GEOCHEMICAL, SEDIMENTOLOGICAL AND REMOTE SENSING STUDIES OF KAYAMKULAM ESTUARY, SOUTH WEST COAST OF INDIA - A GIS APPROACH

Thesis submitted to

THE COCHIN UNIVERSITY OF SCIENCE AND TECHNOLOGY

in partial fulfilment of the requirements

for the degree of

DOCTOR OF PHILOSOPHY

IN

MARINE GEOLOGY

UNDER THE FACULTY OF MARINE SCIENCES

BY

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OCTOBER 2002

CERTIFICATE

I certify that this thesis, entitled **"Geochemical, Sedimentological and Remote Sensing Studies of Kayamkulam Estuary, South West Coast of India - A GIS Approach"** is an authentic record of research work carried out by **Mr. Reji Srinivas** under my supervision and guidance at the Department of Marine Geology & Geophysics, Cochin University of Science & Technology, under the Faculty of Marine Science and no part thereof has been presented for the award of any degree in any university/ Institute.

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PREFACE

"A handful of sand is an anthology of the Universe"

David McCord

The coastal sedimentary environment of Kerala is blessed with a chain of water bodies such as fluvial channels, estuaries and backwaters. These aquatic environments play a significant role in the socio-economic and environmental scenario of the State. The health of these aquatic systems is, perhaps, responsible for the scenic beauty, productivity and unique heritage of this " God's own country ". Unfortunately, the various aquatic systems that sustain the life and greenery of the state are at the verge of severe deterioration as consequence of various kinds of human activities over the past 2 to 3 decades. Stringent efforts are needed to revive the healthy environmental quality of these life-supporting systems. Lack of scientific information regarding the existing environmental setting is the one of the major setbacks challenging wise decision-making and implementation of conservation and management schemes.

The present study is intended to generate the base line information regarding sedimentological and geochemical aspects of one of the major estuarine systems of the Kerala, "the Kayamkulam estuary" (Latitudes 9^{O} 2' to 9^{O} 15' N and Longitudes 76^{O} 25' to 76^{O} 32' E), located in the southwest coast of India. Attempts have also been made to assess the human activities responsible for the Shrinking of the Kayamkulam estuary. This is done, primarily through the study of time series changes of the estuarine system using survey records as well as the remote sensing data base (IRS-IC, LISS III). The informations were transferred in the form of various thematic maps, were integrated using GIS for identifying the major causative factors for environmental degradation of this valuable estuarine / backwater system set naturally in the interface between Kollam and Alappuzha districts.

The present study enfolds information on the environment of deposition and lateral variation in texture, mineralogy and geochemistry with respect to various physico-chemical processes operating in the system. The geochemical analysis of major and trace elements, organic matter and carbonate content helped to establish their distribution pattern in the estuarine substratum in regard to toxic contamination / pollutant loading. The heavy and clay mineral investigations enable to decipher the nature and source contributions of the sediments. For the better understanding and expression of the results, the study area has been broadly divided into three zones namely: the northern, central and southern sectors.

The whole work is addressed into 7 chapters

Chapter I deal with the general introduction, which provides the location, climate, geology, physiography, geological and environmental setting of the study area besides the regional geology and historical perspective. The objectives of the present work are given towards the end of this chapter.

Chapter II provide the details of the field work, methods of sample collection, processing, analytical procedures employed for textural, mineralogical, geochemical and remote sensing and GIS studies.

Chapter III enfolds the textural and sedimentological characteristics of the surfical sediments of the Kayamkulam estuary.

Chapter IV describes the mineralogical constitution of estuarine sediments. An attempt has been made to unfold the provenance of sediments as well.

Chapter V presents the geochemistry of organic carbon, carbonates and major and trace elements in the estuarine sediments. The contamination status of estuarine sediments is also worked out in this chapter.

Chapter VI gives the integration of remote sensing data pertaining to the estuarine system as well as the adjoining areas. Geographic Information System (GIS) has been used to integrate various layers of information gathered in the form of thematic maps.

Chapter VII presents the summary of the whole study and the salient conclusions drawn from the results thereof.

The pertinent literatures cited are furnished towards the end of the thesis.

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CHAPTER I

GENERAL INTRODUCTION

1.1 HISTORICAL PERSPECTIVE

Knowledge of sedimentary processes in lagoons over the past 80 years has grown along different lines of inquiry. Early interest centred on morphological features that relate to geological evolution of lagoons, adjacent marshes, inlets and barrier islands (Davis, 1898; Johnson, 1919; Lucke, 1934). As a guide for petroleum exploration, stimulated the problem of recognizing ancient lagoon and barrier deposits during the 1950's. Sedimentary patterns of modern deposits in the Waddan Sea (Van Stratten, 1954, 1959), in tidal flat lagoons bordering the North Sea, and in lagoons of the USA Gulf coast (Shepard and Moore, 1960; Rusnak, 1960) were determined from textural, compositional and structural features. Some of the patterns and features were related to hydraulic conditions and depositional processes in a general way.

The first notable study directed specifically to sedimentary processes was that of Krumbein (1939) in Barataria Bay of the USA Gulf coast, in which he showed that distributions of particle size were sensitive to hydraulic conditions. Inman and Chamberlain (1955) demonstrated that particle size distributions in Texas Bays, USA Gulf coast, result from different transport processes, mainly bottom wave agitation, and from different amounts and types of sediment supply. The detailed results of

Stewart (1958) in San Miguel Lagoon, Mexico, showed how textural and compositional properties are closely linked to environmental processes.

The problem of fine sediment accumulation in the Wadden Sea and the cause of landward transport from the North Sea led Dutch workers (Van Stratten and Kuenen, 1957; Postma, 1957, 1961, 1967) to study the dynamics of sediment transport by direct observation of suspended sediments and water movement. This approach, related to flow measurements and lag effects, has been applied to problems in estuaries, (Nichols, 1974; Allen and Castaing, 1973), a tidal creek (Boon, 1975) and in lagoon inlets (Byrne, 1975; Certel, 1972). Only a few studies report the effect of wave processes on shoals and flats (Anderson, 1972; Postma, 1957). A practical need to stabilize inlets resulted in studies by Bruun and Gerritsen (1960) defined a ratio of tidal prism to long shore drift for maximum stability. O' Brien (1969) found that the flow area of an inlet is a function of tidal prism. Hydraulic conditions are often complex, so hydraulic models have been employed to predict sediment transport affected by engineering works (Simons, 1966). Increasingly, predictions have been facilitated by numerical models, e.g., Odd and Owen (1972), Leendertse et al. (1973) and April and Brett (1975).

After it was learned that organisms exert a profound effect upon sediments in which they live (Sanders, 1958), numerous studies of animal-sediments relationships emerged. Burrowing in sediment results in particle displacement (Schafer, 1962) and in turn, affects mass properties (Rhoads, 1974). Some deposit-feeders fractionate and sort particles of different sizes (Myers, 1977); others deposit sediment as fecal pellets and pseudofeces (Warme, 1967; Haven and Morales-Alamo, 1972) and thus enhance sediment accumulation. A detailed review of the growing volume of literature on the effects of animals and plants on sediments are beyond the scope of this paper. The reader can refer papers by Pryor (1975); Howard and Frey (1975) and Frey and Basan (1978).

An understanding of chemical processes in lagoon sediments stems from studies of evaporite deposition from models (Scruton, 1953) and filed observations (Evans and Bush, 1973). Chemical conditions for flocculation of clay minerals were treated by White house, et al. (1969), Einstein and Krone (1961) and Gibbs (1977). Postma (1969) showed the effect of hydrography on the concentration of chemical compounds associated with suspended matter. Friedman and Gavish, 1970 and Oppenheimer, 1960, present diagenetic changes of sediment chemistry.

During the past decade, a concern with effects of pollution, dredging and filling, and the need for coastal zone management, has provided an impetus for process oriented studies like the case histories by Orme (1975), Harbridge, et al. (1976) and Nichols and Towle (1977).

Commonly, lagoons have been studied individually and by different methods, or for the special features they may hold. Few workers have studied more than a single lagoon (Emery and Uchupi, 1972). Consequently, the present state of knowledge consists of a random distribution of data. There are few general reviews of lagoonal sedimentary processes but summaries of sediment characteristics are presented by Emery and Stevenson (1957) and Folger (1972). Many useful sediment papers are found in symposia volumes by Trask (1955), Lauff (1967), Castanares and Phleger (1969), Nelson (1972), Institute de Geologie du Bassin d'Aquitaine (1974), Cronin (1975) and Wiley (1976).

1.2 INTRODUCTION

The coastal belt of Kerala endowed with an interlacing network of fluvial channels, lakes and other backwater bodies along the southwest coast of India has a coastline of nearly 580 km, extending from Manjeswar in north to Puvar in south. This is about 10% of the total coastal length of India. The chains of brackish water, lagoons and estuaries of Kerala extends over 325 km in length and the total brackish water area estimated is to be around 2,42,000 hectors (Annon, 1990).

The lakes and backwater bodies occurring in Kerala are known locally as 'kayals'. A *kayal* is a distinct dynamic environment where different energy forces act to supply and distribute sediment from various sources. The interplay of energy and sediment operates in a body of water, which is generally shallow and has communication (restricted or ephemeral) with the major water bodies like sea through inlets. In most cases there shall be a barrier separating the *kayal* from the adjacent sea. An understanding about the various processes operating within each *kayal* is an essential link in any multidisciplinary effort to solve problems in that environment, which is threatened by various natural and man-made factors. Studies revealed that many of the aquatic systems of Kerala pose severe ecological impairments due to the continued discharge of contaminants from urban, agricultural and industrial areas.

Human intervention is another responsible factor for the accelerated degradation of the coastal fragile ecosystems including the *kayals* that are located close to the coastal areas. The conservation and management of these fluvial environments, which support the coastal Kerala, would become difficult in the absence of sufficient information regarding the physicochemical and biologic processes operating within these systems.

The *kayals* are of varying ages and located on geological formations of different genetic history. From a detailed study, Nair and Thrivikramaji (1996) categorized the *kayals* of the coastal Kerala under four broad groups. The details are presented in Table 1.1. As per this classification, the area selected for the present study, the Kayamkulam *kayal* falls within the Type A category. In addition to the water bodies mentioned by Nair and Thrivikramaji (1996), the Kerala state is blessed with numerous other minor water bodies as well; examples are the Pookot lake (Wyanad), Chelur *kaya*l and Chittumala *kayal* (Kollam district), etc. All these water bodies have a prime role in maintaining bar supporting the life and greenery of the Kerala state. It is unfortunate to note that many of these systems are under the threat and also at the verge of disappearance due to accelerated sedimentation, reclamation and other natural and man made activities. These observations point to the urgent need for systematic monitoring, conservation and management of these gifted water bodies of Kerala.

Present investigation is an attempt to study the various physicochemical processes operating within one of the coastal water bodies/ lagoons of Kerala, the

Table 1.1 Classification of *Kayals* in the coastal areas (after Nair and Thrivikaramji, 1996)

Type A	**Type B**	**Type C**	**Type D**
Katinamkulam,Kayamkulam, Vembanad, Chetwai,Tirur, Kanjiramukku,Agalapuzha, Kavvai. *(Very large length-width ratio, coast parallel or nearly parallel disposition for the long axis, separated from the sea by large barrier spits and by inlets, display simple rectilinear or complex rectilinear plan forms.)*	Anjuthengu, Akathumuri, Paravur,Ashtamudi,Kadalundi, Chaliyam, Badagara, Mahe, Tellicherry,Valapatanam, Chandragiri. *(Large length–width ratio, long axis set transverse shore line, major portion of the kayal shore line is set against cliff line, obvious dichotomy between inlet and the gut of the kayal.)*	Puvar, Karichal, Panathura, Akkulam-Veli, Edava, Kalli Purapparamba, Chitrai, Bakal, Kottikulam, Kalanadu, Mogral, Kumbl, Uppala *(Kayals are smaller in aerial extent (<2 sq.km) with its long axis set transverse and very close to the present shore line, seasonal spit develops at the bar mouth may block free exchange of water, wash over sediments, builds wash over fan.)*	Vellayani, Sasthankotta, Vatta. *(Set for back in the coastal land, presently devoid of any direct connection with sea, fresh water supply from land drainage and underground sources, basin are set in older formations)*

Note: Descriptions in parenthesizes are the salient features that characterize the *kayals* under the sited categories

Kayamkulam *kayal*, located parallel to the coast from Sankaramangalam in the south (Kollam district) to Karthikapalli in the north (Alappuzha district). Since surface run off from various natural as well as man-made drainage systems dilutes the saline water in the lagoon, the Kayamkulam *kayal* exhibits the character of an estuary. Further, Soman (1997), who compiled the Geology of Kerala, highlighted the Kayamkulam kayal under the broad category of estuaries (Table 1.2; Fig. 1.1). Because of all these observations and citations, the study area is hereafter designated as 'Kayamkulam estuary' for the presentation and discussion of the findings of this investigation.

1.3 LOCATION OF THE STUDY AREA

The Kayamkulam estuary (Fig.1.2) is a linear water body stretching from Sankaramangalam in the south and Karthikapalli on the north for a length of about 24 kms. The width of the lake varies between a few tens of metres over a kilometre. The water spread area of the lake falls within the jurisdiction of two coastal districts of Kerala, Kollam and Alappuzha districts. The estuary lies between north latitudes $9^{o}2'$ to $9^{o}16'$ and east longitudes $76^{o}25'$ to $76^{o}32'$ and fall within the Survey of India (SOI) topographic sheets 58C/8 and 58C/12.

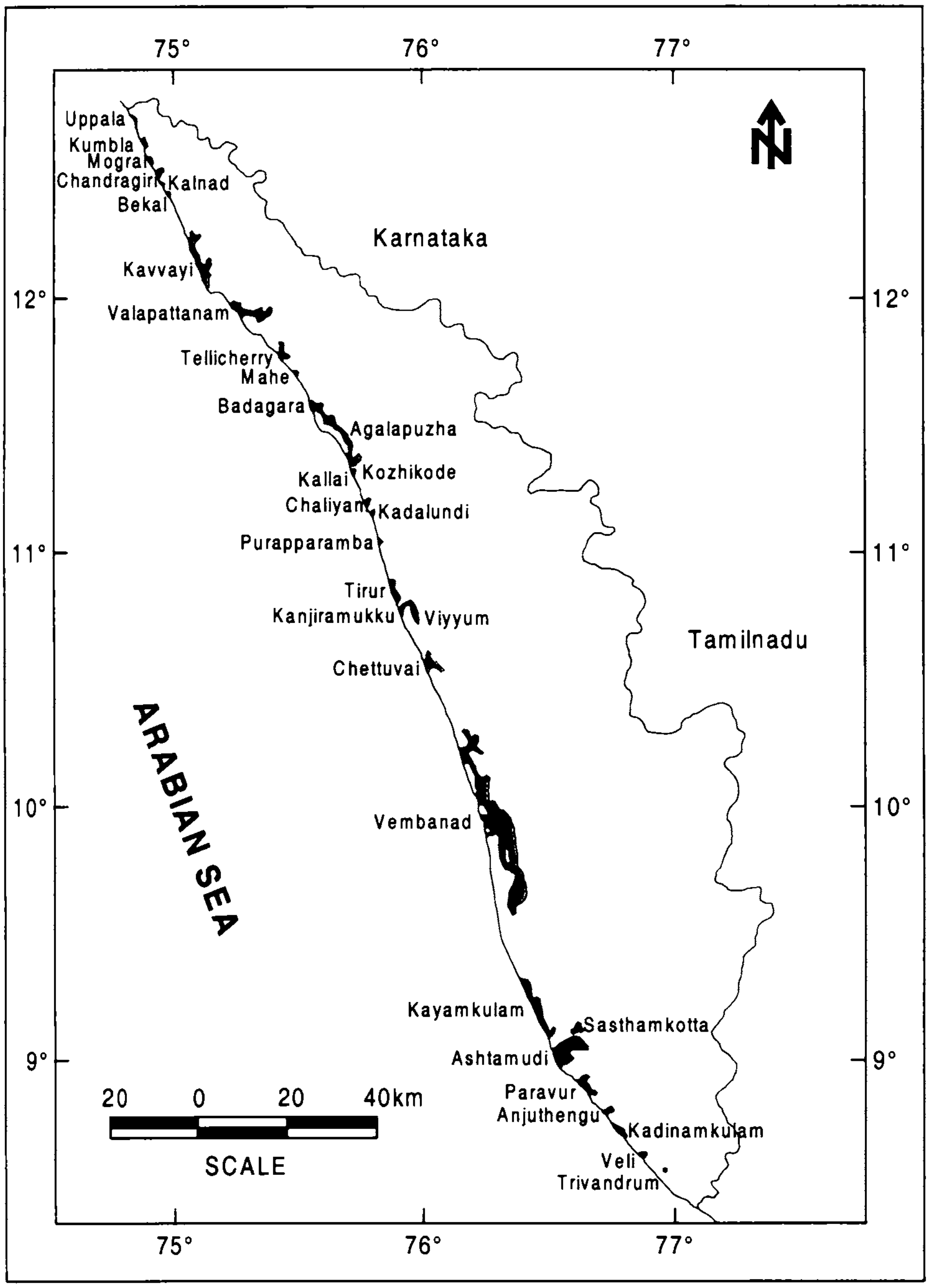
1.4 THE KAYAMKULAM ESTUARY: A BRIEF PROFILE

Kayamkulam estuary is one of the major estuarine systems in the southwest coats of India. The estuary is located close to the Arabian sea and separated from the sea by a narrow barrier beach. The water spread areas of the system fall within

Table 1.2 The estuaries and lagoons in Kerala

Estuaries	Lagoons
Uppala , Kumpla,, Mogral, Chandragiri,	Kavvayi
Kalnad, Bekal, Chittari, Karingote,	Agalapuzha
Ezhimala, Valapattanam, Dharmadom, Tellicherry,	Enamakkal- Manakkodi
Mahe, Kottakkal, Elathur, Kallai,	Muriad
Beypore, Kadalundi, Chettuvai, Ponnani,	Kodunngallur- Varapuzha
Vembanad, Kayamkulam, Ashtamudi,Paravur,	Sasthamkotta
Edava-Nadayara, Kadinamkulam, Veli.	Vellayani

Source : Soman (1997)



SOURCE: K.SOMAN(1997)

Fig.1.1 Location map of Kayals in Kerala

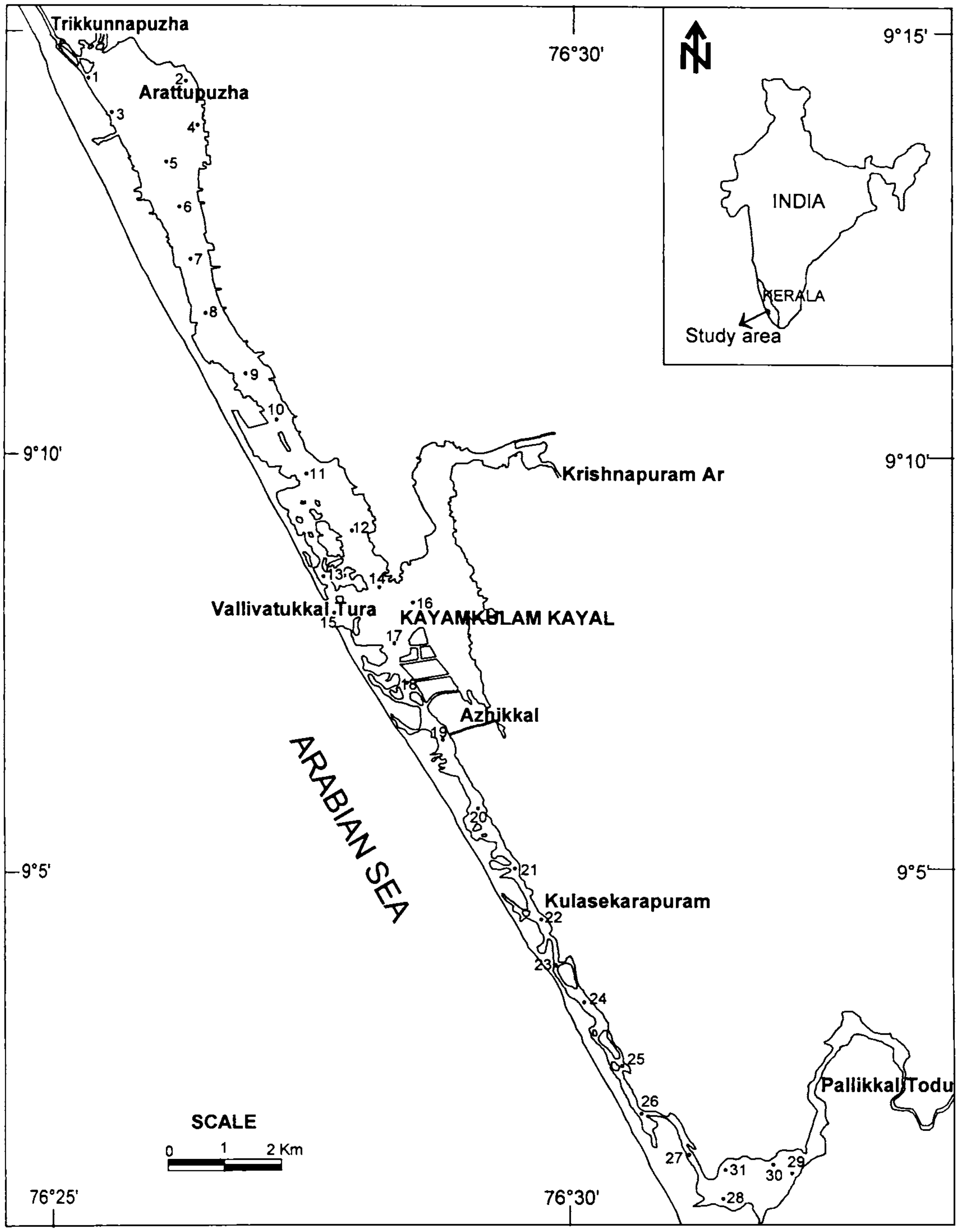


Fig 1.2 Location map of the study area with sampling stations

the Alappuzha and Kollam districts. Three major drainage channels that drain the estuarine basin are Pallikkal thodu in the south, Krishnapuram Ar and the Kayamkulam canal in the central and Thrikkunnappuzha in the north (Fig.1.3). In addition to these, a few low order streams and minor canals as well as distributaries of Pamba River are also debouching into the Kayamkulam basin at different locations. The general drainage pattern is dendritic reflecting the homogenous terrain. The Kollam-Kochi surface water transport canal is also passing through the system. The lake is connected to the Vembanad in the north and Ashtamudy in the south through canals. The Kayamkulam lake is also connected to Achenkovil river though a narrow perennial and shallow canal. The influx of water from land drainages into this coastal lagoon makes the system estuarine most part of the year.

The Kayamkulam estuary differs from a typical estuary from its closed nature, at least for a period of three months every year in the summer season. It is connected to Arabian sea through Vallivathukkal Tura bar mouth, a 'Pozhi' which cut off the lake from the sea by the formation of a sand bar at least for a period of three months (January-May).The fresh water run off from the land during the monsoon flushes out the lake by the forced opening of the bar mouth where by lake enjoys sea water as well as fresh water in flow. The sediment carried out by the fresh water causes the sand bar to form again after the monsoon. This phenomenon is largely responsible for the marked variation in the hydrographical features of the estuary.

Because of the great variety of processes, range of sediment types and morphology observed, it is useful to organize lagoons into a systematic framework.

