms of organic and inorganic nitrates) show the similar characteristic distribution pattern which is comparable to that of dissolved nitrates. Pre-mudbank period concentration of adsorbed and interstitial forms of inorganic nitrates alone showed values of comparable magnitudes (0.16 to 0.35 µg at g^{-1}) whereas in all other cases a notable difference was observed. Post-mudbank interstitial inorganic nitrate concentration (3.23 to 8.27 µg at g^{-1}) was found to be higher than the corresponding adsorbed inorganic nitrate concentration (0.40 to 3.20 µg at g^{-1}). But the mudbank period concentration of interstitial inorganic nitrate (16.00 to 24.05 µg at g^{-1}) was found to be nearly a third of the corresponding adsorbed value (20 to 77.8 µg at g^{-1}). Remarkably greater fluctuations in the surface and bottom values were marked during the mudbank period distribution of sedimental nitrates (especially interstitial and adsorbed form of inorganic nitrates and the interstitial forms of organic nitrates).

In the case of the organic forms, the amount of nitrates leached with NaCl (interstitial) was found to be significantly greater than that leached with NaOH (adsorbed). The ratio of interstitial to adsorbed forms of organic nitrate yields a factor of $\approx$ 10 for pre-mudbank period and $\approx$ 20 for post and mudbank periods.

One of the characteristic features found in mudbank period distribution of sedimental nitrates was that the concentration of all four forms decreased with increase in the distance from the shore.

The seasonal distribution pattern of sediment - nitrate in the non-mudbank area is similar to that of dissolved nitrates, and differs from that of mudbank area in that the post-mudbank values are found to be higher than there of mudbank period. Further the interstitial and adsorbed forms of inorganic nitrates and interstitial organic nitrates showed lower values during the mudbank period in the non-mudbank area, as compared to the mudbank area.

The seasonal distribution pattern of sedimental nitrates is shown in the monthly variation graph (Figure 14). During June and July, the highest values of adsorbed and interstitial forms of organic and inorganic nitrates were observed, whereas March and April recorded the lowest values of these forms. But in the non-mudbank area the highest values were obtained during December. A well defined concentration peak is observed from the monthly distribution of all the four forms of nitrates during the mudbank period i.e., from June to August; whereas the non-mudbank area is characterised neither by such a concentration peak or higher values during the months of June to August. The concentration of different forms of nitrates during the months March to May is lower than that of September to December. Further, for the post-mudbank period, the concentration of nitrates in December is appreciably higher than those of the previous months.

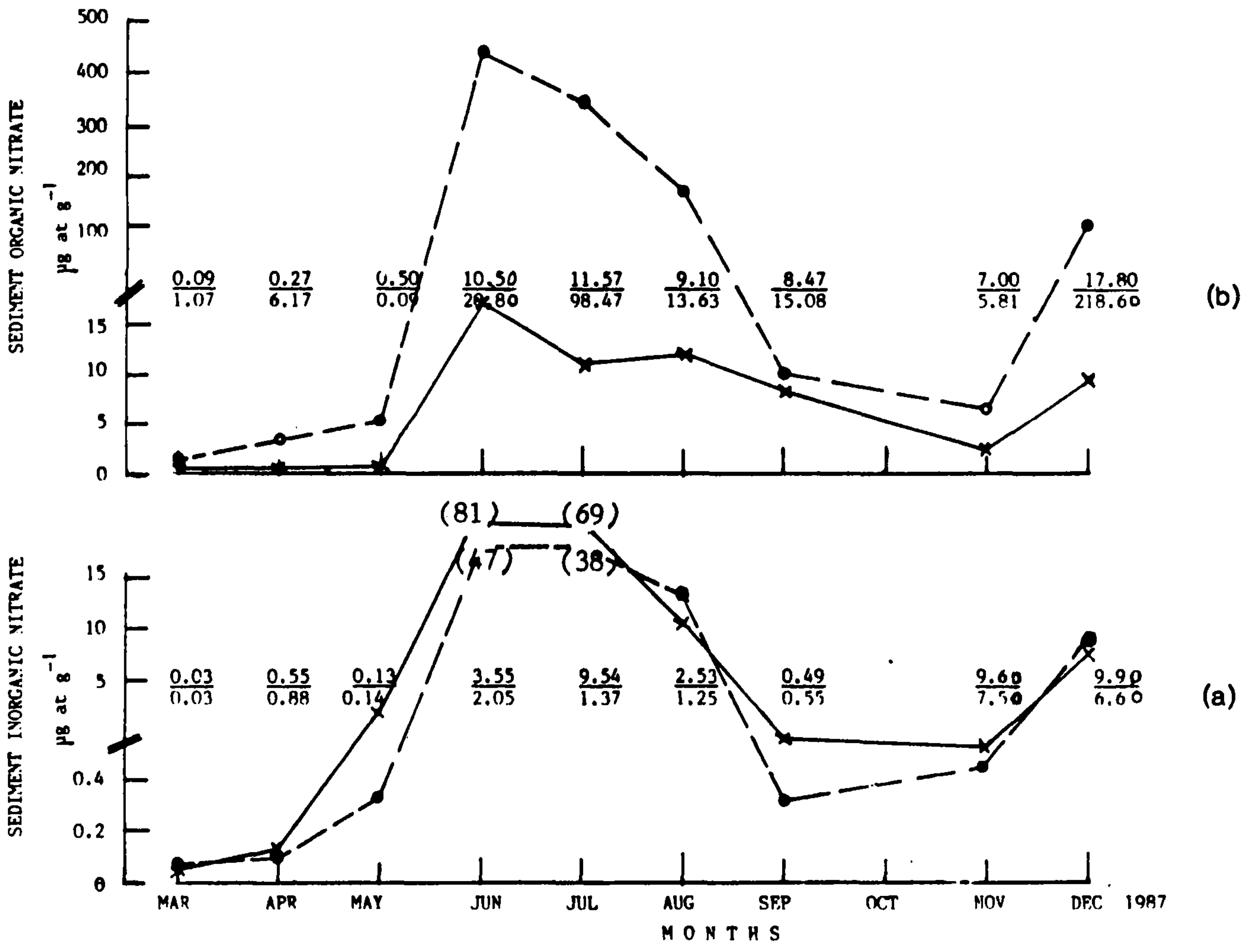

Figure 14. Monthly variation of sediment inorganic (a) and organic (b) nitrate at mud-mudbank area (x——x adsorbed, ●----● interstitial) along with the corresponding non-mudbank area values (top-adsorbed, bottom-interstitial).

Rao et al. (1984) reported the maximum values of dissolved inorganic nitrate during post-mudbank period, lowest during pre-mudbank period and appreciably high values during the mudbank period. But in the present study it is observed that the mudbank period nitrate concentration is greater than post-mudbank period value, regardless of the nature of the nitrate whether it is dissolved or sediment associated.

The slow rate of nitrification during pre-mudbank period as evidenced by high values of ammonia and urea may be the reason for low value of nitrates in this period. The high concentration of all forms of nitrates during the mudbank period may suggest the possibility of high rate of nitrification, resulting in ammonia oxidation and transfer to the upper layers contributing equivalent amounts of nitrate (Sen Gupta & Koroleff, 1973).

In otherwords, the denitrification processes appear to be suppressed during mudbank period and enhanced during pre-mudbank period, which may explain the results of highest and lowest values of nitrate. The loss of nitrate from overlying water, as denitrification has also been observed by Nishio et al. (1982) and Kaspar (1982). In general, the range of denitrification rates observed in coastal marine sediments is greater than that measured in lake or river sediments (Seitzinger, 1988).

The salient features in the distribution of nitrates at the stations of study during the active phase of the mudbank (i.e. mudbank period) may be summarised as follows:

(i) the concentration of different forms of nitrates in the water and the sediment media was highest during this period.

(ii) a dissolved nitrate maximum was obtained in the mid-mudbank region.

(iii) many fold increase in the concentration of organic nitrate as compared to the non-mudbank area was observed.

(iv) sedimental nitrate concentration decreased with increasing distances from the shore and

(v) as compared to the non-mudbank area, sedimental nitrate concentration was found to be significantly high.

During the mudbank season, the sediments contain more of fine textural clay material (table 1). Presence of the fine clay fraction largely increases the available surface area, which inturn increases the nutrient retaining capacity. Hence the mudbank period sediments are able to hold a very high load of nutrients.

It may be noted that during mudbank period the inshore turbidity increases; the colloidal suspension of fine mud supports prolonged sediment - water interactions during the entire mudbank period. So this turbidity processes would largely be responsible to bring out an appreciable amount of nitrates in the dissolved form. The inshore turbidity processes, diminishing with distance, explains the decrease in the sedimental nitrate concentration with increasing distance off-shore. Further, this decrease is reflected in the dissolved nitrate maxima obtained in the mid-mudbank region indicating the high rate of diffusion of sedimental nitrates into the watermedia.

The lower capacity of the non-mudbank sediments to retain nitrates is explained by the higher amounts of calcareous contents and higher amounts of sandy-silt, which provide a lower surface area.

The intensive growth of phytoplankton/zooplankton during the pre-mudbank period (Nair *et al.*, 1984) consumes large amount of dissolved nitrates (inorganic and organic), causing depletion of dissolved nitrates. Further the dissolved nitrate required for the extensive growth of phytoplankton may be supplied by the sedimental nitrates through the processes of diffusion or desorption. As a result, simultaneous depletion in the concentration of sedimental nitrate was observed during this period. Occurrence of comparatively higher amounts of sedimental nitrates in the mid-mudbank area naturally enhances the diffusion processes at that area to a larger extent;

maximising the dissolved inorganic nitrate during the pre-mudbank period. The biological removal may be subdued, to reflect on nominal fluctuations in the minimum and maximum values during this period.

Since the organic forms of nitrates were least available for bio-uptake, the inorganic nitrates were preferably consumed (removed) by the organisms. In both cases, the biological uptake is restricted to the dissolved form only, so that the function of dissolved organic nitrate as a "reserve nutrient" is one of the characteristic feature in the mudbank region.

In the sediments also the organically bound nitrates tend to diffuse into the watermedia on depletion of dissolved nitrates, and is next to that of inorganically bound nitrates. Further, the nature of binding, whether it is adsorbed or interstitially locked, will also determine the extent and rate of diffusion. Since there is greater depletion of nitrate in the watermedia during the pre-mudbank period, irrespectively whether it is interstitial or adsorbed, both the forms of sedimental inorganic nitrates diffused to a larger extent. Nevertheless they show comparable values, but in the case of organic nitrates, adsorbed form may be diffused several times faster than that of interstitial form.

From the foregoing explanation, the interstitial inorganic nitrate concentration was found to be significantly lower in content (about a third) than the corresponding adsorbed inorganic nitrate concentration during mudbank period. When the mudbank is active, the upper stratum of bottom mud continues in a state of liquidity. This continuous agitation of the bottom mud may effectively unlock the interstitially held inorganic nitrate, explaining the considerably low concentration of inorganic nitrates in the sediments during the active phase of the mudbank.

The high values of nitrates observed during post-mudbank period in the non-mudbank area may be due to the contribution from organic detritus - the resultant of planktonic bloom in these months (Segar, 1982). The organic nitrogen compounds are known to form in water by photo- and bio-synthetic processes by aquatic organisms (Riley & Chester, 1971b).

Since the coastal area is always well oxygenated and the mudbank contains high concentration of certain fractions of dissolved nitrates (especially organic form), the probability of nitrate trapping by sediments cannot be ruled out. Mortimer (1941; 1942; 1971) and Rochford (1974) report on the probable regulatory mechanism for trapping of nutrients by sediment. Hallberg et al. (1972) observed a similar trend in the coastal areas of the Baltic sea. Reddy & Reddy (1987) suggested the oxidation of ammonia in the water column to NO_3^- and the downward diffusion of NO_3^- from the water column into the sediment. Since NO_3^- reduction is depended on substrate carbon availability (Burford & Bremner, 1975; Reddy et al. 1982; Reddy & Reddy, 1987) it is inferred that NO_3^- removal from the water column was affected by organic matter content in the sediment.

Phosphorus

The study of phosphorus (as phosphates) as a growth limiting nutrient (Rigler, 1973) in a region of high bio-production like mudbank had received great attention. Phytoplankton normally satisfy their requirement of this element by the direct assimilation of orthophosphate (Riley & Chester, 1971a).

Inorganic phosphate entirely exists practically in the form of orthophosphate ion. Kester & Pytkowicz (1967) have shown that in a sea water of average salinity (35×10^{-3}) (pH 8.0) at 20°C, 87% of the phosphate occurs as HPO_4^{2-}, 12% as PO_4^{3-} and 1% as $H_2PO_4^-$ and that 99.6% of the PO_4^{3-} and 44% of the HPO_2^{2-} is in the form of ion pairs.

In the quantitative studies of nutrients to unravel the high biological production of mudbank area, the role of phosphates as a growth limiting nutrient is of great concern. Seshappa (1953) and Seshappa & Jayaraman (1956) noted the phosphate content in mudbanks during the southwest monsoon. High amounts of phosphate were also observed by Jacob & Qasim (1974) and Nambisan *et al.* (1987). A detailed study in the distributional pattern of various forms of phosphates during the three periods were conducted and the results are discussed hereunder.

Dissolved form

The figure 15(a) and (b) presents the distribution of inorganic and organic phosphates respectively. Corresponding range of values from the non-mudbank area are also shown on the respective Figures. The surface and bottom values did not show much difference in the seasonal distribution pattern of phosphates.

Both inorganic and organic forms of phosphates recorded highest values during mudbank period (2.72 to 7.95 and 12.90 to 25.20 µg at l^{-1} respectively). The post and pre-mudbank period values of inorganic phosphates were interlinked to one another (0.20 to 1.20 µg at l^{-1}) whereas in the case of organic phosphates the post and pre-mudbank values were distinctly different. The post mudbank organic phosphate values (2.56 to 4.60 µg at l^{-1}) were found to be many fold greater than that of pre-mudbank values (0.10 to 0.33 µg at l^{-1}). During the mudbank period, the concentration of dissolved organic fraction was found to be 3 to 4 times greater than that of dissolved inorganic fraction. The periodic trend found in the non-mudbank area showed close similarity to that of mudbank area.

The Figure 9 (b) and (c) shows the monthly variation of inorganic and organic fraction of dissolved phosphates in the mid-mudbank area. Both the forms recorded high values in the active

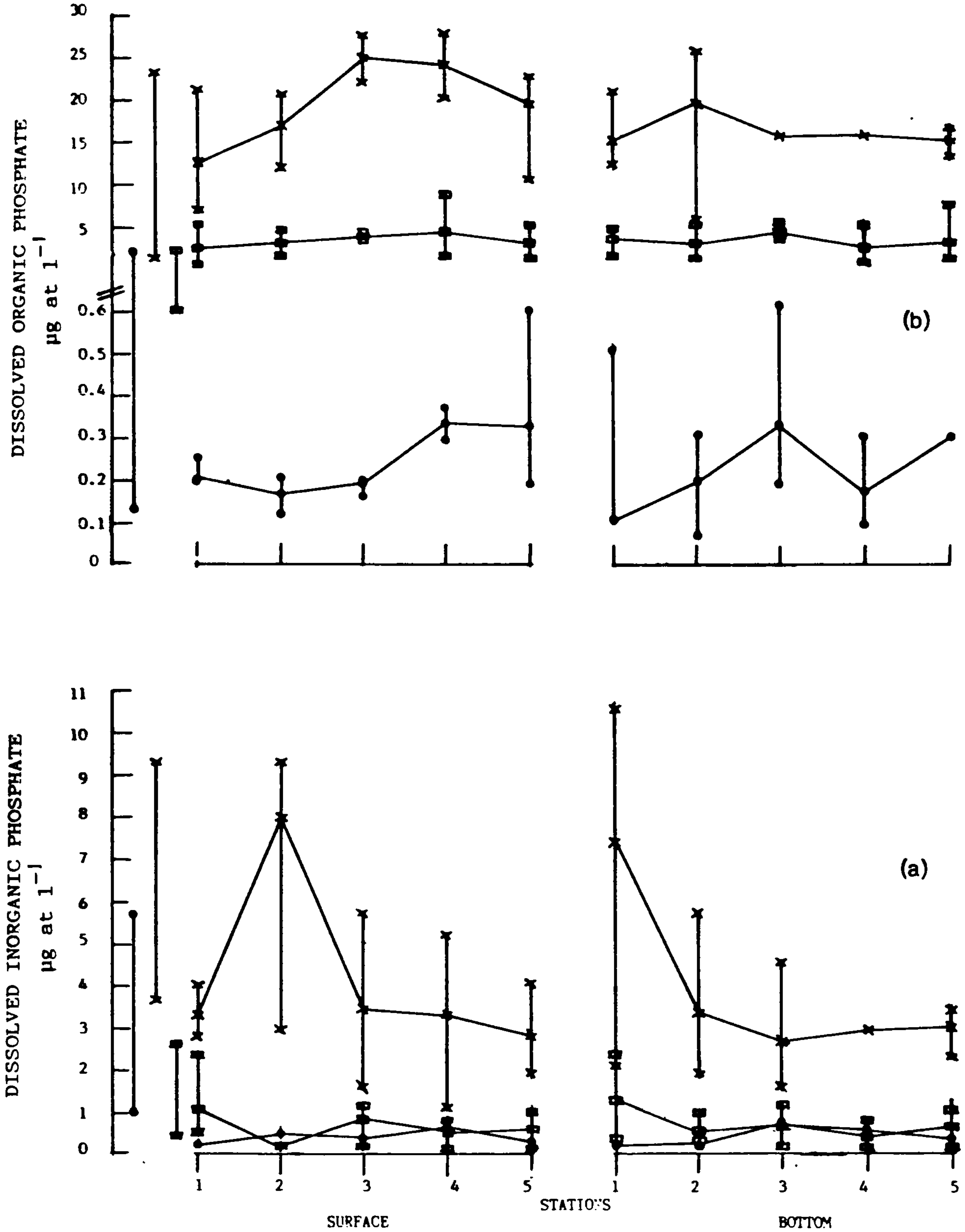

Figure 15. Mean and range of values of dissolved inorganic (a) and organic (b) phosphate during pre-mudbank (●——●), mud-bank (x——x) and post-mudbank (□——□) periods at stations 1-5; range of surface values of non-mudbank area are given on ordinate.

phase of the mudbank. As in the case of nitrates, phosphates also show a "concentration peak" in June-August. Almost steady low concentrations were marked from March to May. In non-mudbank area, the distribution of inorganic phosphate is similar to that of mudbank region i.e. showing higher values in June-July. But the organic fraction shows more or less constant low values from March to December.

Sediment associated form

Table 3 represents the distribution of adsorbed and interstitial forms of sedimental inorganic and organic phosphates along the three periods. The corresponding non-mudbank values are also shown in the respective tables. The adsorbed and interstitial forms of the respective phosphate fraction (inorganic and organic) showed similar distribution pattern.

In all the four forms of phosphates (i.e., adsorbed and interstitial forms of inorganic and organic phosphates) the mudbank values exhibit higher concentrations in the respective distribution table. In the case of inorganic phosphates, the post- and pre-mudbank values ranged between 0.17 to 1.60 µg at g^{-1}, whereas the post-mudbank concentration was found to be slightly higher. But in the case of organic fraction, the situation is reversed, i.e. the pre-mudbank values were found to be higher than that of post-mudbank values. This is more clearly pictured in the distribution of organic adsorbed phosphate. For both inorganic and organic forms of interstitially locked phosphates, the concentration was found to be 4 to 5 times lower than the corresponding adsorbed phosphate in the respective seasons.

Similarly, concentration of mudbank sediment organic phosphates was found to be significantly higher (2 to 5 times) than that of inorganic phosphate. Compared to dissolved phosphates, post mudbank sediment organic phosphate concentration was significantly lower than that of pre-mudbank values. The distribution pattern during the three periods in the non-mudbank area did not provide any distinct periodic difference. Further the levels of mudbank period adsorbed and interstitial forms of organic phosphates in non-mudbank area were found to be much lower than (15 to 20 times) those found in the mudbank area.

The highest values of inorganic and organic phosphates were observed during June and July in the mid-mudbank area irrespective of the forms whether it be adsorbed or interstitial, while the lowest values were observed during April and December respectively (Figure 12(c) and (d)). As in the case of dissolved phosphates and nitrates, the monthly distribution of various forms of sedimental phosphates also exhibited a "concentration peak" during the mudbank period i.e., June to August months. In the non-mudbank area, the highest values of adsorbed and interstitial forms of inorganic phosphates were observed in July and March respectively and that of organic phosphate in March.

From the foregoing results, the significant features sighted during the active phase of the mudbank may be summarised as follows: (1) the concentration of phosphate (both in water and sediment) during this period was found to be the highest in the seasonal distribution of phosphates. (2) amounts of sedimental organic phosphates were found to be about 2 to 5 times higher than inorganic phosphates and (3) organic phosphates in the sediment was found to be about 10 to 100 times greater than that of non-mudbank area.

The higher amount of phosphate in the mudbank compared to that of non-mudbank area is a prime feature of the region. Jacob & Qasim (1974) observed that the total mud phosphates during the mudbank period (0.23 - 3.15 μg at l^{-1} was much higher than those of the interstitial phosphorus (26 to 30 ppm of dry mud) or adsorbed phosphates (10 to 47 ppm of dry mud). The mudbanks act as the store house of phosphates and with respect to the overlying water it is a "reservoir of phosphates" (Damodaran & Hridayanathan, 1966). The content of phosphate in water is shown to be influenced by the dynamics of biological activity under natural conditions (Istvanovics & Herodek, 1985; Istvanovics et al., 1986).

The sediment surface acts as a "physical catalyst" for releasing or trapping of phosphate depending on its concentration in overlying waters. As in the case of nitrates, the presence of very fine clay fractions during the active phase of the mudbank can retain very high load of phosphates. To a larger extent, the phosphate exchange capacity of the sediment is related to the texture of the sediment (Venkataswamy Reddy & Harikumar, 1986). During the mudbank period, with increasing inshore turbidity, higher concentration of dissolved phosphates are evolved consequent to sediment-water interaction.

Again similar to the case of nitrates, the organic phosphorus also plays a crucial role in the mudbank phenomena. Exceedingly very high amount of this fraction may be the "inducer" of the "bio-rhythm" observed in the mudbank. The organic phosphate appears to act as a "reserved nutrient" for future utilization of phosphates in the mudbank subsequent to assimilation of inorganic forms. More so, virtually nothing seems well established on the fate and source of the large amount of organic phosphorus present in the mudbank. Kuenzler (1970) has shown that certain marine algae satisfy their phosphates requirement by direct assimilation of dissolved organic phosphorus, when the inorganic phosphorus level becomes lower enough to limit algal growth.

Seshappa (1953) noted that the laterite formations in mudbanks can retain an appreciable quantity of "adsorbed phosphates" which seems to be a constant source to supplement the local turnover of phosphates in the inshore waters. This explains the observed feature of adsorbed phosphate concentrations being found to be 4 to 5 times higher than that of interstitial phosphates; lower values of interstitial phosphates as compared to that of nitrate may arise from the higher diffussibility or mobility of the pore-water fraction of phosphates.

The sediments have an important role in nutrient uptake and regeneration (Hesse, 1973) and the fluctuations in the phosphate concentration of surficial sediments will potentially influence the phosphate concentration of overlying waters. Logan (1982) suggested the chemical potential of phosphate associated with sediment to be usually higher than that of its dissolved form. An appreciable amount of organic phosphates desorbs from the sediments into the watermedia during the post-mudbank period, resulting in the post-mudbank concentration of sedimental organic phosphate to be lower than that of pre-mudbank period. Consequently, high concentration of dissolved organic phosphates were observed during post-mudbank period than pre-mudbank period. Since the content of phosphate in water is influenced by the dynamics of biological activity under natural conditions (Istvanovics et al., 1986), the high bio-uptake in pre-mudbank period (since primary productivity is very high) and low primary productivity during post-mudbank period resulted in the pre-mudbank period dissolved organic phosphate concentration to be about 10 times lower than that of post-mudbank value. The comparatively high bio-uptake of organic phosphate in the pre-mudbank period is explained by the high primary production reducing the concentration of both inorganic and organic forms of this nutrient to their lowest values in mudbank regions.

However, in the case of dissolved inorganic phosphate, the post-mudbank values were only slightly higher than pre-mudbank values. This reduction in the magnitude of difference in the values of post- and pre- inorganic phosphates may be better understood in the light of high rate of diffusion of sedimental inorganic phosphates to counterbalance the excess biological utilization of dissolved inorganic phosphate during the pre-mudbank period. Consequently, the concentration of inorganic sediment phosphates in the pre-mudbank period was observed to be lower than that of post-mudbank period.

The low pH prevalent during mudbank period may also give rise to the possibility of enhanced phosphate adsorption. This is probably because of the presence of $H_2PO_4^-$ at low pH rather than HPO_4^{2-} ions which dominate the phosphate dissolution systems at higher pH (Kester & Pytkowicz, 1967). A similar situation has been observed by Stirling & Wormald (1977). The magnitude of the ratio of sediment bound phosphate to dissolved phosphate will also influence the phosphate-nutrient controlled bio-rhythm, since the regeneration of phosphatic matter is fast compared to nitrogenous matter.

Relation between different forms of nutrients

The correlation coefficients between the various forms of nutrients in the water media (i.e., dissolved forms) is shown in Table 4. Organic forms of phosphates and nitrates show highly significant correlation in their distribution during the three periods in the mudbank region. This indicates that the mechanism, by which the organic phosphate and nitrate regeneration and removal processes are taking place, may be closely interlinked. Ammonia and urea show a low negative correlation with nitrites, obviously, due to the difference in the conditions for the regeneration and the removal of these forms of nitrogen; ammonia and urea are the reduced forms of nitrogen whereas nitrite is the oxidized form of nitrogen.

Table 4 also shows the correlation coefficients between the different forms of nutrients in sediments. The correlation factor for the interstitial forms of inorganic and organic forms of phosphate and nitrate are significant (+0.82 and +0.97 respectively at $P < 0.01$). Additionally, there is fairly good correlation between the different forms of nitrates and phosphates.

Table 4 also illustrates the correlation of each nutrient in the watermedia to that in sediment. The results indicate that

		DISSOLVED NUTRIENTS								SEDIMENT NUTRIENTS											
		NH_3 S	NH_3 B	UREA S	UREA B	INO PO_4^{3-} S	INO PO_4^{3-} B	ORG PO_4^{3-} S	ORG PO_4^{3-} B	UREA ADS.	UREA INT.	NO_2^- ADS	NO_2^- INT.	INO PO_4^{3-} ADS	INO PO_4^{3-} INT	ORG PO_4^{3-} ADS	ORG PO_4^{3-} INT	INO NO_3^- ADS	INO NO_3^- INT	ORG NO_3^- ADS	ORG NO_3^- INT
DISSOLVED NUTRIENTS	UREA S	0.592								0.789	0.513										
	UREA B		0.196							0.743	0.360										
	NO_2^- S	-0.574		-0.219								0.123	0.754								
	NO_2 B		-0.654		-0.541							0.345	0.686								
	INO PO_4^{3-} S													0.812	0.638						
	INO PO_4^{3-} B													0.795	0.736						
	ORG PO_4^{3-} S															0.675	0.899				
	ORG PO_4^{3-} B															0.855	0.945				
	INO NO_3^- S					0.647												0.541	0.808		
	INO NO_3^- B						0.422											0.440	0.646		
	ORG NO_3^- S							0.962												0.695	0.980
	ORG NO_3^- B								0.983											0.722	0.922
SEDIMENT NUTRIENTS	NO_2^- ADS									-0.747											
	NO_2^- INT										-0.449										
	INO NO_3^- ADS													0.757							
	INO NO_3^- INT														0.824						
	ORG NO_3^- ADS															0.619					
	ORG NO_3^- INT																0.970				

S - Surface, B - Bottom, INO - Inorganic, ORG - Organic, ADS - Adsorbed, INT - Interstitial each form of phosphate and nitrate in watermedia is significantly related to its counterpart in the sediment; but urea and nitrite is not well related. This confirm the role of sediments in nitrate and phosphate uptake and regeneration in mudbank area as is also observed by Hesse (1973). So any fluctuations in the phosphate and nitrate concentrations of surficial sediments will potentially influence their concentration in overlying waters in mudbank region.

Conclusion

The seasonal change in the concentration levels of dissolved and sedimented forms of nutrients are found to potentially influence the nutrient budget of the mudbank area. The turbidity processes occurring during the mudbank period help to increase the supply of dissolved silicate by mixing of bottom waters enriched in dissolved silicate.

Significantly high concentrations of ammonia observed during the pre-mudbank period would play a vital role in the propagation and growth of phytoplankton at a higher rate which may result in a triggering mechanism of "mudbank fisheries". A higher rate of nitrification also results in decrease of ammonia concentration with increase of NO_2^- and NO_3^- concentration during post-mudbank period. Similar to the behaviour of ammonia, the higher concentration of urea observed just before the formation of mudbank signifies the availability of nutrients stored in different forms of nitrogen as a reservoir for later assimilation. Urea content also indicate changes associated with the regeneration and recycling processes of nitrogen forms in mudbanks.

In unison to many upwelling areas, the mudbank area also shows nitrification - denitrification processes; quantitatively this signifies the variability of nitrite concentration during the three periods. The presence of high loads of very fine clay fraction largely increases the available surface area, which in turn increases the nutrient retaining capacity. Many fold increase in the concentration of organic nitrate as compared to the non-mudbank area clearly indicates the role of organic nitrates as reserved nutrient, in the mudbank area. This is one of the characteristic features in the periodic variability of nitrate related to the mudbank fishery of this coastal region.

The content of phosphorus in the dissolved form has been shown to be influenced by the changes in biological activity. Similar to changes in organic nutrient forms of nitrogen, the organic phosphorus also plays a crucial role in "mudbank phenomena". High amounts of organic fraction may be an "inducer" of the bio-rhythm observed here. This fraction also appears to act as a reserved nutrient for near future utilization subsequent to the assimilation of inorganic forms. The magnitude of the ratio of sediment bound phosphorus to dissolved phosphorus also determines the fate of phosphonutrients vis-a-vis bio-rhythm manifestation.

The role of sediments in nitrate and phosphate uptake and regeneration in mudbank area is consanguine to forms of phosphate and nitrate in the overlying watermedia. Studies reveal that fluctuations in the phosphate and nitrate concentration of surficial sediments potentially influence their concentrations in overlying waters. Under these circumstances, the turbidity processes occuring during the active phase of mudbank have a prominent role in regulating the nutrient availability in this zone.

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CHAPTER - 5

CHEMICAL FRACTIONATION OF PHOSPHORUS IN MUDBANK SEDIMENTS

Introduction

The three major micronutrients viz. nitrogen, phosphorus and silicon were studied in the previous chapter; of these, phosphorus was selected for fractionation studies mainly because of the availability of several extractants which can extract specific chemical "species" of the element. The abundance of nitrogen in the atmosphere and the ability of some microorganisms to fix it in available forms make nitrogen compounds less critical in controlling natural productivity than phosphorus, which can be generated only from the existing phosphorus compounds. Silicon is the most abundant element in the lithogenic materials, and its near conservative behaviour in the saline environment makes its sedimentary source less important. The selection of phosphorus for chemical fractionation is based as it is an essential nutrient for the maintenance of life in the sea (Rigler, 1973; Krom & Berner, 1981) and often is the limiting factor for production (Istvanovics, 1988).

Numerous physical, biological and chemical factors determine the rate of transfer of phosphorus from sediment to water and back; the rate depends marginally on the concentration gradients between the two phases (Mortimer, 1971). Advective mixing processes (Hammond *et al.*, 1977) and bioturbation (Davis 1974; Robbins *et al.*, 1979; Goldhaber *et al.*, 1977) will enhance the diffusion of dissolved phosphorus across the sediment-water interface whereas the processes like adsorption and chemical precipitation will retard the migration of phosphorus (Golterman, 1973).

The capacity of sediment to act as "traps" or "buffers" for nutrient phosphorus will largely be determined by two factors viz, the chemical forms in which sedimented phosphorus reach the interface and the subsequent diagenesis. Bostrom (1984) suggested that the relative importance of different environmental factors governing the mobilization (release and transfer between different phases) of sediment phosphorus depends primarily on its fractional composition. The present study involves the separation of different fractions of sedimental phosphorus by various sequential chemical extraction schemes. The fractionation schemes were adopted on the assumption that a specific reagent can preferentially remove a particular phosphorus fraction; thus the extraction procedure may provide information on the form and the mobility of the sedimental phosphorus.

Materials and methods

The schemes and procedures have been detailed in Chapter 2.

Results

A. Analytical schemes

Eight selective extraction schemes were employed to determine the different forms of phosphorus. Sediment samples collected both during the mudbank and non-mudbank periods were studied. As stated by Froelich (1988), all these schemes are intended to estimate the fraction of total solid phosphorus that is biologically "available" - either by desorption, dissolution, or by destruction of host phases, and at best, selective P extractions should be regarded as qualitative indicators of P desorption under rather extreme matrix conditions.

The forms of phosphorus extracted were exchangeable P*, anion exchangeable P, carbonate bound P, labile and resistant organic P, Fe- and Al-bound P, Fe-bound P, Ca-bound P and hydrolysable surplus P. The percentage of the total phosphorus content of the mudbank area sediments of the two periods (mudbank and non-mudbank), extracted by the different extractants, is given in Figure 16, in which the

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* In all cases P stands for phosphorus which is invariably estimated as phosphate-phosphorus.

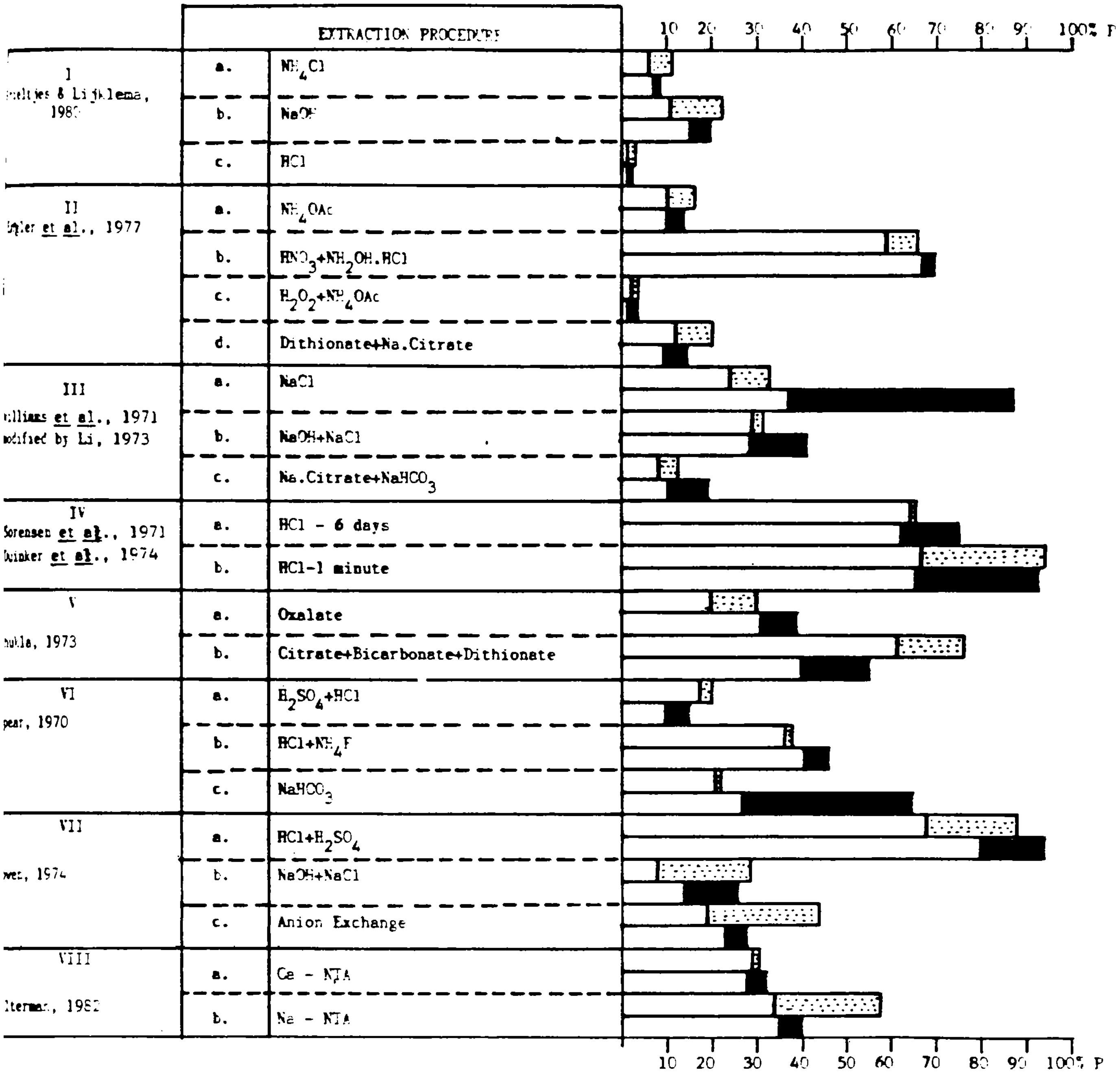

Figure 16. Amounts of phosphorus (in range of values) extracted by different extractants during ▨ mudbank and ■ non-mudbank periods.

dotted column represents the mudbank period sediments and darkened column represents the non-mudbank period sediments. The names of the workers who proposed the schemes originally are also given therein. A total of 18 samples of the mudbank period and 15 samples of the non-mudbank period were studied and the shaded portions indicate the variability recorded.

The proportions of phosphorus extracted was, however, largely variable, schemewise. Further the sum of the fractions determined in each scheme is less than the true total phosphorus values determined by perchloric acid digestion. This was also noted by Williams et al. (1976) in their study. The fractional composition of the mudbank and non-mudbank period sediment phosphorus determined in each scheme is described as follows.

Scheme I

This scheme proposed by Hieltjes & Lijklema (1980) involves the sequential use of three pH conditions i.e. neutral, alkaline and acidic conditions. The extraction in neutral NH_4Cl media (pH-7) determines the exchangeable and carbonate bound P. These fractions of P were 6-12% for mudbank period sediments and 7-8% for non-mudbank period sediments. The extraction in alkaline medium using NaOH for 16 hours determines the amount of Fe- and Al-bound phosphorus in which the mudbank period sediment recorded 11-22% whereas the non-mudbank period sediment gave 15-20%. Final extraction in acidic medium using HCl for 24 hours causes dissolution of Ca-bound P. The sediments of both periods yielded minute amounts (1-3%) of this fraction of phosphorus. The sum of the different fractions of phosphorus extracted in this scheme is less than 40% of the total phosphorus. Hieltjes & Lijklema (1980) originally referred the remaining fraction as the residual phosphorus which is given by the difference between the total phosphorus content and the sum of reactive (inorganic) fractions. They also suggested that the residual phosphorus mainly consisted of organic fraction.

Scheme II

This scheme, originally proposed by Engler et al. (1977), includes four procedures, each of which extracts a particular fraction of phosphorus viz. exchangeable P, carbonate bound P, organic P and Fe-and Al-bound P. The extraction using NH_4OAc at neutral pH (7) yielded the exchangeable phosphorus which was less than 15% of the total P for both mudbank and non-mudbank period sediments. The extractants, HNO_3 and hydroxylamine hydrochloride, (i.e. procedure (b)) yielded carbonate bound phosphorus. This fraction of phosphorus was 59-66% in mudbank period sediments and 67-70% in non-mudbank period sediments. The organic phosphorus extracted from both mudbank and non-mudbank period sediments by using H_2O_2 and NH_4OAc (procedure (c)) was $<$3%. Notably, this fraction of phosphorus accounted for only a very low percentage of total P estimated. The sum of the phosphorus determined by procedure (b) (HNO_3 + $NH_2OH.HCl$) and (d) (dithionate + sodium citrate) was reckoned as the value of Fe- and Al-bound phosphorus. As in the case of exchangeable P, the Fe-and Al-bound P was also slightly higher for mudbank (12-21%) period sediments than non-mudbank (9-14%) period sediments. The extraction using NaOH in scheme I, also gave the same amount of Fe- and Al-bound phosphorus (11-22%) for mudbank period sediments, but slightly higher for non-mudbank period sediments (15-20%).

Scheme III

This scheme was proposed by Williams et al. (1971) and was later modified by Li (1973). Mainly three forms of phosphorus can be determined in the sediments; these are exchangeable P, Fe-and Al-bound P and Ca- bound P. Extraction using NaCl yields exchangeable phosphorus. This fraction showed wide difference in its content between the two sets of sediments; 24-33% for mudbank period sediments and 38-87% for non-mudbank period sediments. This exchangeable P indicates greater variability among any of the sediment samples of non-mudbank period (38-87%). The Fe- and Al-bound P were determined by using a strong alkali (NaOH) along with NaCl for a prolonged extraction time of 16 hours. The Fe-and Al-bound P extracted from the mudbank period sediment had similar values as those of exchangeable phosphorus. But the non-mudbank period sediments gave lesser amounts (29-41%) of Fe- and Al-bound P as compared to its exchangeable fraction. The Ca-bound phosphorus determined in sodium-citrate and sodium-bicarbonate extraction showed slightly higher amount of this fraction during non-mudbank period than mudbank period. As compared to the percentage of other two fractions of P in this scheme, the percentage of Ca-bound P estimated in both sets of sediments was significantly low. Reduced amount of Ca-bound P was also noted in Hieltjes & Lijklema (1980) sequential extraction scheme (Scheme I).

Scheme IV

The scheme IV has two procedures using the same extractant (i.e. HCl), but differing in the duration of extraction time, as proposed by Sorensen *et al*. (1971) and Duinker *et al*. (1974). The scheme enables the estimation of the sum of exchangeable P, organic P, carbonate-bound P and Fe- and Al-bound P. The extraction under a short interval of one minute (procedure (b)) could effectively elute a higher percentage of these forms of P for both mudbank (65-95%) and non-mudbank (63-94%) period sediments. The use of the same extractant for a longer extraction time (Procedure (a)) interval of 6 days reduced its effectiveness (or capacity) in the dissolution of the different fractions of phosphorus; so the P values were lowered to 65% for the mudbank and 63-75% for the non-mudbank period sediments. In general, this scheme indicated that an appreciable amount of different fractions (63-95%) of P can be mobilized by the use of HCl.

Scheme V

Shukla (1973) developed this scheme for the determination of the sum of exchangeable P, carbonate bound P and Fe-and Al-bound P using either oxalic acid and ammonium oxalate (procedure (a)) or citrate, bicarbonate and dithionate (procedure (b)) as extractants. Oxalic acid and ammonium oxalate extraction yielded 22-30% and 31-39% of these fractions of phosphorus from mudbank and non-mudbank period sediments respectively. The extraction using citrate, bicarbonate and dithionate eluted these fractions more effectively. Hence, enhanced percentage of these fractions of P were obtained for both mudbank (62 to 76%) and non-mudbank (40-55%) period sediments. In comparison to non-mudbank period sediments, more than 20% of these fractions of P were leached from mudbank sediments by using the procedure (b)). But, the P fractioned from mudbank period sediment was slightly lower than non-mudbank period sediments, when procedure (a) was used.

Scheme VI

This scheme, proposed by Spear (1970) incorporates three procedures: the first two procedures (a) and (b), using acids determine the sum of exchangeable P, organic P, carbonate bound P and Fe-and Al-bound P, whereas the third procedure using a weak alkaline salt determines the sum of different fractions of P as in acid extraction except the Fe- and Al-bound P fraction. The H_2SO_4 + HCl extraction yielded the lowest percentage of P in this scheme: less than 20% for both mudbank and non-mudbank period sediments. HCl + NH_4F extractant eluted 36 to 46% of total P, with slightly higher fractions from the non-mudbank period sediments. The extraction using $NaHCO_3$ (pH = 8.5) gave a broad range of values for extractable P for the non-mudbank period sediments (27 to 65%). In the case of sediments collected during mudbank period, the range of variability was limited to 22-23%. Except the extraction of non-mudbank period sediments in $NaHCO_3$, all other extraction procedures in this scheme yielded P fractions whose sum accounted for less than 50% of the total phosphorus.

Scheme VII

The scheme has three procedures involving acid, alkali and resin extractions (Cowen, 1974). The H_2SO_4 + HCl extraction could effectively remove 70-90% of exchangeable, carbonate, organic and Fe- and Al-bound phosphorus in 10 minutes time. In scheme VI, it is noted that the same extractants at higher molar concentration was less efficient to remove these fractions from both mudbank and non-mudbank period sediments. Further, the same forms of phosphorus could not be extracted to the same extent but limited to 10-30% using NaOH + NaCl mixture (procedure (b)) for an extended interval of 16 hours. The anion exchange resin (procedure (c)) determined the exchangeable form of phosphorus, and the values were higher for the mudbank period sediments (19-44%). The variability of this fraction was limited within 23 to 28% in non-mudbank period sediments. The amount of exchangeable fraction determined in this scheme was significantly higher than that determined in Scheme II (procedure (a)).

Scheme VIII

The determination of Fe- and Ca-bound phosphorus in this scheme proposed by Golterman, (1982) involves the use of two forms of the chelating agent, nitrilotriacetic acid (NTA). The sodium form of NTA extracts the Ca-bound P wheras the Ca-form of NTA extracts the Fe- bound P. The Ca-NTA treatment eluted more or less the same amount ($\simeq$ 30%) of Fe-bound P for both mudbank and non-mudbank period sediments, while the Na-NTA treatment gave higher range of Ca-bound phosphorus in mudbank period sediment samples (33-58%) compared to the non-mudbank period sediment samples (35-40%). The recovery of Ca-bound P by Na-NTA extraction was more than that by strong acid extraction (HCl in Scheme I).

B) Types of phosphorus

The Fe-and Al-bound phosphorus is determined individually in three procedures of the eight schemes applied. These procedures, i.e. NaOH extraction in scheme I, dithionate + Na-citrate extraction in scheme II and NaOH + NaCl extraction in Scheme III, eluted comparable (20-40%) percentage of Fe- and Al-bound phosphorus except by the dithionate + Na-citrate extraction which shows slightly lower values ($\simeq$ 20%). This is understandable from the scheme II itself: some amount of Fe-and Al-bound P was already leached in procedure (b) (HNO_3 + $NH_2OH.HCl$). The exchangeable form of phosphorus alone is determined in NH_4OAc extraction in scheme II, NaCl extraction in Scheme III and resin extraction in scheme VII. The resin extracts higher amounts of this fraction of P for mudbank period sediments (19-44%) than non-mudbank (23-28%) period sediments. Whereas in the NaCl extraction the exchangeable P shows wide variability in the range of values of the non-mudbank period sediment samples (38-87%) analysed; in the mudbank period sediments the values are comparable (24-33%) to that of resin extraction. Both set of sediments gave low percentage ($\angle$ 15%) of exchangeable P in NH_4OAc extraction.

The HCl extraction in scheme I, sodium citrate + $NaHCO_3$ extraction in scheme III and Na-NTA extraction in scheme VIII determine the Ca-bound phosphorus fraction. A very low amount ($\angle$ 3%) could only be extracted by the acid treatment (HCl). The extraction is more vigorous in the bicarbonate leaching method (12-20%) with slightly higher values for non-mudbank period sediments. Na-NTA extraction was more efficient in the Ca-bound P dissolution, in the sense that it extracted 33-58% and 35-40% of total P, respectively from the mudbank period, and non-mudbank period sediments.

The procedures (a) and (b) of the scheme II combined give the sum of exchangeable and carbonate bound phosphorus which is much higher than those determined in procedure (a) of the scheme I. Since the procedure (b), (scheme II) also includes some Fe- and Al-bound P, the extent of magnification in the value of Ca-bound P may not be specific or reliable. The organic phosphorus fraction determined in the H_2O_2 + NH_4OAc extraction (in scheme II) is unique as none of the other procedures determine this fraction alone. Similar is the case of Fe- bound phosphorus in Ca-NTA extraction (scheme VIII).

The four major fractions of phosphorus viz. exchangeable, organic, carbonate bound and Fe- and Al-bound, were determined, collectively in seven procedures of three schemes (i.e. IV(a) and (b), VI (a), (b) and (c) and VII (a) and (b)). The extraction using lower concentration of acids, (HCl in scheme IV (a) and (b) and HCl + H_2SO_4 in VII (a)) were found to elute an average of 65-95% of total P from both mudbank and non-mudbank period sediments. Only less than 20% of total P was extracted by higher concentration of HCl and H_2SO_4 in scheme VI (a). The leaching efficiency is little more enhanced (36 - 46%) when H_2SO_4 is replaced by NH_4F in scheme VI(b). Further the extraction capacity of $NaHCO_3$ (scheme VI (c)) is found to be inferior to that of NH_4F + HCl (scheme VI (b)), though the non-mudbank period sediments showed much fluctuations in their range of values (27-65%). Only 22-23% of the four fractions of P were eluted from mudbank period sediments by $NaHCO_3$.

Scheme V provides a unique case, wherein, comparisons are possible on the efficiency of two extractants, which are expected to elute similar chemical entities of phosphorus. The citrate + bicarbonate + dithionate extraction (V (b)) was found to fractionate 40-46% more than that eluted with oxalic acid (V(a)) from mudbank period sediments; and in non-mudbank period sediments this fraction is 9-16% higher.

The absolute values of various fractions of P eluted from the mudbank and non-mudbank period sediments by the procedures described in the eight schemes are represented in the pie diagrams (Figures 17 and 18 respectively). The informations contained in these figures relates to the actual amounts of P that are eluted from sets of sediments (mudbank and non-mudbank periods) and hence comparable in efficiency and usefulness of the different schemes. Thus knowing the amounts of phosphorus removed by each of the chemical extractant, it is possible to deduce which of the fractions of sediment phosphorus is most available.

The absolute values of phosphorus determined in schemes I and III for mudbank period sediments are 7.87 and 5.54 µg at g^{-1}. The slightly higher values in scheme I is expectable as it also includes carbonate bound phosphorus in addition to exchangeable Fe- and Al-bound and Ca-bound phosphorus estimated in scheme III. This variability is also observed in the corresponding non-mudbank period sediments (6.01 and 5.64 µg at g^{-1} respectively). Further the scheme I indicates that the mudbank period sediments contain 1.86 µg at g^{-1} more exchangeable and carbonate bound phosphorus fractions as compared to non-mudbank period sediments.

The sum of exchangeable, carbonate bound, organic bound and Fe- and Al-bound phosphorus was determined by schemes II, IV (a) and (b), VI (a) and (b) and VII (a) and (b). However, these procedures show significant variability in the amount of P extracted. The scheme IV, using hydrochloric acid as extractant, recorded the highest values of the sum of the four forms of phosphorus from among the schemes applied in this study. Again, the higher values in IV (b) (44.25 and 34.50 µg at g^{-1} for mudbank and non-mudbank period sediments respectively) as compared to IV (a) (31.75 and 26.00 µg at g^{-1} for mudbank and non-mudbank period sediments respectively), indicate that the HCl extraction is more effective when extraction time is reduced. Bostrom & Pettersson (1982) and Eck Van (1982)

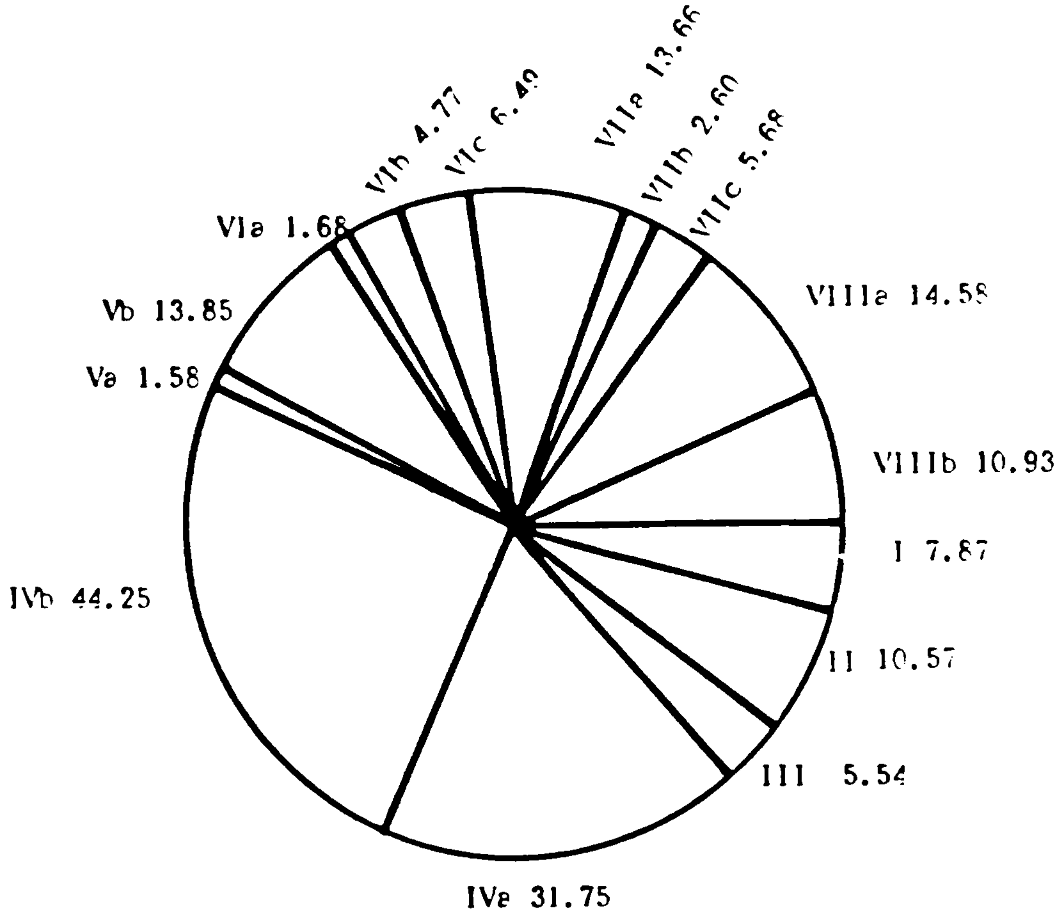

Figure 17. The mean absolute values of phosphorus extracted by different extractants during the mudbank period (µg at g^{-1})

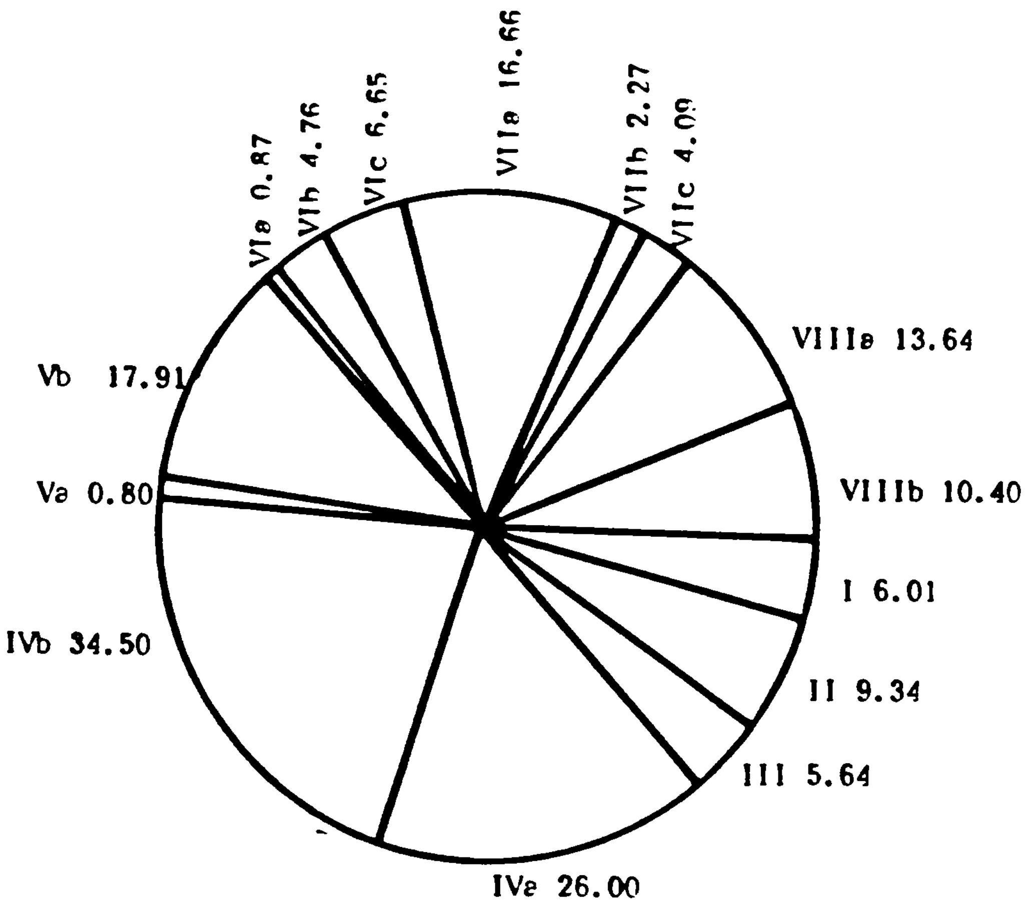

Figure 18. The mean absolute values of phosphorus extracted by different extractions during the non-mudbank period (µg at g^{-1})

also found that considerable quantities of phosphorus are leached in a very short interval of time. Klapwijk et al. (1982) suggested that the amount of P in the HCl extraction was sometimes measured as total P.

It has been noted that the schemes II and VII (a) provide closely resembling values for the above fractions of phosphorus (10.57 and 13.66 µg at g^{-1} for mudbank; 9.34 and 16.66 µg at g^{-1} for non-mudbank). As compared to the scheme IV, the absolute values of the four forms of P extracted by these schemes were found to be generally lower than 50%. Further the scheme VII(b), applying NaOH + NaCl mixture for a prolonged reaction time of 16 hours, gave low, but comparable amounts to the above forms of phosphates for mudbank and non-mudbank period sediments (2.60 µg at g^{-1} for mudbank period 2.27 µg at g^{-1} for non-mudbank period).

The scheme VI (a), using higher concentration of HCl and H_2SO_4, is found to be least effective in extracting these forms of phosphorus from both the mudbank and non-mudbank period sediments (1.68 and 0.87 µg at g^{-1} respectively). But the conditions are more favourable for extraction when using HCl and NH_4F in scheme VI(b); comparable amounts of these forms were eluted from mudbank and non-mudbank period sediments (4.77 and 4.76 µg at g^{-1}).

The procedure VI(c), using bicarbonate, determines the organic fraction along with exchangeable and carbonate bound phosphorus. The amounts of the three forms of phosphorus leached in either group of the sediments (6.49 µg at g^{-1} for mudbank and 6.65 µg at g^{-1} for non-mudbank period sediments) were again comparable. This scheme, which elutes three fractions of phosphorus, is found to be more efficient than the schemes VI(a), VI(b) and VII(b), which were designed to elute an additional fraction of the phosphorus i.e. Fe- and Al-bound phosphorus.

The sum of exchangeable, carbonate and Fe- and Al-bound phosphorus alone is determined in schemes V(a) and V(b). The citrate + bicarbonate + dithionate (V (b)) extraction is found to be very effective in extracting these forms of phosphorus from the sediments as compared to the oxalate extraction (V (a)). It is emphasized that when the scheme V(a) is replaced by V(b), the leaching efficiency is improved by 8 times for mudbank period sediments (1.58 to 13.85 µg at g^{-1}) and 22 times for non-mudbank period sediments (0.80 to 17.91 µg at g^{-1}).

Anion exchange resins such as Dowex 1-x8 are known to separate exchangeable forms of phosphorus which are later eluted in sodium sulphate. The resin is suitable to bring into solution the exchangeable labile as well as moderately bound types of phosphorus. Mudbank period sediments gave slightly higher values of exchangeable phosphorus (5.68 µg at g^{-1}) as compared to non-mudbank period sediments (4.09 µg at g^{-1}). This unifractional extraction scheme (i.e. exchangeable fraction) is merited over some of the multi-fractional extraction schemes (exchangeable , carbonate bound, organic bound, Fe- and Al-bound etc) like V(a), VI(a), VII(b) in its total amount leached.

The nitrilotriacetic acid extraction technique provides the selective separation of Fe-bound and Ca-bound phosphorus in schemes VIII(a) and VIII(b) respectively. The above schemes help in removing large portions of Fe-bound and Ca-bound phosphorus. Appreciable difference were not noted in the amount of these two forms of phosphorus in mudbank and non-mudbank period sediments.

Discussion

Attempts to describe the forms of sedimental phosphorus has been in vogue since two decades. It is an intriguing problem to design a scheme of universal application, since the composition of sediments is highly variable, regionwise. The chemical composition of sediment phosphorus extracted under each scheme is not definitely known; hence "operational definitions" have been provided to give useful information on the composition of phosphorus in sediment. This is to state that the extraction procedures yield operationally defined fractions and cannot be used for identification of discrete phosphorus compounds (Pettersson et al., 1988). These methods are all designed to estimate the fraction of the total solid phosphorus that is biologically "available" - either by desorption, dissolution, or by destruction of host phases (Froelich, 1988). Froelich (1988) concluded that, at least, selective P extraction should be regarded as qualitative indicators of P desorption under rather extreme matrix conditions.

Thus the extraction schemes employed for identifying the different fractions of phosphorus in the sediments collected during the mudbank and non-mudbank periods, provide valuable information to quantify the nature of phosphorus fractions in these high productive waters. The important phosphorus mobilizing factors are more or less closely related to the rate of primary production (Istvanovics, 1988) and also to phosphorus retention capacity, release potential and phosphorus saturation level (Pettersson et al., 1988).

Based on the analytical results obtained by the application of eight different schemes, an integrated fractionation scheme is proposed. This integrated fractionation scheme illustrates the different forms of phosphorus that may be accounted by the use of different reagents extracting different types of phosphorus. Thus the direct relationship between the extractant and the corresponding extractable phosphorus is schematically represented in Figure 19. The definitions of these types are usually derived experimentally and are highly variable as suggested by Pettersson et al. (1988). Though multiple approaches are presented in this figure to determine a single fraction of the phosphorus, care should be taken in as far as interpreting the results, understandably because of the variations in its magnitude.

The scheme I proposed by Hieltjes & Lijklema (1980) is technically simple to perform for routine analysis and provides the most important fractions of phosphorus. However, the different forms of phosphorus: exchangeable, carbonate, Fe- and Al-bound and Ca-bound fractions from this scheme is bounded in its application to sediments conditioned in marine waters. The NH_4Cl can dissolve some phosphorus from Ca-bound and Fe- and Al-bound phosphorus compounds (Hieltjes & Lijklema, 1980). This explains the extremely low fractions of Ca-bound ($<$3%) phosphorus obtained for mudbank and non-mudbank period sediments in HCl extraction of scheme I.

From Figure 19, it is inferred that a suitable procedure to determine the exchangeable fraction may be the use of a mild extractant like ammonium acetate (Engler _et al._, 1977) or the use of anion exchange resin (Cowen, 1974). The anion exchange resin extracts the exchangeable phosphorus possibly by the dissolution of some phosphorus compounds due to "equilibria criteria" (Pettersson _et al._, 1988). The difference in the amount of exchangeable fraction obtained with NH_4OAc and resin extraction may be due to the difference in the composition of NH_4OAc extractable phosphorus as well as the equilibrium criteria for the resin extractable phosphorus. Engler _et al._ (1977) included the labile organic fraction along with exchangeable fraction simply by incorporating 30% H_2O_2 with NH_4OAc.

The carbonate bound phosphorus may be determined either by extracting the residue of NH_4OAc treatment with NH_4Cl or with a mixture of HNO_3 + $NH_2OH.HCl$ (Figure 19). The latter treatment, which had been standardized by Engler _et al._ (1977), extracts a sizable fraction of the carbonate bound phosphorus. This may be due to the association of phosphorus with calcareous materials in the sediments of nearshore region. The former procedure on using NH_4Cl following NH_4OAc treatment did not yield equally large amounts of carbonate bound phosphorus which may be a limitation, again due to the conditioning of the sediments in seawater. A possible explanation for the highly different ratios would be that NH_4Cl can remove phosphorus adsorbed on the freshly formed $CaCO_3$ only.

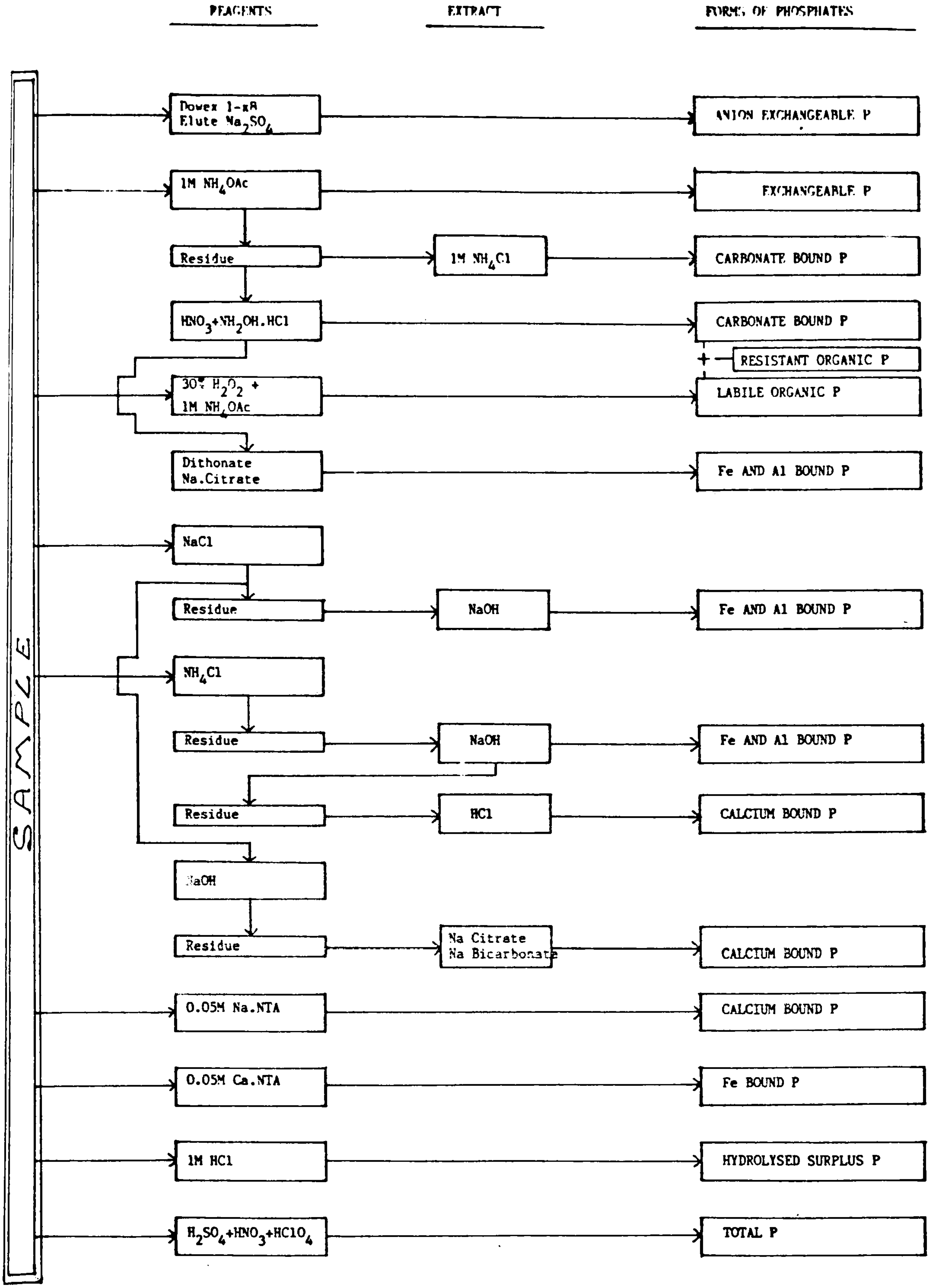

Figure 19. Scheme of analytical procedures used to determine various forms of phosphorus.

Further, the figure shows that the labile organic phosphorus obtained from H_2O_2 + NH_4OAc extraction together with HNO_3 + $NH_2OH.HCl$ extractable carbonate bound phosphorus constitute resistant organic forms of phosphorus. The subsequent treatment of HNO_3 + $NH_2OH.HCl$ fraction with dithionate and sodium citrate accounts the Fe- and Al-bound phosphorus. The bicarbonate/dithionate extraction procedure may have over-estimated the amount of reducible Fe-bound phosphorus due to the partial dissolution of the HCl fraction (like Ca-bound) of the Hieltjes & Lijklema scheme, as was shown by Pettersson et al. (1988) and Istvanovics (1988).

The use of sodium chloride followed by NaOH, determines the Fe- and Al-bound phosphorus. This procedure may bring out only the interstitial and labile bound phosphorus as described by Rochford (1951) and as reviewed by Cowen (1974). The NaOH + NaCl extraction is subsequently followed by sodium citrate plus sodium bicarbonate extraction to determine the Ca-bound P. This scheme originally developed by Williams et al. (1971) modified by Li (1973) proposed the use of NaCl to determine the exchangeable phosphorus. Substantial amount of Ca-bound phosphorus was solubilized by CDB (citrate-dithionate-bicarbonate) reagent (Williams et al., 1976), where the strongly chelating citrate ion plays a major role (Pettersson et al., 1988). Psenner et al. (1985) clearly demonstrated that the CDB extraction method, in addition to reactive phosphorus, measured an equal amount of non-reactive (organic) phosphorus in the sediments of the Piburger Sea, Austria.

The sediment samples treated with NH_4Cl solution followed by NaOH extraction yields Fe- and Al-bound phosphorus and the subsequent treatment with HCl gives Ca-bound phosphorus. But it is to be noted that some Fe-phosphates such as triplite ($Fe_2(PO_4)F$) do not dissolve in NaOH but only in HCl and phosphates like monazite ($CePO_4$) and and xenotime (YPO_4) do not dissolve at all either in NaOH or HCl (Williams et al., 1980).