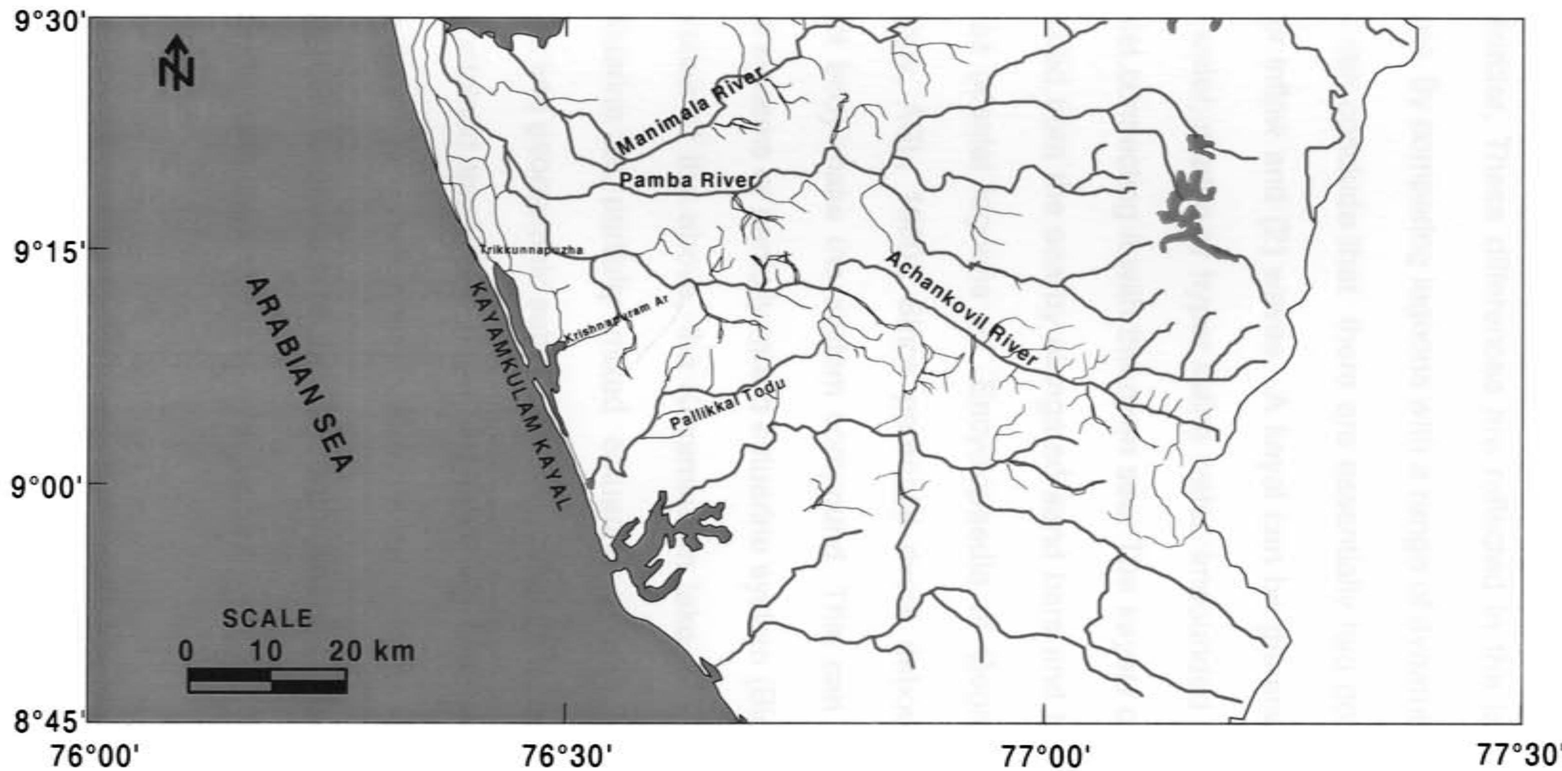


Fig. 1.3 The drainage pattern of the Pallikkal thodu, Krishnapuram Ar and Trikkunna puzha

Different types of lagoon systems result when the dominant energy forces differ in intensity and character. These differences are reflected in the lagoon morphology and sediment types. By comparing lagoons with a range of dynamic attributes and by generalizing, we can conclude that there are essentially two dominant processes: (1) tides plus river inflow and (2) waves. A kayal can be generally described as a body of brackish water, marine or hyper saline water, impounded by a sandy barrier and having an inlet connecting it with the open sea. The *kayals* of the Kerala coast are mostly separated from the sea by elongated sand bars and based on this they can be treated as coastal lagoons (cf. Encyclopaedia of Geomorphology, 1968; glossary of geology, AGL, 1980). Since perennial rivers debouche into the sea through this water body make the system compound. This can be considered as lagoons-estuarine systems or partially mixed estuarine system (Biggs, 1978). Taking into the consideration of the above, the Kayamkulam lake can be considered as under lagoon-estuarine or partially mixed estuarine system. On the basis of geometry, geologic and geomorphic setting, the Kayamkulam kayal comes under the group of those contained the beach ridge and adjoining coastal plains. Kayals of these types have their long-axis running parallel to the coast and are mostly found within the coastal plain formations of the Quaternary period. These are separated from the sea by barrier spits interrupted by tidal passes.

1.5 PHYSIOGRAPHY

On the basis of physiographic and slope maps of Kerala (CESS, 1984), the land of Kerala can be grouped into five distinct zones. They are mountain peaks of the Western Ghats rising above 1800 m from the mean sea level (MSL), the highlands at an altitude range of 600 – 1800 m, the midlands at an altitude of 300 – 600 m, the lowlands of 10 - 300 m and coastal plains of <10 m elevation. However, the major rivers/streams draining into the Kayamkulam estuary originates from the midland zones only. The Kayamkulam estuary sets in the coastal plains having < 10 m altitude from MSL, modified to the present level by a series of coastal evolutionary processes that took place primarily in the Quaternary period (Nair, 1971).

1.6 GEOLOGIC SETTING

1.6.1 Regional Geology

Geologically, Kerala state shows four major rock units, viz: i) Precambrian crystallines, ii) Tertiary sedimentaries, iii) Laterites developed over Pre-Cambrian crystallines and Tertiary sedimentary rocks, and iv) Recent to Sub-Recent sediments.

The Precambrian crystalline rocks comprise chiefly of charnockite and khondalite group of rocks which traversed by granites, pegmatites and basic dykes. The charnockite is seen throughout the state. The Precambrian rocks cover more than 80% of the total area of Kerala (GSI, 1995). The khondalite group comprising garnet-sillimanite gneiss with or without graphite, garnet – biotite gneiss, garnet-quartz, feldspathic gneiss or granulite and quartzite are the predominant rock types in southern Kerala. Tertiary sedimentary formation of Kerala overlies the Precambrians and extends from Cape Comarine in the south to Manjeshwar in the north and comprises two faces of sediments.

(i). The continental facies, the Warkalli Formation, comprises carbonaceous clays with lignified tissues, china clays and friable sandstone.

(ii). The marine facies, the Quilon Formation, composes of sandstone and carbonaceous clays with thin bands of fossiliferous limestone depicting the transgressive events that occurred during Burdigalian (Upper part of Lower Miocene) time. The third lithological unit is the laterites. It is iron-aluminium rich rocks derived from the chemical weathering of either Precambrian crystallines or Tertiary sedimentaries. They found as cap rocks or 'iron hats' over both the Precambrian crystallines as well as the Tertiary sedimentaries.

The Recent to sub-Recent sediments include fringes of parallel sand bars, several flats, alluvial sands and lacustrine deposits. Polymict pebble bed separates this group from the Tertiary sedimentaries. This formation, particularly the beach sands, is the most important one owing to the attractive concentration of valuable placer minerals like ilmenite, rutile, zircon, monazite etc.

1.6.2 Geological Setting of the Kayamkulam Estuary

Hinterland areas drained by the Pallikkal *thodu*, Krishnapuram *Ar* and Thrikkunnapuzha along with other minor channels emptying in the Kayamkulam estuary, are characterised by a variety of geological formations which can be broadly classified under three distinct units, viz., Precambrian cystallines, Tertiary sedimentries, and Quaternary deposits (Fig.1.4). As mentioned earlier, laterite is found cap rocks at some places. The Precambrian crystallines are composed predominantly of garnet-biotite gneisses with associated migmatites, garnet-sillimanite gneisses with graphites (khondalite) and patches of quartz-feldspar-hypersthene granulite (charnockite). These rocks are intruded at many places by acidic (pegmatites and quartz veins) and basic (pyroxene granulite) rocks of various ages. The Precambrians are confined mainly to the eastern part of the watershed area of the estuary. It is followed towards west by Tertiary and sedimentaries represented by sandstones and claystones with seams of lignite (Warkali Formation). Coastal sands and alluvium of Quaternary age dominates the western part close the estuarine basin. This zone is marked by a series of ridges and runnels resulted from the Quaternary sea level oscillations.

1.7 ENVIRONMENTAL SETTING

The Kerala coastal belt is undulating with many rivers traversing the area from the east to the west, and linking the lagoons and backwater bodies. Man-made canals also inter-connect the backwater bodies to provide inland waterway for nearly about 150 km. The near shore sea bottom is composed of sandy sediments upto several meters. The sedimentary deposits vary between 480 and 600 meters in depth till the rock base is reached. This estuarine system opens to the sea at Vallivatukkal Tura. The land use adjoining this estuary mainly consists of coconut plantation and

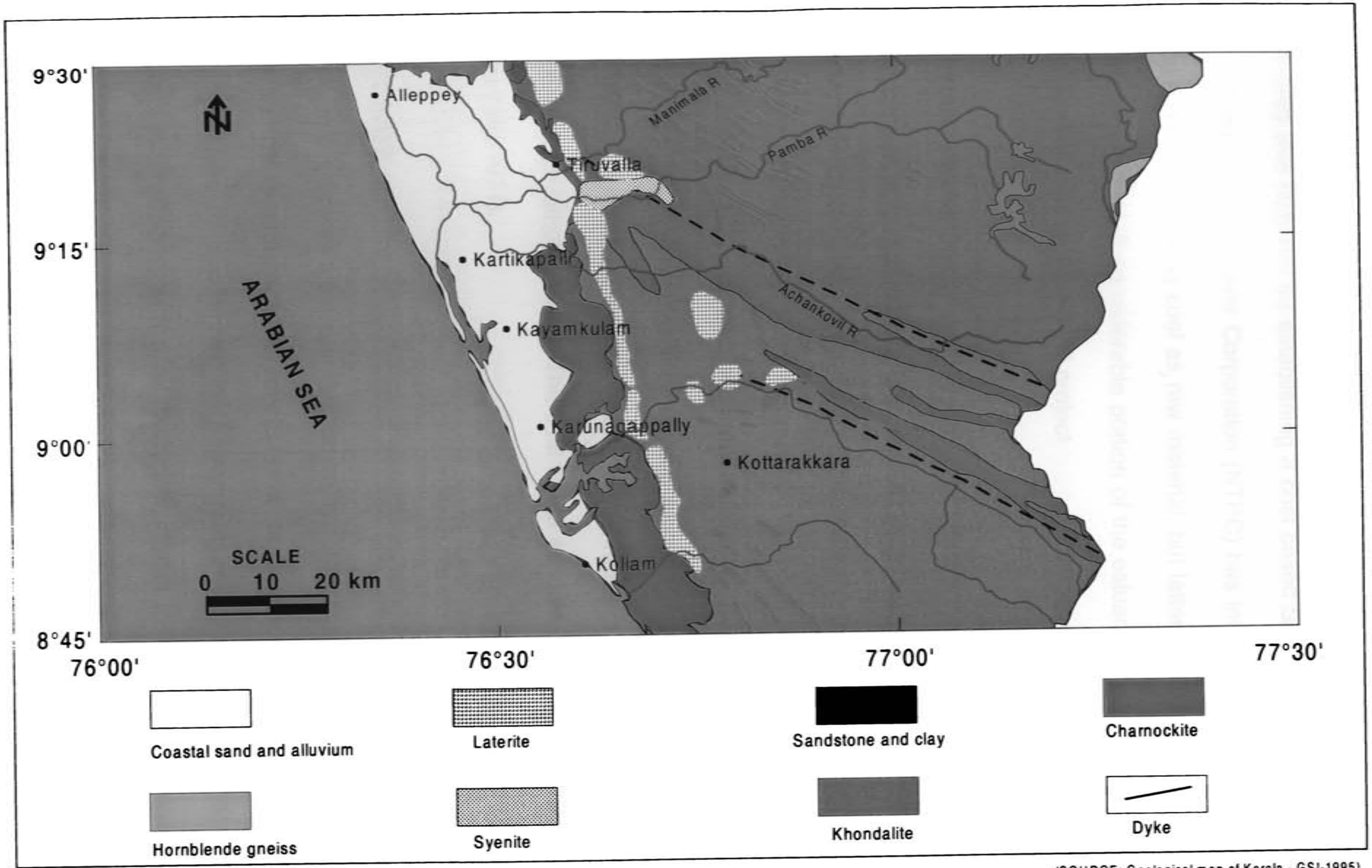


Fig.1.4 Geological setting of the Kayamkulam estuary

fields of paddy cultivation. At the time of beginning of the study the northern arm of the estuary was acquired for establishing a coal based Super Thermal Power plant. The National Thermal Power Corporation (NTPC) has initiated the preliminary work of the power station using coal as raw material, but latter on, they converted to gas based thermal plant. A considerable portion of the estuarine bed at its northern arm has been reclaimed for the NTPC project

1.8 HYDROGRAPHY

The Kayamkulam estuary is a shallow marginal lagoon whose depth varies between 0.5 m and 2.5 m. The salinity of the estuary ranges between 0.5×10^{-3} and 33×10^{-3}. (The lower values observed during peak monsoon and higher values during summer season) and temperature varies between 26.9°C and 32°C (Kuttiyamma, 1980). The dissolved oxygen recorded in the estuarine water varies from 3.2 mg l^{-1} to 6.5 mg l^{-1}. The average tidal range is about 1.25 m near the bar mouth at Vallivathukkal Tura. The tidal range exhibits a progressive decrease far inland (Nair, 1971).

1.9 CLIMATE

The Kayamkulam estuarine region enjoys characteristic tropical humid climate. A dry summer season from February to May (Pre monsoon) is followed by southwest monsoon (June to September) of heavy rain and then post monsoon season (October to December) with a relatively low rainfall to scanty thunderstorms. The climate is an important parameter that affects the various stages of morphogenic processes, and the quality and quantity of particulate materials within the estuarine system.

1.9.1 Temperature

Mean maximum temperatures are between 30° and 32°C in the costal belts but go up to 38° C in the interior part of the watershed areas of the estuary (Pisharody, 1992). The variation in the maximum temperature is of 36° and 37°C along the coast but goes up even high at places further inland. The seasonal and diurnal variations of temperature are not uniform. The stations located near the coasts are influenced by land and sea breezes and have seasonal and diurnal variations of temperature, which are almost of the same range.

1.9.2 Rainfall

Kerala state is blessed with high rainfall amounting in the order between 200 cm and 500 cm; with 60% of rainfall from southwest monsoon. In general, rainfall increases from the coast to the foothills and then decreases towards the hilltops. The state experiences three broad seasons based on the rainfall trend. They are:

(i). South –West Monsoon period (June – September)

(ii). North – East Monsoon period (October – December)

(iii.) Non – Monsoon Months (January – May)

- To find the change in the area of Kayamkulam estuary for the period 1967 to 1999.
- To delineate the land use and health of the vegetation around the estuary and suspended sediment concentration within the estuary using satellite digital image.
- To integrate the various layers of information using Geographic Information System.

Another significant point to note is that, many of the investigations are done only after industrlization or urbanization, and hence background information regarding the heavy metal level of those systems are practically nil. It is in this contest the present study is highly significant since the Kayamkulam and adjacent regions are free of much industrial effluent. So, the trace metal data before commissioning the Super Thermal Power Plant can be taken as excellent base line information for computing/ evaluating postindustrial pollutions.

CHAPTER II

MATERIALS AND METHODS

This chapter deals with the various methods employed in the sample collection, sample processing and their analysis.

2.1 FIELD SURVEY

A systematic fieldwork and sample collections were performed during post-monsoon and pre-monsoon seasons of 1997 – 1998 periods. A total of 48 sediment samples were collected at regular intervals along the Kayamkulam estuary at each period. Surface sediment samples were collected using a stainless steel van Veen grab sampler. The samples were packed in well cleaned, labelled polythene bags and were kept in an inert atmosphere till further processing. For geometric correction of satellite images and land use pattern of the study area, a certain number of ground control points (GCPs) were identified. GCPs are the points, the position of which is known both in satellite image and in supporting maps.

2.2 GRANULOMETRIC STUDIES

2.2.1 Texture

The sediment samples were repeatedly washed with distilled water to remove the soluble salts, and dried at 80°C. The representative sand dominant samples were taken after coning and quartering and were subjected to dry sieving. Sieving was done with the help of mechanical Rotap sieve shaker and the sieve sets were arranged in the descending order of the grain size and sieved at half phi interval following Carver (1971). The weight of each representative fraction is noted and the cumulative weight percentage was calculated. There are two methods for calculating the grain size parameters of the sediments, moment method and graphic method. In moment method grain size parameters are obtained directly from the size data, whereas in graphic method, a graph is drawn with the data and from this quantitative readings are taken following (Folk, 1966). The graphic method has widely been used for understanding the grain size distribution. The grain size in phi values was plotted against cumulative weight percentage on a probability chart and different percentile values for 5,16,25,50,75,84 and 95(∅) obtained from the graph were computed for the determination of various grain size parameters.

2.2.2 Cumulative frequency curves

The cumulative frequency curves is a curve based on the original histogram data, and is obtained by plotting ordinates which represent the total amount of material larger or smaller than a given diameter.

Grain size is plotted on the horizontal axis and cumulative weight percentage is plotted on the vertical axis with a scale running from 0 to 100%. The curve may be drawn using an arithmetic ordinate scale. From the probability chart, the phi values required for the calculation of statistical parameters were determined. Cumulative frequencies of the representative samples were determined from their respective weight percentages. From this cumulative curve, the conventional method suggested by Folk and Ward (1957) was followed and different grain size parameters such as mean, median, mode, standard deviation, skewness and kurtosis are calculated.

2.2.3 Statistical parameters

Four-grain size parameters are generally used to describe the grain size distribution. They are mean, standard deviation, skewness and kurtosis. In addition to these, the median and mode are also of great use in understanding the grain size variations in relation to environment of deposition and energy conditions of the depositing medium (Folk and Ward, 1957)

2.2.3.a Mean grain size (Mz)

Mean is the statistical average expressed in phi (∅) units. Different researchers have suggested different formulae, for calculating these statistical parameters, but the widely accepted one is put forward by Folk and Ward (1957).

$$\text{Mean (Mz)} = \frac{(\varnothing 16 + \varnothing 50 + \varnothing 84)}{3}$$

2.2.3.b Mode

Most frequently occurring particle size.

2.2.3.c Median

The median is a midlying value and should be abandoned as a measure of average size. It is based on only one point of the cumulative curve.

2.2.3.d Standard deviation (σ_1)

Standard deviation is a measure of sorting. Uniformity within a sample of sediment can be measured by these parameters. It is one of the most useful parameters in recognizing the efficiency of the depositional media.

$$\text{Standard deviation } (\sigma_1) = \frac{(\varnothing 84 - \varnothing 16)}{4} + \frac{(\varnothing 95 - \varnothing 5)}{6.6}$$

According to Folk and Ward (1957) the divisional points based on standard deviation are as given below:

Standard deviation (∅)	Sorting
<0.35(∅)	Very well sorted
0.35 - 0.50(∅)	Well sorted
0.50 - 0.71(∅)	Moderately well sorted
0.71 - 1(∅)	Moderately sorted
1 - 2(∅)	Poorly sorted
2 - 4(∅)	Very poorly sorted
>4(∅)	Extremely poorly sorted

2.2.3.e Skewness (Sk)

The asymmetry of the grain size distribution in a sediment sample is measured by skewness. The skewness index by Folk and Ward (1957) is the best measure, as it covers the full curve.

$$\text{Skewness (Sk)} = \frac{\varnothing 16 + \varnothing 84 - 2\varnothing 50}{2(\varnothing 84 - \varnothing 16)} + \frac{\varnothing 5 + \varnothing 95 - 2\varnothing 50}{2(\varnothing 95 - \varnothing 5)}$$

The limits of skewness as given by Folk and Ward (1957) are as follows:

Skewness value	Type of skewness
>0.30	Very finely skewed
0.30 to 0.10	Finely skewed
0.10 to -0.10	Nearly symmetrical
-1.1 to -0.30	Coarse skewed
<-0.30	Very coarse skewed

Sign of skewness is related to the environmental energy (Duane, 1964). Negative skewness (coarse skewness) is correlated with high energy and winnowing action (removal of fines) and positive / fine skewness with low energy levels (accumulation of fines).

2.2.3.f Kurtosis (K_G)

Kurtosis is considered as one of the important textural parameters to distinguish various environments as explained by Duane (1964), and Mason and Folk (1958). It is a measure of the contrast between sorting observed in the central part of the particle size distribution with that of the tails.

$$\text{Kurtosis } (K_G) = \frac{\varnothing 95 - \varnothing 5}{2.44(\varnothing 75 - \varnothing 25)}$$

It represents the degree to which the particles are concentrated near the center of the curve (Platykurtic- broad curves, mesokurtic- middle and leptokurticpeaked curves). Many curves designated as "normal" by the skewness measure turn out to be markedly non-normal when the Kurtosis is computed.

The limits of kurtosis as given by Folk and Ward (1957) are as follows:

Kurtosis value	Type of Kurtosis
<0.67	Very platykurtic
0.67 - 0.90	Platykurtic
0.90 - 1.11	Mesokurtic
1.11 - 1.50	Leptokurtic
1.50 - 3	Very leptokurtic
>3	Extremely Leptokurtic

2.3 PIPETTE ANALYSIS

Pipette analysis is the most popular and widely used method for finding granulometric proportions of mud dominant sediments. By wet sieving, the coarser and the finer fractions can be differentiated. Further, the finer fractions may be dispersed into its individual sizes by adding any dispersing agent, preferably sodium hexametaphosphate for textural and ammonia solution for chemical analysis. The sediment samples were subjected to pipette analysis following the method suggested by Carver (1971) to determine the silt and clay proportions.

2.4 SCANNING ELECTRON MICROSCOPE ANALYSIS OF QUARTZ GRAINS.

Approximately 10g of some selected samples was washed thoroughly with distilled water and soaked with H_2O_2 to remove organic debris. From the dressed sediments, sands of medium grain size fractions were taken for scanning purpose. Quartz grains between 250 to 355 microns were used after treating with stannous chloride and 10% hydrochloric acid to remove the iron coatings if any present over the grains (Goudie and Bull, 1984). According to Krinsley and McCoy (1977), the quartz grains in the size range 200 to 400 microns are generally considered to record all the depositional features in any given environment. Using an optical binocular microscope, samples of quartz grains were mounted on SEM stubs using double-stick tape. It is then sputter coated with gold for one minute. The gold-coated quartz grains were examined with JEOL Scanning Electron Microscope. SEM photographs of a few selected grains were taken to illustrate the shape and micro relief features. The interpretations of photomicrographs thus obtained were utilized following Georgieve and Stoffers (1980) Marshall (1987) and Krinsley and Doonkamp (1973)

2.5 HEAVY MINERAL SEPARATION

About 50g of the sediment sample was washed with distilled water to remove finer fractions (<63u) and afterwards it was treated with diluted HCl to remove the shell fragments and iron coatings on the grains. It is then washed with distilled water and dried in hot air oven. The dressed dried sample was subjected to dry sieving so as to get two size fractions viz. 0.25 – 1.0 mm (medium) and 0.063 – 0.25 mm (fine). The heavy and light minerals were separated using a high density (2.89 gm/cc) liquid bromoform.

2.5.1 Preparation of grain mounts and identification

The heavy minerals were boiled for a few minutes with 6N hydrochloric acid and a tinge of stannous chloride to remove the Fe coating over the detritus heavy grains. A total of 300-400 grains were mounted on glass slides using Canada balsam after heating it into a transparent liquid. Then it was gently pressed with cover glass to drive away the entrapped air. The slides were cleaned with xylene and arranged systematically in a slide box for mineral identification and grain counting. The mineral identifications were performed with Carl Zeiss polarizing microscope.

2.5.2 Grain counting

There are different means of counting methods, of which line counting is followed for this study. The minerals present on each slide were counted separately along lines of specific intervals. Then respective percentages of different minerals were calculated. Some selected minerals were then photographed using a Leitz microscope with MPS photo automat.

2.6 MINERALOGY OF CLAY FRACTION

Clays were separated from the bulk sediment using Stoke's settling velocity. The clay mineral identification was carried out by X-ray diffraction technique.