The use of nitrilotriacetic acid (NTA) is advocated by Golterman (1982) for the differential extraction of sediment phosphorus. Golterman (1977; 1982; 1984) has argued that strong acids and alkaline solutions should be avoided in phosphorus extraction schemes, as they are too aggressive and do not deliver well-defind fractions. A chelating agent like NTA would not disturb clay-bound or organic phosphorus in the estimation of Ca- or Fe- bound phosphorus (Pettersson _et al._, 1988). Inspite of the theoritical considerations, it was noted that NTA often gave better results than EDTA indicating that the reactions are not only controlled by their thermodynamics but that the kinetics are likely to be equally important (Golterman, 1982). The techniques of extraction of Ca-bound phosphorus by Na-NTA and Fe-bound phosphorus by Ca-NTA, are useful especially in the extraction of Fe-bound fraction within a mixture of calcareous sediments of high organic content (Golterman, 1977; 1980). Golterman (1977) has also proposed that Ca-NTA solution will selectively extract Fe-bound phosphorus from sediments leaving Ca-bound phosphorus untouched.

The hydrolysed surplus phosphorus determined in HCl is a widely applicable measure to a number of forms of phosphorus such as exchangeable, organic, carbonate and Fe-and Al-bound. Ray _et al._ (1957) stated that dilute hydrochloric acid may attack some of the less resistant silicates such as certain clay minerals. But Duinker _et al._ (1974) and Agemian & Chau (1976) showed that structural degradation was limited. Rhee (1973) had modified the above procedure slightly for rapid release of the forms, by boiling the solution for a couple of minutes. From the results, the HCl extractable phosphorus was found to have a broad range in values compared to the total, which may be due to the releasing of interstitially locked phosphorus. The total phosphorus content, determined after H_2SO_4 + HNO_3 + $HClO_4$ digestion, forms the basis for deriving all the above observations.

The cumulative percentage of 11 forms of phosphorus extracted from mudbank and non-mudbank period sediments are schematically represented in figure 20. The order-wise arrangements of 11 forms of phosphorus and the corresponding extraction schemes are also indicated at the bottom of the figure. This compilation of results exhibits the characteristic features of the mudbank and non-mudbank period sediments.

It is noted that during the period of mudbank, the anion exchangeable form of phosphorus was double the amount of the non-mudbank period. An anion exchange resin acts as a sink for phosphorus, promoting desorption of phosphorus from particle surface (Logan, 1982) and possible dissolution of some phosphorus compounds due to equilibrium criteria (Pettersson et al., 1988). The exchangeable form determined in the scheme II(a) also provides higher values for mudbank period sediments, though the magnitude is less. The value of exchangeable and anion exchangeable phosphorus differs appreciably in mudbank period sediments (14% and 32%) whereas in non-mudbank period sediments, they have comparable values (11.5% and 16%). This may be due to the releasing of interstitially locked phosphorus of unknown forms. So the higher fraction of exchangeable phosphorus in mudbank period sediments remains potentially mobile and is recycled in the water/sediment column supporting primary production.

It may be pointed out that during the mudbank period, the Fe-and Al-bound (schemes I(b) and II(d)), Ca-bound (scheme III(c)), and Fe-bound (scheme VIII(a)) phosphorus fractions are slightly lesser in content than non-mudbank period sediments. This is probably due to the dissociation of Ca-, Fe- and Al-bound phosphorus fractions during the active phase of the "Bio-Rhythm". However, the slight increase of Fe- and Al-bound phosphorus during non-mudbank period indicated that the adsorption capacity of the Fe- and Al-compounds decreases gradually as their surface becomes saturated with phosphorus during prolonged period of external loading.

Dissolved oxygen is recognised as a factor supporting phosphorus release from sediments (Pomeroy et al., 1965; Fillos &

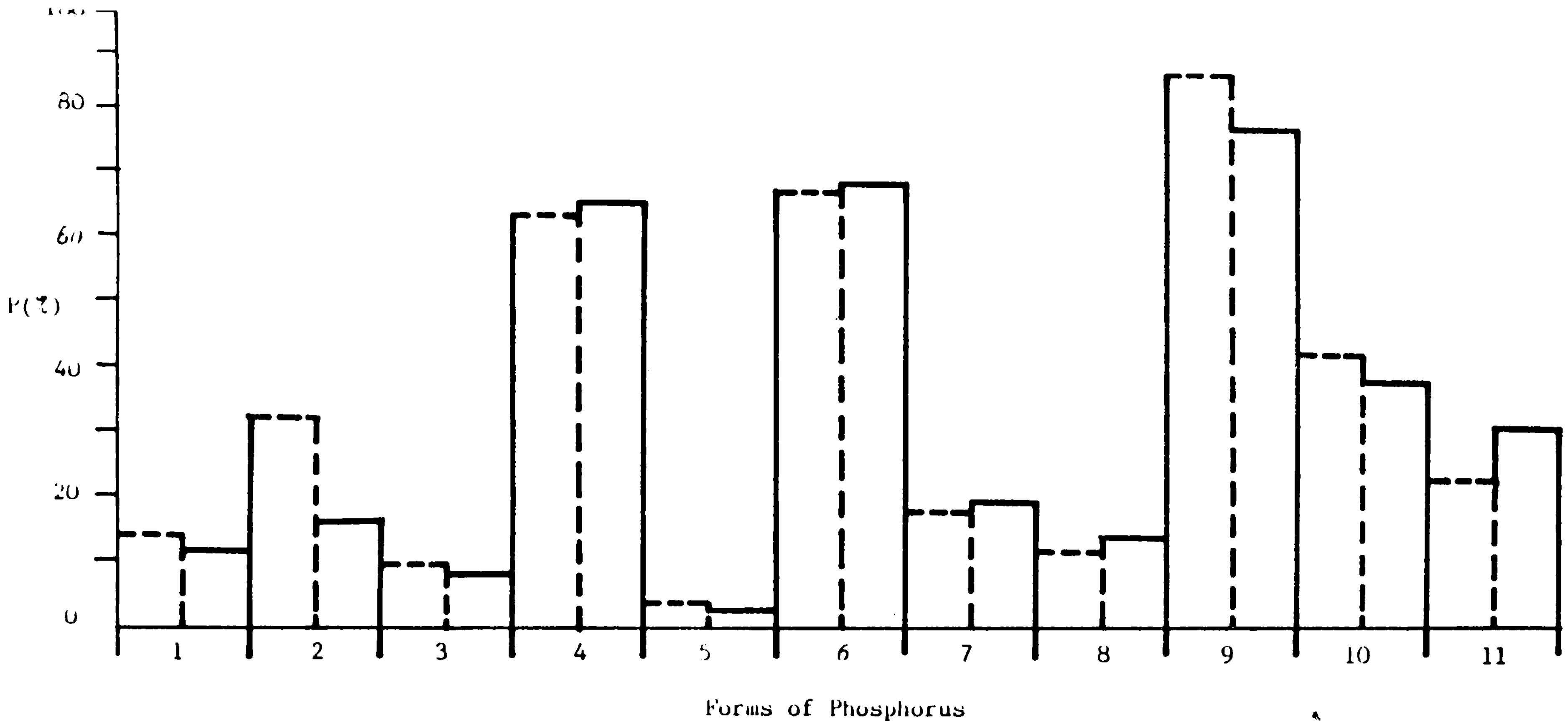

Figure 20. Phosphorus fractions (%) in the sediments collected during mudbank (┆) and non-mudbank (┐) periods. Forms of phosphorus: (Scheme No.) : (1) Exchangeable P(IIa), (2) Anion exchangeable P(VIIc), (3) Exchangeable + Carbonate P (Ia), (4) Carbonate P (IIb), (5) Labile organic P (IIc), (b) Resistant organic P (IIb+IIc), (7) Fe - and Al-bound P (Ib & IId), (8) Ca-bound P (IIIc), (9) Hydrolysed surplus P (IVb), (10) Ca-bound P (Fe - phosphate may also be extracted) (VIIIb) and (11) Fe-bound P (VIIIa).

Molof, 1972; Holdren & Armstrong, 1980; Nakajima, 1983). It is observed that the dissolved oxygen content is generally higher during non-mudbank periods than mudbank period (Chapter 3). Hence removal of phosphorus by adsorption to ferric hydroxides formed by oxygenation of ferrous iron in the vicinity of water-sediment interface, is possible in this area during the well oxygenated non-mudbank periods.

Of the 11 forms of phosphorus presented in Figure 20, the carbonate (scheme II(b)), the resistant organic (scheme II(b) + II(c)) and hydrolysable surplus (scheme IV(b)) phosphorus occupy larger proportions (60-85%). In these three forms, the hydrolysable surplus phosphorus alone shows a distinguishable variability among the two sets of sediments: 85 and 76% for mudbank and non-mudbank period sediments respectively.

The occurrence of higher amounts of carbonate bound and resistant organic phosphorus fractions is viewed as due to the presence of calcareous materials as well as the organic detritus material, cycled within the coastal zone. A part of $CaCO_3$ dissolutes resulting in the mobilization of $CaCO_3$-P; the rate of this process depends on the amount of organic matter decomposing in the sediments (Voros et al., 1983) as well as on the concentration of CO_2 soluble sediment phosphorus (Gelencser et al., 1982). The opposite processes of the adsorption/desorption of phosphorus on/from the carbonates and metal hydroxides as well as precipitation and dissolution of $CaCO_3$ take place simultaneously in coastal environmental conditions at rates controlled by the prevailing hydrographical conditions. Further, the physically adsorbed forms of phosphorus would be easily released from bondage, either by the internal process of digestion in the large organisms or by external modification of the micro-environment by bacteria and other microbiota (Rochford, 1974).

Considering the low Fe-bound P and high Ca-bound P contents of the sediments it is to be inferred that the pH conditions modified by primary production and mineralization play important role in the regulation of the phosphorus modification (Istvanovics, 1988). The phosphorus mobilized in the deeper reducing zones of the sediments diffuses upwards and is trapped in the oxidized surface layers (Carignan & Flett 1981; Herodek & Istvanovics, 1986).

The highest fraction that can be extracted, - the sum of exchangeable, organic, carbonate bound and Fe- and Al-bound phosphorus - is termed collectively as the hydrolysed surplus phosphorus. This fraction may also include the labile organic fraction. But this fraction is found to be comparatively diminished in content (scheme II(c)) for both groups of sediments collected from this region. It is possible that some of the phosphorus is present in a complex organic matrix which is not easily extracted by the above procedure. Logan (1982) defined the labile phosphorus fraction as phosphorus that is adsorbed, easily hydrolysed or easily dissolved.

Below the sediment-water interface, diagenetic regeneration coupled with processes like bioturbation, ebullition and pore water advection, convection and diffusion determine the transport regimes and chemical gradients which deliver dissolved constituents to the interface and eventually to the water above (Klump & Martens, 1981). Ostrofsky (1987) argued that chemical species of phosphorus present in the sediment would certainly be the most important factor regulating the phosphorus release rates.

It may be noted that during the mudbank period, the inshore turbidity increases steadily. The colloidal suspension of fine mud exhibits a calm, viscous and wave-damping coastal area with high alongshore mobile characteristics and supports prolonged sediment - water interactions during the entire mudbank period. This spatial complexity better known as "turbidity process" has a massive role in fractionating the available phosphorus from sediment, which supports high primary production. Moreover, the available phosphorus is not a constant proportion of total sediment phosphorus but is directly related to one particular fraction of the phosphorus.

Istvanovics (1988) regarded the decomposition of the organic matter taking place in the sediments as one of the important phosphorus mobilizing factors. In order to elucidate further information regarding the sediment organic influence on phosphorus mobilization, the interstitial (NaCl-leached) and adsorbed (NaOH-leached) phosphorus were studied in relation to sediment organic carbon* (data compiled vide Chapters 3 & 4). Both these forms of phosphorus show a significant correlation with sediment organic carbon during the mudbank period (Figure 21). But a similar plot (Figure 22) fails to identify any worthwhile relationship during non-mudbank period. The mudbank period sediment phosphorus prominently reflects the organic based cycling of phosphorus to influence the biological processes. Significant relationship between organic matter and phosphorus in high production zones were also reported by Williams _et al_. (1976). Thus a positive feedback exists between sediment phosphorus fractions and primary production in mudbank area.

No significant relationship between extractable P and Fe was observed. This clearly demonstrates that the biogenic sedimentation is the main pathway by which phosphorus gets associated with sediments of mudbank region. Phosphorus concentrations in surface sediment were clearly related to the trophic state as the total phosphorus values were higher for sediments rich in organic material, an observation also made by Flannery _et al_. (1982). However, the possibility of fixing quantitatively the orthophosphates as Fe(III) hydroxy phosphates under oxic condition by an enough concentration of iron (Eck Van, 1982) is remote, since the low Fe/P ratio would drastically reduce the phosphorus trapping effect. In the light of high organic material, kinetic relation between Fe and P fails to take control in this environment too as also reported by Stumm & Leckie (1970). The biological uptake is the significant process keeping phosphate concentration at a constant low level and cycling the available phosphorus between the water and the sediments (Istvanovics _et al_., 1986; Istvanovics & Herodek, 1985).

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*Values derived from sediment organic matter.

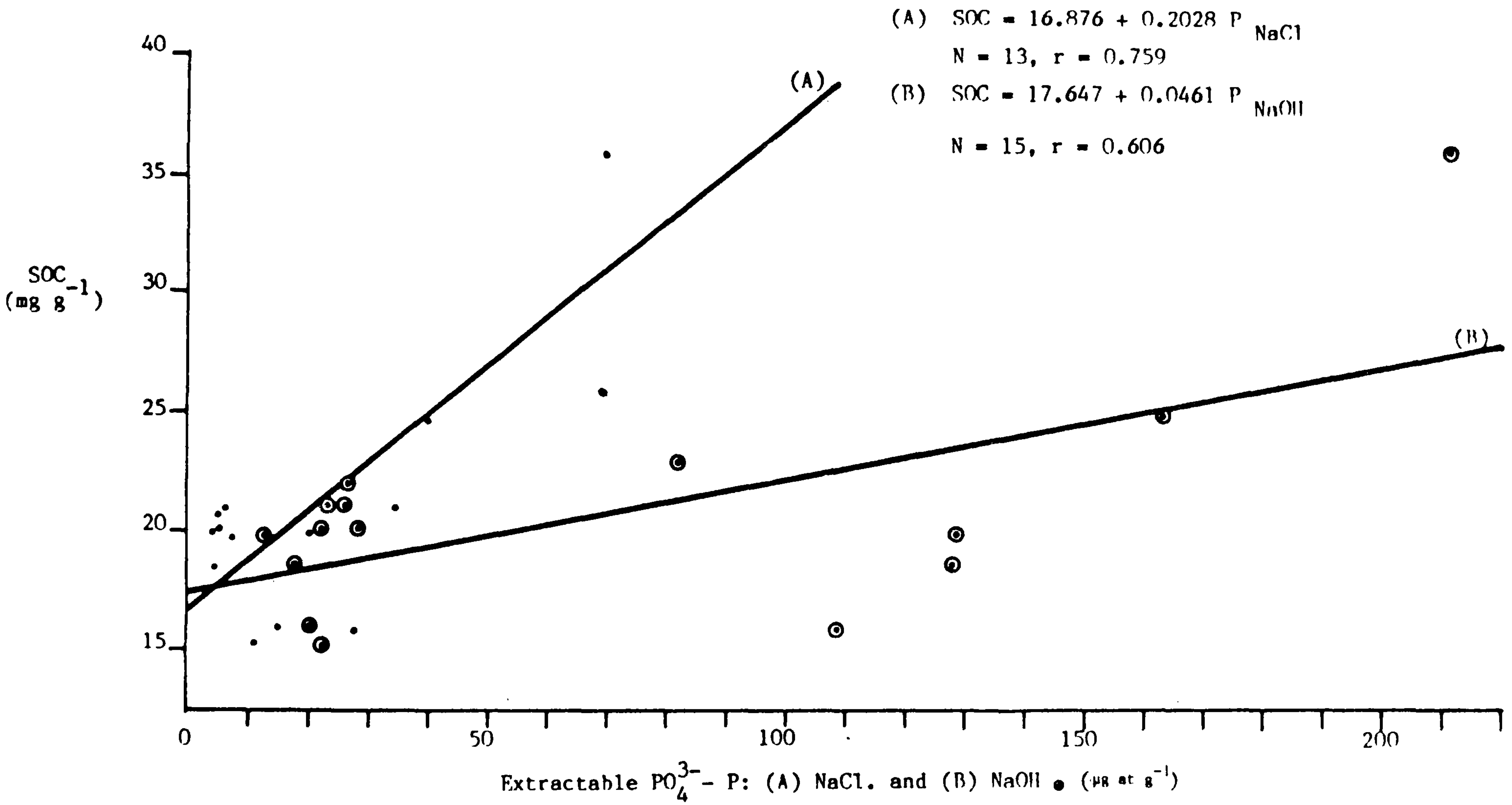

Figure 21. Relationship between NaCl-, NaOH - extracted phosphates Vs sediment organic carbon (SOC) during mudbank period.

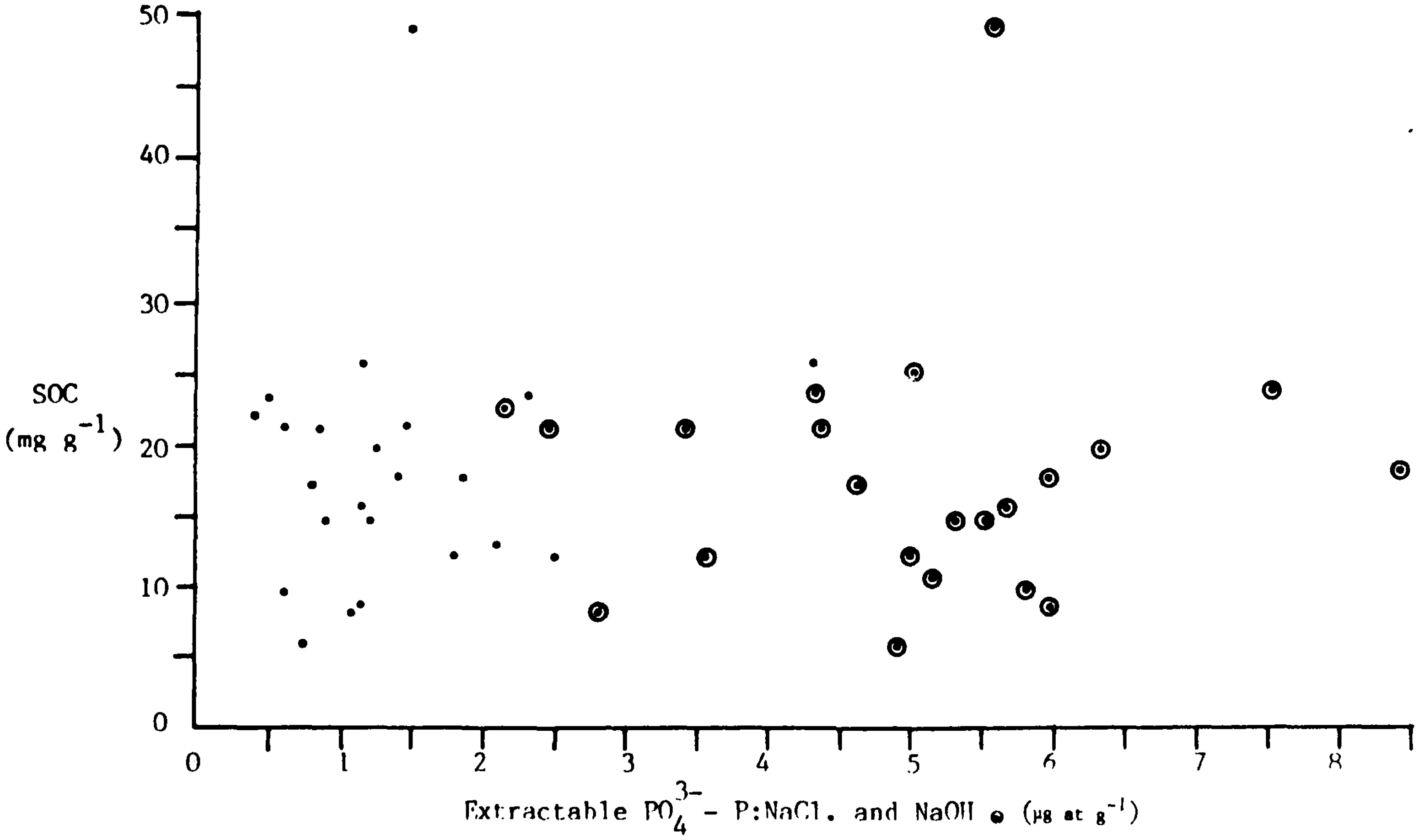

Figure 22. Relationship between NaCl-, NaOH- extracted phosphates Vs sediment organic carbon (SOC) during non-mudbank period.

Conclusion

The "phosphorus buffering" or "trapping" capacity of sediments collected from mudbank area is determined by the chemical forms in which the sedimental phosphorus reaches the interface and the subsequent diagenesis of these forms. The various extraction schemes yield operationally defined phosphorus fraction that may be biologically available - but not the identification of discrete phosphorus compounds.

The higher amounts of exchangeable phosphorus in sediments during the period of mudbank (nearly double that during non-mudbank period) remained potentially the mobile fraction recycled in the water-sediment system. The Fe- and Al-bound, Ca-bound and Fe-bound phosphorus fractions are slightly less in content than non-mudbank period sediment, which indicates the probable dissociation of these fractions during the active phase of the "Bio-Rhythm". The removal of these phosphorus fractions through adsorption on ferric hydroxide formed by oxygenation of ferrous iron in the vicinity of water-sediment interface is yet another important feature.

Larger proportions of carbonate bound and resistant organic phosphorus fractions in either period is viewed as due to the presence of calcareous materials as well as due to the inputs of organic detritus material, cycled within the coastal zone. Further, higher amounts of these fractions of phosphorus trapped in the surficial layers may be mobilized and diffused into the water column depending on the environmental factors such as pH, DO, redox potential and organic matter content. Labile phosphorus fraction was found to be comparatively diminished in content during both the periods explaining the association of phosphorus in the more complexed organic web.

Significant relationship exists between organic matter and phosphorus fractions in the high production period. This indicates the existence of a positive "feedback" between the sedimental phosphorus fractions and primary production in the active phase of mudbank. Finally the absence of any relationship between Fe and phosphorus fraction, demonstrates that biogeneic sedimentation is the main pathway by which phosphorus gets associated with sediments of mudbank region.

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CHAPTER - 6

PHOSPHORUS SORPTION CHARACTERISTICS OF MUDBANK SEDIMENTS

Introduction

The surficial sediments have an important regulatory role in nutrient uptake and regeneration (Hesse, 1973). The fluctuations in the physical and chemical characteristics of surficial sediments will potentially influence the nutrient budget of the zone; this in turn will affect the biological processes. The phenomena like turbulent mixing and bioturbation can alter the depth of the exchanging surface layer (Shaw & Prepas, 1989). As the porosity of the sediment decreases with depth, the activity of the exchanging layer was thought to be restricted almost exclusively to the uppermost few centimeters (ca 2 cm) of sediment (Twinch & Breen, 1982; Lerman, 1979). The role of the surface sediments in sediment-water exchange of nutrients have been highlighted by Twinch & Breen (1982).

Phosphate-phosphorus behaves as a growth limiting nutrient (Ishikawa & Nishimura, 1989) regulating the production and biomass of a particular aquatic ecosystem. In this connection, sediment bound phosphates play an important role in deciding the bioavailability of phosphorus since the surface of sediments act as a "physical catalyst" for releasing or trapping phosphates depending on the phosphate concentration in overlying waters. The phosphate has only one oxidation state in solids as well as in solution, and has no significant atmospheric fluxes; hence the process of phosphate exchange between sediment (or suspended solids) and solution becomes more significant (Stumm & Leckie, 1971). Further, the ratio of the sediment bound phosphate to dissolved phosphate (i.e. the partition coefficient) greatly influences the response of phytoplankton to the phosphorus load in aquatic environments.

It is widely recognized that phosphorus is a highly particle - reactive element and in solution it reacts quickly with a wide variety of surfaces, being taken up by and released from particles through a complex series of sorption reactions (Froelich, 1988). The phosphate retention (sorption) capacity of the "sediment boundary layer", whether benthic or suspended, acts as a buffer to maintain (or control) the concentration of phosphate in the overlying waters (Syers *et al*., 1973; Khalid *et al*., 1977) at some near constant values regardless of biological removal and input reactions (Froelich, 1988). Sediments are capable of taking up large amounts of phosphates from the water when concentrations are increased, and of releasing some phosphates when concentration in the water decreases on biological demand, thereby maintaining a dynamic phosphate equilibrium between the sediment and the overlying water (Syers *et al*., 1973). The continuous adsorption and desorption of phosphates by sediments demonstrate the potential role of sediments, both as a source and a sink for phosphates in the phosphorus cycle. This was clearly demonstrated by Twinch (1981) in his laboratory uptake and release experiments.

The objective of this study was not to determine the exact rates of phosphorus uptake/release by the sediment, but rather to establish the principal difference in the pattern of phosphorus uptake or release under different conditions in laboratory oriented studies. The phosphate sorption characteristics of mudbank sediments were studied in the laboratory under various simulated conditions of environmental significance such as varying regimes of salinity , sediment and phosphate concentrations. The effect of temperature and pH was observed not to significantly affect the results of this study. The effect of pH on sorption at values between 6 and 8.5 is negligible (Carritt & Goodgal, 1954); a higher pH is unlikely to occur in the marine environment because of its buffer capacity (Stirling & Wormald, 1977). Stirling & Wormald (1977) also pointed out that temperature has only a small effect on phosphate adsorption processes.

Materials and methods

The procedures have been detailed in Chapter 2.

Results

I. Desorption characteristics of mudbank sediments at different salinities

a) Mudbank water: Figure 23 represents the time graph to attain quasi-steady state in six sets of samples containing the same amount of sediments and same volume of mudbank water at different salinities viz. 0,5,10,15,20 and 25 x 10^{-3}. In all the cases studied, the desorption of phosphate was taking place rapidly, reaching a quasi-steady state within 20 to 30 minutes. The initial, rapid release of phosphates were observed more at high salinities (i.e. 88% for 20 x 10^{-3}, 73% for 15 x 10^{-3}, 63% for 25 x 10^{-3} etc.), but at steady state, the amount of phosphates retained (adsorbed) in the sediments were higher at higher salinities (96% for 25 x 10^{-3}, 92% for 20 x 10^{-3}) than at lower salinity (90% for 5 x 10^{-3}). The values were recorded only upto 24 hours, since no appreciable changes were observed in the quasi-steady state concentration during the experimental period upto seven days.

b) Synthetic seawater: The influence of salinity (i.e. ionic concentration) on the phosphate sorption capacity of mudbank sediments were repeated with synthetic seawater in order to differentiate from the mudbank water quality. The time-dependent phosphate desorption kinetics are depicted in Figure 24 at different salinities ranging from 0 to 35 x 10^{-3}. As compared to mudbank water medium, the desorption of phosphates in synthetic water takes slightly longer range of time i.e. 15 to 60 minutes to attain quasi-steady state values. In contrast to the mudbank water, high rate of rapid initial release of phosphates was observed at lower salinities (57 to 62% for 5 to 15 x 10^{-3}) than at higher salinities (34 to 39% for 25 to 35 x 10^{-3}). A notable feature is that the amount of phosphates released from the mudbank sediments to the overlying synthetic seawater at different salinities were comparatively very low (0.3 to 3.8%) with higher quasi-steady state dissolved phosphate concentration at lower salinities or more amount of phosphate was adsorbed

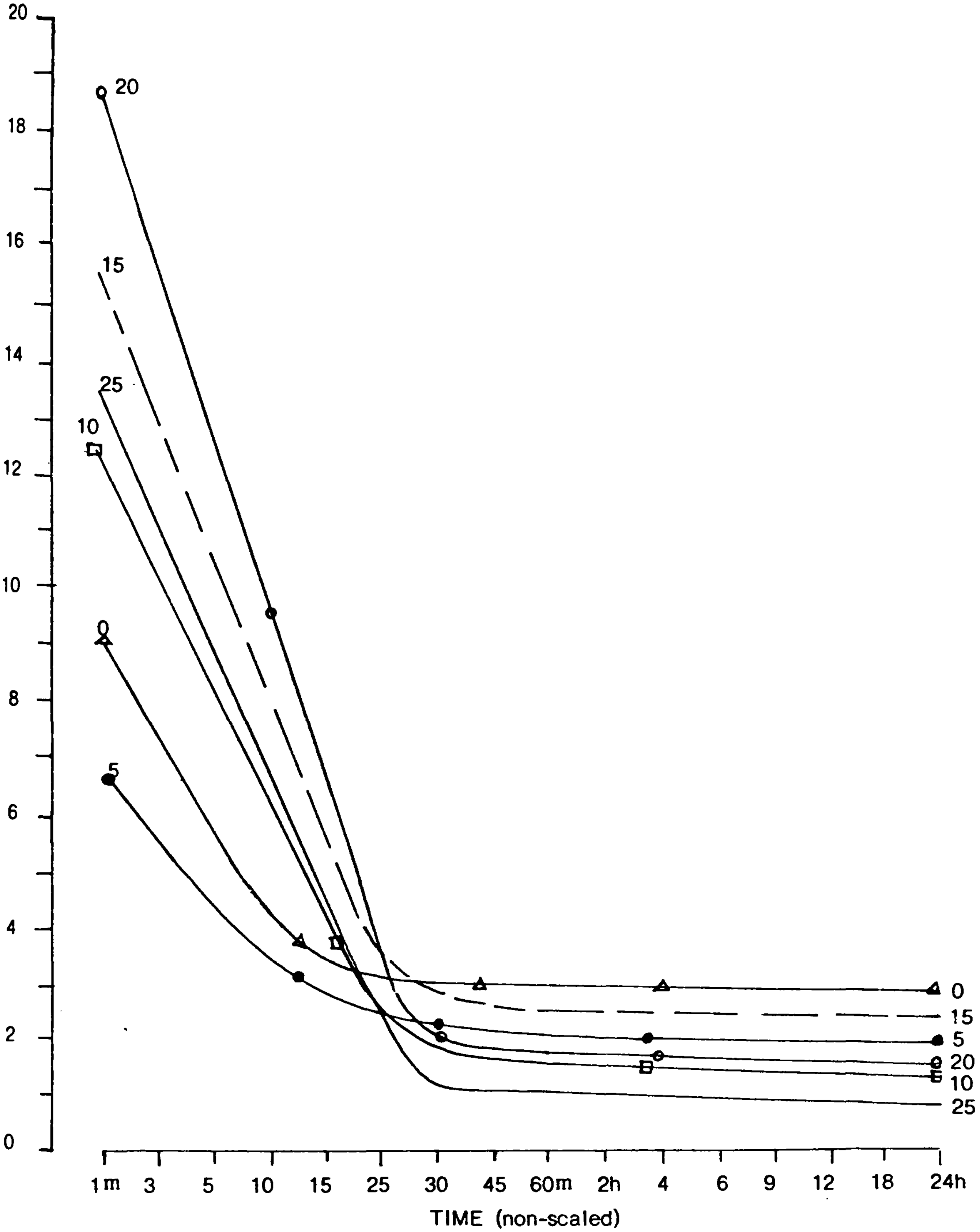

Figure 23. Desorption characteristics of mudbank sediments at different salinities (0,5,10,15,20 and 25x10^{-3})

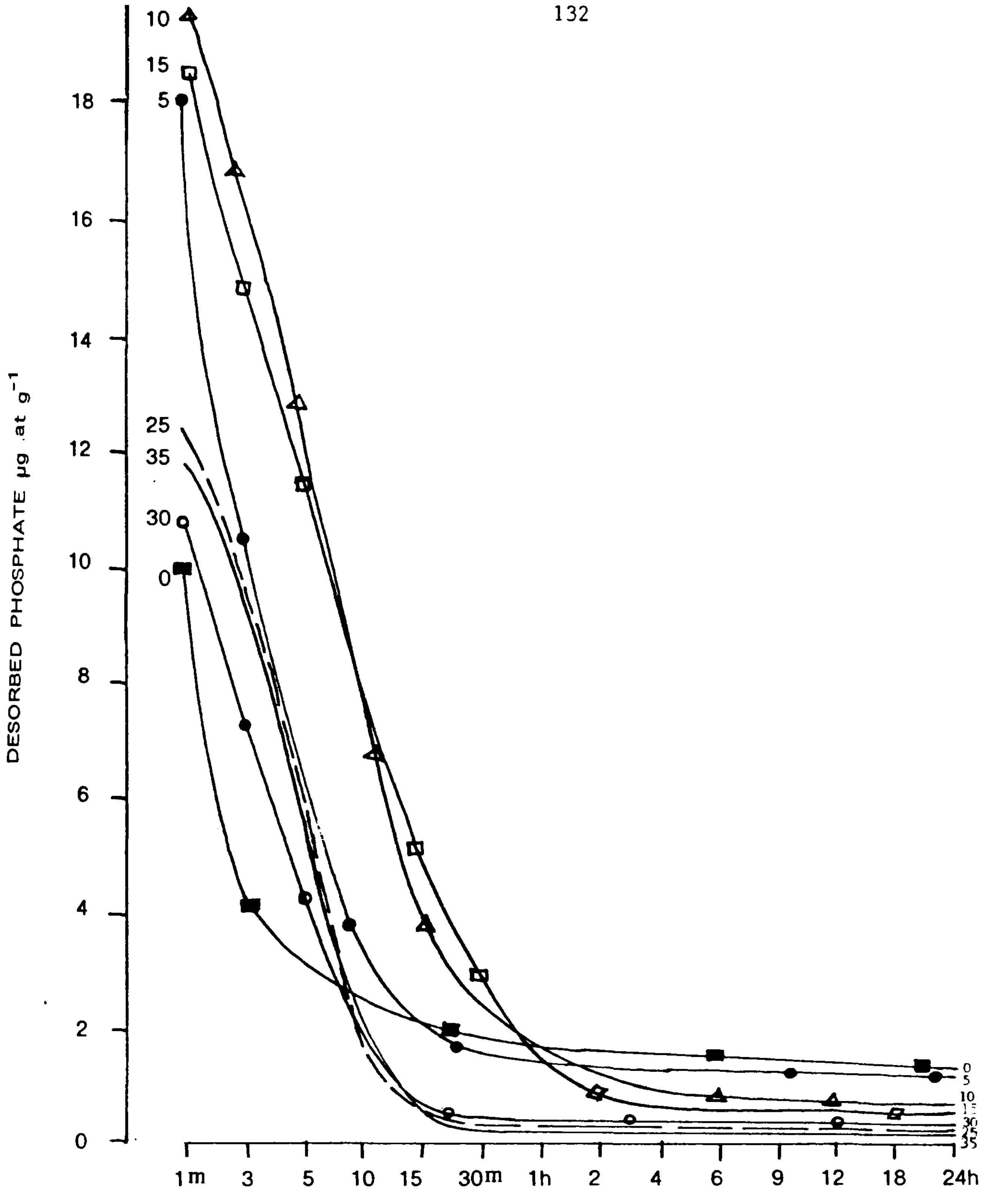

Figure 24. Desorption characteristics of mudbank sediments at different salinities (0,5,10,15,25,30 and 35x10^{-3})

at higher ionic concentration (i.e. higher salinity) when the quasi-steady state is reached.

II. Adsorption characteristics at different concentration of phosphates in mudbank water

Figures 25(a), (b), (c) & (d) represent the amount of phosphate removed (expressed as desorbed phosphate concentration in µg at g^{-1}) from four increasingly incremented concentrations of phosphate (0.005, 0.01, 0.05 and 0.10 µg at ml^{-1}) in mudbank water by a constant amount of leached and unleached mudbank sediment and kaolin. After a rapid adsorption period it passes through the stages of slow and fast sorption processes. This indicates more or less diphasic kinetics in which atleast two exchange mechanisms are involved in phosphate sorption across the sediment-water interface. Except kaolin in 0.05 µg at ml^{-1} solution quasi-steady state was attained approximately in 20 h. The maximum amount of percentage phosphate adsorbed by kaolin, leached and unleached mudbank sediments in the different initial concentration of phosphates are summarised below.

	0.005 µg at ml^{-1}	0.01 µg at ml^{-1}	0.05 µg at ml^{-1}	0.10 µg at ml^{-1}
Kaolin	70	67	57	49
Unleached mud	85	91	94	62
Leached mud	95	97	91	60

From the foregoing results it is evident that kaolin differs markedly in its low capacity (11 to 37% lower phosphate adsorption) to adsorb phosphate as compared to mudbank sediments where the leached mudbank sediment had slightly greater adsorption capacity (97%) than unleached mud (94%). Obviously, all of them show higher degree of adsorption at lower phosphate concentrations; kaolin in 0.005 µg at ml^{-1}, unleached sediment in 0.05 µg at ml^{-1} and leached mud in 0.01 µg at ml^{-1} solutions.

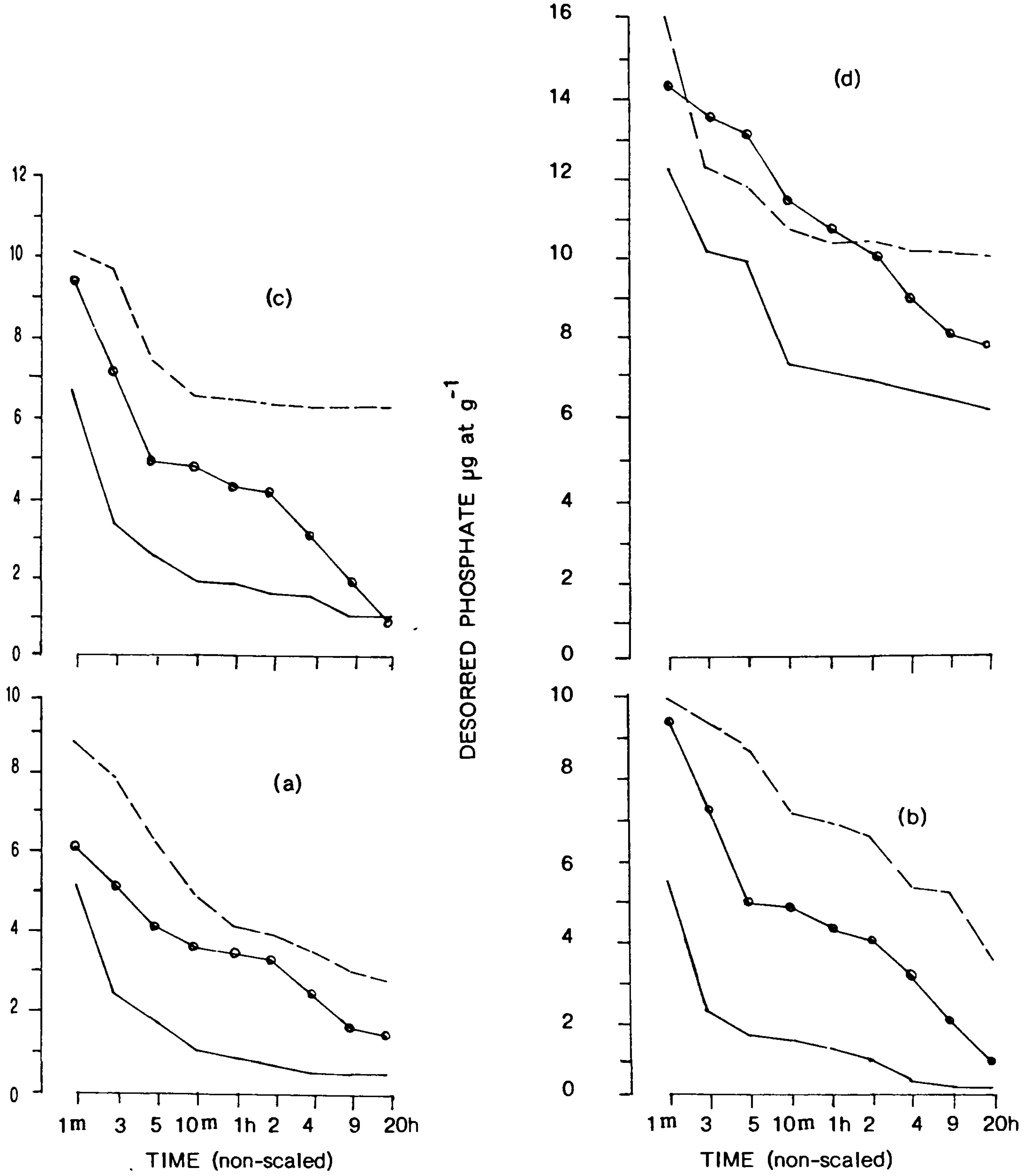

Figure 25. The amount of phosphate removed (expressed as desorbed concentration) from 4 increasingly incremented concentrations, 0.005 (a), 0.01(b), 0.05(c) and 0.10 (d) µg at ml^{-1} in mudbank water by a constant amount of leached (O——O) and unleached (———) mudbank sediments and kaolin (- - -).

III. Adsorption characteristics at different sediment concentrations

Figure 26 represents the time-dependent variations of degree of phosphate adsorption (expressed as desorbed concentration in μg at g^{-1}) by varying quantities of sediments (viz. 2,5,10,25,50 and 100 g) in distilled water (200 ml) containing same initial added phosphate concentration (0.02 μg at ml^{-1}). From the figure (26) the amount of phosphates (in %) adsorbed by different concentrations of sediment were summarised as follows:

Weight of mud (in g)	Phosphate adsorbed (%)
2	8-40
5	69-88
10	79-93
25	93-97
50	97-98
100	98-99

It is observed that there is a sharp increase in adsorption maximum at sediment concentration $>$10 g after which there is only marginal increase in the magnitude of phosphate adsorption; there is almost a completion of adsorption process in the experiment using 100 g of sediment. The attaining of a quasi-steady state at a sediment : solution ratio of 10 g : 200 ml indicates a "control" in the sediment - water phosphate sorption mechanism.

Discussion

I. Desorption characteristics at different salinities

The changes at the sediment-water interface appear to influence the phosphate potential in the "active exchanging layer" of the sediments (Hesse, 1973; Twinch & Breen, 1982). The clay minerals have the property of sorbing certain anions and cations and retaining them in an exchangeable state, i.e. these ions are exchangeable for other anions or cations of the ambient medium. Nearly every ion-exchange process is

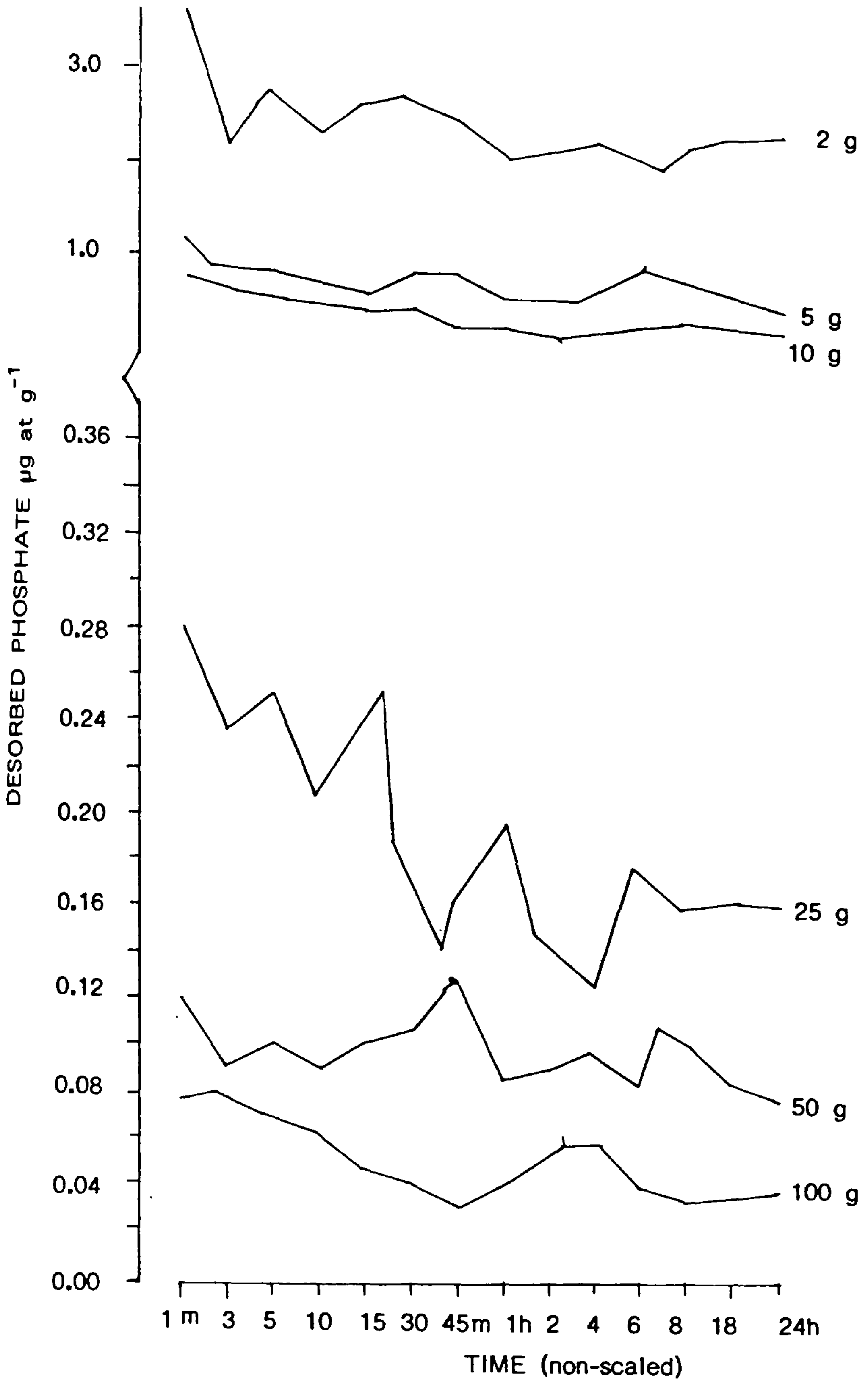

Figure 26. The amount of phosphate removed (expressed as desorbed concentration) by varying quantities of mud (2,5,10,25,50 and 100g) in distilled water containing same initial phosphate concentration.

accompanied by sorption. The clay minerals have the property of sorbing certain anions (like PO_4^{3-}, NO_3^-, Cl^-, SiO_4^{2-}, SO_4^{2-} etc) and retaining them in an exchangeable state (Grim, 1968). In seawater, these anions are easily substituted or replaced. The investigations of anion exchange in clay minerals have been conducted to a considerable extent associated with studies on the adsorption of phosphate by sediments. In some cases the sorption is definitely related to ion-exchange; in other cases the mechanism is not clearly understood.

In order to study the effect of ionic concentrations on the phosphate sorption power of sediment, varying electrolyte concentrations of mudbank water (i.e. different salinities) along with synthetic seawater were used. A plot of C (where C is the dissolved phosphate concentration (µg at ml^{-1}))against C/x/m (where x/m is the amount adsorbed per unit mass sediment (µg at g^{-1}))for the desorption characteristics of mudbank sediments at different salinities of mudbank and synthetic water, is shown in Figures 27 and 28 respectively. The resulting correlation coefficient (r), intercept and slope are summarised in table (5). The similarity in the physico-chemical characteristics of synthetic seawater to that of natural seawater is limited to its major inorganic ionic concentration only.

In the study of ionic effects on the adsorption mechanism of phosphates, typically single slope plots are described by many workers (Green et al., 1978; Ku et al., 1978; Mc Callister & Logan, 1978). The initial rapid (minutes-hours) reaction of phosphates in sediments followed by a slower reaction over days and weeks with the overlying water has been observed by several researchers (Griffin & Jurinak 1974; Rajan & Fox, 1975; Ryden et al., 1977).

In synthetic seawater, the quasi-steady state adsorbed phosphate concentration increases as the ionic concentration of the media increases. In general, the sorption increases as the ionic strength of the background solution increases. Oloya & Logan (1980) also found that there was near instantaneous removal of a large fraction of

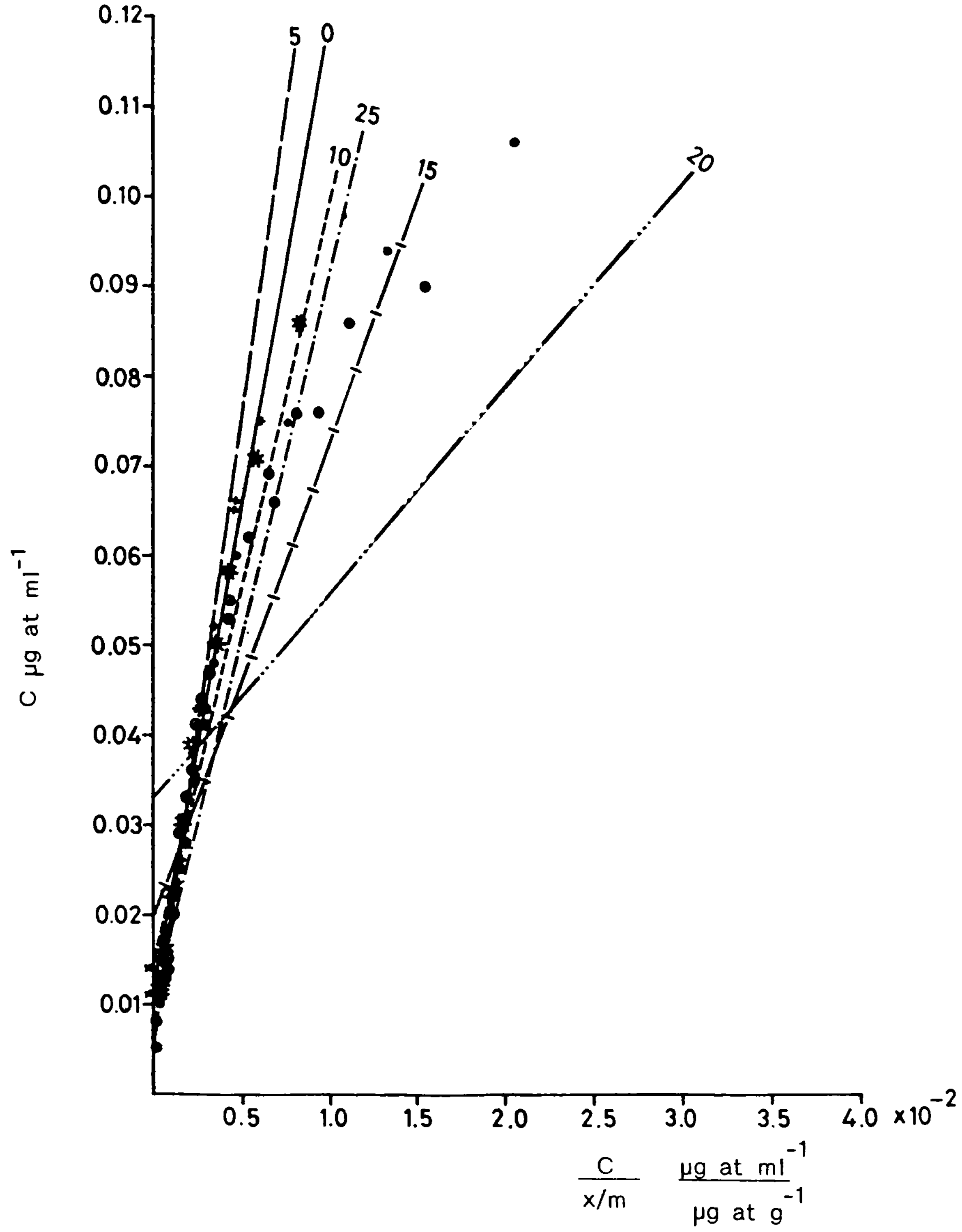

Figure 27. Plot of C against $\frac{C}{x/m}$ for the sorption characteristics of mudbank sediments at different salinities (0,5,10,15,20, 25x10^{-3}) of mudbank water.

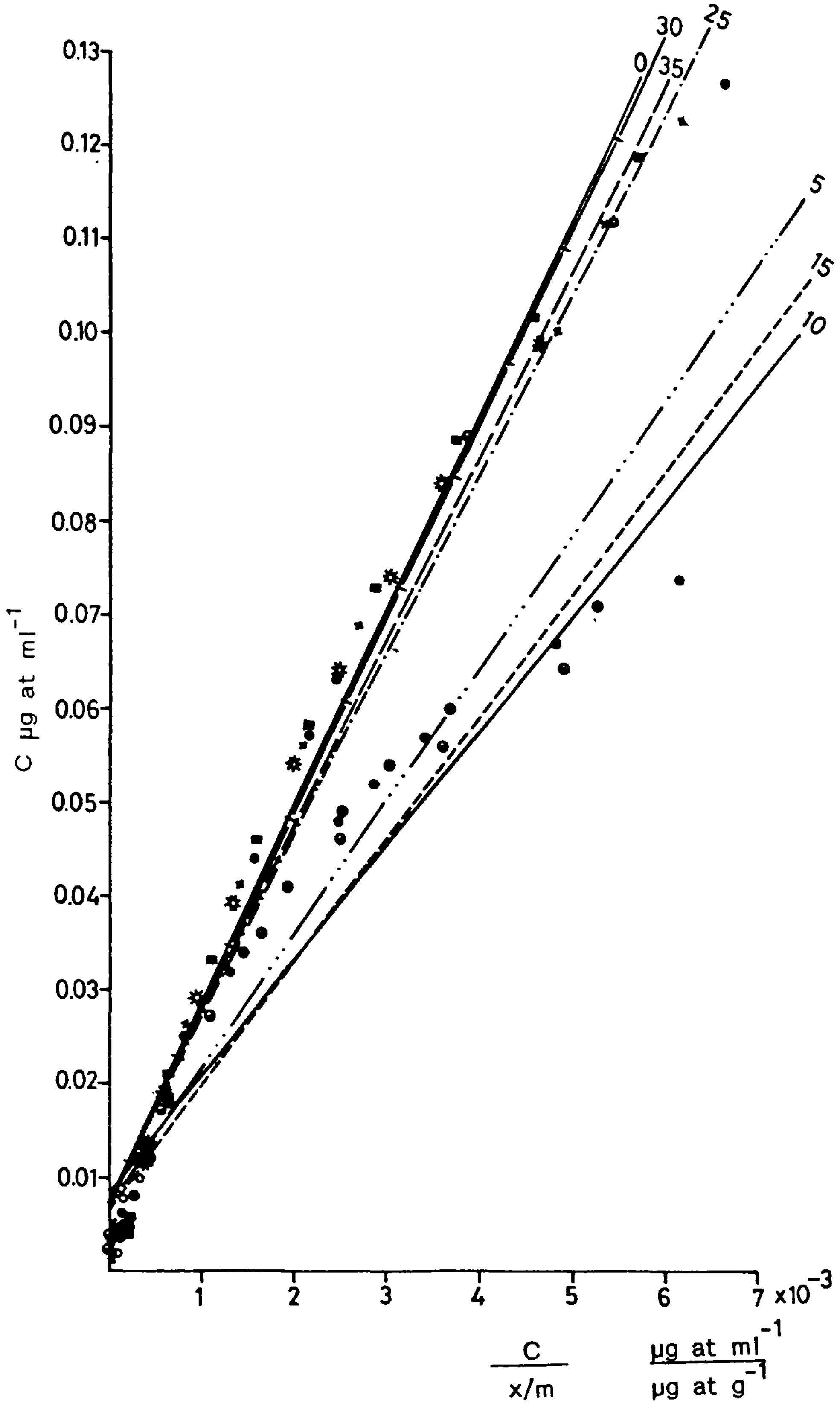

Figure 28. Plot of C against $\frac{C}{x/m}$ for the sorption characteristics of mudbank sediments at different salinities (0,5,10,15,25,30 and 35x10^{-3}) of synthetic seawater.

Table 5. Correlation coefficients, intercepts and slopes obtained from the plot of C against $\frac{C}{x/m}$ (Figures 27 and 28) on the desorption characteristics of mudbank sediments at different salinities (n=10)

Experiment	Salinity x 10^{-3}	Correlation coefficient r	Intercept	Slope
Mudbank water with different salinities	0	0.993	0.0125	10.8283
	5	0.996	0.0061	13.6261
	10	0.974	0.0144	8.5909
	15	0.943	0.0199	5.2600
	20	0.836	0.0336	2.2348
	25	0.964	0.0117	7.8394
Synthetic sea water with different salinities	0	0.995	0.0067	20.9740
	5	0.973	0.0078	13.7359
	10	0.967	0.0085	12.2460
	15	0.971	0.0065	13.1351
	25	0.990	0.0076	19.2280
	30	0.993	0.0068	20.8230
	35	0.992	0.0067	19.8205

phosphates in sediments by dilute electrolytes and desorption could be described by first-order kinetics. This explains the initial rapid release of phosphates at lower salinities in synthetic water in contrast to mudbank water which itself has an appreciable amount of dissolved phosphate.

In experiments with mudbank water, it is observed that the initial rapid release of phosphates increases as the salinity increases. The mudbank water, however, may contain numerous inorganic and organic ingredients, including an appreciable amount of dissolved inorganic/ organic phosphates. This leads to a higher probability for other molecules to compete with phosphate already retained in the sediment; other anions in the watermedia also compete for surface sorption sites and reduce the phosphate adsorption during the initial time (fast reaction), and consequently affect the rate and mass of phosphate released or retained from the layer already present during the slow reactions (i.e. experimentallydetermined after 30 minutes), as explained by Froelich (1988) in the kinetic control of dissolved phosphate in natural rivers and estuaries.

In synthetic water as well as in mudbank water, the mud bank sediments showed the adsorption maximum at higher salinities when the quasi-steady state (or quasi-equilibrium) is reached. This is in agreement with the general view that the sorption increases as the ionic strength of the background solution increases (Nair et al., 1984). The anions like SO_4^{2-}, F^-, OH^-, $B(OH)_4^-$ etc. present in the synthetic water are readily in an exchangeable state rather than getting adsorbed. Obviously in contrast to mudbank water, the synthetic seawater is free from complex inorganic and organic molecules; hence the direct adsorption of phosphates on the surface of the sediment does not suffer any hinderance from these molecules. But the increase in phosphate adsorption with increase in salinity of mudbank water shows that the complex organic or inorganic molecules which may be present in the mudbank water, would help directly or indirectly the linking of phosphates with sediment. For example, sediments containing iron and aluminium hydroxyoxides or surfaces coated with these phases display a very low desorption capacity, probably due to the reaction of phosphate with the oxides themselves (i.e. processes like the chemisorption, exchange with hydroxyls, precipitation of Fe- and Al- phosphates) (Froelich, 1988). It is also probable that adsorption occurs simultaneously at all sites with higher energy sites being filled preferentially during the initial stages of adsorption as indicated by Griffin & Jurinak (1973).

The comparatively higher steady state desorbed phosphate concentration at lower salinities signifies the natural phenomenon that a more mobile sediment phosphorus pool is present in the mudbank area. Consequently the mudbank sediments exhibited an increased phosphate desorption potential, when there is a drop in salinity. Suffice to say, that the phosphates from the sediments are continuously recycled in the natural mudbank water, thereby maintaining an appreciable concentration of dissolved available phosphates during the active phase of the mudbank, in which case the lowest salinity was observed (Chapter 4) among the three periods of study namely pre-mudbank, mudbank and post-mudbank.

II. Adsorption characteristics at different phosphate concentration

Figures 29,30,31 & 32 represent the plot of C against C/x/m which are computed from the results presented in figures 25(a), (b), (c) & (d) respectively. A two slope (biphasic) plot is observed in all cases. The correlation coefficients (r), intercepts, and slopes obtained for the regressional lines are summarized in Table 6.

A biphasic or two-slope sorption pattern can explain the kinetics (mechanism) of phosphate adsorption at different phosphate concentrations. Several researchers (Griffin & Jurinak, 1973; Eisenreich & Armstrong, 1978; Taylor & Ellis, 1978; Ku et al., 1978; Twinch & Breen, 1982) also reported a biphasic (two-slope) sorption pattern as indicative of dual phosphate adsorption mechanisms of sediments, soils and inorganic minerals over a wide range of quasi-steady state soluble reactive phosphorus concentration. In all cases a first phase of short duration ($\approx$ 10 minutes) following second order kinetics was observed; this was followed by a phase of longer time of first order kinetics. The biphasic

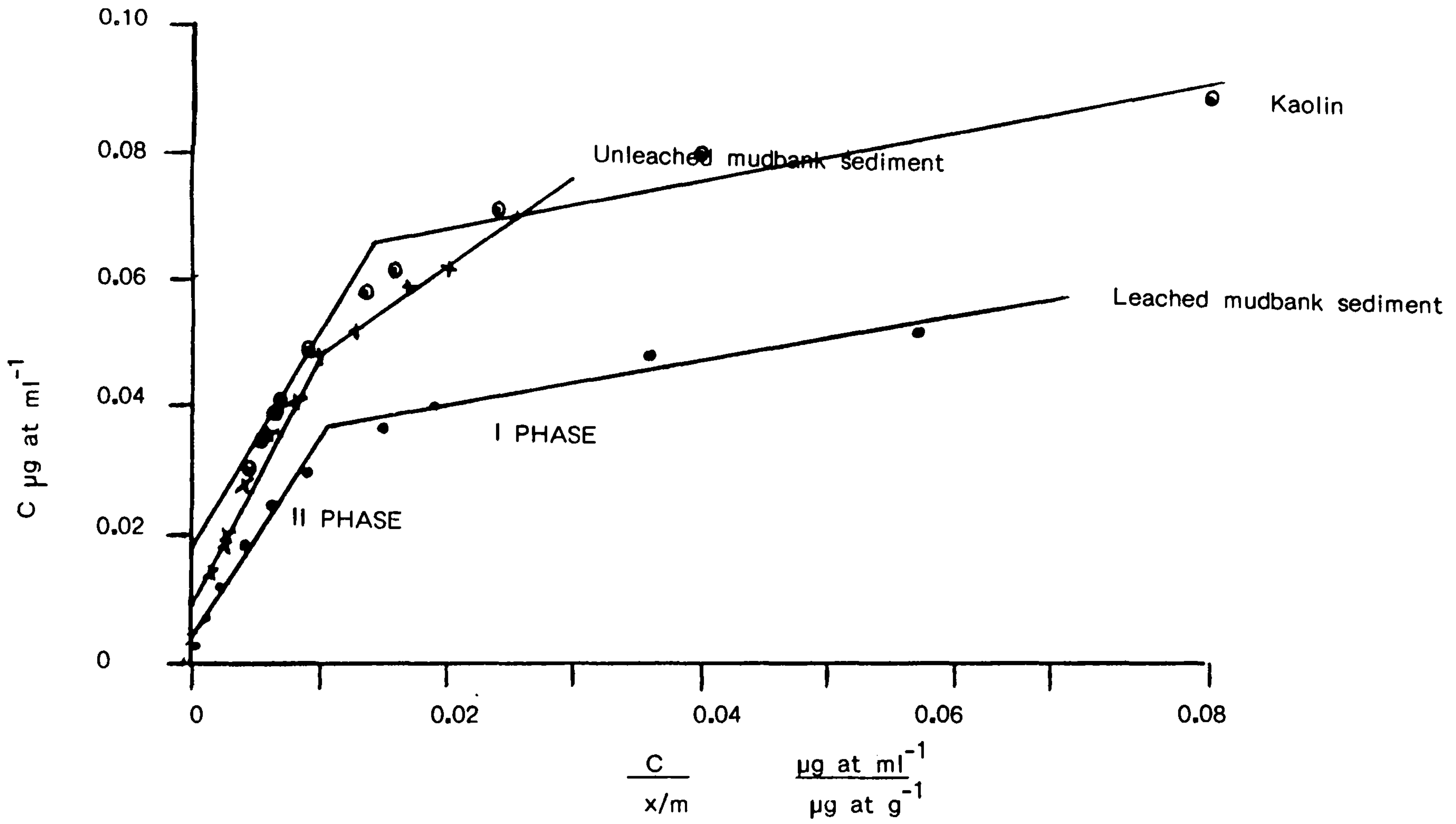

Figure 29. Plot of C against $\frac{C}{x/m}$ on the sorption characteristics of leached and unleached mudbank sediments and kaolin at initial phosphate concentration of 0.005 µg at l^{-1}

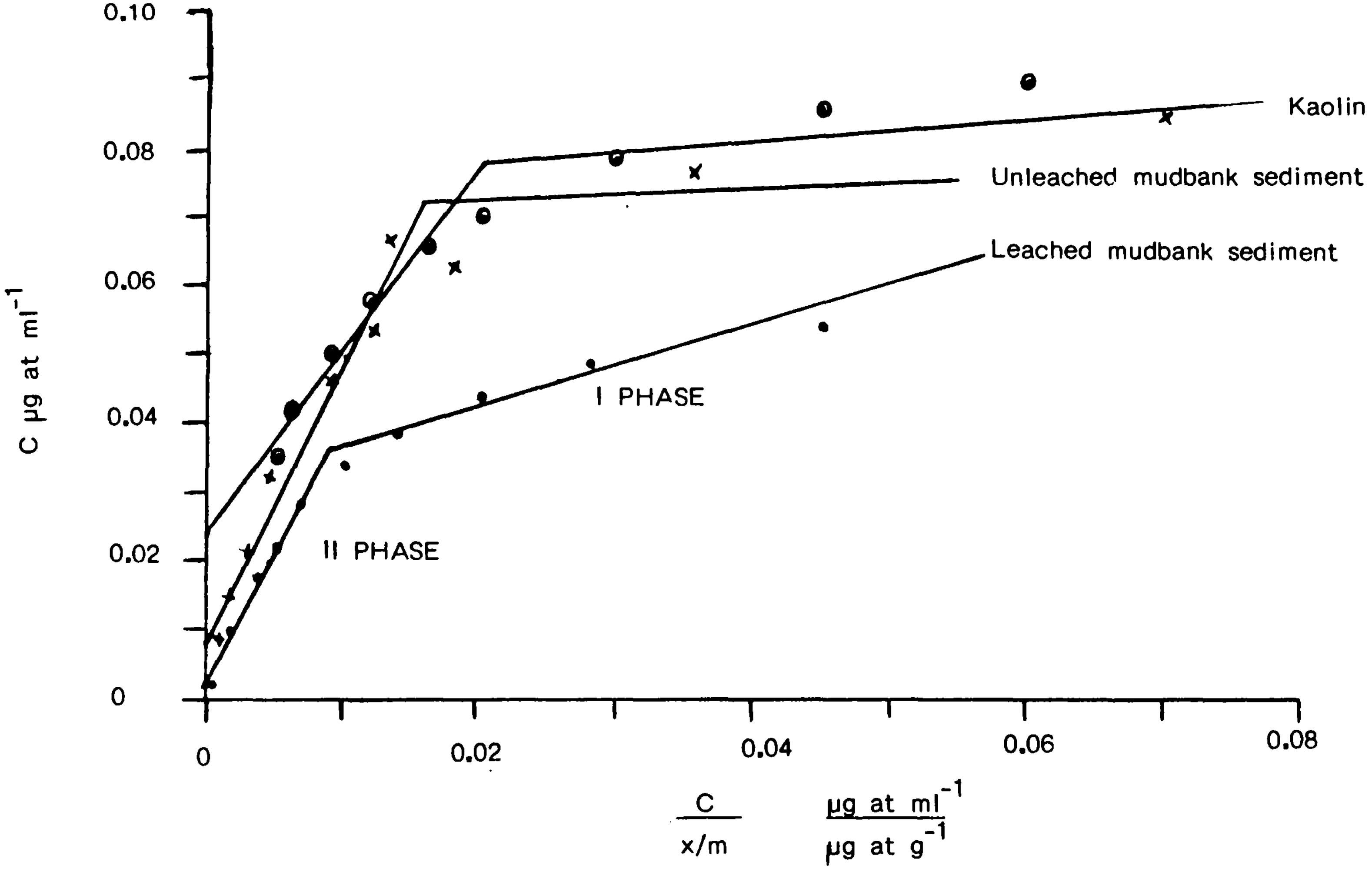

Figure 30. Plot of C against $\frac{C}{x/m}$ on the sorption characteristics of leached and unleached mudbank sediments and Kaolin at initial phosphate concentration of 0.01 μg at ml^{-1}

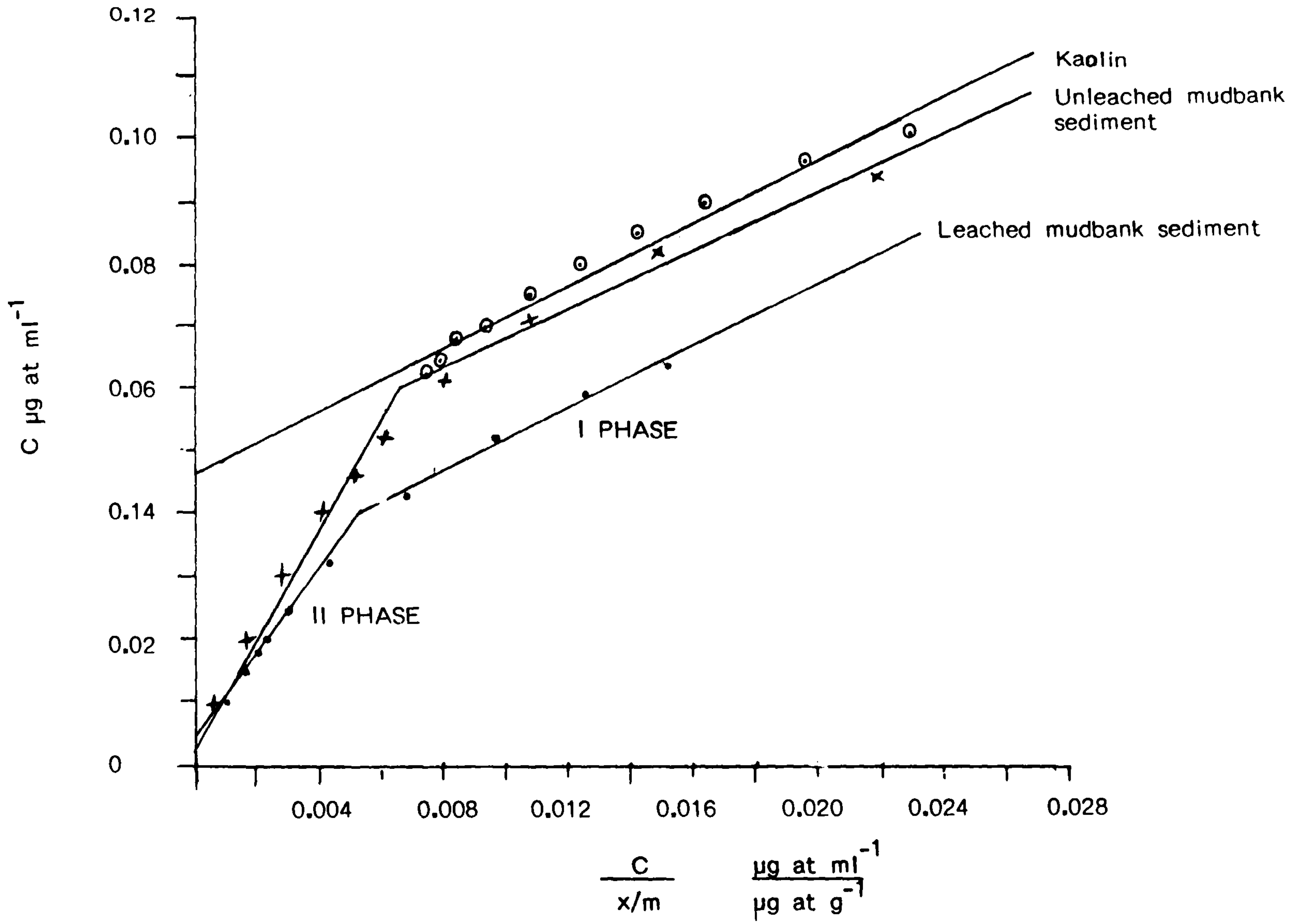

Figure 31. Plot of C against $\frac{C}{x/m}$ on the sorption characteristics of leached and unleached mudbank sediments and kaolin at initial phosphate concentration of 0.05 µg at ml^{-1}