The <2 micron clay fraction was separated following Carver (1971) and was treated with 10 ml H_2O_2 and 5 ml of acetic acid to remove the organic matter and the carbonate content respectively. Thick clay fraction aliquot was used to make slides of almost equal size and thickness by pipetting the sample and smearing on glass slides. The slides were dried at room temperature and placed in the desiccators to prevent dehydration before exposing to X-rays. Clay identifications were carried out by following the scheme suggested by Biscaye (1965).

2.7 GEOCHEMISTRY

2.7.1 Organic carbon content

All the samples were washed free of salt with distilled water and dried at 35^0C. This drying temperature is preferred so as to prevent the oxidation of organic matter. The dried samples were powdered and are used for the organic carbon estimation. The organic carbon for the bulk samples was determined by wet oxidation method following El Wakeel and Riley (1957). The principle is that the organic matter in the sample is oxidized by a known quantity of chromic acid and the amount of chromic acid consumed is determined by titration against ferrous ammonium sulphate to obtain percentage of organic carbon.

$$\% \text{ Organic carbon} = (1 - T/S)\ 10$$

S – Titre value of the standard, T – Titre value of sample

2.7.2 Carbonate content

The principle involved in the determination of the carbonate consists of treating the sample with a known amount of dil. HCl and the estimation of excess

HCl by back titration using standard NaOH solution, Bromothymol blue is used as indicator. The endpoint is the change of colour from yellow to blue. (Hutchinson and Mc Lennan, 1947).

$\% \ CO_3 = (S - T)\ 10$ — S – titre value of the standard; T – titre value of the sample

2.7.3 Major and Minor Elements

Following Carver (1971), clay fractions less than 2 microns were collected after 8 hrs 10 minutes and dried at 50-60°C for chemical analysis .The bulk sediments and the respective clay fractions thus obtained were powdered and digested with a mixture of perchloric acid, hydrofluoric and nitric acid following Shapiro & Brannock (1962) for obtaining solution B.

The digested samples were made up to 100ml using distilled water and it was used for quantitative estimation of various major and trace elements following established conventional standard methods. A brief description of the methods employed and instruments used are listed below:

2.7.3 a Sodium, Potassium and Calcium

Sodium (Na), potassium (K) and calcium (Ca) in the samples were analysed using flame photometer. The dissolution of the sample for this purpose is from "B-solution". The procedure described by APHA (1981) was followed for the determination of these elements. Calibration curves were drawn for the estimation of the above metals.

2.7.3 b Magnesium, Iron, Manganese and Trace Elements

. Magnesium (Mg), iron (Fe), manganese (Mn), and Trace metals [zinc (Zn), copper (Cu), chromium (Cr), cobalt (Co), nickel(Ni), lead (Pb) and cadmium (Cd)] were analysed using atomic absorption spectrophotometer following the methods of Rantala and Loring, (1975). The precision and accuracy of the metal estimations were checked against the international standard samples. All the metal values were in agreement with the published / certified values.

2.8 HEAVY METAL SPECIATION

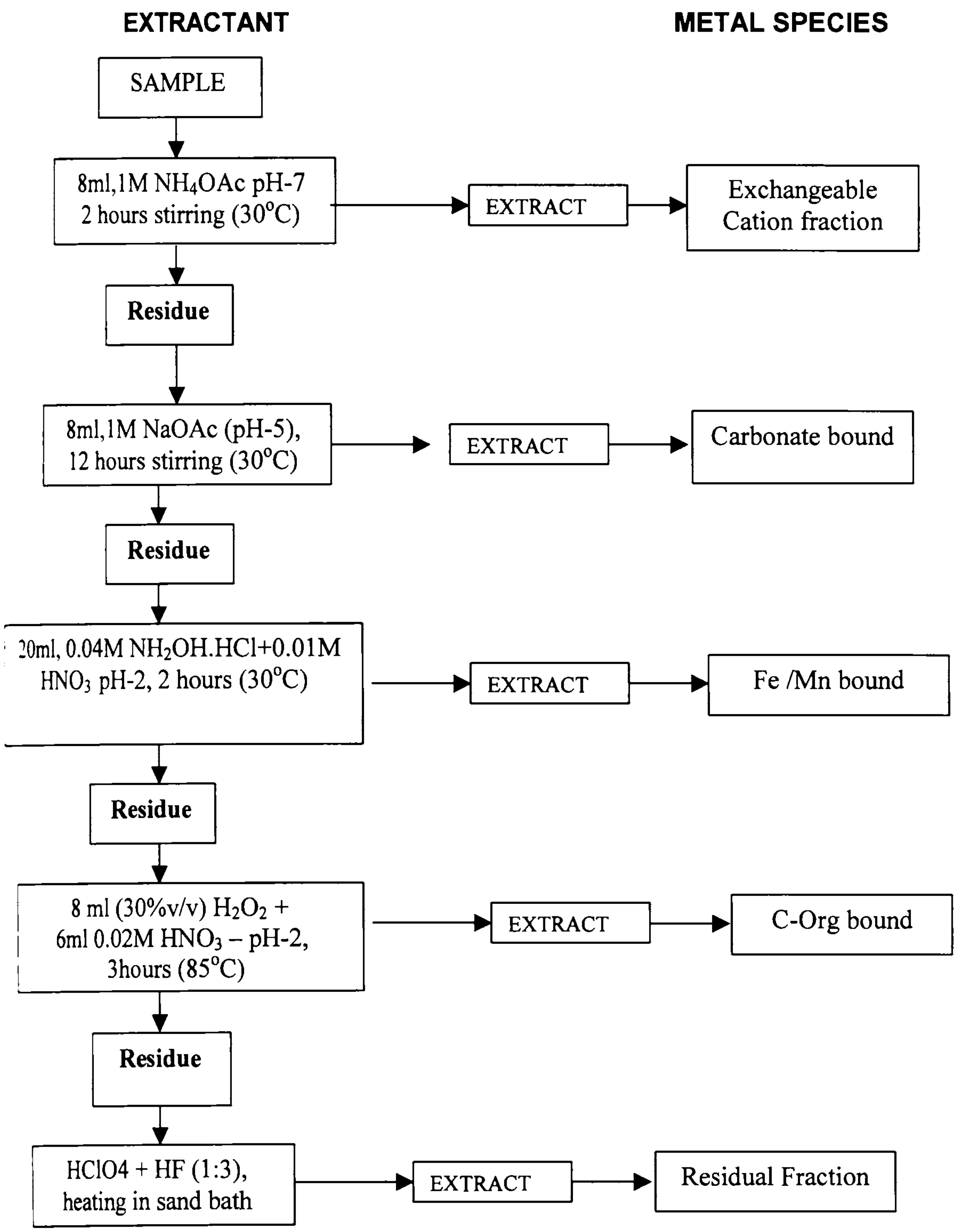
A five step sequential extraction introduced by Tessier et al. (1979) and later modified by Forstner (1982) was used for metal speciation studies. This scheme facilitated the distinction between exchangeable, easily reducible, moderately reducible, organically bound and residual metal fractions. The chemical technique was based on three groups of components occurring in fluvial systems potentially able to enrich the metals in sediments: (i) detrital solids, coated with oxides and organics; (ii) endogenic fraction, transitory in nature, mostly due to insitu processes; and (iii) diagenetic fractions occurring within sediments (Calmano and Forstner, 1983).

Detailed Procedure

a) Easily exchangeable

8 ml of 1M ammonium acetate solutions was added to 1gm of the sediment sample in a test tube and kept it for 2 hours. The above mixture was

The different steps involved in speciation studies are summarized in the flow chart furnished below:



FLOW CHART OF SEQUENTIAL EXTRACTION PROCEDURES

stirred frequently and centrifuged at 3000 RPM for about 30 minutes. 10 ml of the supernatant solution was taken in a plastic bottle after filtering. The above residue was washed in double distilled water and discarded the supernatant solution after centrifuging.

b) Carbonate Bound

8 ml of 1M-sodium acetate solution adjusted to pH-5 with acetic acid was added to the above residue and stirred thoroughly for about 12 hours. 10 ml of the supernatant solution was collected in plastic bottles after centrifuging (RPM-3000 for ½ an hour) and filtering. The residue was washed using double distilled water and discarded the supernatant solution after centrifuging.

C) Fe - Mn oxide bound

20 ml of 0.04 M hydroxyl ammonium hydrochloride and 0.01M HNO_3 were added to the residue and heated the mixture in a water bath at 30^0C for 2 hours with intermittent stirring and then the sample was cooled, after the sample was stirred for 12 hours, then centrifuged and the solution was collected after filtering. The residue was then washed with double distilled water, as described in the above procedure for further explanation.

d) Organic carbon bound

6 ml of 0.02 M nitric acid and 8 ml of 30% Hydrogen peroxide adjusted to pH-2 with nitric acid were added and the mixture was heated to 85^0C for 3 hours with occasional agitation. It was then cooled, centrifuged and the supernatant solution was collected in bottles after it was filtered. The residue was washed with double distilled water as mentioned above.

e) Residual Fraction

The above bulk residue was digested using perchloric acid and hydrofluoric acid in the proportion 1:3. It was then made up to 100 ml using double distilled water and 5 ml of 1:1 hydrochloric acid. Blanks were also run at the same sequence of treatments for all of the above fractions. These solutions i.e., extracted sample solutions were fed into Atomic Absorption Spectrophotometer (Perkin Elmer model 3110) for estimating the trace metals (Cr, Ni, Co, Pb, Cu, Cd, and Zn).

2.9 REMOTE SENSING

Remote sensing and GIS are used to study the Kayamkulam estuary for finding out the change in area, landuse pattern (supervised and unsupervised classification), qualitative mapping of suspended sediment concentration and normalized difference vegetation index (NDVI). Finally, using GIS the non-spatial data (textural, mineralogical and geochemical) are incorporated to the spatial data (GIS coverage containing sample locations) for further analyses and information extraction. IRS- IC LISS III satellite image of 1999 and topographic map of 1967 are the sources of data for the study.

In order to generate an integrated database of Kayamkulam estuary, both spatial and non-spatial data were collected through field survey, and interpretation of satellite image of IRS-1C LISS III and topographic map of Survey of India. Various procedures, adopted in the field and laboratory to collect and process each data set, are explained in detail in the following paragraphs.

2.9.1 Satellite data collection and analysis

The satellite data (1999) of IRS-1C LISS III (both digital and geo-coded FCC) of the study area, available with the Center for Earth Sciences Studies, Thiruvananthapuram, Kerala, were utilized for the study. Geocoded data was helpful in the field to obtain ground control points and digital data was processed in the laboratory using digital techniques. LISS III is one of the three sensors on IRS-1C, which provides multispectral data in four bands; two in visible (0.52-0.59 and 0.62-0.68 microns), one in infrared (NIR, 0.77-0.86 microns) and another one in short wave infrared (SWIR, 1.55-1.70 microns) regions of electromagnetic spectrum. It has a spatial resolution of 23.5 m. in visible and NIR region and 70.5 m. in short wave infrared region. A path-row based full scene product covers an area of 141 x 141 km. The details of the satellite data are given in the table2.1.

Table:2.1 Details of satellite data

Satellite	Sensor	Path	Row	Date of Pass
IRS-1C	LISS III	100	68	24. 02. 1999

2.9.2 Softwares used

Silicon Graphics workstation based ERDAS IMAGINE version 8.3 and ARC/INFO version 7.2.1 and Arc view version 3.1 are used for data processing. All these softwares are very effective and user friendly.

2.9.3 Image analysis

Digital image processing involves the manipulation and interpretation of raw digital images with the aid of a computer. Various steps followed for this purpose include loading of satellite data, rectification and restoration, image enhancement and information extraction. The digital data from CD ROM was imported to the hard disc following the data import option of the software ERDAS imagine. Image rectification and restoration is a pre-processing technique to remove the noise from the image. The various digital image-processing techniques are:

2.9.4 Correction of geometric distortions

Geo-referencing of satellite imagery is one of the most time consuming tasks in remote sensing. There are three basic approaches to geo-referencing satellite images. In the first, a certain number of Ground Control Points (GCPs) are used. With a minimum number of GCPs we can use a polynomial model to relate image and map coordinates and determine the polynomial coefficients by a least squares approach. This mathematical model makes the determination of map coordinates of all image pixels possible. The accuracy is checked with an independent set of GCPs not used in the construction of the least squares model, and the final Root Mean Square (RMS) error is usually taken as a measurement of accuracy.

2.9.5 Image enhancement

Image enhancement is a method of enhancing the visible interpretability of an image. In the present study, to assess the health status of vegetation in the study area, Normalized Difference Vegetation Index (NDVI) is carried out, which is an image enhancement technique.

2.9.6 Normalized Difference Vegetation Index (NDVI)

NDVI is a computation of ratio images using data in infrared and visible bands of the electromagnetic spectrum. It is defined as:

$$NDVI = (IR-R) / (IR+R).$$

Where, IR-Infra red band

R-Red band

This ratio image technique is most commonly used by vegetation scientists to correlate photosynthetic activity and vigour in green biomass by taking advantage of spectral behaviour of vegetation in the IR and Red regions of the EM spectrum. Healthy vegetation reflects 40 to 50% of the incident NIR (0.7 to 1.1 μm) energy with chlorophyll absorption being 80 to 90% of the incident energy in the visible band (0.4 to 0.7 μm). Segmentation of NDVI images helps in differentiating forest cover density and understanding the health of vegetation.

2.9.7 Image classification

Image classification is the process of sorting pixels into finite number of individual classes or categories based on their Digital Number (DN) values. If a pixel satisfies a given set of criteria, then that pixel is assigned to the class corresponding to those criteria. There are two popular methods of classifications. They are:

- Unsupervised classification
- Supervised classification.

2.9.7a Unsupervised classification: Unsupervised classification is more computer-automated. It allows the user to specify parameters, which can be used as guidelines by the computer software to identify the statistical patterns in the data and group them without using any ground truth data. Performing an unsupervised classification is simpler than a supervised classification, because a particular algorithm automatically generates the signatures. To study the suspended sediment concentration of Kayamkulam estuary the 3rd band of the digital data is stacked out and classified into ten categories based on their turbidity level.

2.9.7 b Supervised classification: In this, the user more closely controls the classification than he does in the unsupervised classification. In this process, the user will select pixels that represent different classes in training sets based on ground truth data. Later, the computer software identifies the pixels with similar characteristics and classifies the entire image using the data set given by the user. If the classification is accurate, then each resulting class corresponds to a pattern that he/she has originally identified. Information about the data, number of classes desired, and the algorithm to be used are required before selecting training sets.

2.10 GEOGRAPHIC INFORMATION SYSTEM

2.10.1 Integration of Geographic Information System and Remote Sensing

Survey of India Topographical map of 1967 of the study area is used as the base map. This map is scanned and digitised and used for detecting the change in area of the estuary using the ARC/INFO GIS after projecting the map by giving polyconic option in the software. Later, change detection studies pertaining to erosion/accretion status were carried out. For this purpose, 3rd band is extracted from rectified image of 1999 satellite data. Then the image was classified (supervised) into two classes representing water and land. By subtracting one image (1999 satellite data) from the digitised topomap of 1967, the change in area in terms of erosion and accretion was brought out.

2.10.2 Integration of spatial and non-spatial data

For developing a strong database of Kayamkulam estuary, the integration of spatial and non-spatial data was done. The values of various parameters, such as textural, mineralogical and geochemical characteristics, of sediments were incorporated into the GIS. An attempt has also been made to demarcate the sample locations of heavy metal contamination in the estuary.

CHAPTER III

TEXTURE

3.1 INTRODUCTION

Knowledge of grain size is often critical in order to understand temporal and spatial changes of sediment and their bearing on depositional environments. Texture mainly is the size, shape and mutual relationship existing among different particles constituting the sediments. The characteristics of grain size distribution of sediments may be related to the channel morphology, source materials, process of weathering, abrasion and corrosion of the grains and sorting processes during transport and deposition. The image of grain size spectrum, its properties and statistical parameters are used for getting insight into the formational mechanism of sedimentary frame works especially of estuarine systems (Barbatini and Bothner, 1993; Badarudeen et. al 1996; Allen and Duffy, 1998).

Careful examination of statistical analysis revealed that proper combination of different textural attributes could be successfully used to discriminate various depositional environments of ancient and recent origin (Pettijohn, 1957; Griffiths, 1967; Allen, 1970 and Goldberg, 1980). Apart from this, the particle size distribution can invariably influence the mineralogical (Mishra, 1969; Patro et al., 1989) and chemical (Forstner and Wittmann, 1983) composition of sediments as well.

Among the various attributes of the sediments, grain size is the most important basic parameter as its determination is essential for delineating the various processes associated with sedimentary environments. The analysis of sediment to obtain the size range of particles is known as mechanical analysis and its numerical as graphical representation gives the size distribution of the sediments. The present study is a combination of both the methods, and intended to explore the grain size characteristics of the Kayamkulam estuary. The estuary is unique in several respects; the most important is that it remains closed in winter at least for three months and open in monsoons naturally.

3.2 REVIEW OF LITERATURE

Textural studies on a worldwide scale reveal the existence of significant correlation between grain size distribution and depositional processes. For the past few decades, it is witnessed an up boost of granulometric researches, which brought out the intricate mechanisms of sediment transportation and deposition. Interrelationship between grain-size frequency, distribution and depositional environments and/or processes has been used successfully in many earlier studies to identify the depositional environment and to recognize operative processes of sedimentation of ancient terrigenous deposits (Qidwai and Casshyap, 1978; Goldberg, 1980; Khan, 1984; Ramanamurthy, 1985; Mahendar and Banerji, 1989; Pandya, 1989; Joseph et al., 1997; Majumdar and Ganapathi, 1998). The relation between different size parameters viz. phi mean, standard deviation (sediment sorting), skewness and kurtosis have been well established. Published works are plenty and deal mainly with how best the granulometric parameters are effective in differentiating various depositional environments (Mason and Folk, 1958; Griffiths, 1962; Stapor and Tanner, 1975; Sly et. al, 1982; Padmalal, 1992, and Mohan, 2000). Detailed picturisation of estuarine sediment transports and the role of textural parameters in controlling the deposition of sediments have been carried out by Dyer (1994). Analysis of grain size trend for defining sediment transport pathways in different aquatic environments were worked out by Gao and Collins (1994).

Passega (1957, 1964) has given a new dimension to the statistical procedures of grain size analysis and established the relationship between texture of sediments and processes of transportation. Moment measure is a sensitive environmental discriminator, which incorporates the entire size frequency range of population (Friedman,1961; Seralathan and Padmalal 1994). Passega, (1957) interpreted the distinct patterns of CM plots in terms of different modes of transportation by plotting coarsest first percentile grain size(C) and the median size (M) of sediment samples on a double log paper, Visher, (1969) explained the lognormal sub populations within the total grain size distribution curve as representing suspension, saltation and surface creep or rolling modes of transportational mechanisms. Other noteworthy contributions in the textural attributes of clastic sediments are of Cadigan, (1961), Fuller (1961), Greenwood (1969), John (1971), Davis and Fox (1972), Veerayya and Varadachari (1975) and Stokes et al., (1989).

Textural attributes of sediments from the different environments in Indian scenario have been attempted by many researchers (Sahu, 1964; Rajamanickam and Gujar, 1985; Samsuddin, 1986; Seralathan, 1988 and Jahan et al.,1990). Sediment transport mechanism in the Vellar estuary, east coasts of India were carried out in detail by Mohan (2000). Seasonal variation of textural characteristics of the estuarine and fluviatile sediments of the Netravati river basin has been studied by Narayana (1991). Rajamanickam (1983) and Rajamanickam and Gujar (1985) have investigated the grain size distribution of surficial sediments of west coast of India. Gupta and Dutt (1989) have studied the Auranga river, a seasonal river which carries sand predominantly, to understand the physiography, sediment texture and structure and its transportational behaviour. The river Narmada has been subjected to detailed analysis so as to know the channel physiography, morphology and sediment transport by Rajaguru et al., (1995). Seetaramaiah and Swamy (1994) worked out the textural characteristics of inner shelf sediments of Pennar river, east coast of India. Seralathan and Padmalal (1994) carried out detailed textural studies of Muvattupuzha river and Vembanad estuary. Sediments characteristics in relation to hydrography of Cochin estuary were extrapolated by Nair et al., (1993). Badarudeen et al., (1997) worked out the textural characters of Veli estuary. The sedimentary framework of Ashtamudy estuary, southwest coast of India was studied by Sajan et al., (1992). All these studies were useful for understanding the various processes operating in the respective environments.

3.3 RESULTS AND DISCUSSION

3.3.1 Granulometry and Textural facies

The sand, silt and clay ratios are determined for sediment samples recovered from the Kayamkulam estuary for the pre and post monsoon seasons are furnished in table 3.1. The spatial distribution of sediment facies

Table 3.1 Textural terminology of the sediments of Kayamkulam estuary

	PRE MONSOON				*POST MONSOON*			
Sample No.	**Sand %**	**Silt %**	**Clay %**	**Sediment Type**	**Sand %**	**Silt %**	**Clay %**	**Sediment Type**
1	65	25	10	silty Sand	78	8	14	muddy Sand
2	52	28	20	muddy Sand	80	12	8	muddy Sand
3	61	14	25	muddy Sand	65	25	10	silty Sand
4	84	4	12	clayey Sand	88	5	7	muddy Sand
5	79	12	9	muddy Sand	59	27	14	muddy Sand
6	85	3	12	clayey Sand	22	51	27	sandy Mud
7	88	2	10	clayey Sand	83	5	12	clayey Sand
8	91	2	7	Sand	64	14	22	muddy Sand
9	86	5	9	muddy Sand	81	7	12	muddy Sand
10	83	6	11	muddy Sand	18	70	12	sandy Silt
11	29	66	5	sandy Silt	1	66	33	Mud
12	56	30	14	silty Sand	92	4	4	Sand
13	64	22	14	muddy Sand	72	18	10	muddy Sand
14	10	65	25	Silt	95	2	3	Sand
15	30	35	35	sandy Mud	65	10	25	clayey Sand
16	57	17	26	muddy Sand	93	1	6	Sand
17	44	37	19	sany Mud	95	3	2	Sand
18	76	9	15	muddy Sand	97	2	1	Sand
19	85	8	7	muddy Sand	79	7	14	clayey Sand
20	89	3	8	clayey Sand	90	6	4	Sand
21	48	26	26	sany Mud	63	10	27	clayey Sand
22	58	24	18	muddy Sand	66	14	20	muddy Sand
23	92	1	7	Sand	67	21	39	muddy Sand
24	39	23	38	sandy Mud	11	39	50	sandy Mud
25	91	1	8	Sand	92	5	3	Sand
26	68	9	23	clayey Sand	26	39	35	sandy Mud
27	71	9	20	clayey Sand	86	6	8	muddy Sand
28	65	12	23	muddy Sand	86	8	6	muddy Sand
29	79	9	12	muddy Sand	72	10	18	muddy Sand
30	89	2	9	clayey Sand	56	32	12	silty Sand
31	66	10	24	clayey Sand	20	43	37	sandy Mud

for pre and post monsoon are provided in the Fig. 3.2 a and b, so as to bring out the sedimentary framework for the two seasons. Surface plots were also supplemented to assess the regional variation of sand, silt and clay for the pre and post monsoon Fig. 3.3. The sand, silt and clay contents range from 10% to 92%, 2% to 66% and 5% to 38% respectively for the pre monsoon sediments, and 2% to 95%, 1% to 70%, and 3% to 50% for the post monsoon sediments. The average percentage of sand in post monsoon season (av; 67%) is slightly higher than that of pre monsoon (av; 64%). Contrary to this, the fractions of silt (av; 19%) and clay (av; 17%) in pre monsoon sediments are on higher level to that of post monsoon season (silt: av; 18%, clay: av; 16%). Size spectral analysis of coarser fraction indicates that, more than 85% of the sand grains of this environment fall mainly in the medium to very fine sand grade of Wentworth grain size scale. Textural nomenclature of the sediments based on sand, silt and clay ratios reveal the admixture of different textural classes (Fig.3.1) viz. muddy sand (mS), silty sand (zS), clayey sand (cS), silt (Z), sandy mud (sM), Sand (S), sandy silt (sZ) and mud (M) (Table 3.1).