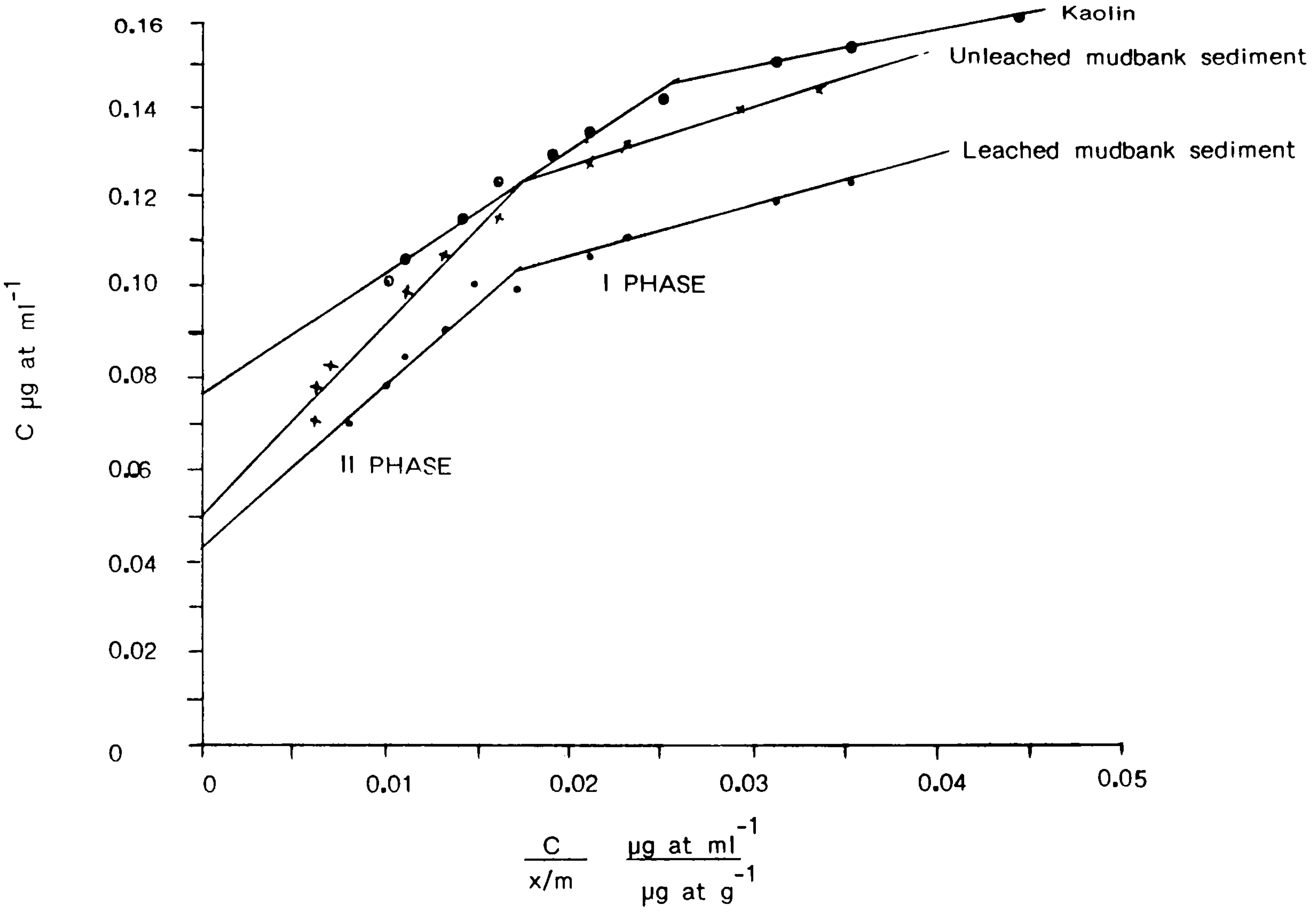

Figure 32. Plot of C against $\frac{C}{x/m}$ on the sorption characteristics of leached and unleached mudbank sediments and Kaolin at initial phosphate concentration of 0.10 ug at ml^{-1}.

Table - 6. Correlation coefficients, intercepts and slopes obtained from the plot of C against $\frac{C}{x/m}$ (Figures 29,30,31 and 32) on the adsorption characteristics of mudbank sediments at different phosphate concentration ($n = 5$).

Adsorbent		0.005 µg ml^{-1}			0.01 µg ml^{-1}			0.05 µg ml^{-1}			0.10 µg ml^{-1}		
		r	Intercept	Slope	r	Intercept	Slope	r	Intercept	Slope	r	Intercept	Slope
Kaolin	I-Phase	0.943	0.0601	0.3848	0.871	0.0743	0.1637	0.985	0.0464	2.5340	0.998	0.1223	0.8345
	II-Phase	0.989	0.0185	3.1530	0.986	0.0246	2.7017				0.988	0.0760	2.6720
Unleached mudbank sediment	I-Phase	0.989	0.0335	1.4459	0.817	0.0711	0.0783	0.986	0.0447	2.3319	0.994	0.9903	1.3186
	II-Phase	0.988	0.0093	4.0248	0.987	0.0085	4.0036	0.974	0.0010	8.9126	0.976	0.0500	4.1561
Leached mudbank sediment	I-Phase	0.971	0.0330	0.3524	0.959	0.0311	0.5474	0.992	0.0270	2.4931	0.994	0.0837	1.0992
	II-Phase	0.980	0.0044	3.1018	0.993	0.0022	3.9473	0.995	0.0043	6.6237	0.986	0.0433	3.4276

kinetics does, however, indicate that at least two exchange mechanisms are involved in phosphate exchange across the sediment-water interface; the rapid and slow phases of exchange occur concurrently and that each phase may consist of more than a single uptake mechanism (Li et al., 1972).

The phosphate adsorption capacity of sediment is thought to be largely dependent on various factors like inorganic clay fraction (Stumm & Leckie, 1970; Golterman, 1973; Syers et al., 1973), organic material content (Hesse, 1973; Slater & Boag, 1978), $CaCO_3$ content (Gunatilaka, 1982; Kuo & Lotse, 1972; Cole et al., 1953), extractable Fe- and Al- (Berkheiser et al., 1980; Gunatilaka, 1982; Syers et al., 1971), phosphate status of the sediments (Hesse, 1973; Twinch & Breen, 1982), the upward and downward migration of porewater (Shaw & Prepas, 1989) etc.

However, adsorption taking place at various sites on the particle surface or subsequent adsorption taking place in layers, may explain the two slopes observed in this study, as also has been observed by Gunatilaka (1982). Griffin & Jurinak (1973) indicated that adsorption occurs simultaneously on all sites with higher energy sites being filled preferentially during the initial stages of adsorption. The two distinct linear regions in the graphs (Figures 29,30,31 & 32) represent the lower concentration range (I phase) and the higher concentration range (IInd phase).

Many workers (Eisenreich & Armstrong, 1978; Ku et al., 1978; Twinch & Breen, 1982) have derived Langmuir constants from these plots to calculate parameters like adsorption maximum, bonding energy constants, number of adsorption sites etc. But in reality, Langmuir monolayer adsorption model is largely ruled out here as the adsorption occurs simultaneously on all sites with higher energy sites being filled preferentially during the initial stage of adsorption (Griffin & Jurinak, 1973). In general, these approaches have not provided useful mechanistic information (White & Taylor, 1977; Posner & Bowden, 1980; Froelich, 1988). Further the natural processes like turbulent mixing, bio-turbation and other hydrographical conditions can hardly be simulated in the laboratory studies. Hence no attempt was made for the calculation of these energy constants from the plots under discussion.

The time-dependent graphs (Figures 25(a), (b), (c) and (d)) show the lowest adsorption maximum for kaolin and the highest for leached sediment. This clearly indicates that the phosphate adsorption capacity of the synthetic mud (kaolin) is lower than that of mudbank sediment. Froelich (1988) also opined that pure clays (e.g.kaolinite) have a limited ability to sorb phosphates beyond the initial adsorption step, while clays containing natural oxide coatings have a higher capacity for phosphate sorption.

The simplest pausible model explaining the complex and variable behaviour of phosphate - particle interactions (Bowden et al., 1977; Barrow, 1983) involves adsorption and desorption (uptake and release) of dissolved phosphates via a two-step process; rapid surface adsorption (or desorption) of phosphate onto/off reactive surface followed by slow penetration (or release) by solid-state diffusion of this surface phosphate into/out of sub-surface horizon within the interior of particles (Froelich, 1988). Barrow (1983) also suggested that the fast adsorption of divalent phosphate (HPO_4^{2-}) on a variable - charged surface induces a slow diffusion towards the interior of the particle. Further the clays in the mudbank sediments also might have different coatings of inorganic (like Fe- and Al- hydroxides) and organic materials as compared to synthetic clay (kaolin). Surficial coatings of Fe- and Al- hydroxides have a higher capacity for adsorbing phosphate in the second step and for maintaining low quasi - steady state phosphate concentrations in solutions (Froelich, 1988). It is however not unlikely that organics and organic coatings are important in the adsorption of phosphate (Martens et al., 1978; Murray et al., 1978; Rosenfeld, 1979). Some workers like Olsen & Watanabe (1957) and Krom & Berner (1980a) conclude that the nature of the clay mineral in a soil seemed to be less important in controlling the adsorption of phosphate than surface area and the degree of weathering or some factors associated with the degree of weathering.

In all the three sets of sediments (kaolin and leached and unleached mudbank sediments), the maximum adsorption was observed not at the highest desorbed phosphate concentrations but rather at some optimum concentrations. For example, the adsorption maximum for kaolin and leached and unleached mudbank sediments were observed at 0.005, 0.01 and 0.05 µg at ml^{-1} respectively. Further, the percentage increase in phosphate adsorption is reduced as the phosphate additions increased. This trend was also reported by Bostrom & Pettersson (1982). Laquer & Manahan (1987) also noted in general, that the adsorption is less favoured as the solution concentration increases. The reduced uptake at higher phosphate application may be simply due to increased saturation of adsorption sites (Holden, 1961; Twinch & Breen, 1982). The actual amount of quasi-steady state dissolved phosphate concentration (in µg at ml^{-1}) in each set of experiment is summarised as follows.

	0.005 µg at ml^{-1}	0.01 µg at ml^{-1}	0.05 µg at ml^{-1}	0.10 µg at ml^{-1}
Kaolin	0.00150	0.0033	0.0215	0.0510
Unleached sediment	0.00075	0.0009	0.0030	0.0380
Leached sediment	0.00025	0.0003	0.0045	0.0400

In the seasonal distribution of nutrients (Chapter 4) the highest values of dissolved inorganic phosphate were observed during the mudbank period. During this period the dissolved inorganic phosphates concentration ranged from 0.003 to 0.008 µg at ml^{-1} (whereas in the pre- and post-mudbank periods, values ranged from 0.0002 to 0.0013 µg at ml^{-1}). This study on phosphate sorption mechanism with mudbank sediments (especially unleached mudbank sediments) revealed that the maximum phosphate adsorption is at 0.05 µg at ml^{-1}. At this adsorption maximum, the value of dissolved inorganic phosphate concentration is 0.0030-0.0045 µg at ml^{-1} which is in good agreement with those determined in the field (0.003 to 0.008 µg at ml^{-1}).

The slightly higher adsorption maximum observed for the leached sediment than the unleached sample may be arising from leaching processes which make the surfaces of the sediment free from foreign particles producing more available surface area (or adsorption sites). However, the slight change in the trend observed in the case of maximum amount of phosphate adsorbed by unleached sediment is difficult to be explained on the basis of the present study.

III. Adsorption characteristics at different sediment concentrations

Higher range of sediment concentration and longer reaction times have failed to establish a quasi-steady state or quasi-equilibrium of a linear form. Cole _et al_. (1953), Kuo & Lotse (1972) and Gunatilaka (1982) also failed to obtain linear regions in their adsorption isotherm model. The figure 26 illustrates the salient features of phosphate sorption by mudbank sediments at varying concentrations of sediment on a time-oriented basis. The increasing sediment concentrations make the exchange processes become polybasic involving the combined effects of several exchange reactions occuring at different rates through different mechanisms (Li _et al_., 1972; Twinch & Breen, 1982). The slow reactions rate via some diffusion-controlled processes cannot be fitted to simple adsorption models (Carritt & Goodgal 1954; Froelich, 1988). Obviously the (ad-/de-) sorption reaction rates are affected by sediment concentrations or soil-solution ratio (Hope & Syers, 1976; Logan, 1982) and labile phosphates (Barrow, 1974; Oloya & Logan, 1980).

Beyond the saturation point of 10 g in a volume of 200 ml (in which 79-93% adsorption takes place) there is a decrease in the rate of adsorption (or there is little further adsorption) as the concentration of sediment increases. At higher concentration of sediments, the desorption of the previously adsorbed phosphate occurring concurrently with adsorption will become a notable factor in maintaining the dissolved phosphate concentration. As pointed out by Logan (1982), here also the difficulty in determining the effect of labile phosphate on equilibrium is due to the difference in rate of desorption of previously adsorbed phosphate and the rate of initial adsorption. Further, the sediments of mudbank appears to act as a buffer system in which the large increase of sediments concentration after the saturation point will have little effect on adsorption. For example, a ten fold increase (100 g) in sediment concentration will only increase the adsorption by about 6% after the saturation point. Froelich (1988) also reported that many solids and sediments display buffer capacities. The steady-state may become an ephemeral phenomenon (Webster & Patten 1979; Newbold et al., 1981; Elwood et al., 1981) as the sediment concentration increased from its saturation level.

Conclusion

The gradients between the sediment - water interface primarily control the fluxes of nutrients from the sediment to the overlying waters and hence the boundary layer processes are of prime interest (Berner, 1977; Krom & Berner, 1980b; Suess, 1981).

It has been found that the ionic concentration (i.e. salinity) influences the phosphate sorption characteristics of mudbank sediments. When the ionic concentration of the media is lower, greater will be the desorption potential. Comparatively, lower salinities were recorded during the mudbank period (Chapter 3) than other periods. The lowering of salinity helps to increase the dissolved inorganic phosphate concentration, i.e. it favours desorption from sediments to overlying waters. But during the mudbank period the high suspended load (1000 to 1800 mg l^{-1}) will largely remove the dissolved phosphate by adsorption. From the sorption study it is found that the saturation level is attained only when the sediment concentration is 50 g l^{-1}. So the benthic and suspended sediments will remove the excess dissolved phosphates generated from the increased desorption potential due to the lowering of salinity.

In short, the mudbank sediments are capable of "buffering" the dissolved phosphate concentration.

Now a question arises whether the mudbank sediment adsorbs the dissolved phosphates to its maximum capacity or saturation level. The study of phosphate adsorption at varying concentrations of dissolved phosphates showed that the mudbank sediment has its maximum adsorption at 0.05 μg at ml^{-1} in which it left 0.0030 to 0.0045 μg at ml^{-1} dissolved inorganic phosphates as unadsorbed (desorbed). From the periodic variability (Chapter 4) of dissolved inorganic phosphate the higher values of dissolved inorganic phosphates were obtained during the mudbank period and the values ranged from 0.003 to 0.008 μg at ml^{-1}. This indicates, clearly, that the mudbank period sediments have not only higher sorption capacity (since experimentally it is proved that it has higher sorption capacity than synthetic clay (kaolin)), but also it adsorbs the phosphate to its maximum capacity during the period of mudbank in which highest concentration of dissolved and sedimental phosphates were recorded (Chapter 4). Hence the two characteristic features of mudbank period, i.e. lower salinity and higher suspended load in which the former supports desorption and the later supports adsorption, make the phosphate buffer mechanism a significant natural process.

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*Not referred to in original

Annexure-1. Chronological table of theories and related works on mudbanks

Year	Author	Hypothesis/Reports	Remarks
1678	Pinkerton	First observational reporting	1860 Administrative report of Travancore.
1775	Capt.Cope	Siting of Alleppey mudbank	Referred as 'Mud Bay'
1860	Crawford	Personal observation of mud cones at Alleppey and advances a hypothesis of subterranean flow of mud.	Probably the first explanation to mudbank formation.
1881	King	Report on Alleppey and Narakkal mudbanks - refers to presence of oil in mud.	Mudbank described as a smooth water anchorage
1886	John Rhode	Theory on transport of fluid mud strata below port of Alleppey.	Postulated as build up of hydraulic pressure in inland lagoon/estuary causing subsurface mud transport to coastal regions.
1938	Bristow	First comprehensive treatise as "History of mudbanks", Vols I and II	Exhaustive observations on formation, maintenance and movement of mudbanks at Alleppey and Narakkal - serves historical reading interest
1938	Ducane	Special report on studies of Narakkal mudbanks.	Varying amounts of carbon and organic debris noted - hydraulic pressure transfer doubted.
1953	Seshappa	Phosphate content of mudbanks along Malabar Coast reported.	Increased phosphate content in the overlying waters during the southwest monsoon noted.
1956	Seshappa		
1956	Seshappa & Jayaraman	Phosphate content of mudbanks reviewed	Higher concentrations noted in comparison to other coastal regions.
1959	Ramasastry	Hypothesis on mudbanks being associated with upwelling and divergence near 20-30 m bottom layer	Resultant vertical acceleration lifts fine mud of bottom into suspension.

1966	Varadachari	Role of estuarine output and mudbank formation discussed.	Shoreline configuration of Kerala State described.
1966	Damodaran & Hridayanathan	Flocculation effect to keep mud in suspension postulated.	Lowering of surface salinity is attributed to flocculation.
1967	Rao	Fishery aspects of mudbanks discussed.	Physico-chemical features of Alleppey bank also considered.
1968	Dora *et al.*	Textural studies on Narakkal mudbank	Predominantly fine clay fraction in mudbank sediments noted.
1969	Varma & Kurup	Mudbank theory explained on the basis of role of waves and rip-currents	Formation is a result of interaction between the inshore and off-shore transport of sediments in suspension.
1971	Moni	Study of mudbanks along the southwest coast of India.	Mudbanks and shore stability of the southwest coast of India discussed.
1972	Kurup	Hypothesis extended to converging littoral currents in the inshore	Role of these currents on formation of mudbanks at south of Alleppey discussed.
1972	Reddy & Varadachari	Wave refraction studies carried out.	Attempts to explain mudbank movement.
1972	Iyer & Moni	Mudbank and shoreline stability evaluated.	Beach stability features studied.
1973	Damodaran	Benthos studied in mudbank region.	Biological aspects ascertained.
1974	Gopinathan & Qasim	Alleppey mudbank characteristics studied in detail.	Role of currents and waves in mudbank formation, maintenance and dissipation explained.
1974	Jacob & Qasim	Chemical studies on Alleppey mudbank	High amounts of total phosphorus and organic carbon noted.
1975	Kurup & Varadachari	Hydrography of Purakad mudbank region reported	Seasonal distribution of temperature and salinity studied.

1976	Nair	Mudbank of Kerala Coast	Review paper.
1977	Kurup	Details the physical aspects of mudbanks.	Role of texture of sediments in mudbanks evaluated
1977	Mathew *et al*.	Diurnal variations of zooplankton related to currents and other ecological parameters.	Biological studies in mudbank regions.
1981	Mac Pherson & Kurup	Mathematical model on wave damping.	Viscous fluid mud bottom causing wave damping suggested.
1981	Kurup *et al*.	Wave damping studies.	Experimental work to relate wave damping to viscosity.
1983	Nair	An interim report on mudbanks off Kerala coast.	Some chemical and sedimentological aspects studied.
1984	Silas *et al*.	Mudbanks of Kerala coast.	Detailed studies on physical, chemical and biological aspects reported.
1984	Mallik & Ramachandran	State of art report on mudbanks of Kerala coast.	Review article.
1985	Ramachandran & Mallik	Studies on Alleppey mudbanks.	Sedimentological aspects detailed.
1986	Shenoi & Murthy	Wave damping studies.	Viscous damping of solitary waves in mudbank region explained.
1987	Nambisan *et al*. 1987	Chemical oceanographic aspects reported.	Studies on chemical aspects of mudbanks.
1987	Balchand *et al*. 1987	Theories and prespectives of mudbanks.	Review article.
1988	Mallik *et al*.	Mudbanks of Kerala coast.	Sedimentological aspects detailed.
1989	Ramachandran	Geochemical characteristics of Quilandy mudbank environment.	Sedimentological aspects detailed.

ANNEXURE - 2

Procedure for preparing artificial seawater (APHA, 1980)

Compound in order of addition	Concentration mg l^{-1}
NaF	3
$SrCl_2 \cdot 6H_2O$	20
H_3BO_3	30
KBr	100
KCl	700
$CaCl_2 \cdot 2H_2O$	1,470
Na_2SO_4	4,000
$MgCl_2 \cdot 6H_2O$	10,780
NaCl	23,500
$Na_2SiO_3 \cdot 9H_2O$	20
Na_4EDTA	1
$NaHCO_3$	200

Annexure - 3. Mean and range of hydrographical parameters during pre-mudbank, mudbank and post-mudbank periods at surface and bottom at mudbank area (stations 1-5) (values in parenthesis indicate non-mudbank area consolidated data in range)

Sl. No	Parameter		Station	Pre-mudbank period		Mudbank period		Post-mudbank period	
				Mean	Range	Mean	Range	Mean	Range
1.	SALINITY $X10^{-3}$	Surface	1	33.54	33.30 - 33.78	31.30	24.27 - 34.15	34.22	32.49 - 34.75
			2	34.10	33.65 - 35.00	30.90	28.79 - 32.97	33.90	30.70 - 36.09
			3	32.60	31.65 - 33.30	31.00	27.09 - 33.49	31.80	29.99 - 34.75
			4	33.05	32.81 - 33.30	29.90	24.27 - 35.50	32.20	29.40 - 34.75
			5	32.55	32.30 - 32.81	29.80	28.75 - 31.05	32.70	30.74 - 34.75
			(Non-mudbank area		34.90 - 36.00		32.90 - 34.10		34.50 - 35.60)
		Bottom	1	34.20	33.10 - 35.00	30.74	27.66 - 33.82	32.60	30.75 - 36.09
			2	35.00	33.10 - 35.60	32.50	30.48 - 33.65	34.20	31.66 - 36.09
			3	33.77	33.65 - 33.90	28.87	27.00 - 33.48	33.10	30.74 - 36.09
			4	35.55	33.40 - 36.10	29.80	26.00 - 33.99	34.30	33.33 - 34.75
			5	33.40	32.90 - 33.90	29.20	28.35 - 30.05	32.20	29.83 - 36.09
2.	TEMPERATURE °C		1	32.7	32.5 - 33.0	29.4	29.0 - 32.0	30.7	30.0 - 32.0
			2	32.8	32.5 - 33.0	30.0	29.0 - 32.0	30.7	30.1 - 31.5
			3	32.7	31.5 - 33.0	30.8	29.5 - 32.0	30.8	30.1 - 31.5
			4	32.8	32.5 - 33.0	30.6	29.5 - 31.7	30.8	30.1 - 32.0
			5	32.8	32.0 - 33.5	30.6	29.5 - 31.7	30.7	30.0 - 32.0
			(Non-mudbank area		29.1 - 32.0		29.5 - 31.5		30.0 - 30.5)

Annexure 3 (Contd...)

Sl. No.	Parameter		Station	Pre-mudbank period		Mudbank period		Post-mudbank period	
				Mean	Range	Mean	Range	Mean	Range
3.	pH	Surface	1	8.00	7.80 - 8.20	7.49	7.30 - 7.64	7.80	7.63 - 7.97
			2	8.05	7.95 - 8.15	7.33	7.05 - 7.60	7.89	7.65 - 8.05
			3	8.10	7.70 - 8.20	7.46	7.00 - 7.74	7.85	7.57 - 8.07
			4	8.10	8.00 - 8.20	7.54	7.20 - 7.74	7.88	7.60 - 8.09
			5	8.08	7.90 - 8.26	7.40	7.13 - 7.74	7.83	7.59 - 7.98
			(Non-mudbank area		7.85 - 7.70		6.83 - 7.15		6.83 - 8.16)
		Bottom	1	8.28	8.25 - 8.30	7.39	7.05 - 7.78	7.72	7.30 - 7.94
			2	8.10	7.90 - 8.25	7.40	7.30 - 7.50	7.79	7.46 - 7.99
			3	8.00	8.80 --8.15	7.31	7.15 - 7.55	7.70	7.33 - 7.98
			4	8.03	7.80 - 8.20	7.35	7.10 - 7.70	7.75	7.36 - 8.09
			5	8.05	7.95 - 8.15	7.10	7.00 - 7.55	7.33	7.01 - 7.62

Annexure 3 (Contd...)

Sl. No.	Parameter	Station		Pre-mudbank period		Mudbank period		Post-mudbank period	
				Mean	Range	Mean	Range	Mean	Range
4 .	DISSOLVED OXYGEN ml l^{-1}	Surface	1	7.50	6.47 - 8.33	7.93	6.64 - 9.22	5.46	5.25 - 5.66
			2	7.55	6.96 - 8.11	6.34	5.34 - 6.96	5.71	5.42 - 5.99
			3	7.10	5.99 - 8.17	6.44	6.15 - 6.64	5.87	5.42 - 6.31
			4	6.44	6.07 - 6.80	6.27	5.82 - 6.72	5.99	5.66 - 6.31
			5	7.40	7.04 - 7.76	6.19	6.15 - 6.23	6.27	6.07 - 6.47
			(Non-mudbank area		4.61 - 5.74		2.75 - 6.23		6.55 - 7.60)
		Bottom	1	6.60	6.10 - 7.00	6.00	5.04 - 6.96	5.38	4.77 - 5.99
			2	6.84	6.39 - 7.28	6.04	4.53 - 7.29	5.18	4.69 - 5.66
			3	6.92	6.88 - 6.96	4.32	3.96 - 4.69	5.00	4.50-- 5.55
			4	7.10	6.90 - 7.20	4.37	4.12 - 4.61	5.40	4.93 - 6.40
			5	6.84	6.80 - 6.88	3.96	3.31- 4.61	5.20	4.80 - 5.60

Annexure 3 (Contd...)

Sl. No.	Parameter		Station	Pre-mudbank period		Mudbank period		Post-mudbank period	
				Mean	Range	Mean	Range	Mean	Range
5.	CHLOROPHYLL mg m^{-3}	Surface	1	3.13	1.29 - 3.84	13.37	6.47 - 20.79	9.54	1.40 - 21.84
			2	6.00	3.49 - 8.49	5.25	2.15 - 6.11	4.00	1.50 - 20.15
			3	7.79	4.93 -11.51	3.09	1.82 - 4.97	3.23	1.19 - 5.71
			4	7.50	3.61 -11.38	7.33	5.54 - 9.12	2.38	0.81 - 3.95
			5	16.98	10.34 -23.62	13.70	4.10 - 23.30	9.72	1.00 - 23.71
			(Non-mudbank area		1.80 -10.48		3.18 - 21.56		3.41 - 7.86)
		Bottom	1	2.46	1.86 - 3.06	8.78	2.54 -15.02	6.09	3.10 - 10.55
			2	10.56	6.46 -21.63	10.00	3.77 -13.75	7.09	1.47 - 14.97
			3	8.05	6.20 -11.20	7.51	1.11 -12.01	4.29	1.81 - 8.82
			4	14.10	8.30 -19.92	11.50	8.80 -15.14	6.41	3.54 - 9.26
			5	20.77	19.44 -22.10	15.75	7.30 -20.09	10.39	3.38 - 22.20

Annexure 3 (Contd....)

Sl. No.	Parameter	Station		Pre-mudbank period		Mudbank period		Post-mudbank period	
				Mean	Range	Mean	Range	Mean	Range
6.	DISSOLVED ORGANIC CARBON mg l^{-1}	Surface	1	3016	2810 - 3338	1259	926 - 1849	3253	2865 - 3844
			2	1778	799 - 2757	1470	776 - 2528	3203	2845 - 3533
			3	2823	2458 - 3037	1722	565 - 2981	3302	2556 - 3835
			4	3283	3265 - 3301	1334	304 - 1849	3400	1917 - 4659
			5	3377	3134 - 3621	1550	761 - 2339	3405	2288 - 4608
			(Non-mudbank area		2315 - 3441		547 - 773		915 - 1964)
		Bottom	1	2316	1369 - 3263	914	583 - 1245	3064	2577 - 3533
			2	2536	1452 - 3033	1100	692 - 1400	3087	2524 - 3766
			3	2296	1452 - 3338	1604	643 - 2905	3133	2535 - 3553
			4	2905	2546 - 3265	918	643 - 1094	3253	2555 - 3960
			5	3102	2659 - 3546	1100	750 - 2849	3158	1704 - 5009

Annexure 3 (Contd...)

Sl. No.	Parameter	Station	Pre-mudbank period		Mudbank period		Post-mudbank period	
			Mean	Range	Mean	Range	Mean	Range
7.	MOISTURE %	1	64.27	62.14 - 66.14	70.39	64.50 - 79.10	67.71	65.66 - 68.38
		2	71.30	63.50 - 78.00	71.70	65.80 - 79.30	65.12	63.47 - 66.56
		3	68.84	65.10 - 72.20	70.10	69.20 - 71.03	64.57	63.08 - 65.61
		4	62.95	61.90 - 64.10	66.90	62.80 - 70.01	64.65	62.57 - 65.77
		5	63.61	63.20 - 64.01	69.90	70.50 - 69.20	68.15	61.60 - 69.17
		(Non-mudbank area		28.00 - 41.00		31.00 - 44.00		27.00 - 55.00)
8.	SEDIMENT ORGANIC MATTER mg g^{-1}	1	19.66	15.43 - 23.90	21.11	18.58 - 22.55	16.95	14.80 - 18.38
		2	21.50	16.07 - 25.57	21.95	19.97 - 24.72	24.11	12.20 - 40.27
		3	22.49	21.05 - 23.93	16.01	15.73 - 35.88	11.07	8.84 - 14.61
		4	21.32	21.18 - 21.45	20.05	19.90 - 20.19	14.97	12.18 - 17.15
		5	22.00	18.37 - 25.63	20.85	20.25 - 21.46	8.94	5.58 - 12.86
		(Non-mudbank area		18.20 - 21.40		18.46 - 24.00		12.36 - 98.60)

Annexure - 4. Mean and range of nutrients during pre-mudbank, mudbank and post-mudbank periods at surface and bottom at mudbank area (stations 1-5) (Values in paranthesisindicate non-mudbank area consolidated data in range)

Serial No.	Parameter		Station	Pre-Monsoon Mean	Pre-Monsoon Average	Monsoon Mean	Monsoon Average	Post-Monsoon Mean	Post-Monsoon Average
1.	Dissolved Ammonia µg at l^{-1}	Surface	1	10.0	9.9 - 17.0	13.0	12.2 - 15.6	4.5	4.1 - 4.9
			2	15.5	14.0 - 19.9	9.4	5.0 - 21.2	4.2	3.6 - 5.0
			3	26.4	13.0 - 28.0	5.0	1.7 - 10.5	4.5	3.5 - 5.2
			4	24.9	12.5 - 39.9	7.1	2.2 - 12.1	3.8	3.5 - 5.1
			5	29.9	19.9 - 51.0	3.6	2.0 - 7.0	4.6	3.9 - 7.0
			(Non-mudbank area		2.4 - 33.4		17.5 - 19.0		1.7 - 29.6)
		Bottom	1	6.0	4.2 - 10.5	13.8	8.5 - 18.0	5.0	3.9 - 5.2
			2	20.5	19.0 - 23.2	13.9	12.1 - 16.0	5.3	4.7 - 6.0
			3	15.7	14.0 - 19.9	4.3	2.4 - 6.1	5.3	3.5 - 4.0
			4	32.5	20.5 - 49.0	10.9	10.4 - 11.4	6.5	6.5 - 9.2
			5	28.3	24.5 - 41.0	5.3	5.1 - 5.5	4.9	3.5 - 5.5
2.	Dissolved Urea µg at l^{-1}	Surface	1	10.0	4.9 - 12.3	2.0	0.6 - 3.2	5.8	5.0 - 8.9
			2	8.5	7.3 - 18.6	2.5	2.4 - 2.6	5.5	3.7 - 7.3
			3	7.5	6.0 - 8.4	1.3	0.8 - 2.4	3.4	1.9 - 7.8
			4	7.2	5.0 - 8.0	1.7	1.0 - 4.3	2.8	2.3 - 5.8
			5	8.7	6.9 - 9.1	3.0	1.5 - 4.4	4.8	4.2 - 8.2
			(Non-mudbank area		3.6 - 4.6		1.1 - 2.5		1.1 - 3.2)
		Bottom	1	16.0	13.0 - 16.7	2.1	0.6 - 3.0	5.8	5.7 - 6.0
			2	12.5	7.4 - 16.0	2.2	1.3 - 2.2	4.9	2.0 - 8.0
			3	10.2	4.7 - 13.1	7.1	6.9 - 7.2	3.5	1.2 - 9.0
			4	7.9	6.0 - 8.7	3.7	1.2 - 7.3	2.7	1.0 - 6.4
			5	8.0	6.0 - 8.7	7.5	6.5 - 8.5	5.9	5.1 - 8.9

Annexure - 4 (cont....)

3.	Dissolved Silicate μg at l^{-1}	Surface	1	16.3	14.8 - 27.7	40.2	44.3 - 36.0	22.7	18.8 - 28.6
			2	16.5	9.7 - 32.3	31.8	21.5 - 38.7	28.8	14.7 - 42.9
			3	16.2	21.9 - 15.1	46.2	21.2 - 78.2	17.0	15.5 - 22.8
			4	17.5	12.8 - 22.1	44.1	25.6 - 62.5	35.2	14.8 - 54.4
			5	23.4	28.0 - 18.9	43.0	56.7 - 29.3	38.1	18.1 - 58.4
			(Non-mudbank area		18.7 - 27.6		56.6 - 74.7		36.6 - 60.2)
		Bottom	1	16.5	15.5 - 20.5	48.8	45.0 - 50.6	30.3	26.1 - 37.0
			2	16.7	14.7 - 18.8	41.8	40.0 - 43.5	32.8	23.4 - 38.1
			3	20.2	18.4 - 21.9	45.0	28.0 - 72.8	35.9	19.8 - 46.4
			4	20.6	15.3 - 25.9	57.8	38.0 - 68.2	36.3	20.0 - 52.7
			5	19.3	14.9 - 23.9	55.0	46.0 - 70.1	34.3	21.7 - 42.7
4.	Dissolved inorganic phosphate μg at l^{-1}	Surface	1	0.30	0.15 - 0.44	3.30	2.80 - 4.00	1.13	0.41 - 2.41
			2	0.49	0.40 - 0.58	7.95	3.00 - 9.30	0.23	0.20 - 0.25
			3	0.44	0.40 - 0.77	3.46	1.68 - 5.71	0.76	0.20 - 1.20
			4	0.66	0.42 - 0.90	3.33	1.10 - 5.20	0.53	0.20 - 0.80
			5	0.30	0.30 - 0.30	2.80	1.91 - 4.00	0.66	0.20 - 1.01
			(Non-mudbank area		1.00 - 5.70		3.60 - 9.30		0.40 - 2.60)
		Bottom	1	0.25	0.20 - 0.30	7.40	2.10 -10.60	1.20	0.30 - 2.40
			2	0.22	0.15 - 0.31	3.35	1.91 - 5.70	0.55	0.35 - 1.00
			3	0.71	0.60 - 1.34	2.72	1.61 - 4.50	0.70	0.20 - 1.20
			4	0.54	0.47 - 0.60	2.98	2.80 - 3.00	0.45	0.20 - 0.80
			5	0.37	0.30 - 0.44	3.00	2.32 - 3.40	0.20	0.70 - 1.10

Annexure - 4 (Cont....)

5.	Dissolved Organic Phosphate µg at l^{-1}	Surface	1	0.20	0.20 - 0.25	12.90	7.00 - 21.30	2.56	0.60 - 5.20
			2	0.16	0.12 - 0.20	16.76	12.10 - 20.70	2.73	1.60 - 4.70
			3	0.19	0.17 - 0.20	25.20	22.30 - 27.80	3.60	2.90-- 4.60
			4	0.33	0.30 - 0.36	23.94	20.50 - 27.90	4.60	1.40 - 9.00
			5	0.33	0.18 - 0.60	19.50	10.50 - 22.50	3.80	1.50 - 5.20
			(Non-budbank area		0.13 - 2.10		1.30 - 23.00		0.60 - 2.38)
		Bottom	1	0.10	0.50 - 0.10	15.00	10.50 - 21.00	3.56	1.60 - 5.00
			2	0.19	0.30 - 0.07	19.66	6.00 - 25.40	2.90	1.40 - 6.10
			3	0.33	0.19 - 0.62	16.15	15.20 - 16.80	3.76	3.80 - 5.70
			4	0.17	0.10 - 0.30	16.20	15.70 - 16.60	2.63	1.30 - 5.10
			5	0.31	0.30 - 0.31	15.00	13.30 - 16.70	3.80	1.70 - 7.80
6.	Dissolved Nitrite µg at l^{-1}	Surface	1	0.16	0.05 - 0.30	0.34	0.08 - 0.60	1.19	0.18 - 2.0
			2	0.23	0.11 - 0.32	0.29	0.05 - 0.30	1.45	0.80 - 2.1
			3	0.21	0.19 - 0.24	0.23	0.15 - 2.80	1.06	0.50 - 1.70
			4	0.20	0.20 - 0.24	0.57	0.05 - 3.90	0.77	0.11 - 1.60
			5	0.17	0.15 - 0.19	0.30	0.50 - 0.10	0.62	0.80 - 1.40
			(Non-mudbank area		0.38 - 1.19		1.40 - 8.90		0.30 - 2.79)
		Bottom	1	0.09	0.05 - 0.12	0.47	0.36 - 0.57	0.94	0.13 - 2.10
			2	0.15	0.03 - 0.34	0.23	0.10 - 0.36	1.14	0.19 - 2.10
			3	0.23	0.22 - 0.25	0.70	0.20 - 4.30	1.64	1.30 - 1.90
			4	0.20	0.18 - 0.22	0.43	0.10 - 0.90	1.06	0.09 - 2.20
			5	0.19	0.18 - 0.19	0.30	0.20 - 0.40	0.54	0.07 - 1.00

Annexure - 4 (cont....)

7.	Dissolved inorganic Nitrate µg at l^{-1}	Surface	1	0.51	0.42 - 0.59	10.53	5.50 - 24.80	6.00	2.0 - 14.6
			2	0.35	0.31 - 0.60	11.75	10.60 - 30.10	4.60	1.7 - 15.1
			3	0.91	0.13 - 1.75	26.40	20.60 - 57.40	5.40	0.70 - 15.4
			4	0.24	0.03 - 0.45	18.70	2.90 - 34.50	3.70	1.0 - 9.8
			5	0.13	0.01 - 0.25	18.0	11.60 - 24.40	3.60	1.8 - 8.7
			(Non-mudbank area		0.82 - 8.30		16.80 - 49.90		20.20 - 71.60)
		Bottom	1	0.33	0.32 - 0.34	12.26	12.26 - 18.50	4.32	2.50 - 10.20
			2	0.35	0.35 - 0.43	24.00	19.00 - 36.00	5.90	2.00 - 15.40
			3	0.62	0.44 - 0.91	62.85	20.80 -104.01	9.02	4.90 - 21.60
			4	0.14	0.01 - 0.26	12.20	7.90 - 17.50	4.40	0.60 - 11.10
			5	0.23	0.02 - 0.45	16.00	14.00 - 22.80	4.20	0.50 - 11.90
8.	Dissolved Organic Nitrate µg at l^{-1}	Surface	1	50.90	50.80 - 51.0	1550	1399 - 1822	148.5	100.7 - 196.2
			2	51.70	48.00 - 55.4	1842	1837 - 1848	118.0	53.6 - 199.1
			3	48.60	40.70 - 56.5	1812	1798 - 1827	149.0	54.1 - 200.5
			4	50.90	45.70 - 56.2	1837	1835 - 1839	110.6	51.7 - 189.4
			5	45.3	39.7 - 50.9	1650	1386 - 1890	146.8	55.4 - 201.6
			(Non-mudbank area		2.6 - 40.0		44 - 210		110.0 - 480.0)
		Bottom	1	53.8	52.4 - 55 .1	1740	1650 - 1800	124.7	56.0 - 199.4
			2	55.9	55.8 - 56. 1	1860	1830 - 1910	126.0	54.8 - 195.8
			3	43.8	32.2 - 55.4	1810	1788 - 1833	120.7	44.2 - 201.[illegible]
			4	63.1	56.7 - 69.6	1786	1760 - 1813	127.0	54.4 - 199.9
			5	59.5	51.7 - 87.3	1500	1363 - 1550	125.0	30.3 - 199.8

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Distribution pattern of salinity and silicon and their inter relationship in Cochin backwaters

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Abstract. Time series curves for salinity and reactive silicon at surface and bottom for the years 1976-77 and 1985-86 are preseted for Cochin backwaters. Pre-monsoon salinity gradient in the horizontal direction coupled with salinity instruction of northward deflection is a significant feature. Stratification is pronounced in the lower reaches of Periyar while southern part appears well mixed. During South-West monsoon, the estuarine conditions are transformed to freshwater except at bar-mouth, whereas post-monsoon is a transition period. High monsoonal riverine input of silicon are quantitatively lost in the estuary, largely influenced by salinity. A negative correlation exists between salinity and silicon indicating chemical conservative behaviour. The decinnial variation in the estuary are explained in the light of above results.

Keywords. Estuarine mixing; stratification; salinity gradient; silicon and inter-relation.

1. Introduction

The Cochin estuary is a water body of major port activities in the country. In recent years, several man-made changes have occurred in this ecological system. The construction of Thannirmukham bund lead to the deterioration and stagnation of water in the agricultural Kuttanad region, resulting in large changes in the hydrography of Cochin backwaters. Also inter-basin transfer (Periyar river to Muvattupuzha river) of water gave rise to new management problems.

Salinity — nutrient changes and distribution in the Cochin backwaters is largely affected by the intrusion of sea water and fresh water inflow in addition to the urban drainage and agricultural, industrial discharges. Eventhough considerable work has been done on the hydrography of this estuarine system. (Ramamirtham and Jayaraman 1963; Sankaranarayanan and Qasim 1969; Sankaranarayanan *et al* 1986) detailed account of inter-relationship between salinity and silicon remains unpublished.

The variation in the concentration of the reactive silicon during estuarine mixing is one of the interesting problems of estuarine chemistry. Liss (1976) and Aston (1978) have given a review on the silicon cycles in estuaries. Studies have shown that removal of silicon in estuaries by floculation and precipitation depends largely on salinity gradients. In some estuaries, the removal of silicon from river water is explainable in terms of simple dilution mechanism (Burton *et al* 1970; Fanning and Pilson 1973) or as the result of physical, chemical and biological processes taking place in estuaries in varying degrees (Kamatani and Takano 1984). The present investigation assesses the seasonal and spatial variation in salinity and reactive silicon in Cochin estuary during 1976-77 and 1985-86 and analyses its inter-relationship.

The backwaters from Alleppey to Azhikode (09° 40' — 10° 12' N, 76° 15' — 76° 25' E) from a tropical estuary with two seasonal openings into the Arabian sea, one at Parur (North) and the second at Andhakaranazhi, and a permanent opening at Cochin. During flood tide, the sea water enters the estuary *via* Cochin barmouth (12 m depth) and the flow reverses during the ebb tide. The magnitude of influence of the tide progressively decreases with increasing distance from barmouth.

Out of the six major rivers, discharging fresh water into the Cochin backwaters, the Periyar joins on the northern part. A large number of heavy industrial concerns manufacturing fertilizers, insecticides and other chemicals are situated on this river bank. The Muvattupuzha river joins the southern part of the backwaters. Discharges from other rivers influence the hydrology of the backwaters only during monsoon when gates of Thannirmukham bund are kept open.

2. Materials and methods

The locations of the sampling stations during two different surveys (figures 1 and 2) were so fixed as to give a fairly good coverage of the prevailing complex environmental conditions. Both surface and bottom samples were collected at fortnightly intervals from September 1976 to May 1977 and June 1985 to May 1986. Surface samples were collected by using a clean plastic bucket and bottom water samples by using a Hytech water sampler. Salinity and reactive silicon were estimated by standard methods as given by Strickland and Parsons (1972). In order to understand the seasonal and spatial variations of chemical parameters, the season were divided into three distinct periods, namely (i) monsoon (June — September), (ii) post-monsoon (October — January) and (iii) pre-monsoon (February — May).

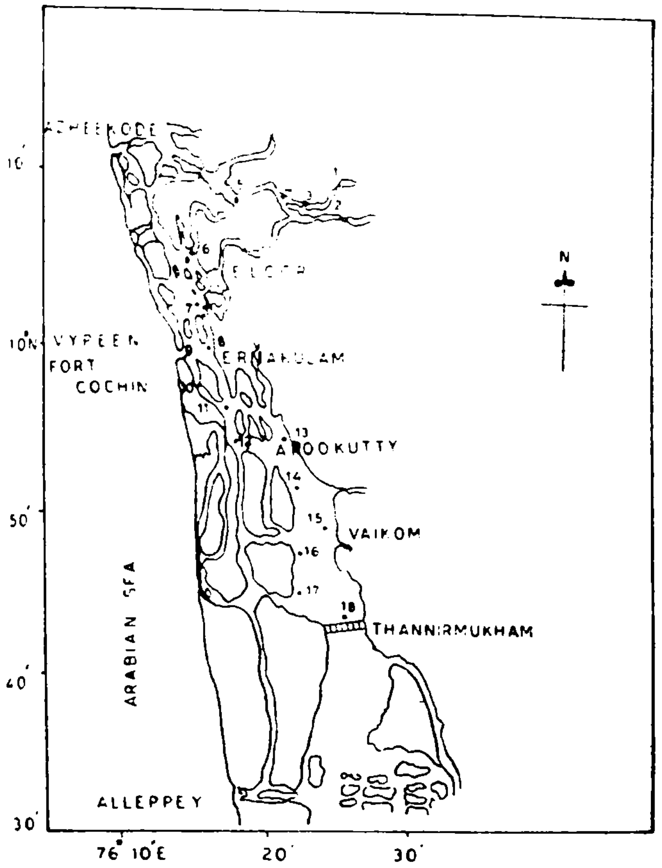

Fig. 1 Map of Cochin Backwaters, showing location of stations (1976–1977)

3. Results

3.1. *Salinity*

1976-77:

The estuary is evidently influenced by the influx of fresh water and intrusion of sea water. Bar-mouth region at stations 9 and 10 recorded high surface salinities > 30 x 10^{-3} during pre-monsoon (January — April). With the onset of monsoon, rapid decrease in salinity was observed at stations lying close to the bar-mouth. During monsoon period, surface salinity values ranged between ~0–5x10^{-3} along with entire estuary. Fresh water conditions were found at stations 1–6 throughout the year and also at stations 13 to 18. Horizontal surface salinity gradient on the northern side was stronger than on the southern side.(Fig 3)

Bottom salinity chart indicates that during pre-monsoon, salinity >10 x 10^{-3} was observed at all stations. During monsoon period the barmouth region alone showed salinity >25 x 10^{-3} while rest of the estuary indicated fresh water condition. Higher salinity values were observed on the southern parts than on the northern part. Horizontal gradients were strong between stations 8 and 9 and also between stations 11 and 13 during monsoon and post-monsoon.

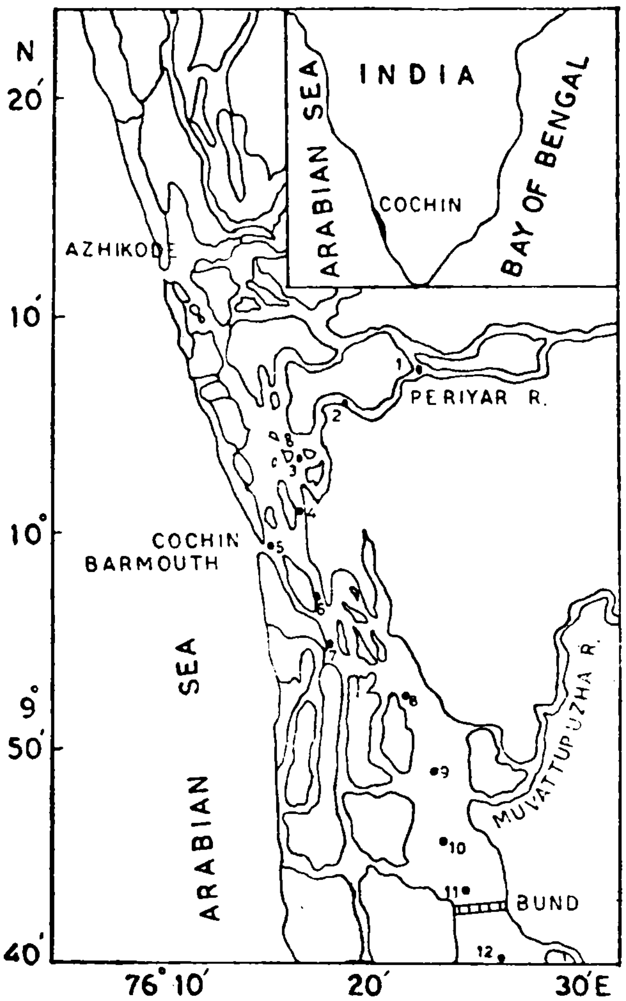

Fig. 2 Map of Cochin Backwaters, showing location of stations (1985–1986)

1985–86 :

The distribution pattern of surface and bottom salinity as time series curve along all the stations is presented in figures 4 (a) and (b). In the northern region, along stations 1 to 5 during monsoon, very low salinity values ranging between 0 to 12 x 10^{-3} at the surface and higher values ranging between 0 to 28 x 10^{-3} at the bottom were encountered. In the southern region along stations 6 to 12 low values of salinity ranging between 0 to 10 x 10^{-3} at surface and 0 to 16 x 10^{-3} at bottom were observed during monsoon. Fresh water conditions were observed at stations 9 — 12 during monsoon

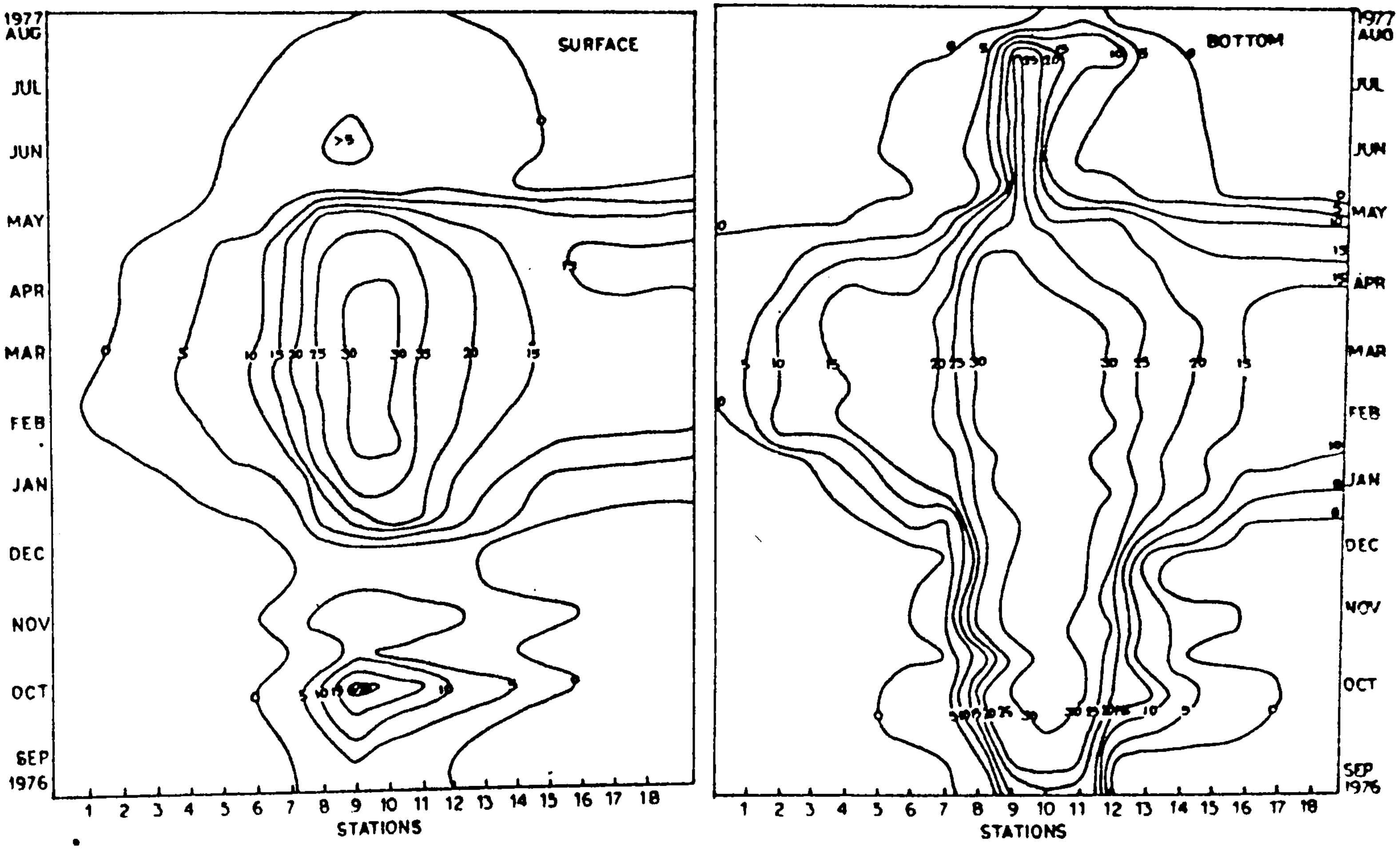

Fig 3. Time series curve of salinity (‰) at surface and bottom (1976-1977)

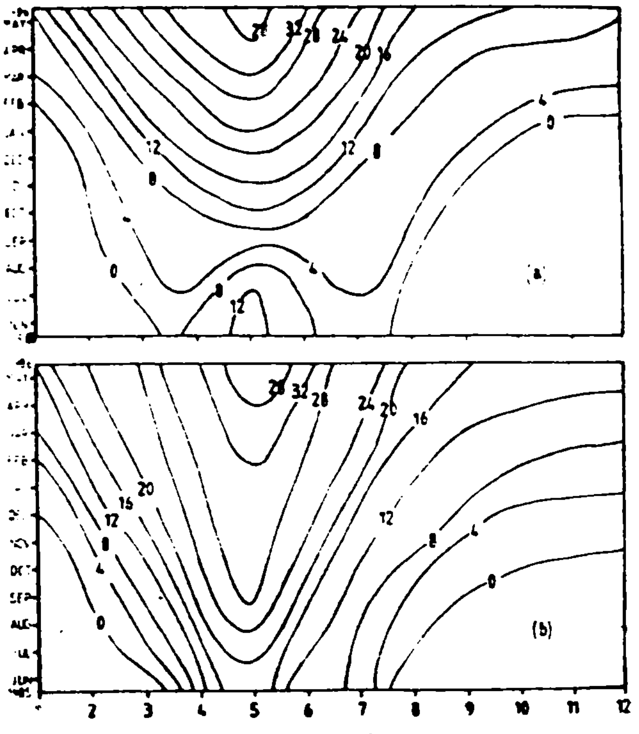

Fig. 4 Time series curve of salinity (10^{-3}) at (a) surface and (b) bottom (1985–1986).

and post-monsoon at surface. A gradual increase in salinity could be observed as the season progressed through post-monsoon and pre-monsoon. The highest value of 35 x 10^{-3} was recorded at surface and bottom at stations 4 — 6 during pre-monsoon. Horizontal bottom salinity gradient was stronger in the northern region.

3.2. *Reactive silicon*

(a) 1976-77 :

Distribution pattern of inorganic reactive silicon both at surface and bottom waters are given in figures 5 (a) and (b). Distribution of reactive silicon showed a regular pattern, *ie.*, high concentrations were recorded at the fresh water region which gradually decreased towards the seaward side. During postmonsoon and premonsoon (on the northern part of the backwaters) identically similar conditions were recorded for silicon varying between 75 to 150 µg at Si/l with the highest value (150 µg at Si/l) between stations 3 and 4 at bottom during the end of postmonsoon. On the sourthern part, postmonsoon values decreased to a minimum as the season advanced to premonsoon. The lowest values varying between 0 to 15 µg at Si/l were observed at barmouth region during pre-monsoon. The horizontal concentration gradint of silicon on both arm ends of the backwaters was similar to the salinity gradient pattern during postmonsoon and pre-monsoon.

(b) 1985 - 1986 :

Distribution of reactive silicon [figures 6 (a) and (b)] showed high concentrations at the fresh water region which gradually decreased towards high saline water areas. Also, there was a general decrease in the silicon content from June 1985 to May 1986. Reactive silicon values ranged from 25 µg at Si/l at the barmouth region to 180 µg at Si/l at the southern region. Bottom values were slightly higher than surface values in the southern region. Distribution pattern of reactive silicon is very much similar to that of salinity throughout the estuary.

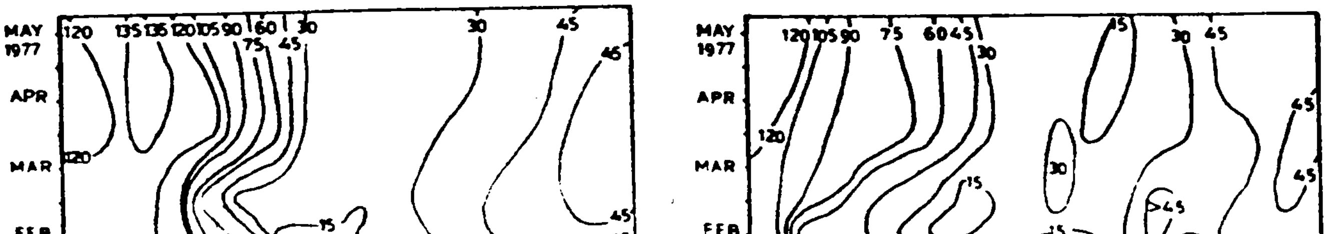

Fig. 5 Time series curve of reactive silicon (µg at Si/l) at (a) surface and (b) bottom (1976–1977)

In the northern region, monsoonal values (110 μg Si/l to 160 μg at Si/l at surface and 90 to 175 μg at Si/l at bottom) decreased as the season progressed towards postmonsoon and premonsoon. However, from monsoon to postmonsoon, gradual decrease of silicon concentration from station 1 to 5 was observed. During premonsoon, stations 3 - 5 recorded slightly higher values of silicon. The intrusion of sea water through station 5 and subsequent mixing with river water, largely influenced the distribution of silicon in the northern part of the system.

3.3. *Regressional behaviour between salinity and silicon*

Coefficient of correlation and regression equations between salinity and silicon during different seasons are given in table 1. The marked rivers ecorrelation values between salinity and silicon during premonsoon and postmonsoon suggests that silicon behaves conservatively in the estuary. The simple mixing of silicon rich river water with sea water may be the major process regulating the distribution of silicon in this estuary.

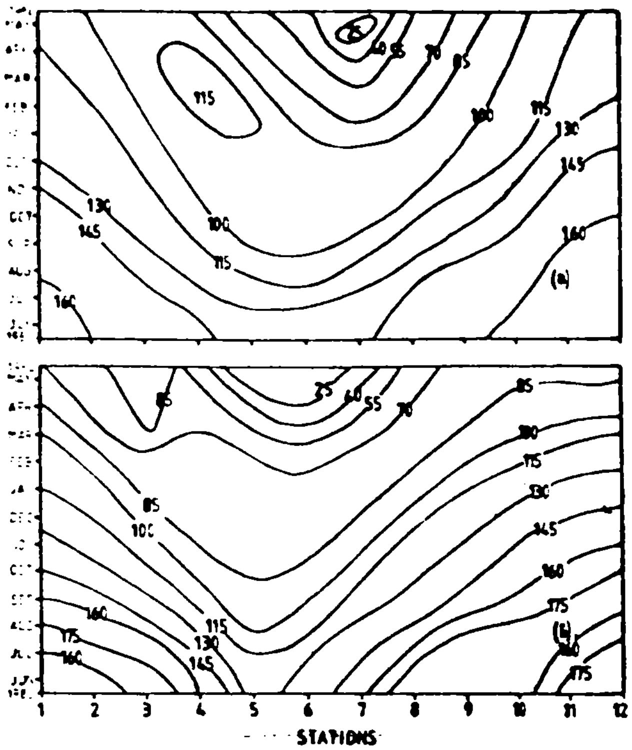

Fig. 6 Time series curve of reactive silicon (μg at Si/l) at (a) surface and (b) bottom (1985 - 1986)

Table 1: Correlation between reactive silicon and salinity in Cochin backwaters

Year	*Season*	*Correlation Coefficient*		*Regression Equation*	
		Surface	*Bottom*	*Surface*	*Bottom*
1976-77	Premonsoon	—0.9045	—0.8272	$Sio_4 = 113.1968 - 3.9068 \times S\%$	$Sio_4 = 99.4958 - 2.7594 \times S\%$
	Postmonsoon	—0.8892	—0.9760	$Sio_4 = 105.9117 - 2.7657 \times S\%$	$Sio_4 = 109.4327 - 2.8494 \times S\%$
1985-86	Monsoon	—0.7095	—0.9140	$Sio_4 = 153.1084 - 3.7075 \times S\%$	$Sio_4 = 165.9423 - 3.3979 \times S\%$
	Postmonsoon	—0.6495	—0.8096	$Sio_4 = 130.4453 - 2.1827 \times S\%$	$Sio_4 = 136.330 - 2.44 \times S\%$
	Premonsoon	—0.4260	—0.5681	$Sio_4 = 106.4710 - 1.3055 \times S\%$	$Sio_4 = 118.7055 - 1.9488 \times S\%$

4. Discussion

During 1976-77 investigation, surface salinities during premonsoon in the northern parts of the estuary were near fresh water conditions. However, in 1985-86 the fresh water conditions altered giving rise to higher values of 20×10^{-3}. Bottom salinity charts for 1976-77 and 1985-86 indicated that large areas were periodically subjected to intrusion of sea water ($5-25 \times 10^{-3}$). However, it is possible to clearly define the bottom salinity wedge on the northern parts during all these years of study. Horizontal salinity fields generated by tidal currents indicate strong gradients during 1976-77 on the northern side; the nature of salinity gradients in 1985-86 are not similarly predominant. This resultant longitudinal change in the salinity pattern indicates that the variation may have occurred due to the diminished influx of fresh water from the Periyar river. In this context, it is not worthy that inter-basin transfer of water from Periyar river to Muvattupuzha river may have caused the above hydrological change.

Stations lying closer to the barmouth indicate salinities greater than 15×10^{-3} at both surface and bottom during premonsoon during all the years of study. The region adjacent to Thannirmukham bund indicated a changed hydrological pattern. During 1976-77.

salinity value ranged from 10 to 20×10^{-3} (surface and bottom) which altered to lower values of 4 to 10×10^{-3} during 1985-86. This feature is due to: (i) restricted movement of the water body lying adjacent to the bund on the estuarine side (possibly trapped water), and (ii) fresh water influx from Muvattupuzha river diluting the estuarine waters. It is suggested that in years to come larger areas of the southern parts may still exhibit lower salinity values and eventually transform to fresh water conditions. No significant variations in salinities are observed during 1985-86 between surface and bottom layers as also observed during 1976-77 in other locations of the southern parts (less than 10×10^{-3}). It is inferred that the southern parts exhibit a well mixed region. Salinities greater than 25×10^{-3} (surface and bottom) are restricted to barmouth region which were noted as cores of high salinity region in the respective figures.

The main mechanism controlling estuarine circulation during monsoon period is the discharge of river water giving rise to stratification. However, the observed vertical gradient lies close to the barmouth region. This in turn, denotes that with the onset of monsoon except the barmouth region the entire estuary attains fresh water conditions. This is also the period when both arms of the estuary is being flushed out, attributable as a characteristic phenomenon in a tropical estuary. The core of high salinity at bottom layers giving rise to stratification, observed persistantly during the initial stages of the monsoon, of much significance for this estuary, may be due to the dredged channel at the Cochin barmouth region. To a large extent the barmouth region acts as a barrier between the two arms of the estuary giving rise to varied environmental settings on either sides of the water body.

Postmonsoon season is essentially a time for stabilization of the relative forces acting in the estuary namely the tidal currents verses fresh water influx. It has not been possible to exactly derive the features of salinity patterns during this time of the year. Hence, this is termed as a transitional period from the monsoon fresh water conditions to the characteristic premonsoon estuarine situation.

The silicon inputs from Periyar river in the range of 100 - 120 μg at Si/l are progressively depleted towards the higher salinity zone (bar-mouth values are 15-30 μg at Si/l). The process of removal giving rise to horizontal gradients are found to be lying in the lower reaches of Periyar. This feature is observed during the entire study period. It is worthwhile to note that these gradients lie in the region where rapid salinity changes occur. The maximum rate of removal, hence, is explicit from the features observed or otherwise theoretically predicted.

Silicon distribution on the southern parts of the estuary has a distinct variation over the decinnial years. Whereas the values ranged only from 15 to 45 μg at Si/l during 1976-77, much higher inputs were observed during the year 1985-86 ranging from 100 to 120 μg at Si/l. This feature has likely resulted from the fresh water inflow through Muvattupuzha river.

The rain water runoff has been indentified to be one of the important source of silicon entry into this estuary. Subsequent to the onset of monsoon, the contributions from either arms of the estuary in the range of 165 to 180 μg at Si/l are observed to be consistant, which are directly transported across the barmouth (without appreciable removal in the estuary). This transport of dissolved silicon is a significant feature probably due to the non-saline condition prevailing during this season.

As observed in the case of salinity distribution during the entire study period, the silicon values also exhibited a transitional behaviour for postmonsoon season. The fresh water inputs are in the range of 90 - 135 μg at Si/l from either arms of the estuary. Postmonsoon is reported to be the season for active biological production involving the utilization of available nutrients for this estuary (Qasim and Wyatt 1972; Gupta and Pylee 1964). The relative influence of this phenomenon along with the chemical activity behaviour may be studied in greater detail.

It is recognized that the behaviour of silicon in estuaries is wide and ranging. As regards to the Cochin backwaters, the silicon behaviour is characterised by the seasonal variations as well as the hydrological processes. The transport of silicia-rich fresh water across the boundaries of the estuary, abstaining all removal processes, turn out to be a marked feature for the Cochin backwaters. The agencies bringing about loss of silicon is, however, pronounced during non-monsoon months only.

The chemical behaviour of reactive silicon could be better understood by plotting salinity values against silicon values. This is presented as correlation diagrams (figures 7 and 8). The strong inverse correlation between salinity and silicon suggests that silicon behaves conservatively in this estuary. Analysis of thsese diagrams indicates that 75 to 80% of silicon was removed at salinities greater than 20×10^{-3} during premonsoon 1976-77 [figure 7 (a)]. However, the present data shows a marked difference in this behaviour. Inferences from premonsoon diagram during 1985-86 [figure 8 (c)] indicate that only 40 - 50% removal (100 - 120 μg at si/l) occurs though the riverine inputs during both times of the year. This is also largely true for the postmonsoon season in this estuary. The finding

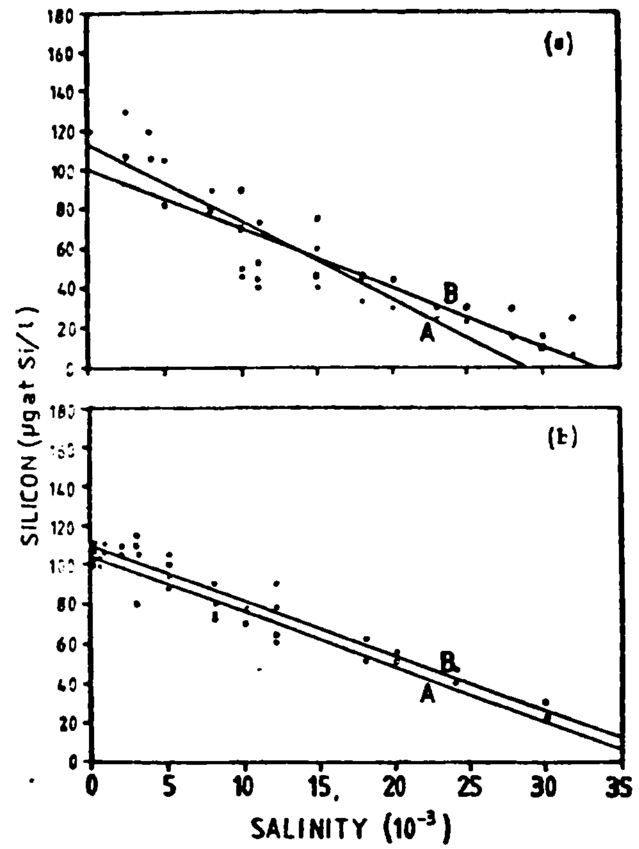

Fig. 7 Relationship between salinity and silicon (Surface.; line — A, bottom ●; line — B) during (a) premonsoon and (b) monsoon (1976–1977)

of lower correlation value during 1985-86 premonsoon season between salinity and silicon calls for continued, additional investigations in this estuary to delineate the long term trends occurring in water chemistry.