Close examination on the distribution of different textural attributes in the northern segments divulges predominance of muddy sand for both pre and post monsoon. Except that for post monsoon, the silty sand has changed to muddy sand at the extreme northern part of the northern segment.

The sand, silt and clay contents vary from northern to central, and then to southern regions of the study area. In the northern segment for the pre monsoon not much changes are noticed and sand, silt and clay do not show any specific trend of variation while for the post monsoon sand increases

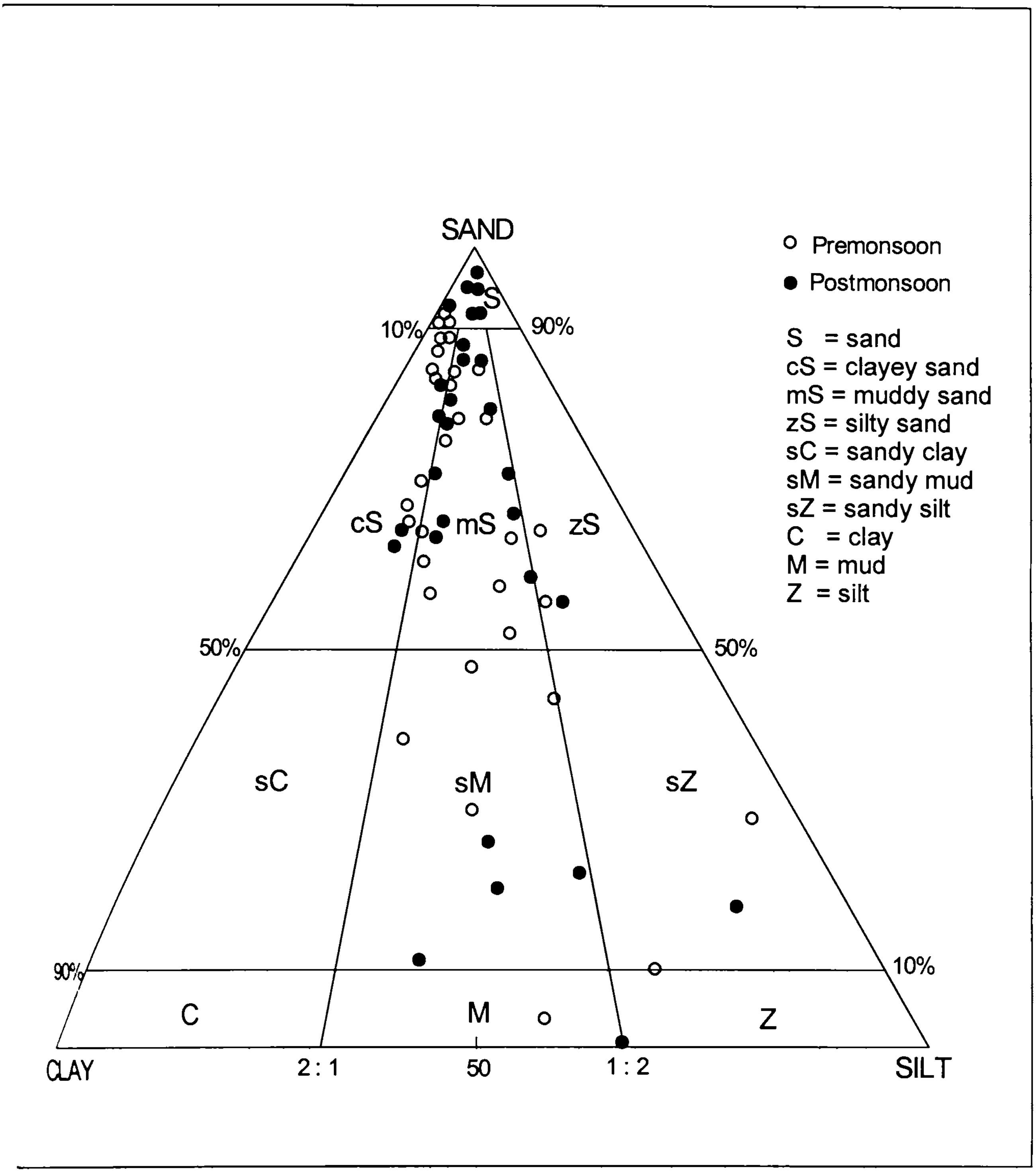


Fig 3.1 Textural nomenclature of the Kayamkulam estuarine sediments for the pre and postmonsoons based on sand - silt - clay ratios (Folk & Ward, 1957)

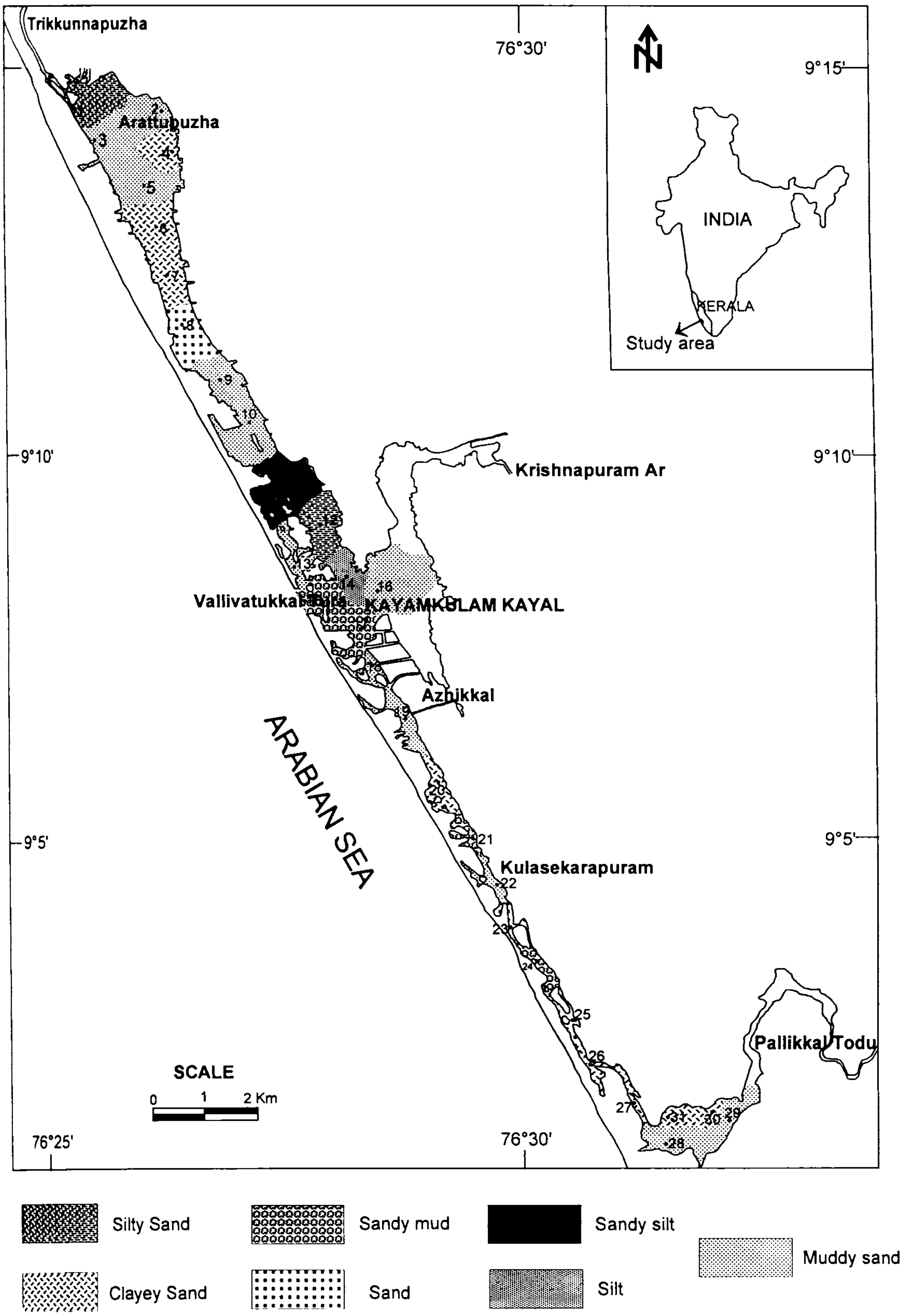


Fig. 3.2a Spatial distribution of the sediment facies in the substratum of Kayamkulam estuary (Pre monsoon)

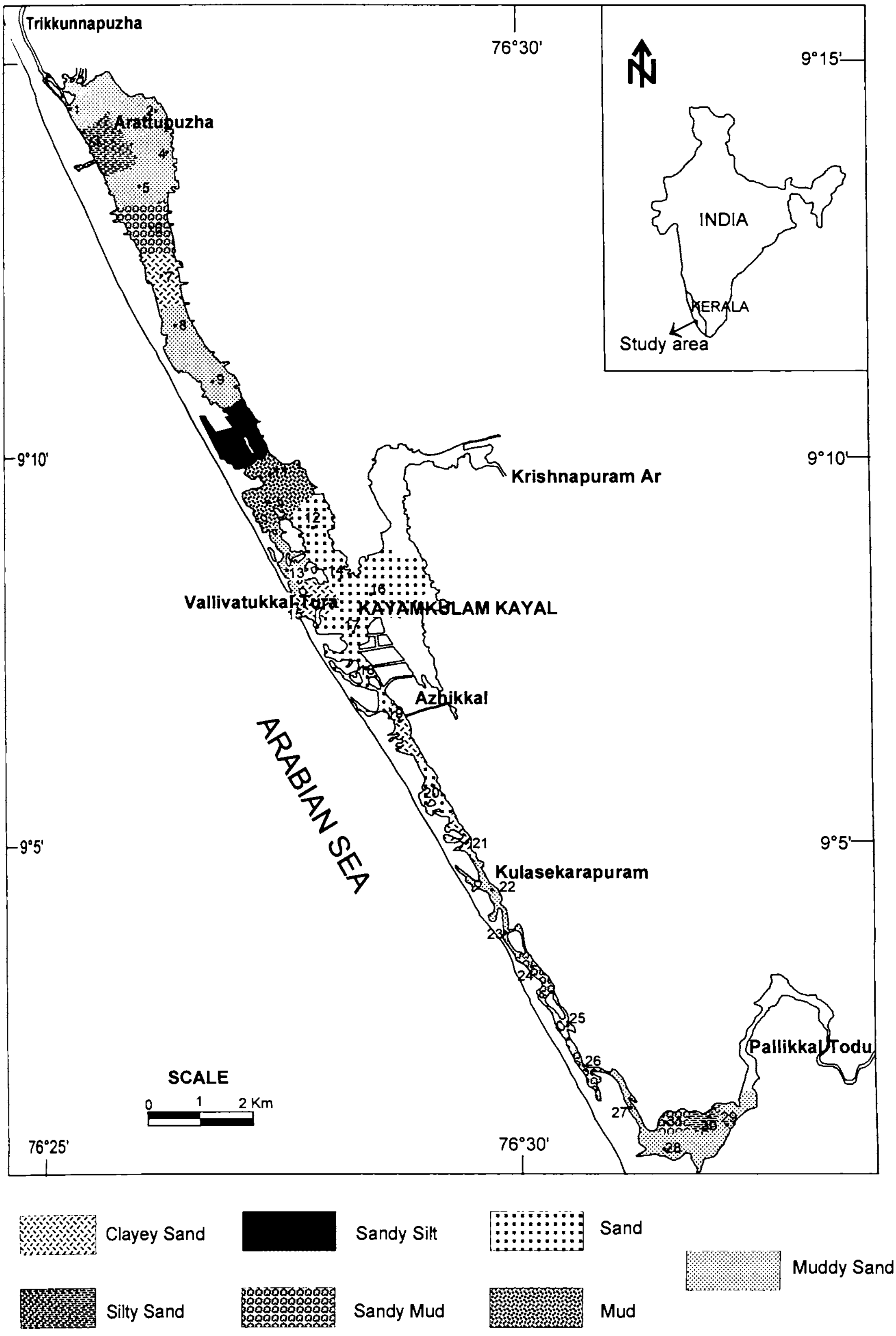


Fig. 3.2b Spatial distribution of the sediment facies in the substratum of Kayamkulam estuary (Postmonsoon)

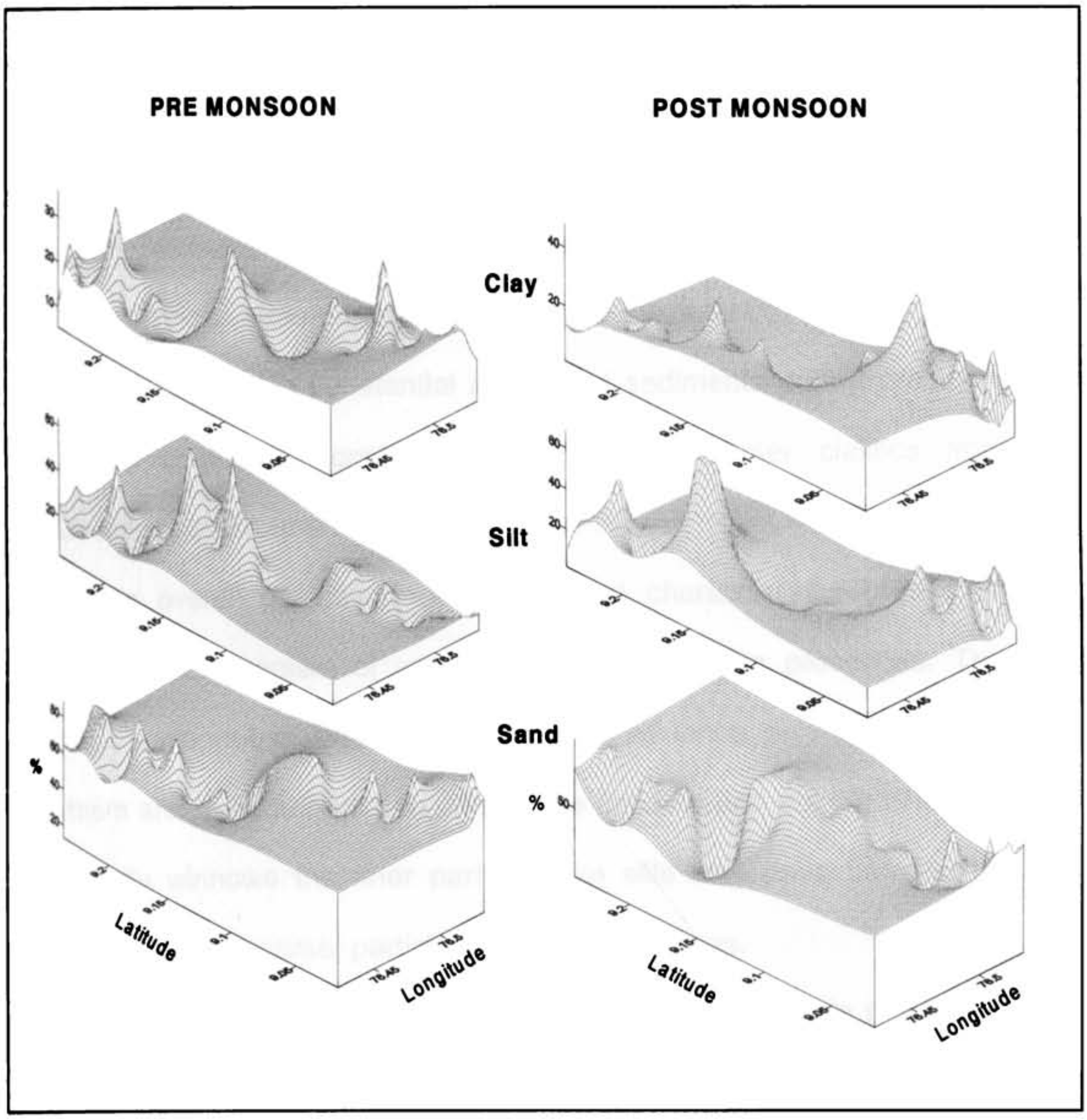


Fig.3.3 Surface plot of Sand-Silt-Clay in the sediments of the Kayamkulam estuary

towards the central region, and thereafter, decreases towards the southern region. Similarly, silt decreases initially and then increases towards the central part of the estuary. Clay, in general, decreases first and thereafter increases towards the central region. The variation of sand, silt and clay for the pre and post monsoon clearly reflects the source as well as the transporting agent. The northern segment is characterised by numerous palaeo ridges and runnels as evidenced from the False Colour Composite (IRS-IC, LISS III) of the study area (Fig.6.1). Although Thrikkunnapuzha, a man made cannal, and a network of undefined minor streams, which drain into the estuary, are not competent agents to transport a substantial amount of sediments during pre monsoon, they can contribute considerable amount of coarser clastics from the palaeoridges and runnels during monsoon.

An overall evaluation of the textural characteristics of this estuary reveals the mechanism of sedimentary transportation processes. The tidal waters, compared to the middle segment, influence only marginally in the northern and the southern segments. The flooding and ebbing of tidal waters constantly winnows the finer particles like silts and clays back to the sea leaving the more coarser particles as lag concentrates.

In the central and southern regions, a trend similar to that of northern segment is exhibited. But the variation in the sand, silt and clay fractions in southern region could be explained in terms of the contribution from the Pallickkalthodu originating from the midland emptying into the southern region. It can contribute substantial amount of finer clastics from the hinterland area particularly during monsoon season. Hence, the southern region is marked for comparatively higher content of silt and clay for the post monsoon. But for the pre monsoon, onward transportation of the finer fraction to the central region may be by the fluvially induced local currents at the southern region that holds good for the higher content of the clay and silt at the central region. Moreover, during pre monsoon, the tidal activities are very much restricted and hence prevent the winnowing of the fines by the tides. Hence, comparatively higher content of sand and lower amount of fines at the central zone compared to that of southern and northern region. For the post monsoon, the winnowing action of tides is very effective, whereby the fines are carried away to the near shore areas leaving behind the coarser particles.

From the general distribution pattern of sediments, an increase in the proportion of silt and clay in the similar direction to that of sand can be attributed to short fluvial current induced by the undefined canals and streams during the monsoon period .The general trend of the sand along with the silt and clay reflects the tidal influence over the sediment distribution in the estuary.

The deviation from the general sediment distribution pattern for the Kayamkulam estuary, if any, can be explained in terms of the local turbulence induced by the changes in the fluvial channel morphology of the estuary. Further the annual maintenance of the surface transport canals, sand mining and construction activities can also impose local changes in the textural attributes of estuarine sediments.

3.3.2 Statistical Parameters

The various statistical parameters such as phi mean, standard deviation, skewness and kurtosis computed for the pre and post monsoon sediments of Kayamkulam estuary is furnished in Table 3.2. The mean size of clastic sediments is the statistical average of grain size population expressed in phi (Ø) units. Standard deviation or sediment sorting is the particle spread on either side of the mean/average. The sediment sorting will be good, if the spread sizes are relatively narrow. Skewness of sediments reflects the environment of deposition and is a measure of the asymmetry of grain size population. In textural analysis, skewness is considered as an important parameter because of its extreme sensitivity in subpopulation mixing. Kurtosis or the peakedness of the frequency curve is, on the other hand, a measure of the contrast between sorting at the central part of the size distribution curve and that of the tails.

In the pre monsoon season, the sediment substratum of the Kayamkulam estuary records phi mean values of 2.46 - 3.34 (fine - very fine sand) with an average of 2 phi. And in post monsoon, phi mean ranges between 2.25 and 3.4 (fine - very fine sands, av; 1.04). It is computed that, more than 90% of the pre monsoon sediments and 80% of the post monsoon sediments accommodate particles of phi mean values between 2 and 3. This observed constancy of phi mean values reiterate the selective entrainment process operating in the environment.

The pre monsoon sediments of the study area exhibit moderately well sorted to poorly sorted sediments and that of post monsoon show well sorted to

Table: 3.2 Textural Parameters for the Pre Monsoon and Post Monsoon Sediments of Kayamkulam Estuary

		Pre monsoon				Post monsoon			
	Sample	Mean(phi)	Standard deviation	Skewness	Kurtosis	Mean (phi)	Standard deviation	Skewness	Kurtosis
	1	2.61	0.92	-0.10	1.15	2.73	1.14	-0.35	1.04
	2	2.14	0.98	0.03	0.92	3.09	0.98	-0.42	1.64
	3	2.63	0.85	0.02	1.08	3.05	0.98	-0.42	1.64
	4	2.10	1.02	-0.02	0.88	2.29	1.09	0.00	1.05
	5	2.40	0.98	-0.19	1.02	2.08	1.02	-0.03	1.00
N	6	2.38	0.96	-0.15	0.90	2.19	1.01	-0.08	1.09
	7	3.11	0.82	-0.43	1.04	1.87	0.96	0.08	1.01
	8	2.58	0.96	-0.17	1.10	2.26	0.95	-0.01	1.07
	9	2.18	0.85	0.02	1.12	2.05	0.87	-0.02	1.11
	10	2.19	0.93	0.02	1.11	2.05	1.01	0.11	1.00
	Average	2.43	0.93	-0.10	1.03	2.37	1.00	-0.11	1.16
	11	2.86	1.01	0.05	1.16	2.18	0.96	0.08	0.99
	12	3.34	0.56	-0.43	0.99	2.01	0.97	0.04	0.94
	13	2.96	0.55	-0.48	0.94	2.12	0.93	0.07	0.99
	14	2.91	1.12	-0.67	1.10	3.40	0.59	-0.59	1.16
	15	1.61	0.67	-0.12	1.20	2.10	0.47	0.02	1.00
C	16	2.08	0.89	-0.02	1.20	2.13	0.93	-0.03	0.97
	17	2.77	0.95	-0.21	0.83	2.39	0.97	0.00	1.13
	18	2.30	1.02	0.01	0.76	1.96	0.81	-0.07	1.20
	19	2.15	1.10	0.04	0.89	2.22	1.15	-0.19	1.08
	20	1.73	0.84	-0.20	1.19	2.26	1.03	-0.15	1.02
	Average	2.47	0.87	-0.20	1.03	2.28	0.88	-0.08	1.05
	21	2.14	0.86	-0.05	1.01	2.16	0.83	0.02	1.15
	22	2.12	0.94	-0.07	1.04	2.10	0.88	0.04	1.23
	23	3.13	0.64	-0.11	0.79	1.58	0.99	-0.07	1.10
	24	3.18	0.74	-0.14	0.85	1.84	0.83	-0.06	1.20
	25	2.03	0.94	-0.03	0.96	1.04	0.87	-0.09	0.93
	26	2.56	0.85	-0.09	1.46	2.64	0.97	-0.19	0.63
S	27	2.04	0.79	-0.02	1.25	2.60	0.99	-0.10	0.78
	28	2.87	0.88	-0.05	0.87	2.24	1.03	0.10	1.58
	29	1.92	1.11	-0.02	1.05	1.90	1.05	-0.05	1.19
	30	2.04	1.13	-0.06	1.10	2.12	1.13	-0.06	1.20
	31	3.20	0.79	-0.64	0.86	3.19	0.79	-0.60	0.91
	Average	2.48	0.88	-0.12	1.02	2.13	0.94	-0.10	1.08

N-NORTHERN, C- CENRTAL,S-SOUTHERN

poorly sorted particle dispersal pattern. The sediment sorting in the former season ranges from 0.55 to 1.13 ϕ, (av; 0.89 ϕ) and that of the latter varies from 0.47 to 1.55 ϕ, (av; 0.94 ϕ). By taking the verbal limits of Folk and Ward (1957), more than 65% of the sediments of the Kayamkulam estuary, in both seasons, belong to the moderately sorted category, and the rest is in the poorly sorted category.

The skewness values of the sediment samples vary from 0.67 to 0.05 (av; 0.14) and 0.59 to 0.11(av; 0.10) respectively, in the pre and post monsoon sediments (Table 3.2). Negatively skewed sediments floor major parts of the area in both the period of sample collections. Predominance of negatively skewed sediments underpins the already mentioned process of removing fines by the winnowing action of tides. These values also exemplify the concentration of coarser clastics in the northern segments.