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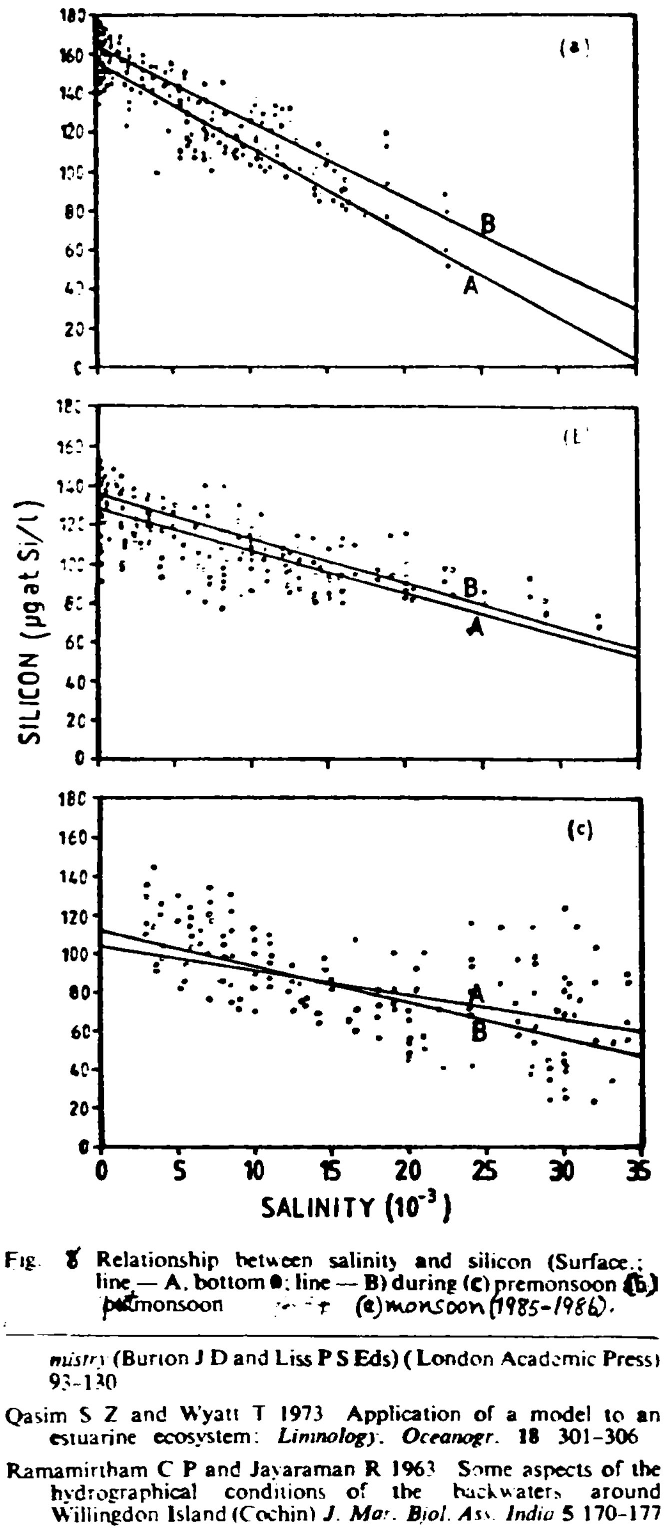

Fig. 8 Relationship between salinity and silicon (Surface.; line — A, bottom ●; line — B) during (c) premonsoon (b) postmonsoon (a) monsoon (1985-1986).

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Environmental Contamination and Toxicology

Sublethal Effects of Copper and Mercury on Some Biochemical Constituents of the Estuarine Clam *Villorita cyprinoides* var. *cochinensis* (Hanley)

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The usefulness of sentinal organisms in environmental pollution monitoring or surveillance programs has been well established (Goldberg et al 1978; Topping 1983). A particularly significant attribute of sublethal physiological response is that it is amenable to both laboratory and field measurements unlike traditional toxicant testing. Such methods could be employed to develop environmental quality models to predict the biological effects of potential pollutants as well as to directly monitor the effects in the environment (Widdows 1985). This paper describes the effect of sublethal amounts of two well known aquatic pollutants namely Cu and Hg on an estuarine clam _Villorita cyprinoides_ var. _cochinensis_.

The changes in carotenoid content (total and unsaponifiable), metabolic rate, lactic acid as well as glycogen contents of the tissues of the clam exposed to sublethal amounts of Cu(II) and Hg(II) were investigated over a range of time.

MATERIALS AND METHODS

The clams (size 25-30 mm) collected from Cochin backwaters (8° 55′ N 76° 17′ E), were acclimatized in the laboratory for 3 to 4 days (salinity=13 x 10^{-3}, temperature 28 ± 1° C, pH = 7.6 ± 0.2, dissolved oxygen = 3.6 mL/L. The animals (25 per 5-L test medium) were exposed to 300 and 600 ug/L each of Cu and Hg for 96 h. The metals were added as aqueous solutions of $CuSO_4 . 5H_2O$ and $HgCl_2$ (British Drug House AnalaR; India). Controls were maintained throughout The test medium was renewed once every 24 h. Animals were not fed during the experimental period. Duplicates were run in all cases. Mortality observed was less than 10 % during the whole period. The 96 - h LC 50 was 1214 ug/L for Cu and 1570 ug/L for Hg

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(Nambisan and Lakshmanan 1982 unpublished data).

Total and unsaponifiable carotenoids were extracted and estimated by the procedure of Karnaukhov et al (1977). The total carotenoids were extracted with acetone. Saponification was carried out by means of 60% potassium hydroxide at a temperature of about 28° C for 14 h, and unsaponifiable carotenoids were extracted using light petroleum ether. Optical density was measured in 1 - cm cuvette using a Hitachi Spectrophotometer(model 200-20) at wavelength of carotenoid absorbtion maxima 450-460 nm. Oxygen uptake of the animals was measured in Erlenmeyer flasks using Winkler techniques(Strickland and Parsons 1972). Liquid paraffin was used to seal the water-air interface. Lactic acid and glycogen were determined by standard procedures (Colowick 1957). The results were analyzed statistically according to Snedecor and Cochran (1967); the significant difference between experimental groups and control groups were determined using student's t-test. The precision of all determinations was within the range ± 5%.

RESULTS AND DISCUSSION

The results are presented in Tables 1 and 2 and Figure 1. In animals exposed to 300 ug/L and 600 ug/L Cu, the carotenoid concentration increased sharply with time and reached a maximum value in about 48 h. The total carotenoid content increased 2 times in the former and 4 times in the latter, the increase being proportional to the concentration of metal ions in solutions. In 300 and 600 ug/L Hg exposed animals the total carotenoid content increased to 0.318 and 0.673 mg/100 gm (wet wt.) respectively within 48 h (control = 0.18). After 48 h the carotenoid content (total and unsaponifiable) decreased. The control values remained remarkably steady(variations ±5%) throughout the entire experimental period.

A corresponding change in metabolic rate (oxygen uptake/h/g dry body wt) of animals was noticed at all stages, with progress of time. Cu-exposed animals generally suffered a greater reduction in the oxygen uptake than Hg-exposed animals. In 600 ug/L Cu and Hg the metabolic rate was depressed by 32% and 28%, respectively, during 48 h. After 48 h, the metabolic rate in both Cu and Hg exposed animals was found to increase, being more pronounced in 300 ug/L exposed animals.

The lactic acid content in the tissue of the clam increased with progress of time and was proportional to the metal concentration. The tissue lactic acid content increased to 94.4 and 136.1 ug/g in 300 and

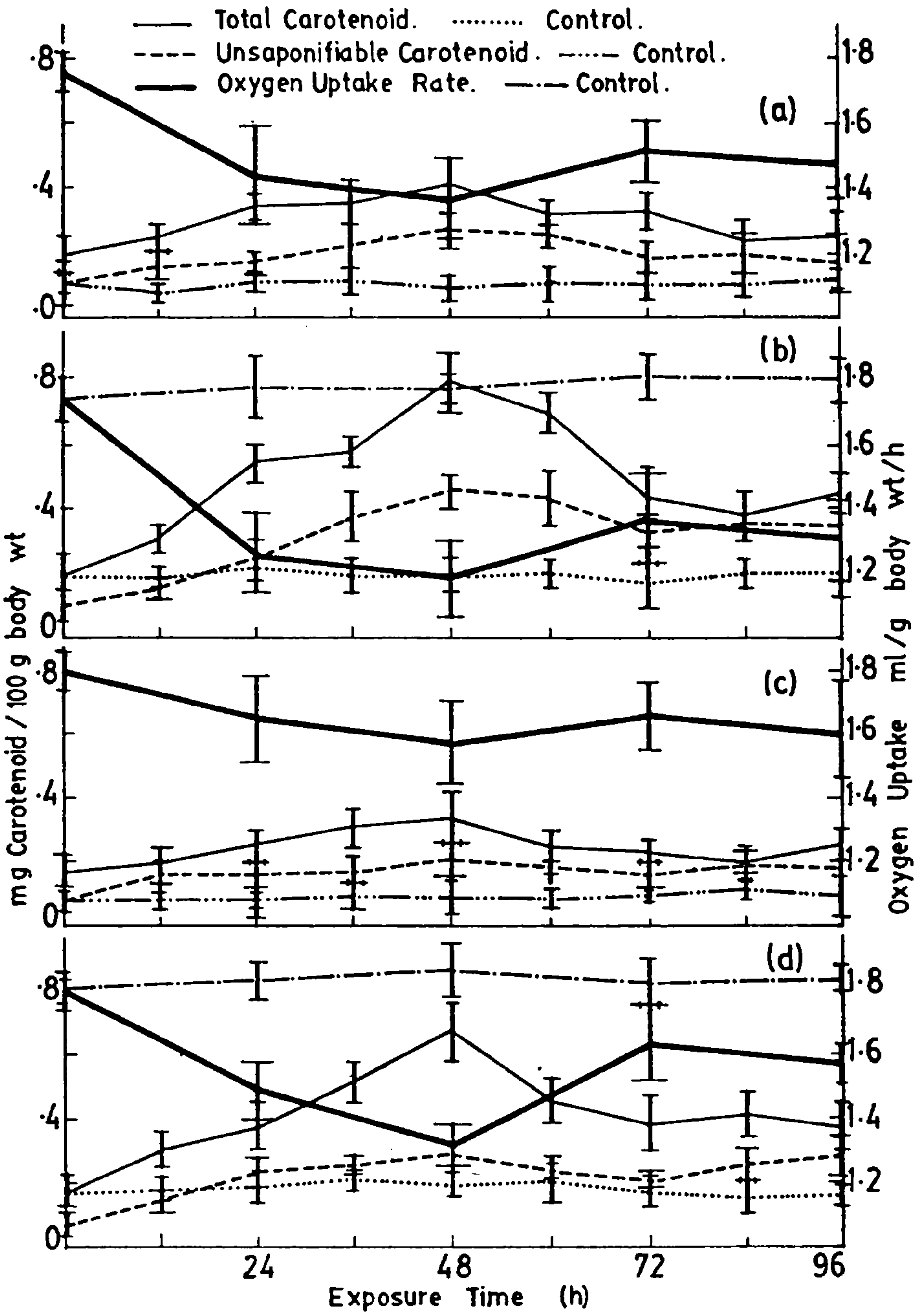

Figure.1.Carotenoid concentration and oxygen uptake rate in V.cyprinoides exposed to (a) 300 µg L⁻¹ Cu (b) 600 µg L⁻¹ Cu (c) 300 ug L⁻¹ Hg (d) 600 ug L⁻¹ Hg, Vertical bars indicate standard deviations (n = 5). Controls are same for (a) and (b), (c) and (d).

Table 1. Changes in the tissue lactic acid content of the clam *V. cyprinoides* exposed to sublethal concentrations of Cu and Hg for varying lengths of time.*

Conc. of metal ions ug / L	Lactic acid, ug / g wet wt; $\bar{x}\pm$ S.D. (n=5) Exposure time				
	3 h	6 h	9 h	12 h	24 h
Cu 300	30.3±2.2	45.3±4.4	44.6±3.5	56.5±5.2	94.4± 9.6
600	43.3±3.2	72.5±7.9	78.5±8.3	95.3±8.7	136.1±11.4
Hg 300	26.3±3.2^a	39.7±2.7	64.9±4.3	60.5±8.3	82.1± 9.7
600	38.4±5.0	56.4±7.1	81.9±7.4	78.6±6.4	124.1±11.3
Control	22.7±2.4	21.0±1.1	18.3±2.7	22.3±1.8	19.5±2.2

Table 2. Changes in the muscle glycogen content of the clam , *V. cyprinoides* exposed to sublethal concentrations of Cu and Hg for varying lengths of time.*

Conc. of metal ions ug / L	Glycogen, ug / g wet wt; $\bar{x}\pm$ S.D. (n=5) Exposure time					
	12 h	24 h	36 h	48 h	60 h	72 h
Cu 300	1793±29.2	1585±32.2	1480±26.5	1409±43.2	1396±49.0	1285±32.7
600	1545±36.7	1211±44.7	1061±42.5	980±30.8	968±20.8	910_42.9
Hg 300	1866±35.8	1744±24.4	1630±42.5	1567±26.1	1560±31.6	1570±34.4
600	1674±42.2	1438±38.4	1371±32.0	1225±34.7	1193±57.0	1188±59.9
Control	1944±23.7	1950±30.5	1959±24.5	1940±31.9	1963±46.9	1954±29.2

* All values significantly different from control ($P < 0.05$) except the one superscribed^a (student's t-test)

600 ug/L Cu-exposed animals and to 82.1 and 124.1 respectively in the Hg-exposed animals during 24 h (control = 20.2) (Table 1).

Glycogen levels, however, were generally found to decrease. The glycogen content of the 300 and 600 ug/L Cu-exposed animals decreased to 1285 and 910 ug/g respectively in 72 h (control = 1952 ug/g). The corresponding values for the Hg-exposed animals were 1570 and 1188 ug/g respectively(Table 2).

These results indicate, that Cu and Hg pollution lowers the normal metabolic rate and glycogen levels of the organism and increases the carotenoid as well as the lactic acid content in the tissues. A distinct inverse relationship is observed between carotenoid content of the clam and its metabolic rate.

The steady increase observed in the carotenoid content may be due to the physiological adaptive responses of the animal to compensate the external stress of metal concentrations and the consequent inhibiton of the respiratory processes. An increase in the carotenoid concentration with increase in environmental pollution has been reproted earlier (Karnaukhov et al. 1977; Karnaukhov 1979). Krishnakumar(personal communication) also has reported that the carotenoid concentration in the mussel <u>Perna viridis</u> increases directly with increase in metal concentrarion. Karnaukhov (1971) has reported that carotenoids participate in the oxidative metabolism of the mollusc <u>Lymnaea stagnalis</u> by providing a large number of unsaturated double bonds as an intracellular oxygen reserve. Therefore, the increase in the carotenoid content can be taken as an indication of the animal's adaptation to the hypoxic conditions.

Heavy metal - induced decrease in metabolic rate in <u>Uca pugilator</u> has been reported (Vernberg et al 1974). Cupric ions were shown to cause respiratory and cardiovascular depression in <u>M. edulis</u> and the effect was attributed to the passive binding of cupric ions with organic ligands (Scott and Major 1972).

The increase in tissue lactic acid content and decrease in glycogen levels may be due to the heavy metal intoxication, which induces appreciable mucus secretion-- even in animals exposed to 300 ug/L Cu and Hg considerable mucus secretion was observed. Lakshmanan and Nambisan (1985) have shown that Cu and Hg intoxication had caused lactic acid accumulation and glycogen depletion in tissues of <u>V. cyprinoides</u> and <u>P. viridis</u>. A similar reduction in glycogen content and increase in lactate concentration in tissues due to copper intoxication in the fresh water teleosts(fish) was reported(Shaffi 1978).

The animals are able to adjust the initial stress or may have released partly that stress and shown symptoms of normal behaviour. The increase in oxygen consumption accompanied by a decrease in carotenoid content after 48 h may be due to this. Moreover, accumulation studies of heavy metals on many organisms have shown that the initial rate of uptake was very high at lower concentrations and the rate decreases with time. (Vernberg et al. 1974). Donaldson and Dye (1975) have observed that Sockeye salmon has adjusted the stress imposed by the low concentration of Cu within 4 h.

It is not yet clearly understood whether physiolcgical changes during a sublethal exposure represent deleterious effects of the toxicant or merely the normal adaptive mechanism of the organisms (Dixon and Sprague 1981). As they have pointed out there is a physiological mechanism functioning within the animal to mitigate the toxic effects of heavy metals. Considerable energy was required to establish the adaptive mechanism, less energy was required to maintain it. A long period of increased oxygen consumption was necessary to restore normal metabolic process damaged by metals.

From the point of view of the organism and polluters the ability to adapt to metals seems to be a favorable aspect to the animal. However, it should be remembered that many of these tolerant organisms contain two to three orders of magnitude higher concentrations of metals than normal and, so far as we know at present, these may be transmitted to non-adapted predators, including man (Bryan 1976).

In conclusion, the animals went through two classical stages of stress response, ie; the alarm reaction and the stage of resistance (Donaldson and Dye 1975). Because metals such as copper are more toxic at low salinities, the pressure to adapt is probably greatest under these conditions. Only a detailed study with a longer time of exposure can reveal whether the animals can successfully accomodate ,and adapt to the stressor.

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ON THE DETERMINATION AND DISTRIBUTION OF HYDROXYLATED AROMATIC COMPOUNDS IN ESTUARINE WATERS

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A modified methodology to determine the hydroxylated aromatic compounds in aquatic waters and sediments has been developed. Interference in seawater samples were overcome by addition of citrate solution permitting the blue colour development on reduction of tungsto- and molybdo- phosphoric acids by the aromatic hydroxylated groups present in lignins and tannins. The above procedure was adopted to study the fate of tannin and lignin like substances (TALLS) in tropical estuarine and coastal waters and sediments receiving pulp-paper effluents.

KEY WORDS: Hydroxylated aromatic compounds, estuarine waters.

INTRODUCTION

Natural waters contain numerous organic compounds of which hydroxylated aromatic compounds have special significance from the viewpoint of terrestrially derived plant constituents. The studies on the determination of such compounds consisting of lignins, tannins and other derivatives found abundantly in pulp-paper mill effluents have also received considerable attention in the near past. Lignin and tannin are found in natural streams receptient of run off from the forestry areas apart from its concentration during pulping processes. The discharge of pulp paper mill effluents into coastal waters have resulted in the deterioration of the environmental conditions necessitating investigations into such areas so adversely affected. This paper proposes a modified methodology to determine quantitatively the content of lignins and tannins in the aquatic environment and further discusses the application in a tropical water way receiving mill effluents. Since both lignins and tannins contain "hydroxylated aromatic groups" it is more appropriate to report experimental values as tannin and lignin like substances (TALLS) or simply as hydroxylated aromatic compounds with regard to the procedure adopted to estimate them.

EXPERIMENTAL

The estimation of "hydroxylated aromatic compounds of "lignin like" and "tannin

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like" substances was performed initially as detailed in APHA.[1] The principle involved is the development of a blue colour on reduction of tungsto-phosphoric and molybdo-phosphoric acids by the aromatic hydroxylated groups present in lignins and tannins. This procedure had to be modified for sea water samples to allow the development of blue colour by suppressing the effects of Mg and Ca hydroxides and/or bi-carbonates using tri-sodium citrate. Sediments leached in 0.05 N NaOH were also found suitable for estimation by the modified procedure.

The tannin-lignin reagent and carbonate-tartarate reagent was prepared according to the prescribed procedure. Additionally a solution of 1.6 M tri-sodium citrate ($Na_3C_6H_5O_7 . 2H_2O$) was prepared. The salt dissolved readily on gentle stirring to yield a clear solution. A stock solution of 1.000 gm of tannic acid (high purity "Loba-chemic" powder—$C_{76}H_{52}O_{46}$) was prepared in distilled water and made up to 1000 ml. This solution was stored in a brown bottle at 5 °C. Secondary standards were prepared daily by diluting 10 ml to 1000 ml to give a concentration of 10 $\mu g\, ml^{-1}$. All reagents used were of MERCK/BDH (GR) grade.

ANALYTICAL PROCEDURES

a) Collection of Samples

Surface samples were collected using a clean bucket. The water samples were filtered (Whatman GF/C (0.45 μm)) and stored in precleaned stoppered glass containers in dark (≈ 5 °C). Analysis of all samples were performed within a day of collection.

To 10 ml of the sample added in rapid succession 5 ml of citrate solution followed by 1 ml of tannin-lignin reagent and 10 ml of carbonate-tartarate reagent and mixed well and allowed to stand for 30 minutes for colour development. Reagent blanks were similarly prepared omitting the sample.

Mud samples were collected (using a stainless steel van-Veen grab) and undisturbed top 2 cm layer skimmed to ice-box storage in closed glass—petri dishes for transporting to laboratory. The sediments were leached using 0.05 N NaOH in large beakers; 5 ml of supernatant liquid was withdrawn for analysis as described for water samples. The sediment to solution ratio was maintained at 500 mg: 250 ml. The blank solution was 0.05 NaOH minus sediments.

b) Estimations

A Hitachi UV-Visible Spectrophotometer (model 150–20) was employed to record the spectrum along with photometric readings using 5 cm cells. Cell to cell and blank corrections were applied to all sets of readings.

Salinity of the water samples was determined by the method reported by Strickland and Parson.[2] Dissolved organic carbon (DOC) and sediment organic carbon (SOC) were estimated by the method of El-Wakeel and Riley.[3]

RESULTS

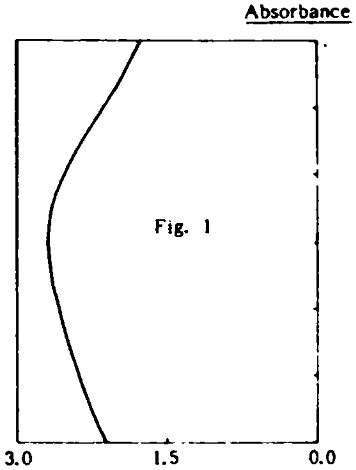
Water Analyses

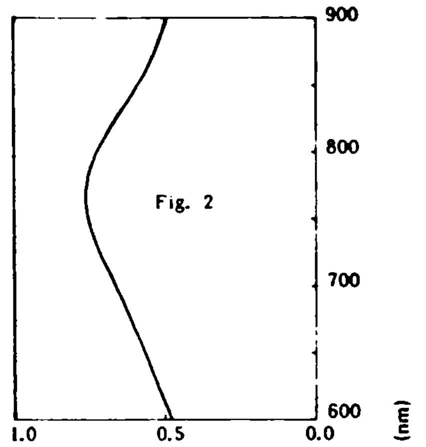
Absorbance spectrum of the pulp-paper effluents treated with experimental reagents (no citrate solution) is given in Figure 1. The wavelength scan was performed from 600.0 nm to 900.0 nm for the absorbance scale 0.000–3.000 which indicated a single maximum at 760.0 nm. In order to compare the closeness of this spectrum containing hydroxylated aromatic compounds (lignin like and tannin like) a suitable volume of the standard tannic acid solution was treated with experimental reagents. The wavelength scan was repeated for this standard solution and the resultant spectrum (Figure 2) indicated a spreadover (single maximum peak in the wavelength band 763.7 to 771.2 nm) exhibiting close likeness to the effluent absorbance spectrum, justifying the use of tannic acid as the standard. Addition of citrate solution to the above standards/effluent sample solutions did not interfere with the results.

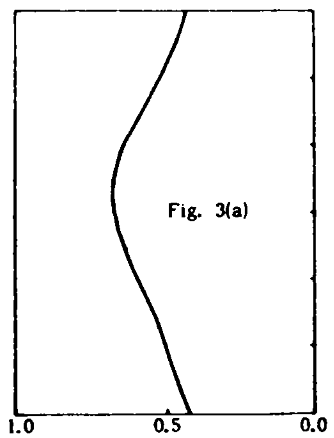
Natural water samples were next tested for their TALLS without the addition of citrate solution. The type of samples included fresh water, estuarine water (2 to 30×10^{-3}) and coastal waters (35×10^{-3}). Results indicate excellent percentage recovery for the freshwater samples (Table 1). However, the estuarine/coastal waters having a salt content more than 2×10^{-3} indicated sharp interference in the spectrophotometric readings. To overcome the salt-interference effects, a 1.6 M solution of tri-sodium citrate was added to the estuarine/coastal samples prior to the addition of experimental reagents. This facilitated the suppression of interference from salt content and the results are given in Table 2. Duplicate runs on freshwater samples (spiked and non-spiked) in presence of citrate solution once again gave identical results. Figure 3(a) and (b) gives the spectrum of spiked double distilled water with and without citrate solution respectively. Similar absorbance spectra were available for freshwater sample, spiked or not. A sample of coastal water was also examined under the modified conditions mentioned above. Figure 4 illustrates the spectrum of the coastal water with a single maximum at 765.2 nm. Table 3 gives the reproducibility and accuracy of the method for aquatic waters.

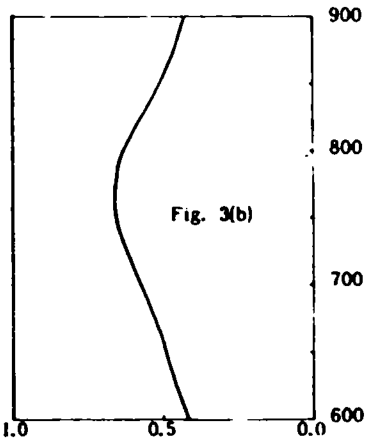
Sediment Analyses

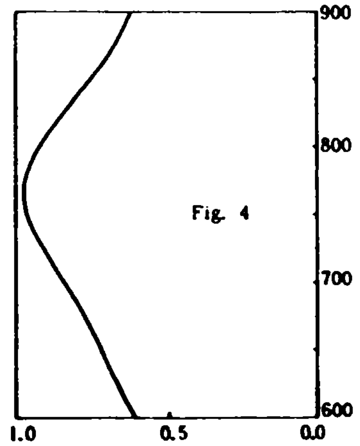
A set of sediment samples were subjected to 0.05 M NaOH leaching for 72 hrs and subsampled at 5, 15, 45 and 120 minutes and thereafter at random upto 72 hrs. Leaching process was observed to be completed in 90 minutes time. Use of stronger NaOH solutions considerably delayed the colour development on addition of experimental reagents. Additionally, use of citrate solutions with stronger NaOH reagent gave rise to a white precipitate, which did not redissolve in excess of citrate. Sediment samples were spiked for the determination of recovery which indicated good results (94–102%). The standard deviation was ±0.15 and the confidence limit (9 determination, 95%) being 3.5200 ± 0.1063 μg/g.











Absorbance spectra of:
Figure 1 Pulp paper effluents
Figure 2 Tannic acid standard
Figure 3(a) Spiked double distilled water with citrate
Figure 3(b) Spiked double distilled water without citrate
Figure 4 Coastal waters

Table 1 Concentration of TALLS in freshwater samples (mg l^{-1})

Sl. no.	*Concentration of freshwater samples*	*Concentration spiked*	*Concentration determined*	*% Recovery*
1.	0.55	+0.50	1.30	96.0
		+2.50	3.09	101.6
		+5.00	5.54	99.8
2.	0.80	+5.00	5.74	98.8
		+10.00	10.66	98.6
3.	4.86	+5.00	9.83	99.4

Table 2 Concentration of TALLS with addition of citrate solution as salt effect suppressant for estuarine and coastal waters (mg l^{-1})

Sl. no.	*Salinity* (× 10^{-3})	*Sample concentration*	*Concentration spiked*	*Concentration determined*	*% Recovery*
1.	10.4	0.91	+0.50	1.44	106.0
			+5.00	6.25	106.8
2.	19.7	2.69	+5.00	7.59	98.0
3.	30.4	4.56	+0.50	5.07	102.0
			+2.50	7.05	99.6
			+5.00	9.54	99.6
4.	34.5	7.05	+0.50	7.53	96.0
			+5.00	12.00	99.0

Table 3 Reproducibility and accuracy of the method for aquatic waters

Sample		*Number of samples*	*Mean concentration determined* (mg l^{-1})	*Standard deviation* (mg l^{-1})
Distilled water	(1)	5	2.8406	0.3577
Spiked	(2)	7	51.2868	1.3580
Freshwater (non-spiked)		7	2.5280	0.4461
Freshwater	(1)	6	4.9833	0.1602
(spiked)	(2)	6	55.4501	1.1077
Seawater (non-spiked)		5	2.5600	0.4774
Seawater	(1)	8	3.2810	0.4189
(spiked)	(2)	6	54.3540	0.2880

From the foregoing experimental conditions, the folllowing modifications in the procedure for the determination of hydroxylated aromatic compounds were incorporated (1) addition of citrate solution to all water samples (fresh/estuarine/coastal water) prior to addition of other reagents. (2) leaching of sediments to be performed with 0.05 N NaOH for 90 minutes and followed by the addition of citrate and other reagents to the withdrawn supernatant fractions. (3) the absorbance of the solution to be determined at 765 nm in the linear conc. range of

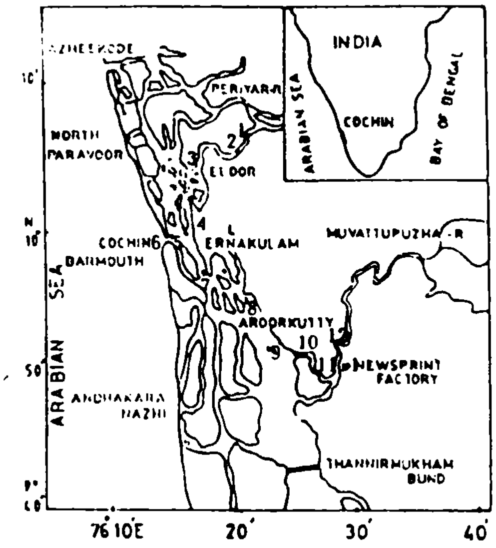


Figure 5 Location map of stations in Cochin estuary.

0.10 to 50.00 mg/l against tannic acid as a reference standard. Very low concentrations of reducing substances like ferrous iron and sodium sulfite did not interfere with the above results.

Field Survey

Abundance of TALLS in Cochin backwaters and along the freshwater river reaches were determined by the above modified method. Water and sediment samples were also drawn from the coastal zone adjacent to the estuary. Figure 5 gives the location map of the stations from where collections were made during the months of October, November and December 1987. The results of the survey are presented in Figure 6 (surface waters) and Figure 7 (sediments). Data on DOC, SOC and salinity are also presented in the above distance scaled station figures. Station (2) on the northern part of the estuary (Periyar river) and station (11) situated on the southern part of the estuary (Muvattupuzha river) receive effluents discharged from chemical factories and pulp-paper mill respectively; ambient conditions are shown by stations upstream of these two. Station 6 (Cochin Barmouth). connects the estuary to the Arabian Sea. More details on the environmental setting of this tropical positive shallow estuary is available elsewhere.[4-7]

Hydroxylated aromatic compounds of terrestrial origin are found in the range of conc. 0.6 to 0.9 mg/l (stations 1 and 12) in the fresh water flowing into the Cochin estuary. The concentration trends indicate large inputs on the southern part of the estuary (2.0 to 25 mg/l) from the pulp-paper mill. However there appears to be only slight enhancement in the concentration on the northern parts mainly

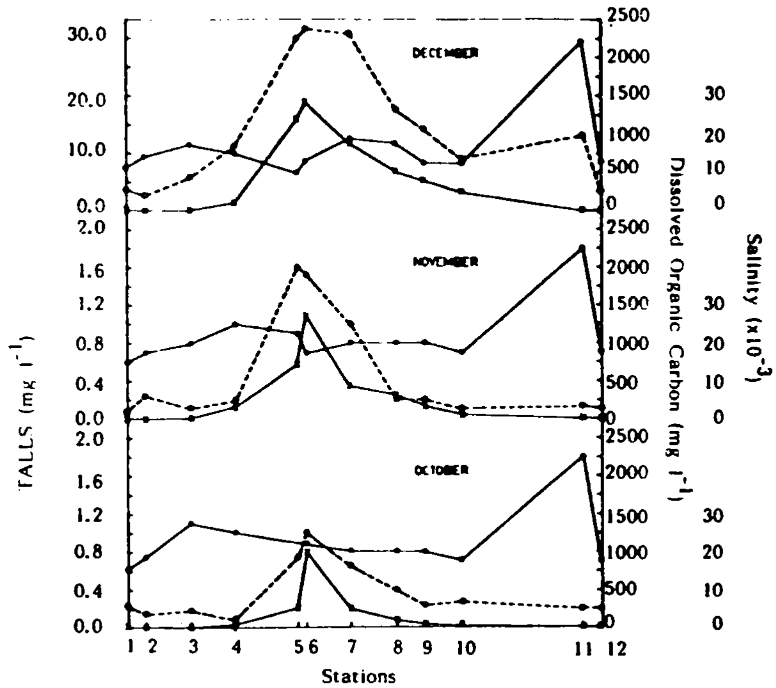


Figure 6 Distance scaled station figure showing variation of TALLS (·——·), Dissolved Organic Carbon (0-----0) and Salinity (x——x) for the months October, November and December 1987.

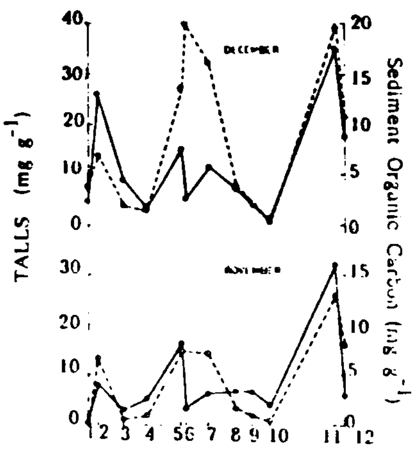


Figure 7 Distance scaled station figure showing variation of TALLS (·——·) and Sediment Organic Carbon (0-----0) for the months November and December 1987.

Table 4 Coastal waters and mud samples determined for TALLS

Distance from shore (m)	*Water samples*				*Mud samples mg g^{-1} wet wt.*	
	TALLS (mg l^{-1})		*DOC (mg l^{-1})*		*TALLS*	*SOC*
	21.11.87	*2.12.87*	*21.11.87*	*2.12.87*	(*2.12.87*)	(*2.12.87*)
25	5.6	4.3	3338	4100	20	3.2
500	6.3	4.6	3037	4000	17	5.7
1000	4.4	2.8	3263	3900	18	8.6
2000	3.8	2.3	3301	4300	11	9.7
3000	2.6	2.5	3621	4800	11	11.5

contributed by the coconut husk retting grounds (located between stations 2 and 3) rather than from station 2 housing industrial units. Gradual decrease of the concentration of hydroxylated aromatic compounds content is observed on the southern parts within the lower river reaches of the Muvattupuzha river bringing down the content to near natural levels. The distribution of the analysed substance shows no significant variability within the estuarine waters. The dissolved organic carbon estimated at all stations for the three months (Figure 6) show marginal variability (250 mg/l to 500 mg/l) in the freshwater or in low salinity regions. During December, however, the values are slightly higher coinciding with the higher concentration of TALLS. The regions around barmouth exhibit higher concentration of DOC (500 to 2500 mg l^{-1}). The singular maximum DOC distribution in this estuary with low values on either arms of the estuary coincides with the entry of seawater into the estuary which is diluted disproportionately on either arms. Surface salinity distribution more or less coincides with dissolved organic content.