The pre monsoon sediments of Kayamkulam estuary exhibit leptokurtic (0.76) to platykurtic (1.46) particle distribution. The post monsoon sediments on the other hand, shows very platykurtic to very leptokurtic (0.63 to 1.64, av; 1.10), particle distribution, indicating the change in sediment transportational / depositional mechanism between the two sampling seasons.

3.3.3 Bivariate Plots

The interrelationship between grain-size and frequency distribution has been widely used to discriminate the depositional environments and also to recognize the various operative processes of sedimentation of ancient and poorly sorted particle dispersal pattern. The sediment sorting in the former season ranges from 0.55 to 1.13 ϕ, (av; 0.89 ϕ) and that of the latter varies from 0.47 to 1.55 ϕ, (av; 0.94 ϕ). By taking the verbal limits of Folk and Ward (1957), more than 65% of the sediments of the Kayamkulam estuary, in both seasons, belong to the moderately sorted category, and the rest is in the poorly sorted category.

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3.3.3 Bivariate Plots

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In the present study an attempt has been made use of the bivariate plots for elucidating the depositional mechanism. The bivariate plots between various statistical parameters for the sediments of the study area are furnished in Fig.3.3.a-f for pre and post monsoon seasons respectively.

From the bivariate plot of phi mean *vs.* standard deviation (Fig. 3.3.a), it is seen that in the northern segment, sorting improves with decrease in grain size both for the pre and post monsoon season. But for the central region during pre monsoon, no specific relationship exists. The southern region, on the other hand, exhibits a similar pattern as that of the northern segment. The plots of phi mean and standard deviation show negative correlation in both the seasons. Majority of the samples for the pre and post monsoon falls in the fine to very fine sand with an average standard deviation of 0.89ϕ and 0.94ϕ, respectively (Table 3.2). As the phi mean increases the sorting capacity of the sediments decreases. From this, it is inferred that the Kayamkulam estuary and the nearby environment do not follow the theoretical consideration of sediment sorting. This may be attributed to various factors including contributions of sediments from older sediments like ridge and runnel systems, mixing activities etc.

The bivariate plots of phi mean V*s* skewness for the sediments of Kayamkulam estuary (Fig. 3.3b) for both pre and post monsoon seasons, all

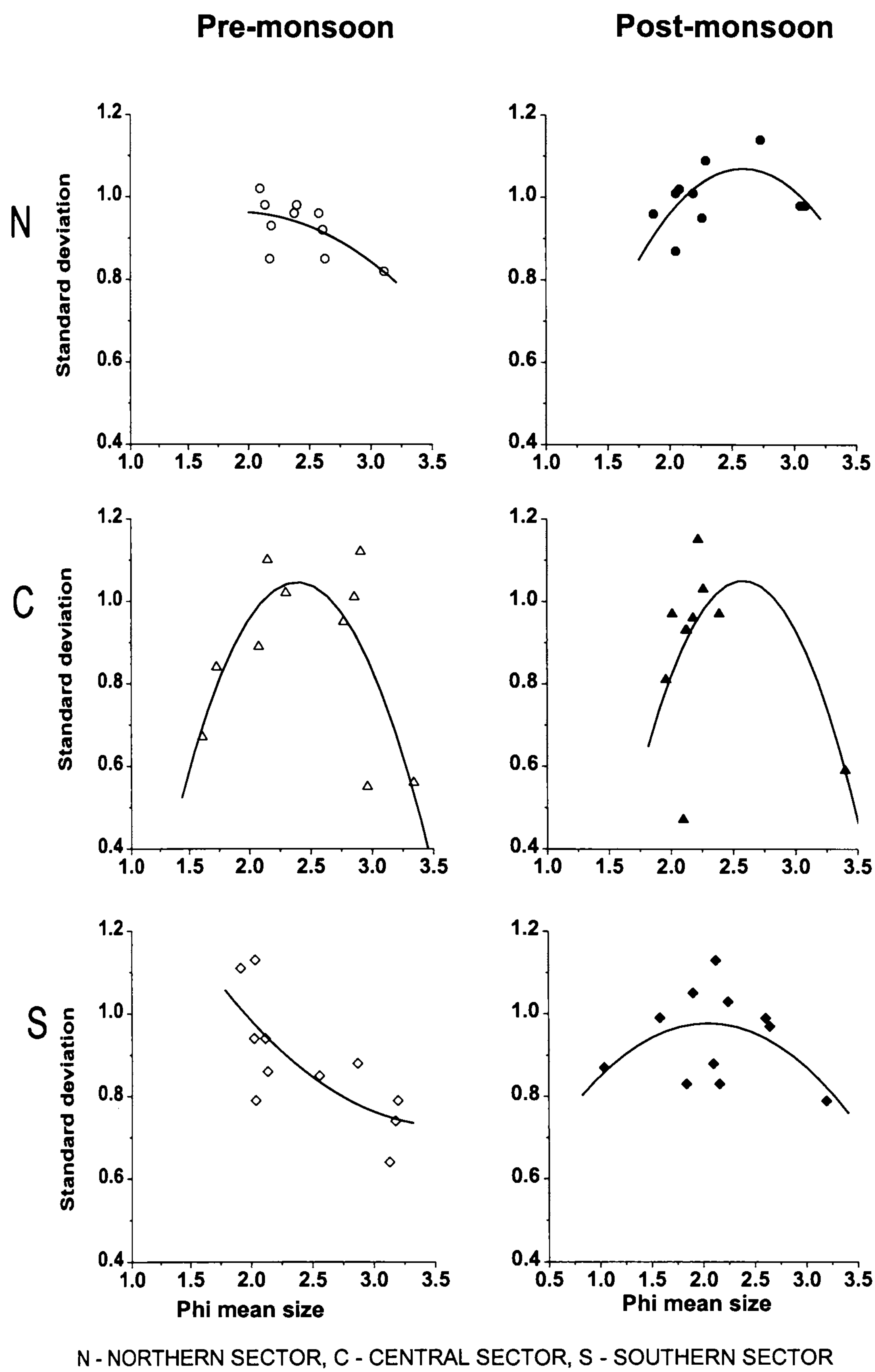
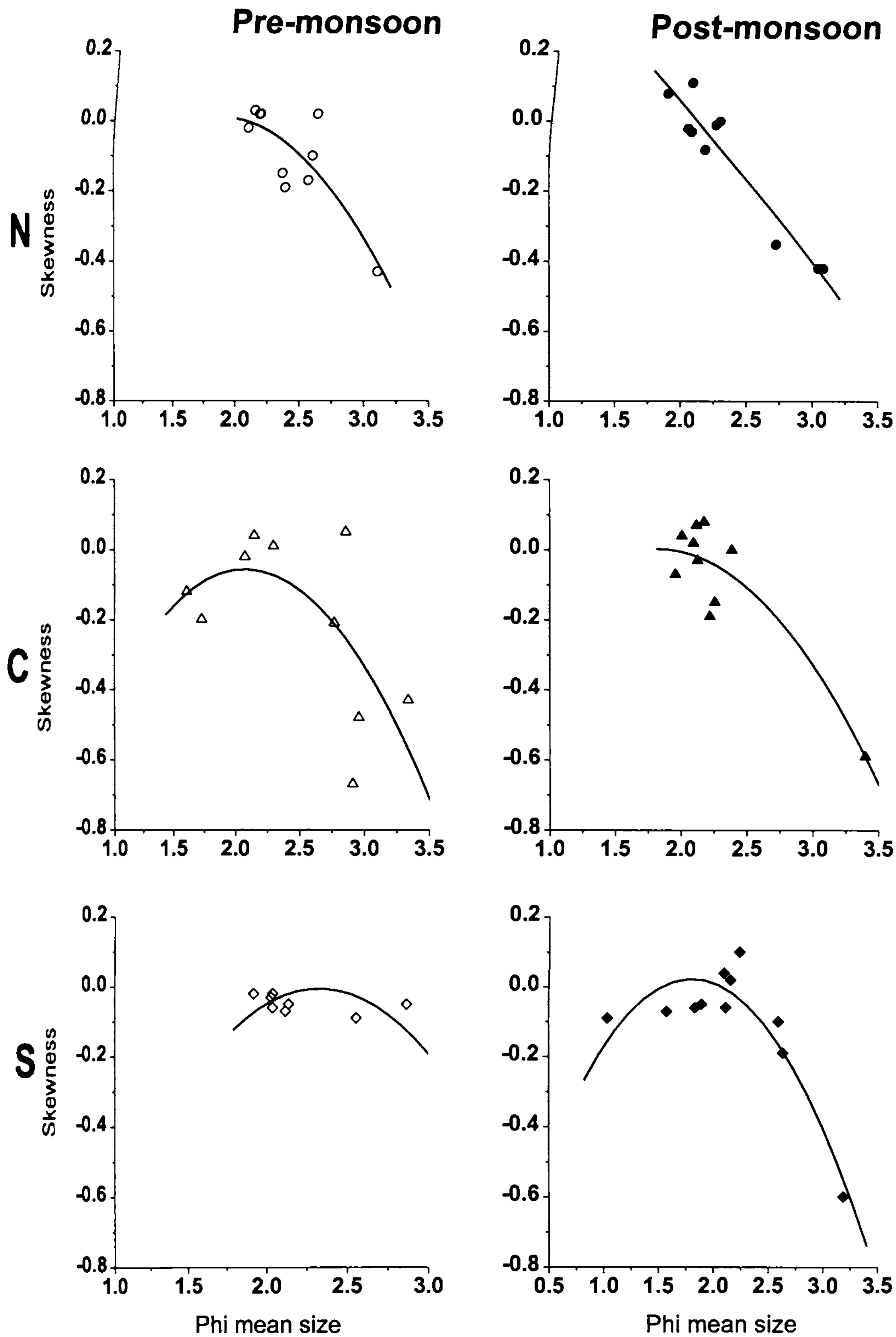
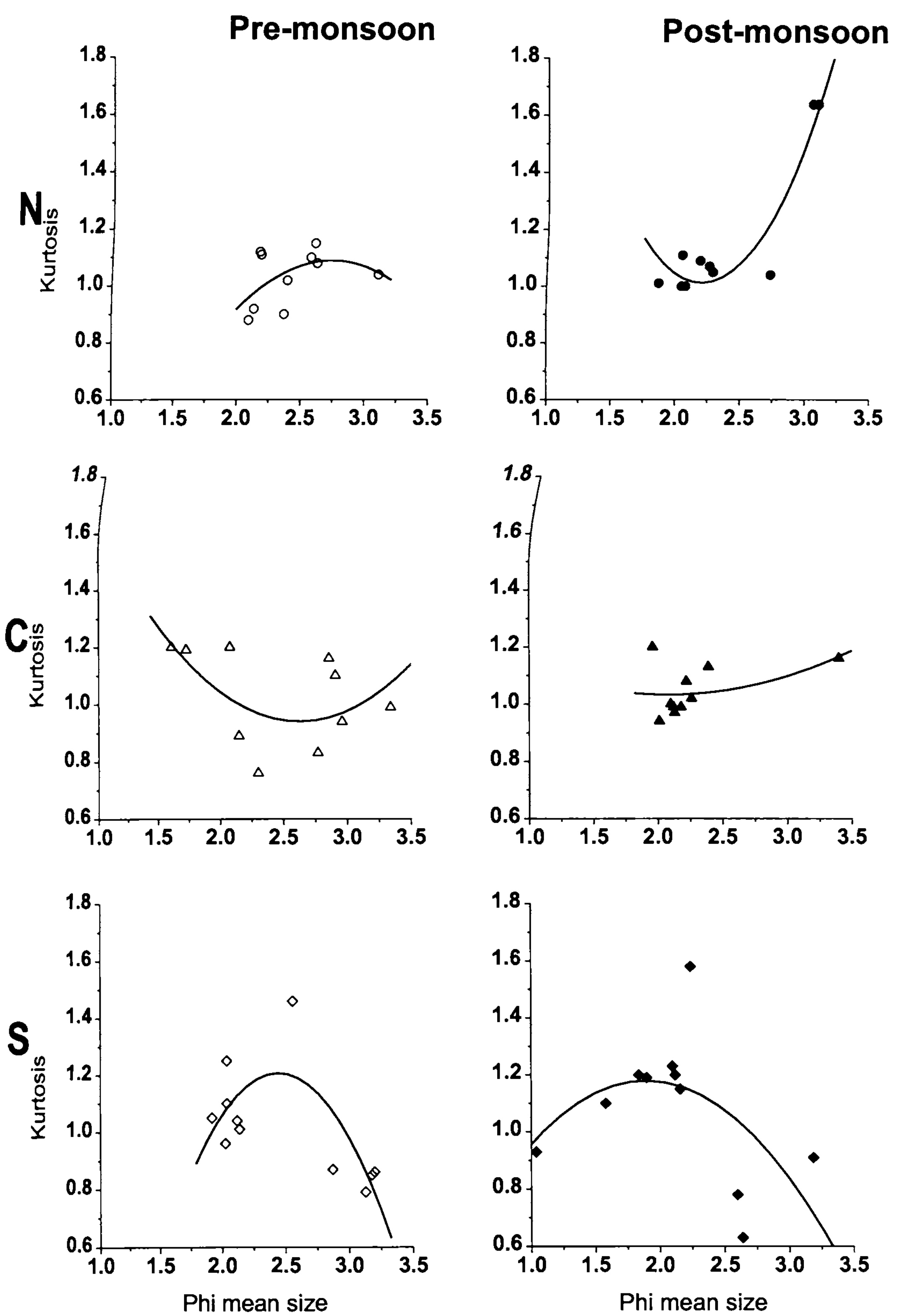


Fig. 3.3a Bivariate plots of phi mean size Vs Standard deviation



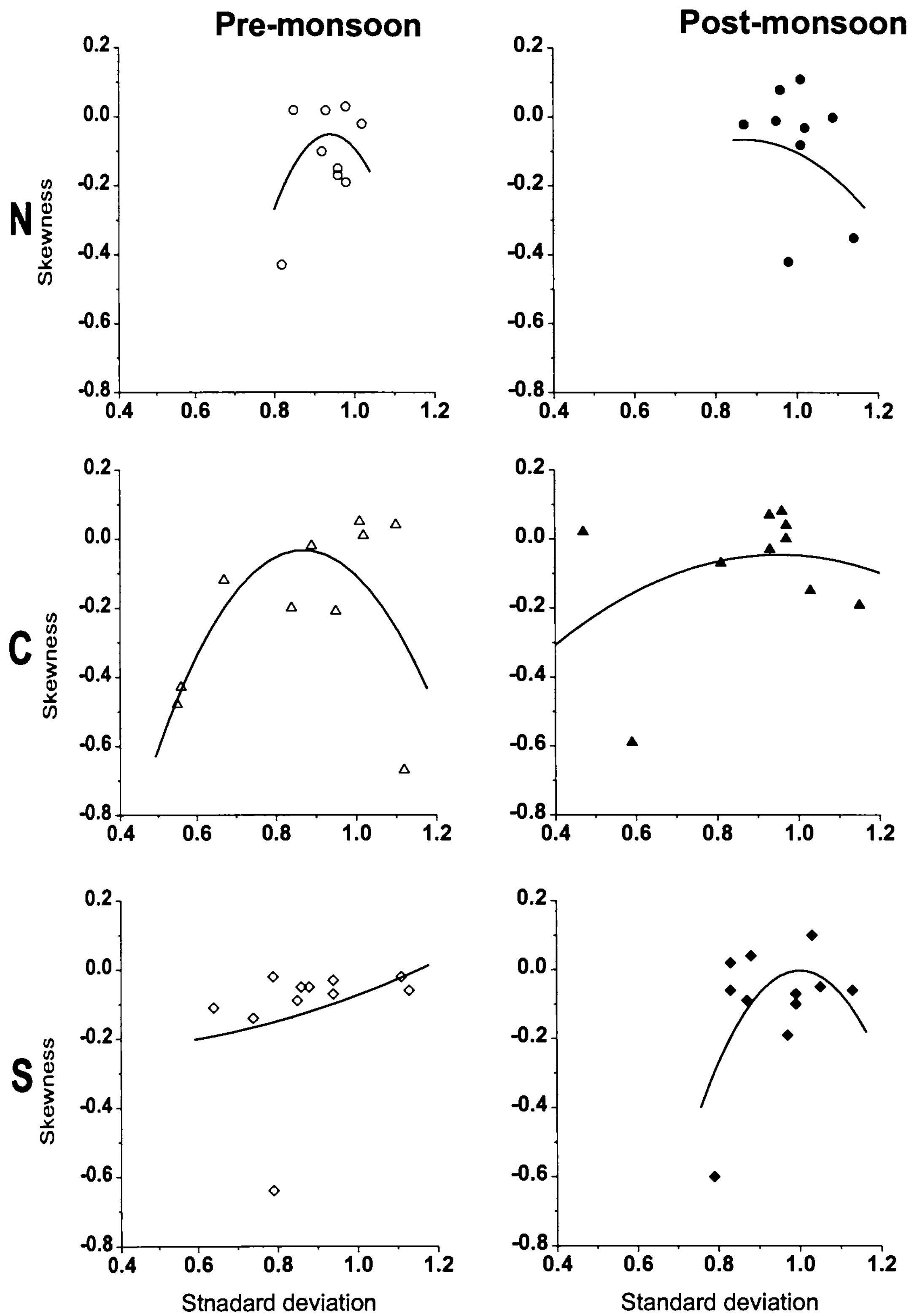
N - NORTHERN SECTOR, C - CENTRAL SECTOR, S - SOUTHERN SECTOR

Fig. 3.3b Bivariate plots of phi mean size Vs Skewness.



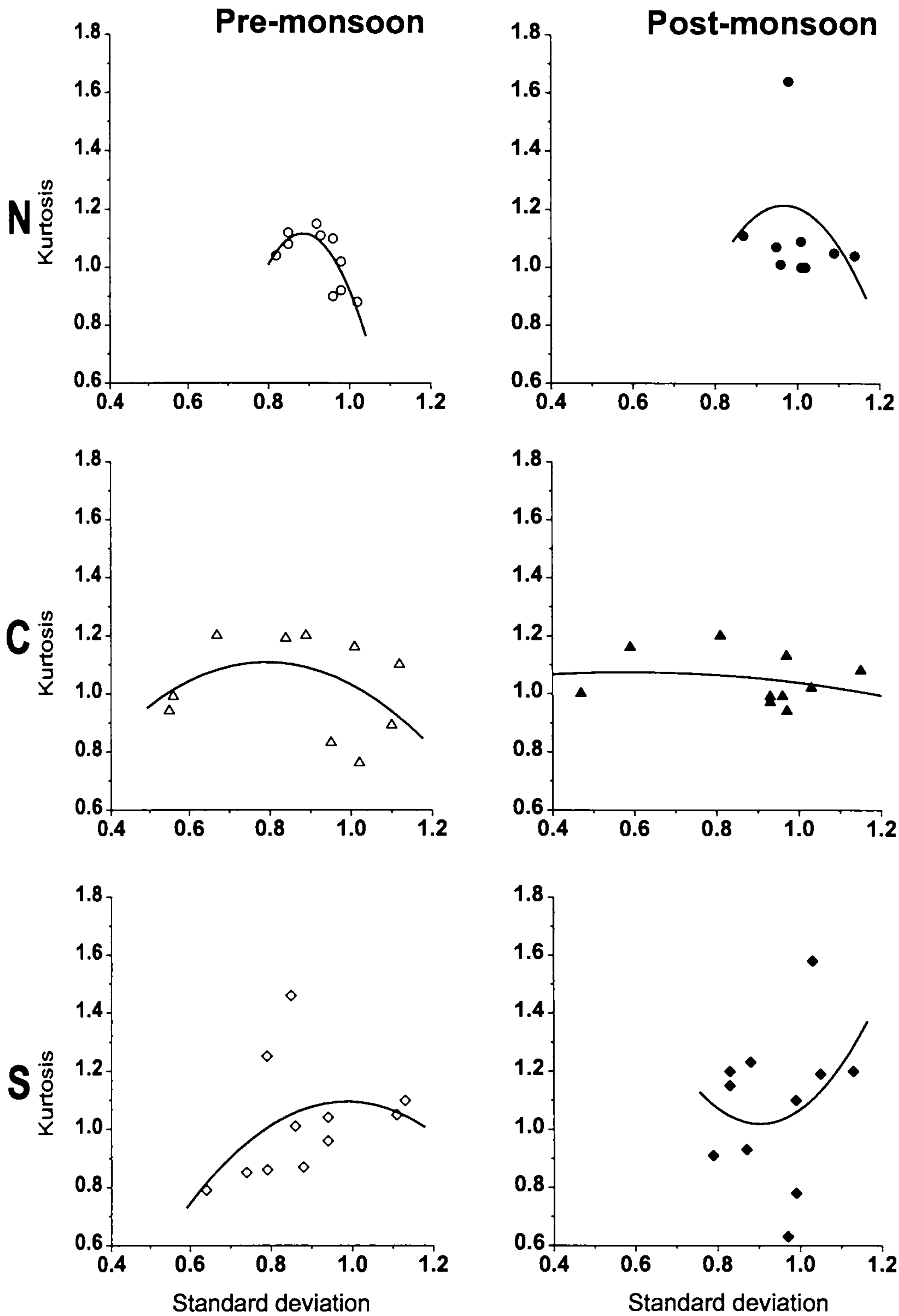
N - NORTHERN SECTOR, C - CENTRAL SECTOR, S - SOUTHERN SECTOR

Fig. 3.3c Bivariate plots of phi mean size Vs Kurtosis.



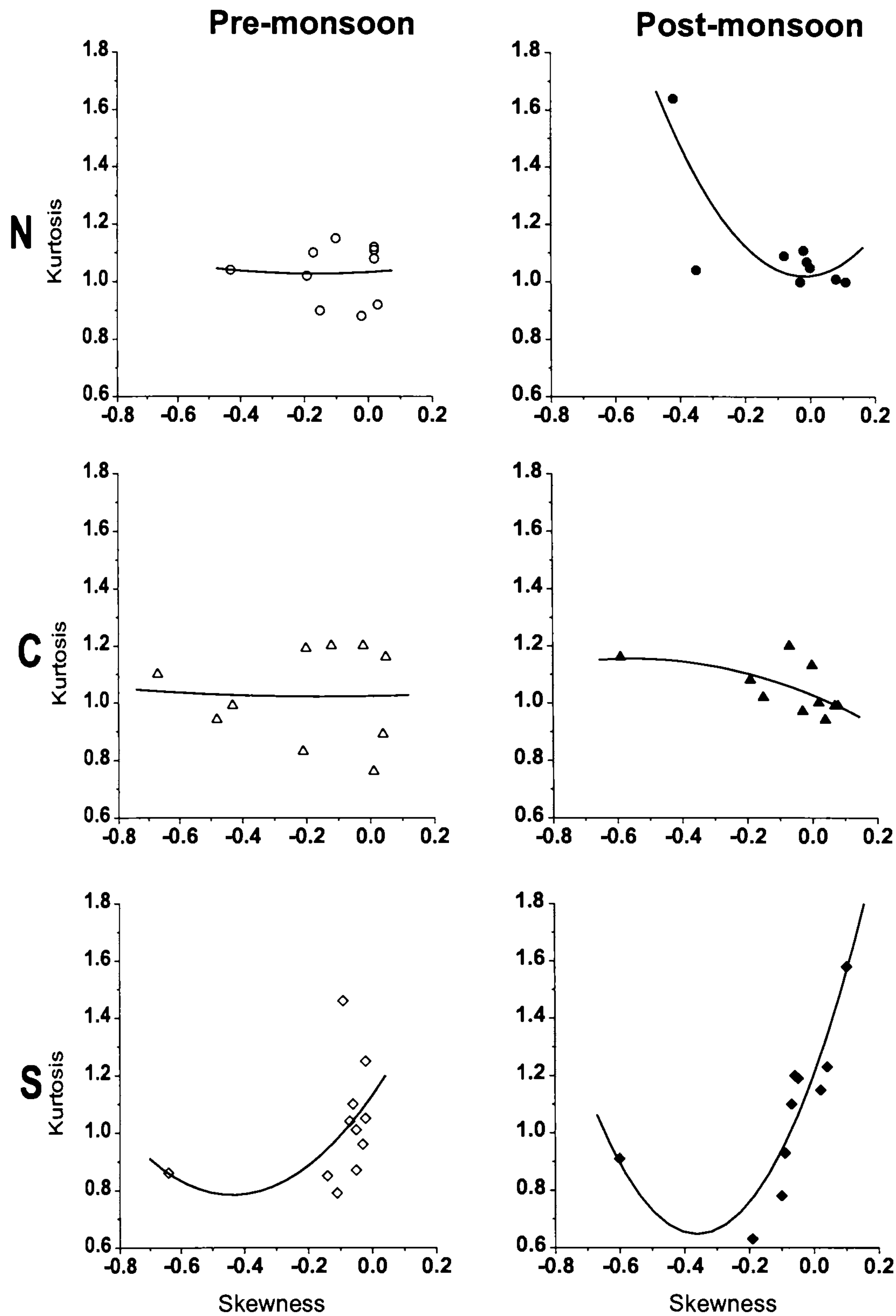
N - NORTHERN SECTOR, C - CENTRAL SECTOR, S - SOUTHERN SECTOR

Fig. 3.3d Bivariate plots of Standard deviation Vs Skewness.



N - NORTHERN SECTOR, C - CENTRAL SECTOR, S - SOUTHERN SECTOR

Fig. 3.3e Bivariate plots of Standard deviation Vs Kurtosis.



N - NORTHERN SECTOR, C - CENTRAL SECTOR, S - SOUTHERN SECTOR

Fig. 3.3f Bivariate plots of Skewness Vs Kurtosis.

three zones exhibit a similar pattern of change, the change being the sorting becomes better with the coarser as the fines gets depleted.

The phi means V*s* kurtosis bivariate plots, (Fig. 3.3c) reveal that for northern region, in the pre monsoon, the spread decreases with increase in phi mean size. In the post monsoon season, a similar trend is observed but with the polygonal in opposite direction reflecting the addition or removal of fines. The post monsoon is characterised by only addition of fines rather than marked removal.

The sorting becomes poor with the addition of finer particles for the pre monsoon in all the three segments studied, while in post monsoon sorting increases with the removal of fines (Fig. 3.3.d).

In the pre monsoon, sorting becomes moderate and the spread is between 5 and 95 % for northern, central and southern segments, while for the post monsoon, sediments sorts only moderately and the spread is between 25 and 75 % (Fig. 3.3.e) for all sectors of the Kayamkulam estuary.

The bivariate plots of skewness *vs* kurtosis (Fig. 3.3.f) for the pre monsoon show that the well sorted fine mode loses its sorting for the spread between 5 and 95 %. This change is noticed for the entire estuary and is due to depletion of finer sediments from the coarser fractions. But for the post monsoon the reverse of the process takes place.

3.3.4 CM Pattern

The CM pattern worked out for the Kayamkulam estuarine sediments for the pre and post monsoon is shown in Fig. 3.4a and b. The values of first

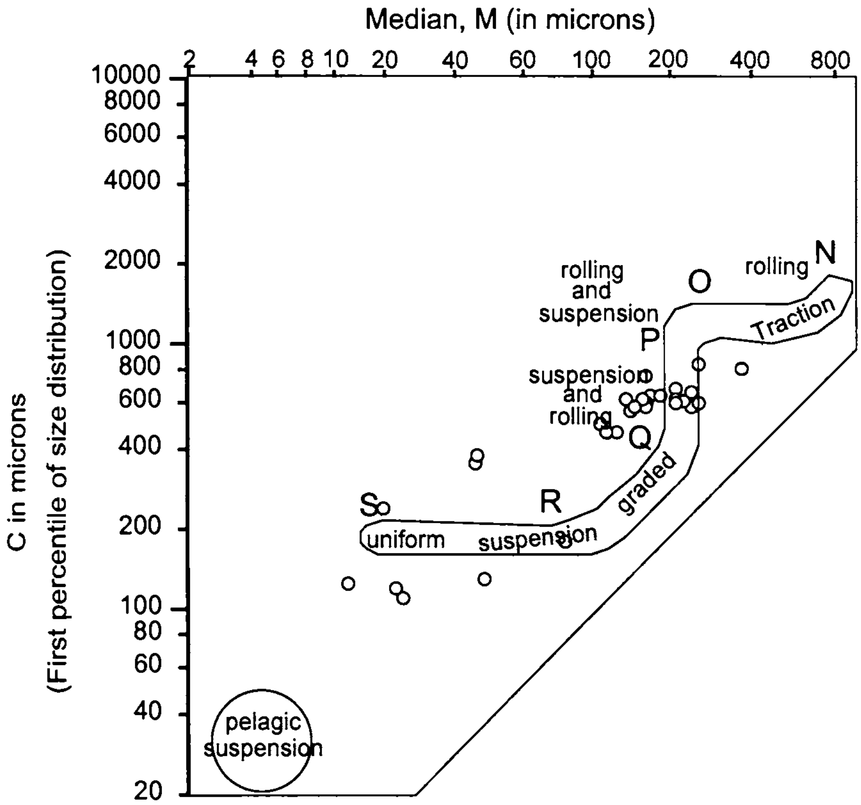


Fig. 3.4a CM pattern of the sediments of Kayamkulam estuary for the pre monsoon period (After Passega, 1972)

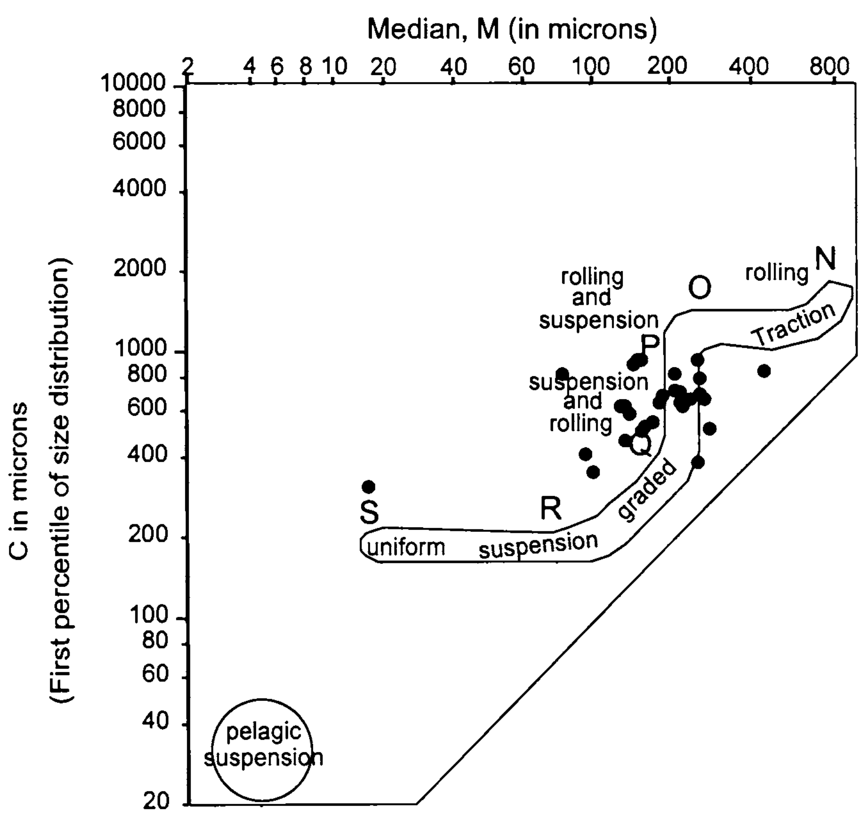


Fig. 3.4b CM pattern of the sediments of Kayamkulam estuary for the post monsoon period (After Passega, 1972)

percentile (C) and median (M) of size distribution (in microns) are presented in table.3.3. The CM pattern depends upon the type and energy conditions of the depositional agent. The pattern (Fig.3.4a&b) represents a complete model of tractive current (depositional process) as shown by Passega (1964), which consists of several segments such as NO, OP, PQ, QR and RS indicating different modes of sediment transport. The plots exhibits specific segregation pattern. The entire samples of both post and pre monsoon seasons are scattered in the sectors OQ and OR. The scattering is imparted due to the drastic differences in the hydrodynamic regimes prevailing in the area. The entire samples in both seasons have first percentile values falling in between 200 and 1000 microns. This group reflects suspension and rolling mode of transportational history, indicating the complexity in the hydrodynamic processes operating in this system.

From the CM pattern of both the pre and post monsoon seasons, it is clear that the Kayamkulam estuary doesn't have 1^{st} percentile values greater than 1000 microns. Majority of the samples are distributed in PQ and QR segments. Thus the first percentile values ranges from 200 μ to 1000 μ. The depositional processes as inferred from the CM pattern for the sediments of Kayamkulam estuary for the pre and post monsoon are mainly suspension and rolling as well as graded suspension.

3.3.5 MICRO TEXTURES OF QUARTZ GRAINS

Study of surface irregularities on quartz sand grains using Scanning Electron Microscopy (SEM) has developed into a major method for

Table: 3.3 One percentile (C) and median (M) values for the sediments of Kayamkulam estuary

	Pre monsoon		Post monsoon	
Sample No	C(in Microns)	M(in Microns)	C(in Microns)	M(in Microns)
1	465	110	925	140
2	620	120	925	135
3	640	150	890	130
4	680	190	710	190
5	600	145	620	120
6	600	190	620	117
7	125	90	620	115
8	640	165	580	125
9	500	95	620	205
10	620	190	640	165
11	120	14	700	200
12	180	68	840	435
13	130	32	790	240
14	110	15	820	67
15	810	350	380	235
16	560	125	660	220
17	355	30	620	205
18	380	30	660	250
19	580	144	540	155
20	600	190	680	170
21	580	220	500	140
22	610	205	460	120
23	600	190	690	240
24	660	220	410	83
25	620	140	510	262
26	580	130	310	61
27	600	235	520	144
28	465	100	640	200
29	840	235	820	190
30	760	144	925	235
31	240	13	350	89

distinguishing sedimentary environments and transport mechanisms. Surface textures on coarse sand grains are primarily developed due to the impact of collision and breakage of particles during transportational processes. Features due to chemical activity can also be discerned through SEM studies. Examination of surface textures of clastic particles is extensively used to determine the source and provenance of sediments, different stages of diagenesis and secondary mineralisation and related chemical overgrowths.

Each environment is characterised by unique processes and energy levels peculiar to that environment. It also gives specific features or textures characteristic of that environment. A quartz grain taken from beach bears typical textural signature on its surface. This imprints are totally different from those produced by action of rivers, wind or glacier. Surface textures are of two types of which the first deals with the dullness or polish of the fragment and the other concerns the markings on the surface. (Krinsley, Doornkamp, 1973, Baker 1976 and Marshall 1987). Waugh (1970) used the surface textural studies to extrapolate the extent of diagenesis in ancient deposits. The development of quasi-quantified diagenesis to SEM analysis has clearly shown that no single surface texture or feature can be used to identify the post environmental history of a deposit, but it is the combination of features that enable the determination (Margolis, 1968; Carter, 1984)

A total of 15 quartz grains collected from the Kayamkulam estuary have been examined under Scanning Electron Microscope under two broad magnification levels.

1) Low magnification studies performed between 110 and 190X, and

2) High magnification studies performed under 2000X, 3000X.

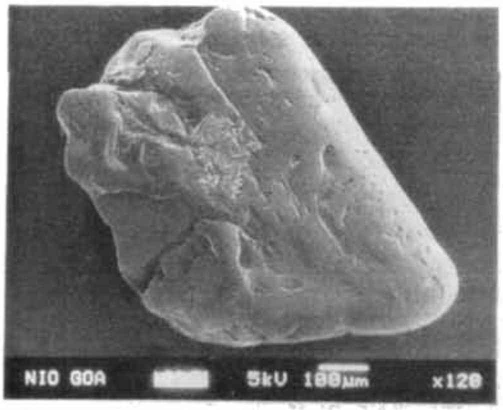
The major observations made from the low magnification analysis are given in Table 3.4 and the representative images of the type grains subjected SEM studies from northern, central and southern parts are given in Plate 3.1.a. The surface textural features and granulometric characteristics exhibit marked difference among the three zones. A substantial proportion of the quartz grains collected from southern part shows sub angular corners or edges, low degree of polishness etc. indicating river transported sediments. On the contrary, the quartz grains of the central and northern parts, exhibit high degree of polishness, sphericity, roundness, characteristic subaqueous impact pits etc. The mixed nature of quartz grains from present and palaeo-beach ridges (ie, the present day ridges) are very evident in the SEM studies.

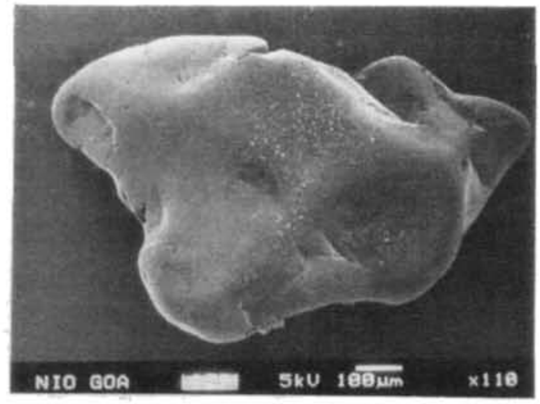
A close up of surface features at high magnification studies (Plate3.1.b) reveal the extent of subaqueous activity to which the particle has been subjected. The bulbous surface is with a spectrum of micro relief structures including chatter marks, impact pits (v-shaped), a few dissolution structures etc. All these impact pits are indicative of intense mechanical action and the long residence time in a beach environment.

In short the SEM studies of quartz grains also supports the earlier views deduced from the granulometric studies.

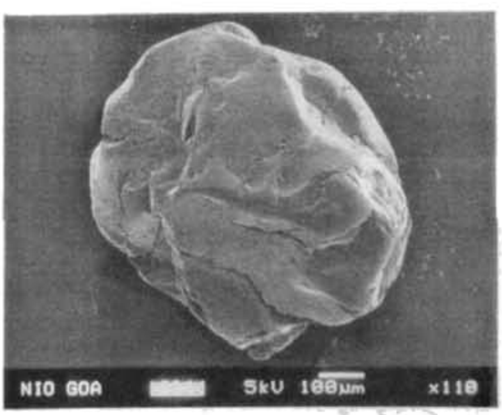
Table 3.4 Surface textural features on quartz grains observed under low-magnification SEM images, Kayamkulam estuary.

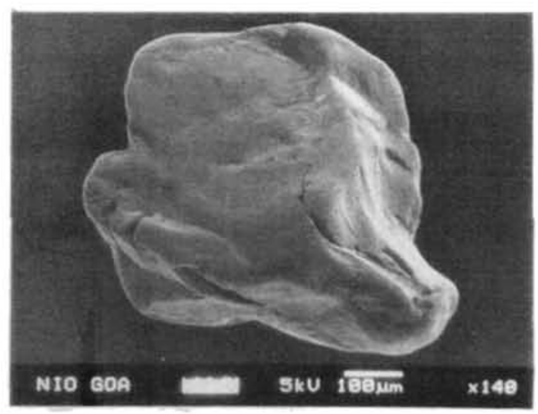
Sector	Sampling stations	Number of grains studied	Grain Magnification	General Observation
Northern part	1 & 7	5	110X to 120X	Grains are subspherical to elongate with rounded to subrounded corners / edges. Some of the grains exhibit high degree of polishness and with well-developed bulbous edges. Traces of 'V' pits and dish shaped features are often present. Grain breakage structures are seen over certain grains.
Central part	12 & 15	6	110X to 140X	Spherical to subspherical grains with well rounded edges / corners. Polishness of the grain surface is moderate to high. Impact pits and grain breakage structures are also seen.
Southern part	27 & 29	4	130X to 190X	Grains are generally elongate, with stout and blocky surface features, corners / edges are subangular to subrounded, polishness of the grains is also not so distinct. Solution pits are seen in some of the grains.



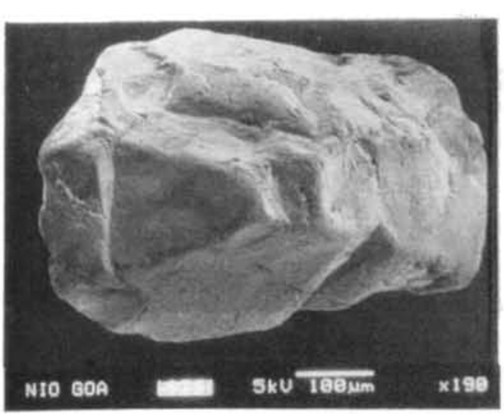


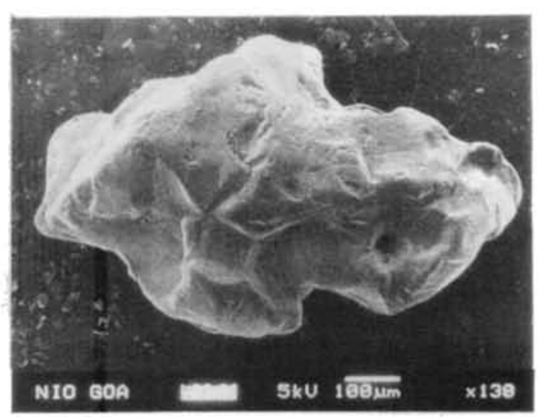
NORTHERN PART





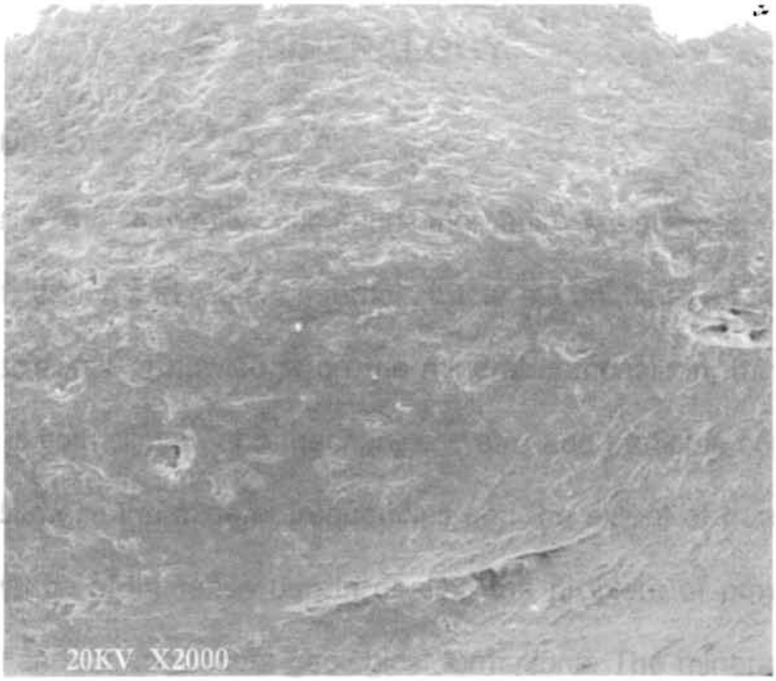
CENTRAL PART





SOUTHERN PART

Plate. 3.1a Surface features of the quartz grains in the Kayamkulam estuary, observed under SEM (low magnification)



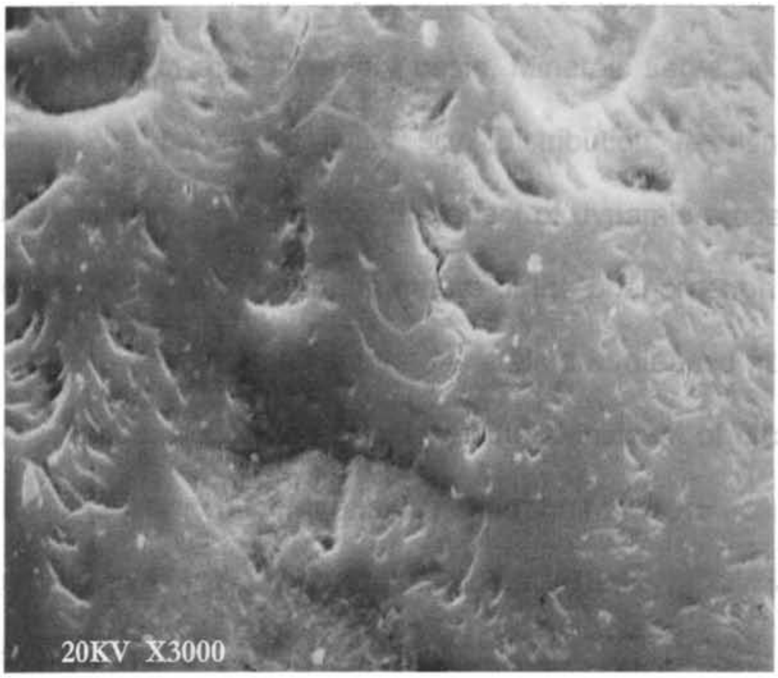


Plate. 3.1b Surface features of the quartz grains in the Kayamkulam estuary, observed under SEM (high magnification)

CHAPTER IV
MINERALOGY

4.1 INTRODUCTION

Minerals, the naturally occurring inorganic substances with definite chemical composition and regular internal structure, constitute an integral part of rocks and sediments. Knowledge on the mineral composition, mineral stability with respect to both climate and mechanical wear, and particles constituting the relationship between the mineral frequencies and the extent of transportation of sediments, will be of immense use in dealing the problem of provenance and correlation of ancient and recent geological formations. The mineralogical make of detrital constituents of the sediments is of profound importance in bringing out the depositional history of a sedimentary basin. Minerals serve as a source of information about the nature of initial size distribution resulting from the mechanical disintegration at the source, the effect of dynamic processes on the original size distribution and assertion in nature of the phenomenon of hydraulic equivalence of sizes. From the moment the minerals are released from their host rocks, a series of processes come into effect. The significant of factors likely to affect the reliability of heavy mineral analyses and their interpretation have been discussed and evaluated by many researchers (Blatt 1967, Hubert 1971, Pettijohn et al., 1972, Morton, 1985).

The mineralogical makeup of sediments is also used for the evaluation of various physico-chemical processes involved during weathering, transportation and deposition. The knowledge of relative abundance of heavy, light and clay minerals in the sediments render insight on to the nature of contribution and energy conditions of the depositing medium. Studies on the mechanisms of fluvial and alluvial placer evolution have facilitated a better appreciation of process operating in the entrainment. Concentration and hydraulic equivalence relationships of light and heavy minerals have been studied by many researchers. (Slingerland,1977, Komar and Wang 1984, Komar et al., 1989, Peterson et al., 1986, Komar 1987).

Heavy mineral fractions in sediments are often composed of diverse mineral species, in which each grain conveys its own history. It is the sedimentary petrologists task to decipher the message encoded in the mineral assemblages and apply them for the purposes of a) determining provenance b) tracing sediment transport paths c) mapping sediment dispersal patterns; d) outlining and, in suitable cases, correlating various sand bodies, e) indicating the action of particular hydraulic regimes and concentrating processes, f) locating potential economic deposits, and g) elucidating digenetic processes.

Heavy minerals are often the only means of reconstructing provenance in sedimentary sequences. Pettijohn et al.,(1972) suggested that the diversities in heavy mineral assemblages are more in the youngest sediments than ancient ones, and further, a number of heavy mineral species may gradually decrease as the age of the sediment increases. It is commonly believed that heavy minerals have a limited value of time-stratigraphic correlation. Lithostratigraphic units are commonly associated with a specific suite of heavy mineral assemblage.

Depositional breaks or unconformities are often characterized by marked changes in the heavy mineral suites. This emphasizes the stratigraphic significance of heavy minerals. Heavy mineral studies have been proved to be important contributors to the analyses of sedimentation associated with tectonically active hinterlands. Heavy minerals are sensitive indicators of sedimentary processes and are useful in signaling even the minute change of the depositional environments or facies (Mange and Maurer, 1992).

Study of the mineralogical constitution of sediments should always accompany the study on textural characteristics, as the texture has a direct bearing on the mineralogical constitution of sediments. High-density accessory mineral constituents of sediments are called heavy minerals. In their parent rocks they are present either as essential rock forming minerals (e.g. Amphiboles, pyroxenes, micas) or are accessory components, such as zircon, apatite, tourmaline etc, occurring in a wide variety of rock types. These accessory components of sedimentary rocks have specific gravity greater than 3 and commonly represents a small percent (usually less than 1 percent) of detrital sedimentary components, the rest of which is mostly quartz.