For November and December 1987, (data for October not collected) as observed (see Figure 7) the sediments also contained relatively higher amounts of hydroxylated aromatic compounds (30–35 mg/g) derived from the effluent discharged at the outfalls. Proceeding downstream of the two rivers into the estuary the concentration decreases to near ambient values (2 to 7 mg/g). The SOC profiles are comparable to the TALLS values for both the months in the freshwater and low salinity regions. However, the distribution of SOC in and around barmouth region noticeably differs from the other parts of the estuary and also with the distribution of tannins and lignins. Corresponding to the DOC values, SOC values are also higher in this part of the estuary.

Coastal waters and muds exhibit varying values for both TALLS and DOC (Table 4). The concentration of TALLS in water decreases from a value of 6 mg/l (25 m from shore) to 2.5 mg/l (3000 m from shore). The mud collected from the same region indicate values decreasing from 20 mg/g to 10 mg/g. The associated carbon values reveal higher values than in the estuarine waters. The concentration in water increases from 3000 to 3600 during October and 4000 to 4800 mg l^{-1} in December in the offshore direction; correspondingly SOC values increase from 3.2 to 11.5 mg/g of wet mud.

DISCUSSION

The pulp-paper mill effluents contain a partly identifiable mixture of organic molecules varying from simple carbohydrates to complex lignin derivatives which have a very high potential to damage the aquatic environment. A list of numerous such organic compounds has been compiled by Michael Fox.[8] These effluents inhibit the growth of microflora as most of the waste products are slow degradable substances. Studies in this direction have proved the biodegradable nature to extend for more than a hundred days.[9-11] The very resistant nature of lignins, investigated by Poole *et al.*[12] is suggestive of long term damaging effects on the ecosystem. As the short-time degradable processes appear to be limited,[13] this facilitates the study of lignin-like compounds as an excellent tracer of pulp mill effluents or such other lignin/tannin containing pollutants in the aquatic environment. Two recent studies by Michael Fox[8] and Lytle and Lytle[14] have indicated the transport of organic wastes using lignin as a chemical tracer.

The present study helps to record the extent of axial transport of pulp-paper mill effluents on the southern parts of Cochin estuary as well as to probe the media for other hydroxylated aromatic sources. The study reveals the presence of such compounds both in the dissolved form as well as in the estuarine beds. Though the lignin degradation process have not been closely probed into, the study gives an insight on the fate of effluents on dispersal in the water way. Evidently most of the dissolved aromatic compounds are observed to be removed within the lower river reaches downstream of the outfall. Likewise in the vicinity of the outfall the river bed also indicated high concentration of TALLS. The removal of lignin from the water media may by itself be a complex phenomena accountable by either one or a combination of the following processes: (a) coagulation (b) formation of lignosulphonates (c) sorption on particulates (d) limited bacterial oxidation (e) dilution by receiving waters and (f) formation of compounds undetectable to the analytical methods.

Though not well established, processes like coagulation as well as the formation of lignosulphonates are not ruled out in this study. Several workers[9,15-17] report the coagulative nature of mill effluents in freshwater/seawater and discusses the presence of lignosulphonates which are very resistant to biological degradation processes. Day *et al.*[18] and Woodward *et al.*[19] have noticed the disappearance of lignin like compounds from the watermedia and has attributed this to the adsorption of lignosulphonates as well as craft mill lignins onto the microbial cell wall. The removal of lignins and tannins within two km downstream of outfall from a pulp-paper mill was mostly attributed to the dilution by receiving waters for explaining the short-term removal by Michael Fox.[8] For the case under study, this explanation is also relevant as the organic effluents are diluted in the Muvattupuzha river by about 10 times.[20] Limited bacterial oxidation of the readily degradable products in these effluents may also occur simultaneously in partly reducing their content downstream. Bouveng and Solyom[21] reported the presence of two or three fractions of lignin compounds in aquatic environments: one which is readily degradable in short time intervals and another partly degradable in freshwater but inert in seawater while a third part, which forms the larger fraction, is relatively non-degradable due to some structural forms. They have also commented that there exists no direct co-relation between changes in DOC or colour with changes in TALLS. In our study too, the DOC values do not co-relate well with the values of TALLS.

The effluent outfall region as well as those regions, where coconut husk retting is practised, the level of suspended solids content ($> 80\,\mathrm{mg/l}$) were higher than from those of the other parts ($\approx 30\,\mathrm{mg/l}$) of the estuary. And these areas contain higher amounts of hydroxylated aromatic compounds too. Higher concentration of lignin in sediments at pulp-paper mill outfalls has already been reported.[22] Leslie[23] in his study on the organic effluents have noted that suspended particles were dispersed and sedimented within two km of the outfall. However this was subjected to many hydrodynamical conditions. In our study, we have noted rapid sedimentation of wood fibrous material in the near-downstream ($< 7\,\mathrm{km}$) river reaches of Muvattupuzha and in the vicinities of husk retting grounds. The NaOH leaching process has been reported to attack a major part of the organics from the sediments.[24] Whereas mud—NaOH leachings have resulted in extracting sizable portions of lignin-like complexes, its alikeness in variation with SOC, revealed the significance of the procedure adopted for the study. The experimentally verified and adopted technique thus proves a useful analytical tool to detect as well as quantify the hydroxylated aromatic compounds in the rivers/estuaries/coastal regions and in their beds. The presence of higher SOC in the barmouth region is exclusively attributed to the higher biomass/productivity in the estuary during these months in the estuary as reported by Nair *et al.*[25] The study may also be extended to the coastal waters and sediments to trace the presence of these compounds and to track their transport.

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A SURVEY OF THE PROTEIN CONTENT IN ESTUARINE WATERS

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A survey of the protein content in a tropical estuary and its nearshore regions are reported for two seasons—postmonsoon (November 1987) and monsoon (June 1988)—using a modified dye binding method. The content of protein varied from 0.05 to $8.0\,\mu g\,l^{-1}$ in the fresh and estuarine waters with little variability between surface and bottom values. The enhanced biological production during postmonsoon months causes a higher level of protein in the lower estuary compared to low values in the freshwater, riverine end. Increased terrestrial runoff and discharge of industrial waste mainly from seafood processing units are linked to the higher concentrations of protein in monsoon, more than double the content during postmonsoon. Auxiliary data on chlorophyll$_a$, organic NO_3^-—N, PO_4^{3-}—P, urea and dissolved organic carbon support the above contention. Interparametric relationships suggest seasonally varying correlation between protein and chlorophyll$_a$, urea and DOC, signifying the role of biological control.

KEY WORDS: Protein, dye binding, estuarine waters.

INTRODUCTION

Proteins are highly complex substances that are universally present in the cells of living organisms or biological fluids and directly involved in the chemical processes necessary for the maintenance of life.[1] More recently, proteins have been found useful in numerous industrial applications in the field of food processing, wool manufacturing and in selected plant fertilizers. With increasing use and applications, the presence of proteins in the aquatic environment has attracted much attention.[2,3] The advent of a sensitive analytical methodology has made it now feasible to determine protein, with accuracy, in estuarine or seawater particulates as well as in sediments.[4-7]

This study aims at determining the level of protein in the waters of Cochin backwaters and adjoining coastal regions and its relationship to relevant environmental parameters. The investigation also highlights the role of industrial activity in regulating the Cochin downestuary protein content.

The waterbody is situated on the southwest coast of India extending from Azhikode at north and Alleppey at south (9° 40′–10° 10′ N and 76° 10′–76° 30′ E) which exhibits the features of a typical positive estuary with a permanent opening at Cochin barmouth (Figure 1—station map). Two rivers, viz. the Periyar at the northern end and the Muvattupuzha at the southern end emptying into this

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estuary show seasonality in discharge, largely influencing the hydrographic conditions downestuary. A number of industrial units (chemical, fertilizer, metallurgical, insecticides, etc.) are located on the banks of Periyar river (in the vicinity of station 2) while a large pulp-paper factory is situated on the bank of the Muvattupuzha river (at station 10). Effluent discharges from the factories as well as the city sewage works are identifiable sources causing water pollution in these backwaters.[8-10] More details on the environmental setting of this tropical shallow estuary are available elsewhere.[11-14]

MATERIALS AND METHODS

The reaction involving proteins with acidic Coomassie blue determines microquantities of protein in natural waters. On interaction, the dye reacts with the NH_2 group of the protein, staining it dark blue on a glass fibre membrane filter, followed by quantitative conversion of the stained complex into a solution, the extinction of which is measured at 590 nm. This methodology originally described by Bradford[4] and modified by Setchell[15] is detailed by Agatova and Torgunova.[16] Two surveys were conducted in November 1987 (postmonsoon season) and June 1988 (southwest monsoon season) at surface and bottom of stations 1–11 in the Cochin estuary (Figure 1). Preconditioned 0.45 μm GF/C grade glass fibre filters (roasted at 450 °C for 5 hours and preserved in dessicator over silica gel) were used to filter 25 ml of the samples [at surface (0.5 m depth) and bottom (0.5 m above bed)] using a Hytech sampler and preserved in plastic bottles) on a millipore filtration unit with mild suction.

Some seawater samples from adjoining nearshore regions were also similarly analysed. The filters were placed in 20% TCA solution for 30 s in a petri dish to fix the protein sorbed on the filter. Next the filters were placed in the dye solution (0.25% Coomassie brilliant blue R-250 in 7.5% acetic acid and 5% methanol stored at 5 °C for a maximum of 2 weeks) for 30 min, intermittently shaking. After staining, the filters were rinsed successively three or four times in 7.5% solution of acetic acid, the end of this process being indicated by an absolutely clean filter margin. After the removal of excess dye, the filters were washed with distilled water and the proteins extracted with 3 ml of 0.12 N sodium hydroxide (in 80% methanol) applying centrifugation (6000 rpm for 15 min). The filters were macerated with a glass rod in the centrifuge tube for complete transfer of complex into solution. The protein dye complex (colourless in alkaline medium) was treated with 0.5 ml of 3 N HCl and allowed to stand for 5 min to develop the blue colour which was read photometrically on Hitachi Model 150-20 at 590 nm against a control mixture prepared by passing double distilled water through a filter processed in the same manner as above. Calibration graphs of bovine serum albumin (BSA) as standard determinations, both in freshwater and saline water ($10, 20, 30 \times 10^{-3}$) were used to calculate the protein concentration. The filtering assembly was rinsed in hot soda solution followed by double distilled water (repeated before each filtration). The reagents used were of Merck/Suprapur BDH grade.

Chlorophyll$_a$ was extracted in 90% acetone and analysed by the method

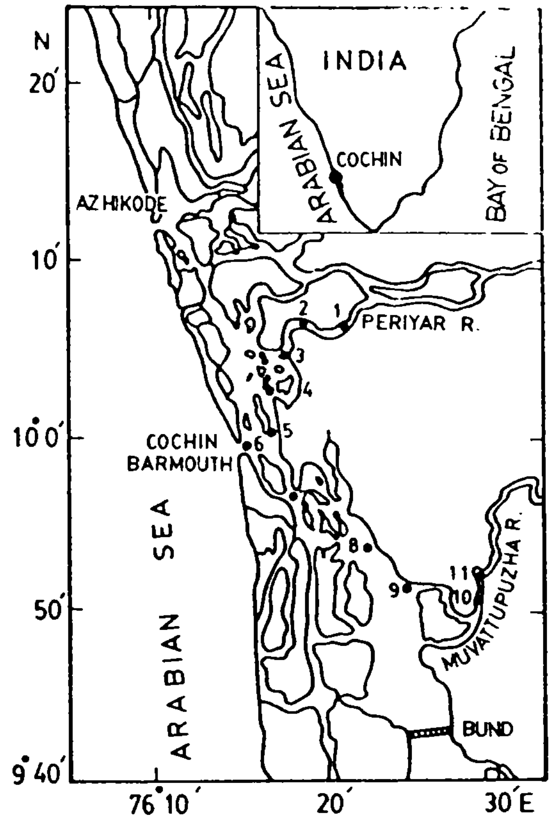

Figure 1 Location map of stations 1-11 in Cochin estuary.

proposed by Strickland and Parsons.[17] Organic NO_3^-—N was determined by the ultraviolet oxidation method[17] and organic PO_4^{3-}—P by the destruction of the C—O—P bonds by irradiation of the sample with strong UV light at wavelength $\simeq 250$ nm as suggested by Armstrong and Tibbits[18] and modified by Grasshoff.[19] Urea was estimated by the modified diacetyl monoxime spectrophotometric methods of Koroleff[20] and dissolved organic carbon by the method of El-Wakeel and Riley.[21]

RESULTS AND DISCUSSION

The distribution of dissolved protein, chlorophyll$_a$, organic NO_3^-—N, organic PO_4^{3-}—P, urea and dissolved organic carbon (DOC) are presented as distance scaled diagrams for both the surveys (Figures 2a and 2b).

Protein

The northern parts of the estuary exhibit increasing concentrations downestuary, both at surface and bottom, with nominal change in the upper reaches (stations 1–3) during November 1987 (Figure 2a). The content of protein was high

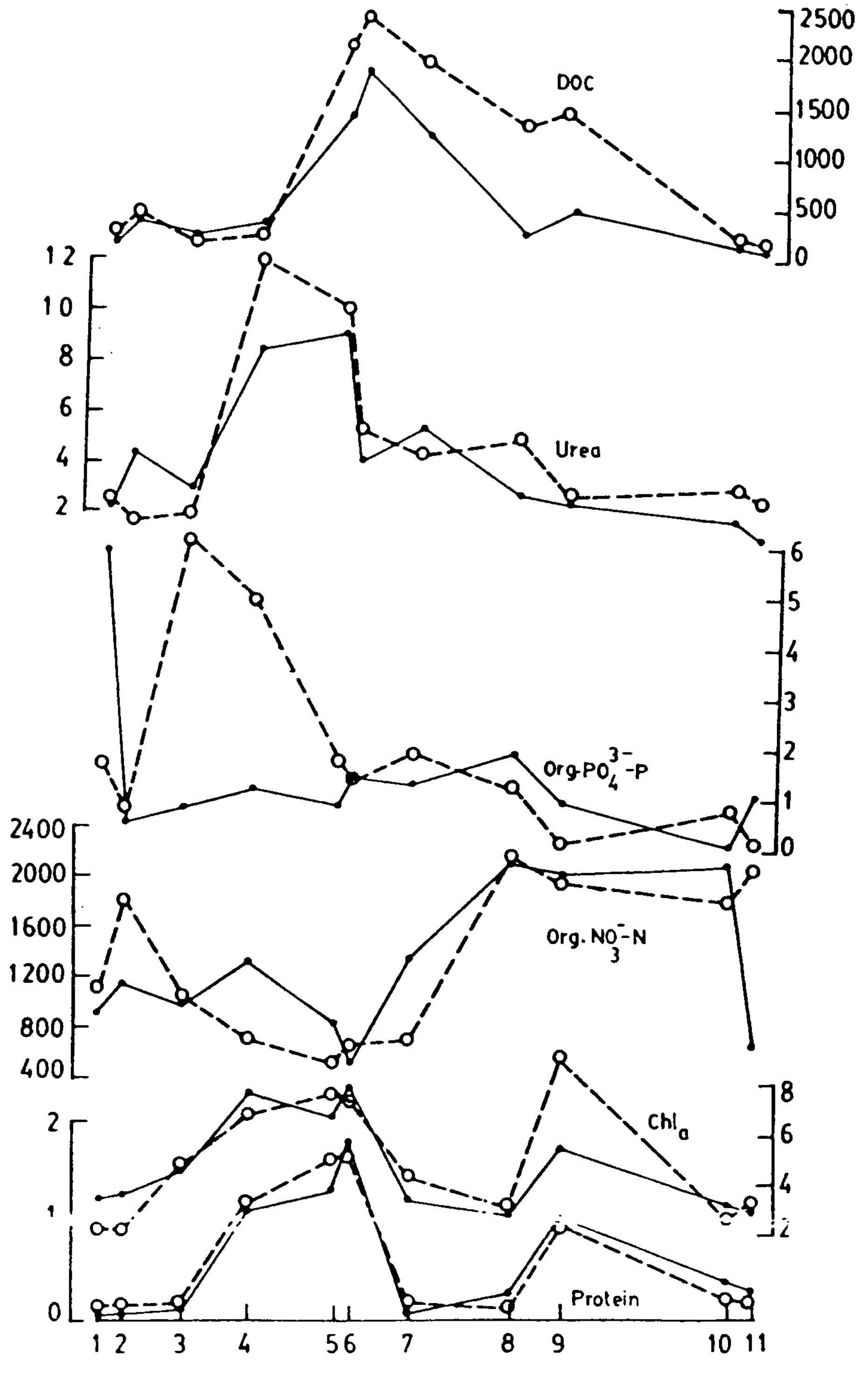

Figure 2a Distribution of protein (μg l^{-1}), Chl$_a$ (μg l^{-1}), Org. NO$_3^-$—N (μg at l^{-1}), Org. PO$_4^{3-}$—P (μg at l^{-1}), Urea (μg l^{-1}) and DOC (mg l^{-1}) in Cochin estuary during postmonsoon 1987 (—— surface; - - - bottom values).

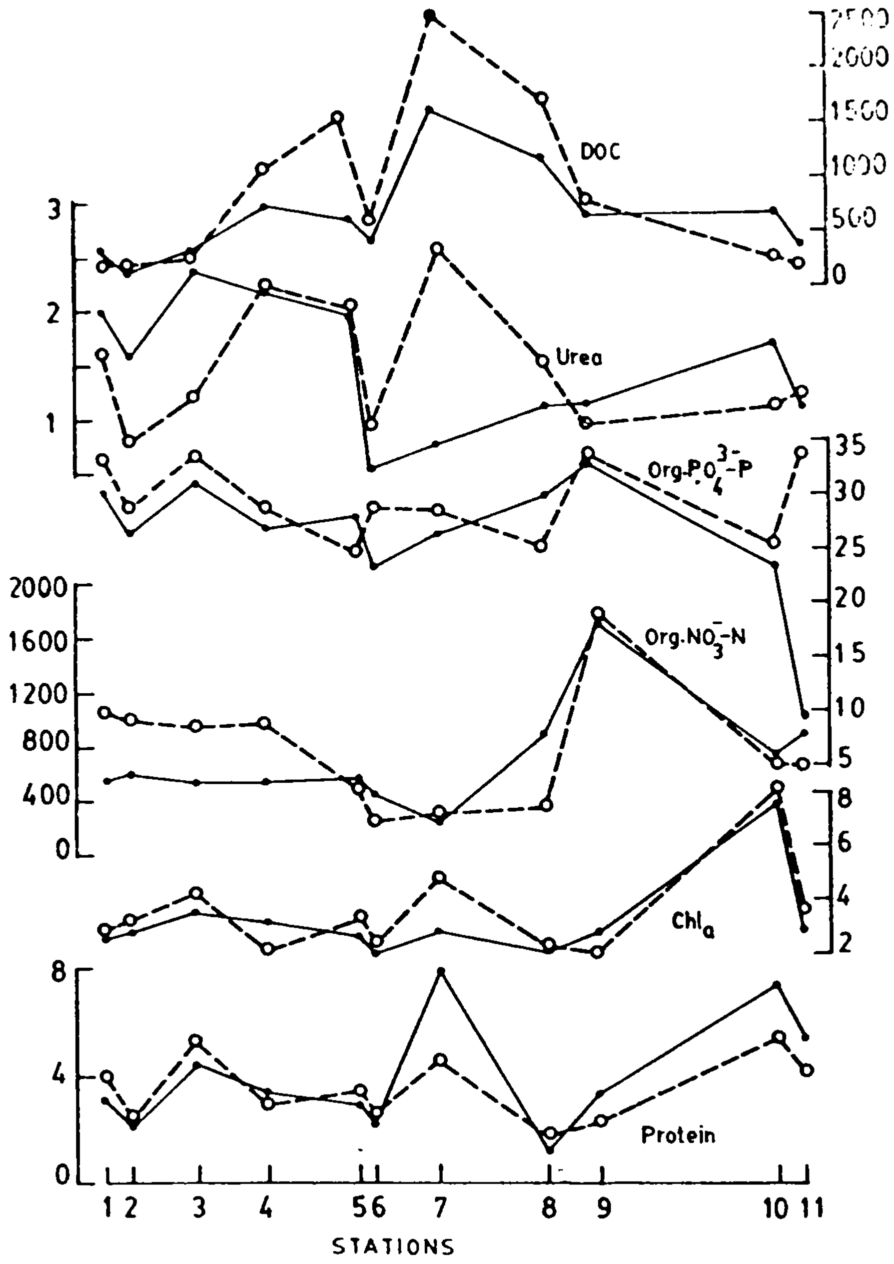

Figure 2b Distribution of protein (μg l^{-1}), Chl$_a$ (μg l^{-1}), Org. NO$_3^-$—N (μg at l^{-1}), Org. PO$_4^{3-}$—P (μg at l^{-1}), Urea (μg l^{-1}) and DOC (mg l^{-1}) in Cochin estuary during monsoon 1988 (—— surface; - - - bottom values).

(1.10–1.80 $\mu g\,l^{-1}$) in the high biological production zone (stations 4–6) signifying its association with planktonic activity. This region of middle and lower Periyar reaches are noted for enhanced production during the postmonsoon season.[22–24] The vast expanse of backwaters on the southern parts (stations 7–9) does not exhibit special features but Muvattupuzha river reach of the upper estuary on the southern parts show gradually increasing content from station 11 (fresh water) to station 9 at river mouth. It is observed that agricultural non-point inputs influence the concentration of protein during this season as this region is a confluence of a number of closely linked tributaries passing through vegetation fields. The level of protein in the freshwater arms of the estuary in the 1987 survey exhibited low values, 0.05 $\mu g\,l^{-1}$ on the northern parts and 0.20–0.30 $\mu g\,l^{-1}$ on the southern parts.

The concentration of protein during the survey in 1988 (monsoon) was more than double the previous level, a feature associated with increased terrestrial run-off (Figure 2b). The distribution features were reversed, in that the northern parts of the estuary exhibited gradually decreasing concentrations downstream with an intermediate high value at station 3 and a bi-modal distribution pattern for the southern parts. The barmouth region showed low levels, a complete reversal of the results of November 1987 study. Station 10, in the vicinity of outfall of the pulp-paper mill, appears to indicate the presence of compounds containing proteins in pulp-paper discharges and further downstream, at station 7, the concentration again peaks (8.0 $\mu g\,l^{-1}$ at surface and 4.6 $\mu g\,l^{-1}$ at bottom) due to siting of city sewage outfall and wastes derived from seafood industries.

Chlorophyll$_a$

The pigment content during postmonsoon (1987) truly represents the changing conditions due to biological production, prominently noted on the northern parts of the estuary. The chlorophyll$_a$ values did not exhibit much variation during monsoon of 1988 in the same locality but on the southern parts, especially in the Muvattupuzha river reaches, the concentration appears to be influenced by discharge from the pulp-paper factory. It has been already noted that the aeration lagoon experiences heavy growth of algae due to presence of excess nutrients.[10] The surface or bottom values do not differ much in content during both surveys, however the trend of chlorophyll$_a$ variation follows the distribution pattern of proteins emphasizing the linkage between the protein associated with the pigments. The end member values are low at 2.5–3.5 $\mu g\,l^{-1}$ in the freshwater zones, but barmouth region (stations 4–6) contained chlorophyll$_a$ in the range 6.8–7.8 $\mu g\,l^{-1}$ during postmonsoon, 1987, a situation reversed in 1988 monsoon to very low values (2.0–3.2 $\mu g\,l^{-1}$). The higher bottom values at station 9 in 1987, a region of river water and low saline estuarine water confluence, may be due to seepage from agricultural fields of neighbourhood than biological production.

Organic NO_3^-—N and PO_4^{3-}—P

In the absence of any marked distribution features in the inorganic forms of nitrates or phosphates, attention was focussed on the organic forms of the two micro-nutrients. Noteworthy, the organic NO_3^-—nitrogen distribution trends are inverse to that of the content of protein pattern during both the surveys. Surface and bottom values seldom differ, but the parametric distribution between the two surveys varied significantly. With decreasing values downestuary in Periyar river, associated with seasonal higher biological production in 1987, the southern region (stations 7–10) indicate a build-up and storage of organic forms of nitrates (2000–2200 $\mu g l^{-1}$). The discharge from newsprint factory (at station 10) is the only source for large amounts of nutrients, mostly neoteric, retained intact, a finding supported by low chlorophyll$_a$ values. During monsoon (1988), the NO_3^-—N content does not exhibit variation in the northern parts; barmouth area contains lower levels (200–400 $\mu g l^{-1}$) and southern parts signify single modal distribution. The inverse relationship between organic form of NO_3^-—N and protein involve the biogenic control of nutrients, an aspect requiring detailed study.

The organic PO_4^{3-}—phosphorous is distributed in varying amounts; the concentration values are nearly 5 to 15 times higher during monsoon, with little or not much variation compared to few random values on the northern parts, but otherwise, very low levels during postmonsoon for Cochin estuary. The land derived phosphates, mainly decomposed from plant detritus may significantly contribute to the higher values in monsoon, apart from contributions to this estuary from organic fertilizers/wastes leached in runoff water. It has not been possible from these two surveys to arrive at any definite conclusion regarding the nature of variability between protein vs. organic PO_4^{3-}—P, presumably because the governing factors of distribution for these two chemical constituents are different and non-compatible.

Urea

The distribution of urea in Cochin estuary follows the general variability trend of protein, but the relative amount of either vary inversely. The content of urea in November 1987 varies widely on the northern parts (1.80–12.0 $\mu g l^{-1}$) at both surface and bottom; values on the southern parts gradually increase downestuary from concentrations of 1.5–3.0 to 4.4–5.4 $\mu g l^{-1}$. The rapid decrease between stations 5 and 6, observed during 1987 as well as 1988 coincide with equally changing salinity conditions in a region of high turbulence and mixing. Urea concentration also simply reflects the local biological processes.[25] The distribution of urea during 1988 monsoon is more complex with wide variation between surface and bottom values. This signifies the role of urea as an important nitrogen source for marine phytoplankton, utilised in varying proportions.

Dissolved Organic Carbon (DOC)

The DOC values are distributed differently in the two surveys of 1987 and 1988. Whereas the range of values are the same, postmonsoon of 1987 exhibits increasing content downestuary from either river, especially in the lower estuarine reaches. The DOC values maximize at the barmouth region associated with production. This feature is not repeated in monsoon of 1988 where the region close to barmouth indicated low values against increasing trends downestuary from either arms of this backwater system. This sharp variation either as increase or decrease in all the parameters considered here reflects the chemical reactivity in higher saline waters superimposed on hydrodynamical influences on mixing high saline seawater with moderately saline estuarine waters.

Relationship to Chlorophyll$_a$, DOC and Urea

The relation between protein estimated by the dye binding assay and chlorophyll$_a$, DOC and urea is given in Figure 3. The data set compiled in 1987 postmonsoon and 1988 monsoon exhibit different seasonal interrelationship. The results of postmonsoon were observed to be significantly related ($n=22$, $p<0.01$) $r=0.92$, 0.60 and 0.59 in 1987 for chlorophyll$_a$, DOC and urea respectively; the interrelation during monsoon 1988 is only ($n=22$) $r=0.63$, 0.01 and 0.05. This suggests the biogenic control of protein content in this estuary during the high production season as terrestrial runoff dominated enhanced levels of protein observed during monsoon. The estimates on protein, likely related to nitrogenous base materials did not, however, correlate well with the organic nitrate forms.

CONCLUSION

The interest in the study of protein content in aquatic waters is generated by the fact that much of the organic fraction of dissolved and particulate matter is proteinaceous.[26] Study of this parameter is related to planktonic nutritional state,[27] metabolic activities based empirically on the ratio of protein to carbohydrate[28] and recognised on the magnitude of its contribution to both detritus and plankton.[29,30] Initially protein was determined by the analysis of marine phytoplankton on the nitrogen content basis[31,32] as N × 6.25 superseding Lowry method.[33] Later Packard and Dortch[29] reviewed the fluorescamine reactions[34,35] in which proteins are converted to fluorophors and measured fluorometrically. However, this estimate accounts for proteins in primary amines, small molecular weight peptides and other substances of biological importance found in cell free homogenates.[36,37] A well studied and widely applicable methodology was proposed by Bradford[4] based on dye binding assay, relatively insensitive to many common reagents which seriously interfere with protein determination by other methods. This methodology is comparable to the Lowry technique[33] as reported by Setchell[15] and even several times sensitive when one may specifically measure protein without non-protein artifacts.[4] The dye binds protein but not small peptides or amino acids, nor is there evidence that it combines with other biologically important material.[5,38,39] Table 1 represents the data compiled on the protein content from different geographical locations revealing its variability under varying environments.

An appreciation of the dye binding assay method is made in the study of protein content in Cochin estuary which reveals the usefulness in describing the estuarine conditions under seasonal influence from biological activity. The two

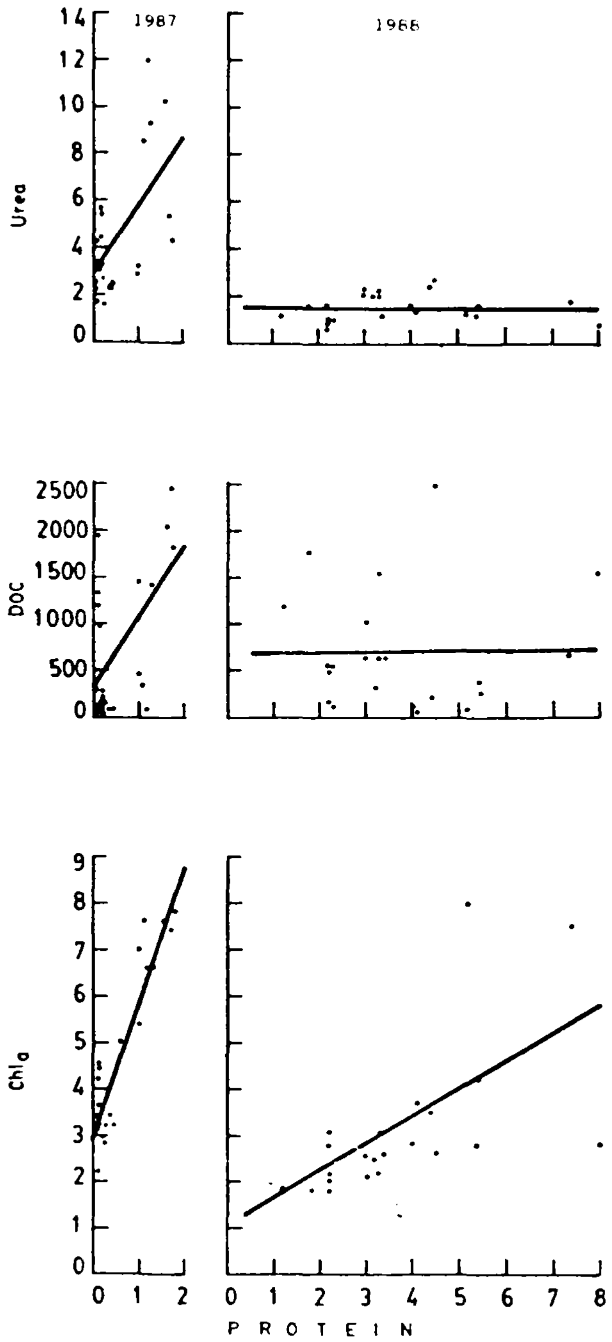

Figure 3 Relation between Chl$_a$ (μg l^{-1}), DOC (mg l^{-1}) and Urea (μg l^{-1}) vs. protein (μg l^{-1}) during postmonsoon 1987 and monsoon 1988.

Table 1 Protein content at various geographical locations including Cochin estuary and nearshore regions

No.	*Geographical location*	*Protein content* ($\mu g\ l^{-1}$)	*Reference*
1.	Minonoska Bay	0.012–0.018^{a}	Agatova and Torgunova (16)
2.	Furugel'm Island	0.026–0.106^{a}	Agatova and Torgunova (16)
3.	Novgorodka Bay	0.073–0.229^{a}	Agatova and Torgunova (16)
4.	Gulf of Maine	2.0 –212	Setchell (15)
5.	Lake Ontario	4.0 –680	Pick (28)
6.	William's Bay	250 –465	Chistenko (40)
7.	Atlantic Southeast	90 –397	Chistenko (40)
8.	Atlantic Oceanic waters	14.88 – 87.50^{c}	Chester and Stoner (41)
9.	North Atlantic surface waters	16.63 –309.75^{b}	Packard and Dortch (29)
10.	Peru (upwelling 0–250 cm zone) > 250 cm	28.0 –1157 50.0	Garfield *et al.* (42)
11.	Peru current	62.13 –2132^{c}	Macisaac and Dugdale (44)
12.	Tropical zone of Indian Ocean	28 – 136	Fischer (45)
13.	Indian Ocean Central	4.38 – 11.78^{c}	Chester and Stoner (41)
14.	Pacific eastern	45.50 – 64.75^{c}	Macisaac and Dugdale (43)
15.	Mediterranean	11.38 – 87.50^{c}	Macisaac and Dugdale (46)
16.	Costa Rica Dome	22.75 – 121.63^{c}	Postel (47)
17.	Cochin Estuary	0.05 – 8.00	This study
18.	Nearshore regions, off Cochin	0.45 – 1.49	This study

^{a}Dissolved fraction.
^{b}Fluorometric determination.
^{c}Micro-Dumas method.

seasons selected in this study exhibit varying characteristics—the northern parts of the estuary showing increasing concentrations downestuary during postmonsoon season in association with higher biological production supported by data on chlorophyll$_a$, urea and DOC. The region of highest production, in the vicinity of barmouth accounted for higher levels of proteins. The relationship between protein vs. chlorophyll$_a$, urea and DOC also show strong linearity in this estuary during postmonsoon months. A similar finding has also been reported in the Gulf of Maine where proteins significantly correlated with chlorophyll$_a$ during bio-production.[15] Subsequent to changed environmental conditions in monsoon, it has been particularly noted that the protein content nearly doubles the postmonsoon level, a feature closely associated with changes in terrestrial runoff and inputs of (organic) detritus material. The trend in distribution of protein also reversed during these months and interparametric relationship too is not at significant levels as again observed in Lake Ontario and Jacks Lake, Ontario.[28] The distribution trends in the organic fraction of NO_3^-—N appeals to us to visualize the changing protein levels under varying estuarine conditions to be regulated largely by biological activity rather than purely non-conservative physical or chemical mechanisms.

It has not been possible to define any better relationship between the two parameters nor extend any hypothesis to relate protein variability with inorganic or organic forms of phosphates in this water body.

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