The size, shape, and type of minerals present in the sediments, were studied in order to decipher the provenance of modern sands. Since heavy minerals are deposited according to the difference in size, shape and density, a single size fraction seldom represents the entire mineralogical composition of sediments (Friedman, 1961; Mishra, 1969; Blatt et al., 1972 and Patro et al., 1989). The diagnostic properties of minerals have been studied microscopically and constitute the most important aspects in the observation of these heavy minerals.

The clay minerals are the main constituents of one class of sediments, which on accumulation and compaction yield shales or mudstones. Whether in sedimentary deposits or not, the clays are usually the products of either weathering or hydrothermal alteration. Different clays results according to physico-chemical conditions and the nature of parent materials, e.g. feldspars, micas, volcanic glasses, or ferromagnesian minerals. Probably most common of the clay minerals are those of kaolinite group and they are formed principally by the hydrothermal alteration or weathering of feldspars, feldspathoids and other silicates. Field occurrences indicate that the rocks, which alter to kaolinite, are usually the more acid types (granites, quartz diorites, etc.). The kaolinite more often is a product of weathering and transportation.

The major factors controlling the properties of clay minerals are clay mineral composition, content of organic material, exchangeable ions and texture. The clay mineral composition refers to the identity and relative abundance of all the clay mineral components. Certain clay minerals, which may be present in very small amount, may exert a tremendous influence on the attributes of a clay mineral, if it is not adequate to determine only the major clay mineral component. Thus a small amount of clay is likely to provide a material very different from another clay with the same composition in all ways except for the absence of smectite. In order to make a complex clay mineral determination, it is frequently necessary to fractionate the clay grade to concentrate minor constituents so that adequate analytical data is obtained.

Illite is a dominant clay mineral in shale and mudstones and also occur in other sedimentary rocks. It may also have a hydrothermal origin and they are often founds in alteration zones around hot springs or metalliferrous veins. Laboratory experiments suggest that for both hydrothermal and sedimentary occurrences, the formation of illite is generally favoured by alkaline conditions and by high concentration of aluminium and potassium.

Montmorillonite and beidellite are the principle constituents of bentonite clay deposits. These have been formed by alternation of eruptive igneous rocks, usually tuffs and volcanic ashes and contain varying amounts of cristoballite, zeolites, biotite, quarts, feldspar, zircon etc. Certain cations may be sorbed by the clay minerals in a non-exchangeable state. Potassium is the commonest ion that is " fixed" to a considerable degree. Illite will fix potassium and most of the K^+ fixed in soil is probably due to the action of this clay mineral. Kaolinite exhibits an inert behaviour towards K^+ either in a moist condition or after drying. The ammonium ion and the potassium ion are fixed in soils by the same mechanism.

4.2 REVIEW OF LITERATURE

The size distribution of heavy minerals in sedimentary deposits was explained by Rubey, (1933). The interrelationship between the source rock characteristics and the transportational processes was stressed by Rittenhouse, (1943). The rate of chemical alteration is greater in coarser grained sediments than in less permeable fine grained ones due to the free movement of intrastratal solution through the former (Blatt and Sutherland,1969). Bradley (1970); Van Andel and Poole (1960); Lowright et al., (1972); Stapor (1973); Slingerland (1977); Flores and Shideler (1978); and Statteger (1987) used the heavy mineral assemblages in unravelling the transportational and depositional histories of sediments. The diversities in heavy mineral assemblages are more in the youngest sediments than ancient ones, and further, the number of heavy mineral species decreases in the latter due to the prolonged action of intra-stratal solution, (Pettijohn, 1941). Contrary to this Krynine (1942) pointed that provenance is main factor that determines the mineralogical diversity.

In the west coast of India, studies were carried out in regard to heavy mineral in recently deposited sediments. Siddiquie et al., (1979) and Chaterjee et al., (1968) were made detailed studies on the heavy mineral assemblage in the sediments of Mangalore coast. Siddiquie et al., (1972) studied opaque heavy mineral distribution and their assemblage for provenance evaluation. Kidwai et al. (1981) classified the Vengurla and Mangalore shelves into four provinces on the basis of heavy mineral distribution. Venkataratnam (1968) reported the heavy minerals in the shelf sediments of Visakhapatnam – Pudimadaka and Pulicat lake – Pennar river confluences. Mallik (1981) studied the distribution pattern of heavy minerals off Kakinada. Heavy mineral distribution pattern of Madras and Visakhapatanam was studied by Pragatheeswaran et al. (1986). By using heavy mineral assemblages, Reddy et al (1992) studied the Kalingapatanam – Bhavanapadu shelf sediments. Allen, (1970), Carver, (1971), Blatt et al, (1972), Komar and Wang, (1984), Komar et al, (1989), Sajan, (1988), and Rao (1991), have studied in detail on the role of progressive sorting based on size and specific gravity differences.

Brown and Dey, (1955) have studied the heavy mineral deposits between Quilon and Cape Comorin on the southwest coast of India. Prabhakara Rao (1968), Purandra et al; (1987), Mallik et al, (1986); Unnikrishanan (1987) investigated heavy mineral suites of the beach sands of Kerala. Heavy mineral concentrates in the shelf region of the west coast of India have been evaluated by Siddiquie et al., (1979). Sajan (1988, 1992) worked on the heavy minerals in the sediments of Ashtamudy lake. Samsuddin (1990) evaluated the heavy mineral assemblages of the beach, strand plain and inner shelf sediments of the northern Kerala coast. Padmalal (1992) discussed mineralogical composition of Muvattupuzha River and Central Vembanad estuarine sediments.

According to Grim (1953), the clay mineral composition sediment provides a clue in unravelling the conditions under which it was deposited. Apart from this, according to the same author it is highly possible that the clay minerals might have played a significant role in the origin of petroleum by acting as catalyst in the alteration of original buried material to hydrocarbon compounds. Clay mineral researches, therefore, provide significant information on the origin of petroleum and important for the location of source beds of petroleum.

Scientists have studied clay mineral in sediments especially of the marine and estuarine environment for many years. Shaw (1973) studied the mineralogy of the clay of the recent surface sediments from the Alicia basin, North Eastern

Mediterranean. The transport mechanism and depositional environment of clay minerals in South East Indian Ocean sediments was studied by Piper and Slatt (1977) evaluated the Late Quaternary clay mineral distribution on the Eastern continental margin of Canada. Regional distribution of clay minerals was brought out by Rao and Rao (1977) for the sediments of the Eastern part of Bay of Bengal. Gibbs (1977), in his classic study on the bottom sediments of the Amazon shelf and Tropical Atlantic revealed the mechanisms of clay mineral segregation in the marine environment. The setting velocity, diameter and density for flocs of illite, kaolinite and montmorillonite were also analysed by Gibbs (1985). Reddy et al., (1992) studied the clay mineral distribution from Bhimunipatnam to Pudimadaka along central eastern continental shelf of India. Rao (1991) investigated the clay mineral distribution in the continental shelf sediments from Krishna to Ganges river mouth in east coast of India. Based on this study he concluded that the abundance of individual clay minerals in the sediments depends on the energy conditions of depositional environment and the organic matter content in the overlying waters. Rao and Rao (1977) have made exhaustive studies on the clay mineral distribution in Bhimunipatnam-Kalingapatnam shelf sediments, east coast of India.

Seralathan and Seetaramaswamy (1987) studied the clay mineral characteristics of the modern deltaic sediments of the Cauvery River and indicated that the clay fraction of marine sediments has higher capacity of trapping organic matter than the riverine sediments. Sajan and Damodaran (1986-88) brought out the clay mineralogy of Ashtamudy estuary and concluded that the clay minerals has undergone limited chemical changes and reflexes source material supplied to the estuary. The clay mineral distribution on the Kerala continental shelf and slope were carried out by Nair et al., (1982). Clay mineralogy of inner shelf sediments of Cochin, west coast of India was studied by Reddy et al., (1992).

4.3 RESULTS AND DISCUSSIONS

4.3.1 Heavy Minerals

The sand fraction of surface sediments of the Kayamkulam estuary has been analysed for its mineralogical composition. For heavy mineral analysis, the samples free of shell fragments and iron coatings were sieved in to two-size fractions viz. 1mm – 0.25mm (medium) and 0.25mm – 0.063mm following the method of Krumbein and Pettijohn (1938). The weight percentages of heavies for the two size fractions are given in table 4.1 and the number percentages of heavy minerals are given in table 4.2 a and b. The surface plot of the total heavies in the medium and fine sediments of the Kayamkulam estuary for the pre and post monsoon is given in the Fig 4.1 the regional distribution of individual heavy minerals in the medium and fine fractions are given in Fig. 4.2 a and b. Inter relationship of heavy minerals were drawn up from the correlation matrix provided in table 4.3 a and b. From the table it is evident that, the content of heavies does not exhibit much variation in the medium sand for the pre and post monsoons. The average weight percentage of heavies in the medium sand fraction for pre monsoon and post monsoon seasons are 1.48% and 1.08%,

Table 4.1 Weight percentage of heavy minerals in the medium and fine grained fractions

PRE MONSOON

	Sample No.	% Medium	% Fine
	1	0.51	8.17
	5	1.16	7.97
N	7	0.34	4.47
	10	0.65	8.85
	Average	**0.67**	**7.37**
	15	6.05	9.09
	16	0.59	5.14
C	17	0.85	7.31
	Average	**2.50**	**7.18**
	21	1.00	20.74
	25	1.36	30.02
S	27	1.84	28.86
	31	1.95	5.53
	Average	1.54	21.29

POST MONSOON

	Sample No.	% Medium	% Fine
	1	0.52	5.01
	4	0.96	10.57
	5	0.99	13.07
N	7	0.99	20.45
	10	0.49	33.06
	Average	**0.79**	**16.43**
	12	0.37	7.91
	14	0.77	0.98
	15	3.76	22.16
C	16	0.49	6.22
	17	1.15	24.20
	18	0.56	11.98
	Average	**1.18**	**12.24**
	21	0.98	17.46
	25	0.26	27.36
S	27	1.81	14.42
	28	2.08	17.45
	Average	1.28	19.17

N - NORTHERN SECTOR, C - CENTRAL SECTOR, S - SOUTHERN SECTOR

Table 4.4 a NUMBER PERCENTAGE OF HEAVY MINERALS IN PREMONSOON

MEDIUM FRACTION

	SAMPLE No.	OPAQUES	NON OPAQUES						
			ZIRCON	GARNET	AMPHIBOLES	PYROXENE	MONAZITE	RUTILE	SILLIMANITE
	1	70.00	3.00	17.00	2.50	4.00	0.00	1.00	2.50
	4	69.50	12.00	8.00	1.00	6.50	0.00	0.50	2.50
N	5	59.00	15.25	16.00	7.50	1.75	0.00	0.00	0.50
	7	52.00	10.00	22.00	4.00	8.00	0.00	0.00	4.00
	10	69.00	11.00	12.00	1.00	4.00	0.00	0.00	3.00
	AVG	63.90	10.25	15.00	3.20	4.85	0.00	0.30	2.50
	12	73.00	7.00	9.00	2.25	6.00	0.00	1.00	1.75
	14	82.00	9.00	3.60	0.00	3.60	0.00	0.00	1.80
	15	59.80	2.50	25.75	4.10	4.10	1.50	2.25	0.00
C	16	82.25	3.75	10.00	0.00	1.75	0.00	1.00	1.25
	17	65.20	4.50	15.00	1.80	9.00	0.90	0.00	3.60
	18	73.00	6.00	12.50	2.00	3.50	0.50	1.00	1.50
	AVG	72.54	5.46	12.64	1.69	4.66	0.48	0.88	1.65
	21	70.00	6.00	9.00	1.50	7.50	0.00	2.00	4.00
	25	78.00	5.00	7.00	1.00	5.00	1.00	1.00	2.00
	27	72.00	2.25	13.00	5.50	6.25	0.00	0.25	0.75
S	28	79.30	6.30	6.00	0.90	4.80	0.00	0.90	1.80
	29	79.50	7.00	3.00	3.00	4.50	0.00	1.00	2.00
	31	73.10	4.00	13.00	1.00	7.30	0.60	0.00	1.00
	AVG	75.32	5.09	8.50	2.15	5.89	0.27	0.86	1.93

FINE FRACTION

	SAMPLE No.	OPAQUES	NON OPAQUES						
			ZIRCON	GARNET	AMPHIBOLES	PYROXENE	MONAZITE	RUTILE	SILLIMANITE
	1	86.50	2.75	6.75	1.00	0.75	0.50	0.00	1.75
	4	82.90	3.95	2.95	1.00	7.30	0.00	0.15	1.75
N	5	78.05	5.85	4.15	1.85	7.95	0.00	0.00	2.15
	7	73.00	7.00	9.00	2.25	6.00	0.00	1.00	1.75
	10	76.65	5.00	5.25	1.95	8.05	1.50	0.00	1.60
	AVG	79.42	4.91	5.62	1.61	6.01	0.40	0.23	1.80
	12	70.50	7.50	4.00	2.50	13.00	0.00	0.00	2.50
	14	82.00	3.95	3.65	1.50	6.75	0.00	0.30	1.85
	15	88.50	3.00	3.50	1.00	2.00	0.00	1.00	1.00
C	16	82.00	5.50	4.50	1.00	3.35	0.25	1.00	2.40
	17	76.10	5.45	5.00	1.50	8.80	0.00	0.00	3.15
	18	83.70	2.95	4.65	0.80	6.10	0.00	0.00	1.80
	AVG	80.47	4.73	4.22	1.38	6.67	0.04	0.38	2.12
	21	78.70	3.65	4.70	1.30	9.00	0.00	0.30	2.35
	25	79.55	3.65	5.15	1.35	7.95	0.00	0.00	2.35
	27	76.60	5.40	5.35	1.00	9.50	0.00	0.15	2.00
S	28	77.65	5.40	4.50	1.35	7.70	0.00	0.30	3.10
	29	79.25	3.70	5.80	0.50	7.10	0.00	0.50	3.15
	31	74.00	7.50	3.50	1.00	10.75	1.75	0.00	1.50
	AVG	77.63	4.88	4.83	1.08	8.67	0.29	0.21	2.41

N-NORTHERN, C-CENTRAL, S-SOUTHERN

Table 4.2 b NUMBER PERCENTAGE OF HEAVY MINERALS IN POST MONSOON

MEDIUM FRACTION

	SAMPLE No.	OPAQUES	NON OPAQUES						
			ZIRCON	GARNET	AMPHIBOLES	PYROXENE	MONAZITE	RUTILE	SILLIMANITE
	1	58.10	14.60	10.00	7.00	3.50	1.00	1.00	4.80
	4	77.50	4.50	11.00	1.25	2.50	0.50	0.50	2.25
N	5	61.00	9.00	15.00	2.50	8.00	0.50	0.50	3.50
	7	79.75	7.50	7.50	0.00	1.75	0.75	0.25	2.50
	10	61.00	7.00	15.00	3.00	9.00	0.00	0.00	5.00
	Average	67.47	8.52	11.70	2.75	4.95	0.55	0.45	3.61
	12	80.50	5.40	10.00	0.00	0.90	0.60	0.00	2.60
	14	51.00	5.00	20.00	6.00	10.00	0.00	6.00	2.00
	15	72.00	6.50	9.00	2.00	7.00	0.00	0.00	3.50
C	16	65.50	12.50	12.50	3.00	4.25	0.00	0.00	2.25
	17	84.30	5.20	5.70	0.90	1.20	0.90	0.90	0.90
	18	73.75	6.25	6.75	0.00	8.50	0.25	0.75	3.75
	Average	71.18	6.81	10.66	1.98	5.31	0.29	1.28	2.50
	21	75.00	7.00	7.50	1.00	6.00	0.00	1.50	2.00
	25	62.30	5.40	10.80	5.40	10.70	0.00	0.00	5.40
	27	81.50	3.50	4.50	1.50	5.50	1.00	0.50	2.00
S	28	61.75	8.25	20.00	6.75	0.80	0.00	2.05	0.40
	29	71.20	5.60	14.50	3.50	0.18	0.00	5.03	0.00
	31	84.60	3.30	4.40	2.20	1.10	1.10	0.00	3.30
	Average	72.73	5.51	10.28	3.39	4.05	0.35	1.51	2.18

FINE FRACTION

	SAMPLE No.	OPAQUES	NON OPAQUES						
			ZIRCON	GARNET	AMPHIBOLES	PYROXENE	MONAZITE	RUTILE	SILLIMANITE
	1	74.2	4.0	12.5	0.8	5.1	0.3	1.3	2.0
	4	76.0	5.8	9.3	1.3	6.5	0.3	0.0	1.0
N	5	76.0	8.5	7.5	1.0	5.5	0.0	0.0	1.5
	7	71.0	7.5	13.0	1.3	5.0	0.0	0.3	2.0
	10	71.0	13.0	8.0	2.0	2.0	1.0	1.0	2.0
	Average	73.6	7.8	10.1	1.3	4.8	0.3	0.5	1.7
	12	83.4	2.0	5.6	1.0	6.3	0.0	0.3	1.5
	14	83.3	4.0	2.0	0.5	8.0	0.5	0.0	1.8
	15	83.8	3.0	6.3	1.0	4.5	0.0	0.3	1.3
C	16	75.3	7.0	3.3	1.3	9.3	0.8	0.5	2.8
	17	82.9	2.9	5.6	0.3	6.8	0.4	0.1	1.1
	18	67.0	5.0	12.0	2.0	9.5	0.0	1.0	3.5
	Average	79.3	4.0	5.8	1.0	7.4	0.3	0.4	2.0
	21	77.8	5.6	8.5	0.9	5.1	0.0	0.2	2.1
	25	84.1	4.3	5.7	0.6	4.5	0.0	0.0	1.0
	27	80.6	4.7	6.7	0.8	5.3	0.0	0.0	2.1
S	28	82.4	2.6	7.0	0.0	6.0	0.3	0.1	1.6
	29	78.6	4.0	5.9	0.8	8.0	0.8	0.3	1.8
	31	78.8	5.5	12.0	1.0	2.3	0.0	0.0	0.5
	Average	80.4	4.4	7.6	0.7	5.2	0.2	0.1	1.5

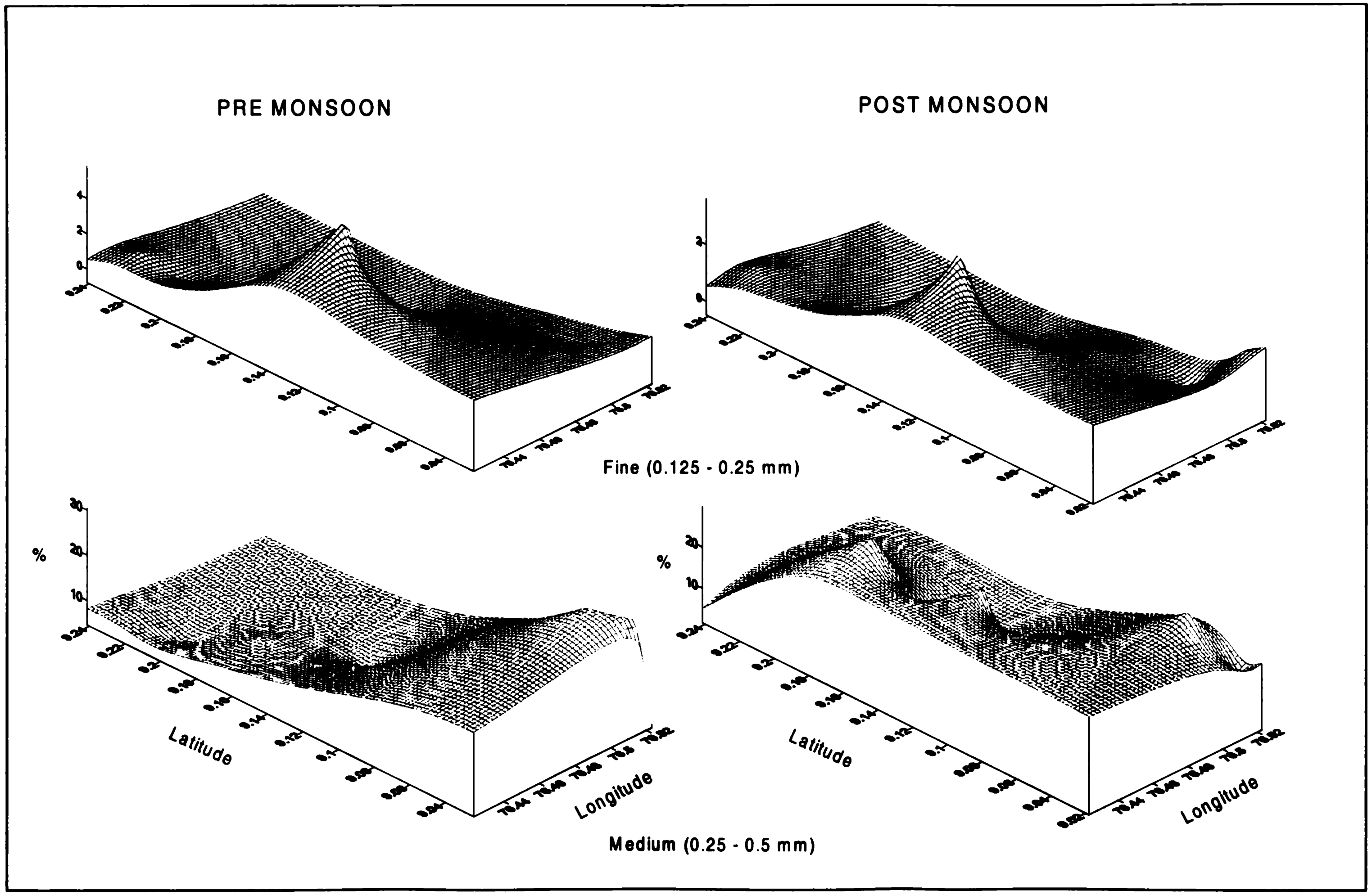


Fig.4.1 Surface plot of the heavies in the sediments of Kayamkulam estuary for the pre and post monsoons

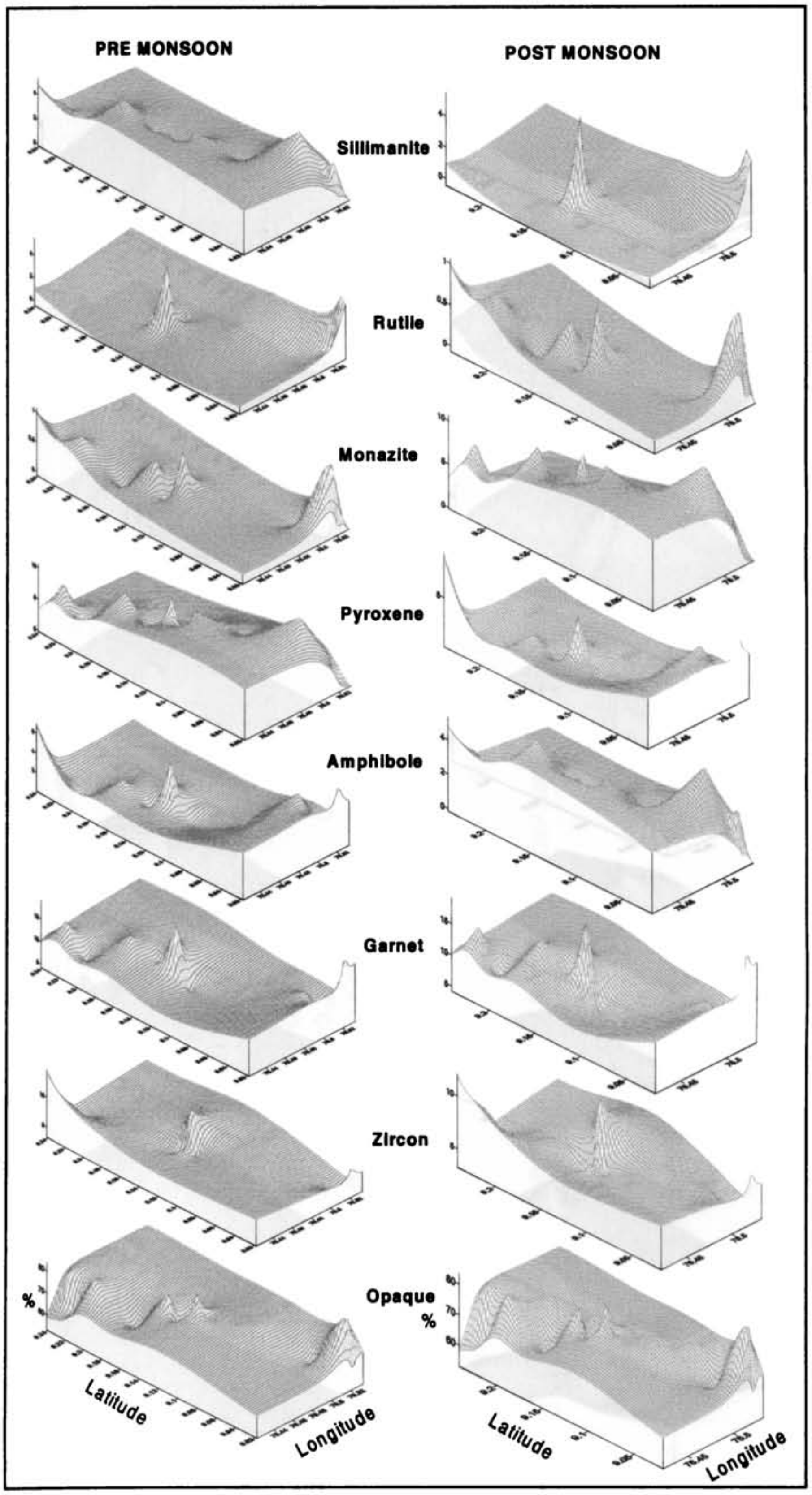


Fig.4.2a Surface Plot of the heavy minerals in the medium fraction of the Kayamkulam estuarine sediments for the Pre & Post monsoons

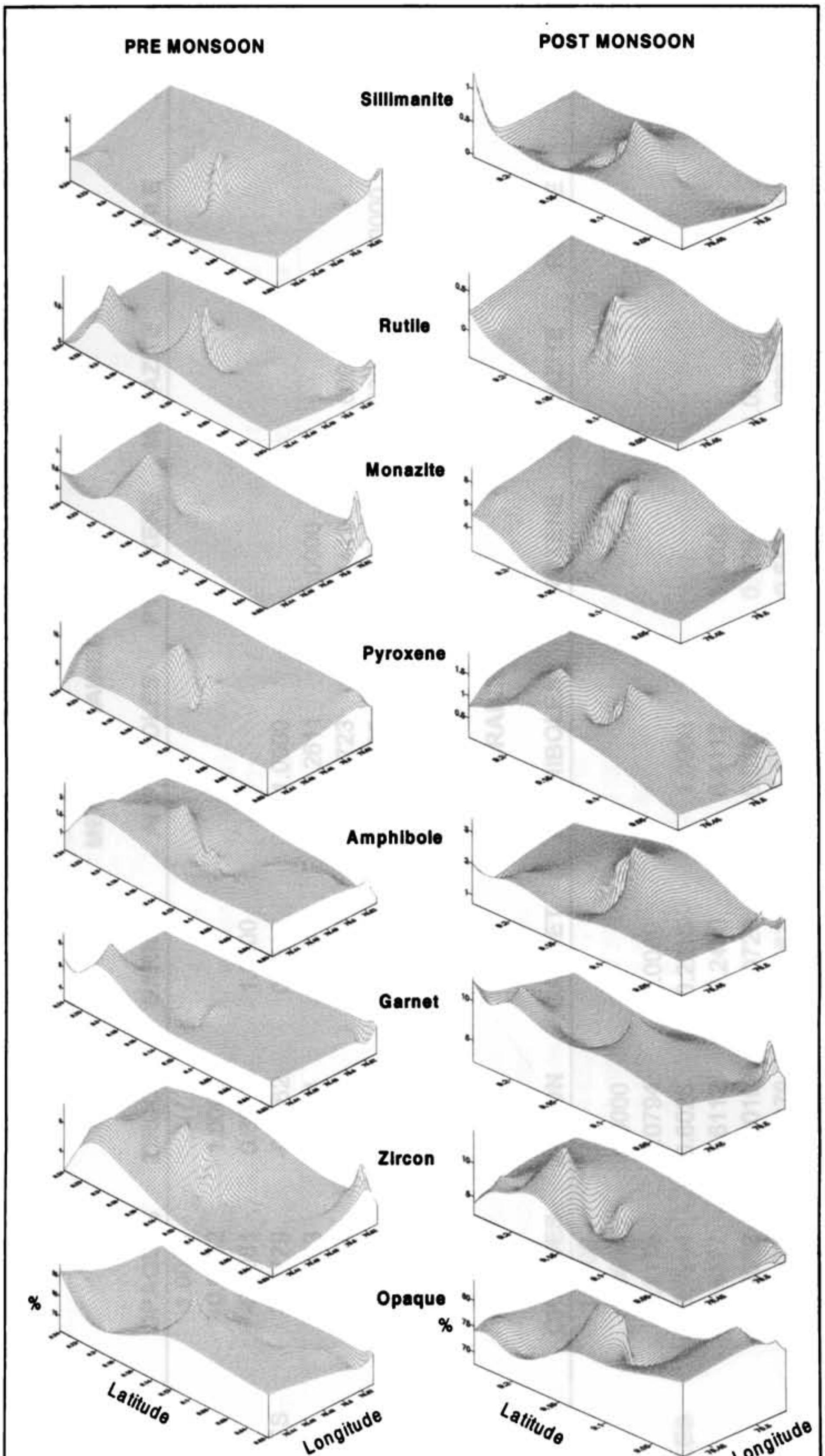


Fig.4.2b Surface plot of the Heavy minerals in the fine fraction of the Kayamkulam estuarine sediment for the Pre & Post monsoons

Table 4.3 a CORRELATION MATRIX OF THE HEAVY MINERALS IN THE SEDIMENTS OF KAYAMKULAM ESTUARY FOR THE PRE MONSOON

MEDIUM GRAINED

	OPAQUES	ZIRCON	GARNET	AMPHIBOLES	PYROXENE	MONAZITE	RUTILE	SILLIMANITE
OPAQUES	1.0000							
ZIRCON	-0.6692	1.0000						
GARNET	-0.9081	0.3673	1.0000					
AMPHIBOLES	-0.0779	-0.0562	0.1315	1.0000				
PYROXENE	-0.3683	0.0434	0.2290	-0.2611	1.0000			
MONAZITE	-0.0454	-0.4109	0.2642	0.0723	0.1419	1.0000		
RUTILE	0.1969	-0.4736	-0.0439	0.0495	-0.1361	0.3300	1.0000	
SILLIMANITE	-0.3430	0.3638	0.1083	-0.5371	0.5839	-0.2750	-0.1304	1.0000

FINE GRAINED

	OPAQUES	ZIRCON	GARNET	AMPHIBOLES	PYROXENE	MONAZITE	RUTILE	SILLIMANITE
OPAQUES	1.0000							
ZIRCON	-0.8614	1.0000						
GARNET	-0.2179	0.0794	1.0000					
AMPHIBOLES	-0.6344	0.6026	0.2215	1.0000				
PYROXENE	-0.8277	0.6112	-0.2490	0.4112	1.0000			
MONAZITE	-0.2052	0.3010	-0.0720	0.0105	0.1294	1.0000		
RUTILE	0.2292	-0.0079	0.2587	-0.0848	-0.5111	-0.2627	1.0000	
SILLIMANITE	-0.3646	0.1388	0.0949	0.0044	0.3385	-0.3809	-0.1411	1.0000

Table 4.3 b CORRELATION MATRIX OF HEAVY MINERALS IN THE SEDIMENTS OF KAYAMKULAM ESTUARY FOR THE POST MONSOON

MEDIUM GRAINED

	OPAQUES	ZIRCON	GARNET	AMPHIBOLES	PYROXENE	MONAZITE	RUTILE	SILLIMANITE
OPAQUES	1.0000							
ZIRCON	-0.6110	1.0000						
GARNET	-0.8453	0.2722	1.0000					
AMPHIBOLES	-0.8680	0.5471	0.7663	1.0000				
PYROXENE	-0.2852	-0.3456	0.1854	0.0234	1.0000			
MONAZITE	0.6969	-0.3112	-0.6451	-0.5392	-0.3527	1.0000		
RUTILE	-0.2350	-0.3306	0.5597	0.2773	0.1368	-0.3211	1.0000	
SILLIMANITE	-0.2299	0.3966	-0.2038	0.0690	0.2936	-0.0790	-0.7334	1.0000

FINE GRAINED

	OPAQUES	ZIRCON	GARNET	AMPHIBOLES	PYROXENE	MONAZITE	RUTILE	SILLIMANITE
OPAQUES	1.0000							
ZIRCON	-0.5264	1.0000						
GARNET	-0.4942	-0.2890	1.0000					
AMPHIBOLES	-0.4947	-0.2589	0.5507	1.0000				
PYROXENE	0.0104	-0.6506	0.1218	0.5316	1.0000			
MONAZITE	0.1229	-0.1959	-0.3557	-0.1182	0.5809	1.0000		
RUTILE	-0.4968	-0.1906	0.5668	0.4578	0.3312	0.0955	1.0000	
SILLIMANITE	-0.6971	0.1740	0.2355	0.5145	0.3703	0.0737	0.6053	1.0000

respectively. However the heavies are concentrated several fold higher in the fine sand fraction than medium sands. The concentration of heavies in the fine sands of pre monsoon and post monsoon are 12.38% and 15.29%, respectively. A sector wise analysis of the heavies reveal that, in general, the heavies exhibit an increasing trend towards the southern sector expect for the pre monsoon medium grained heavies in the southern sector.

The sector wise distribution of heavies in the medium and fine grained sand reveals that, in the pre monsoon period, the weight percentage of heavies exhibits a marked increase in the central sector with an average of 2.5% (range: 0.59-6.05%), whereas in the post monsoon period, the heavy mineral maxima shifts towards southern sector with an average of 1.28% (0.26 – 2.08%). The respective heavy mineral contents of the other sectors in the pre monsoon season are: 1.54%(1-1.95%) for the southern sector and 0.67% (0.34-1.16%) for the northern sector. The concentration of heavy minerals in the post monsoon for medium grained 0.79%(0.49-0.99%) for the northern sector; 1.28% for the southern sector and 1.18%(0.37-1.15%) for the central sector. The heavies in the fine sand were also evaluated in a sector wise mode. In the pre monsoon, the maximum percentage of total heavies is observed in the southern sector (av; 21.29%; 5.53 – 30.02%), which is followed by northern sector (av; 7.37%; 4.47 – 8.85%) and least in the central sector (av; 7.18%; 5.14 – 9.09%).

The observed heavy mineral diversity in Kayamkulam estuary is indicative of the input of heavy rich sediments from the hinterland regions by the Pallickal Thodu which drain in to the southern part of the estuary. The sediments were further modified by constant ebbing and flooding activities through the bar mouth. The intense marine activities in the near by areas can concentrate the heavy mineral contents in the areas, removing the lighter particles in to sediment population The density based segregation is a major causative factor for the observed higher heavy mineral content in the finer sands as well. Rubey (1933) states that the grains of different densities if deposited together should have the same setting velocities or the dense minerals should be smaller by an amount predictable on the basis of settling velocity equation.

4.3.2 Heavy mineral assemblage

The heavy mineral suite of the Kayamkulam estuary comprises a spectrum of minerals, which include opaque, garnet, zircon, pyroxene, sillimanite and amphiboles as the major and monazite, rutile as the minor constituents (Plate 4.1). The number percentages of these minerals are furnished in table 4.3 a and b. The characteristic features of the minerals and their spatial and seasonal variations are depicted below:

4.3.2a Opaque

Magnetic separation of a few samples revealed that magnetite and ilmenite constitute the major members among the opaque minerals of Kayamkulam estuarine sediments. In the present study, the mineral, which does not transmit light through it, is collectively referred to as opaques. Generally the opaques are sub angular to sub rounded. Opaque is the most abundant group of

MINERALS IN PLATE 4.1

1. Garnet - open polars
2. Garnet - crossed polars
3. Zircon - open polars
4. Zircon - crossed polars
5. Pyroxene - open polars
6. Pyroxene - crossed polars
7. Rutile - open polars
8. Rutile - crossed polars
9. Hornblende - open polars
10. Hornblende - crossed polars
11. Monazite - open polars
12. Monazite - crossed polars
13. Sillimanite - open polars
14. Sillimanite - crossed polars
15. Opaques

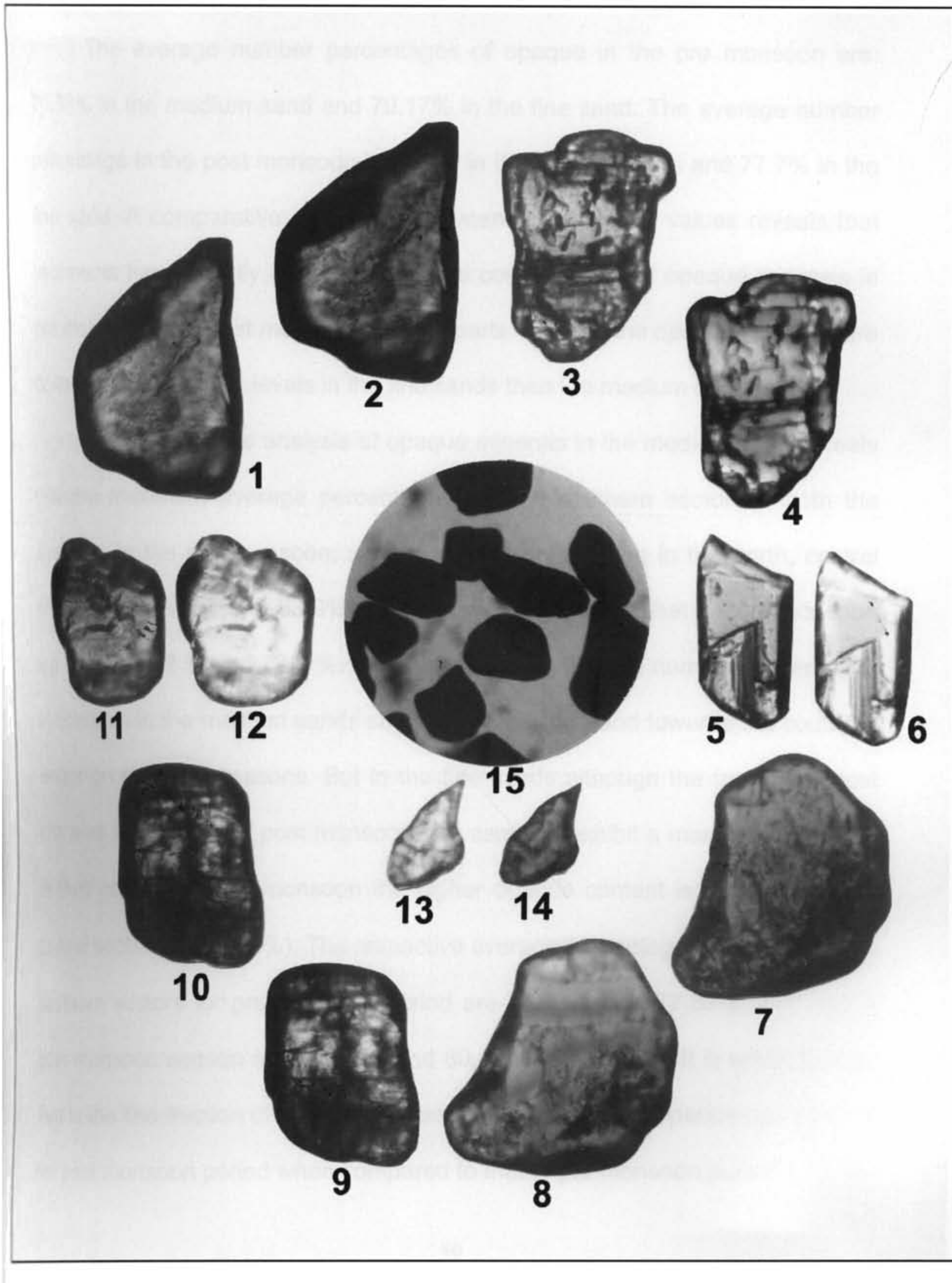


Plate 4.1 Heavy minerals in the sediments of Kayamkulam estuary

minerals among the heavy mineral of the study area both in the pre monsoon and post monsoon seasons.

The average number percentages of opaque in the pre monsoon are: 70.58% in the medium sand and 79.17% in the fine sand. The average number percentage in the post monsoon is 70.6% in the medium sand and 77.7% in the fine sand. A comparative evaluation between the seasonal values reveals that sediments have slightly higher percentage concentration of opaque minerals in pre monsoon than post monsoon counter parts. Further, the opaque minerals are concentrated at higher levels in the fine sands than the medium sands.

The sector wise analysis of opaque minerals in the medium sand reveals that the maximum average percentage is in the southern sector for both the seasons. In the pre monsoon, average content of opaque in the north, central and southern sector are: 63.9%, 72.54% and 75.32 % and that in post monsoon are 67.5%, 71.2 % and 72.7 %. From this it is clear that the number percentages of opaques in the medium sands show an increasing trend towards the southern sector on both the seasons. But in the fine sands although the trend is almost same as in the case of post monsoon, the samples exhibit a marginal difference in their content. In pre monsoon the higher opaque content is observed in the central sector (av; 80.47%). The respective average percentages in the north and southern sectors for pre monsoon period are 79.42%, and 77.63%, and that in post monsoon season are: 73.64% and 80.4 %, respectively. It is worth to note that in the fine fraction of the southern sector, the content of opaques is higher in the post monsoon period when compared to that of pre monsoon period reiterating heavy mineral contribution from the hinterland areas by the Pallickal Thodu.

4.3.2b Garnet

Garnet identified of colourless to pink and pinkish brown. The most abundant non-opaque mineral noticed in the study area is garnet. The average number percentage of garnet in the pre monsoon period is 12.04% (3 - 25.75%) in the medium sand and 4.89% (2.95 – 9.0%) in the fine sand. Similarly, the average number percentage in the post monsoon is 10.9% (4.4 – 20%) in the medium sand, and 7.8% (2 -13%) in the fine sand. The sector wise distribution reveals that in the pre monsoon the average number percentage for north, central and southern sectors are: 15.0% (8 – 22%); 12.64 % (3.6 – 25.75 %) and 8.5 % (3 – 13 %), respectively in the medium grain fraction, and 5.62 % (2.95 – 9 %), 4.22% (3.5 -5%) and 4.83 % (3.5 – 5.8 %) in the fine grain fraction. In the post monsoon, the average number percentage of north, central and southern sector are: 11.7 % (7.5 - 15%), 10.7% (5.7 – 20%) and 10.3 % (4.4 – 20 %) in the medium grain fraction and 10.1% (7.5 – 13%), 5.8% (2 – 12%) and 7.6 % (5.7 - 12 %) in the fine grain fraction. It is observed that in the medium grained heavies both for pre and post monsoon seasons the average percentage of garnet decreases towards the southern sector. But, in the fine sand, the least average number percentage is seen in the central sector of both the seasons.

4.3.2c Zircon

The morphological characters of zircon are determined by the physical and chemical conditions. Therefore, zircon morphology is widely regarded as a petrogenetic indicator. Zircon crystals vary from rounded to sub rounded showing overgrowths.

Zircon is the second most abundant non-opaque mineral in the study area in both the seasons and also in different fractions. The average number percentage of zircon during the pre monsoon is 6.93% (2.25 - 15.25%) in the medium sand and 4.84% (2.75 – 7.5%) in the fine sand. The average number percentage in the post monsoon is 6.93% (3.3 – 14.6%) in the medium sand fraction and 5.4% (2.0 – 13%) in the fine grain fraction. The higher average percentage of zircon is observed in the medium grain fractions. By comparing the number percentage for two seasons, it is clear that post monsoon period has the higher zircon content than pre monsoon.

The sector wise analysis reveals no significant trend in the distribution of zircon in the Kayamkulam estuary. But in the medium sand fraction of both the pre and post monsoon shows that the percentage is decreasing towards the southern sector. The number percentage of pre monsoon medium sand is 10.25% (north), 5.46 % (central) and 5.09% (southern). The fine fraction in the same period shows the least percentage in the central sector. The average number percentages of north, central and southern sectors are: 4.91% (2.75 – 7%) 4.73% (2.95 – 7.5%) and 4.88% (3.65 – 7.5%), respectively. Heavies of the medium sand fraction of the post monsoon shows a decreasing trend towards the south and the respective sector-wise averages are 8.5% (4.5 – 14.6%), 6.8% (5 - 12.5%) and 5.5% (3.3 – 8.3%). The average percentages of north, central and southern sectors for fine fractions are 7.8%, 4.0% and 4.4%, respectively. But in the fine sand fraction the least average percentage is observed in the central sector.

4.3.2d Amphiboles

Hornblende is identified as the predominant amphibole mineral in the heavy mineral assemblage, which is of bluish green to green in colour.

The number percentages of amphibole are furnished in the table 4.2a and 4.2b. The average amphibole count in the pre monsoon is 2.34% in medium sand and 1.35% in the fine sand. The medium and fine sand fractions of the post monsoon account for 2.73% and 1.86%, respectively. A comparative evaluation between the two seasons (pre and post monsoon) revels that in the post monsoon the medium-grained fraction has higher percentage while in the fine sand pre monsoon period has higher percentages amphiboles. From the sector wise data presented in the table 4.2a and b shows that in the pre monsoon period the north, central and south sectors contain average amphibole yielded an average value of 3.2% (1 – 7.5%), 1.69% (0 – 4.1%) and 2.15% (0.9 – 5.5%) in the medium grain fraction; and 1.61% (1 – 2.25%) 1.38% (0.8 – 2.5%) and 1.08% (0.5 - 1.35%) in the fine grain fraction. Similarly the number percentage for the post monsoon are 2.8 %, 2% and 3.4% in the medium grain fraction and 1.3%, 1% and 0.7% in the fine grain fractions. .It is observed that the central sector has the least percentage of amphibole in the medium sand fraction for both the seasons. In the fine sand a decreasing trend in the content of the amphibole from northern to southern sector is noticed for the both seasons.

4.3.2e Pyroxene

Hypersthene, enstatite and diopside are the predominant pyroxene members identified in the Kayamkulam estuary. On the basis of occurrence, pyroxenes rank third position in the study area. The average content of pyroxene in the pre monsoon are 5.13 % (1.75 – 9%) in medium sand and 7.11% (0.75 – 13%) in the fine sand. The average percentages of pyroxene in fine sand for the post monsoon season are 4.7% (0.2 – 10.7%) in medium and 5.8% (2 – 9.5%) respectively. From the above, it is observed that the average content of pyroxene is higher in pre monsoon period both in the medium and fine sand fractions.

The sector wise analysis shows that in the pre monsoon season fine sand shows an enrichment of pyroxenes towards the southern sector. The average percentages pyroxenes in the medium sand for pre monsoon period in the northern, central and southern sectors are 4.85% (1.75 – 8%) 4.66% (1.75 - 9.%) and 5.89% (4.5 – 7.5%) and in fine fraction they are 6.01% (0.75 – 8.05%), 6.67% (2 – 13%), 8.67% (7.1 – 10.75%). Similarly in the post monsoon period, the content of pyroxene is 5% (1.8 - 9%), 5.3% (0.9 – 10%) and 4% 0.2 – 10.7%) in the medium sand and 4.8% (2 – 6.5%), 7.4% (4.5 – 9.5%) and 5.2% (2.3 - 8%) in the fine sand fractions for the north, central and southern sector respectively. In the pre monsoon the southern sector has the higher percentage but in post monsoon the central sector has the highest percentage of pyroxenes in both the medium and fine fractions.

4.3.2f Sillimanite

Most of the sillimanite exhibits prismatic character. The average content of sillimanite in the pre monsoon is 2.02% in medium sand and 2.1% in the fine sand. While for the post monsoon, it is 2.7% for the medium and 1.73% for the fine sand fractions. The sector wise distribution pattern of sillimanite in the north, central and southern sector for pre monsoon period are 2.5%, 1.65% and 1.93% in the medium sand, and 1.8%, 2.12% and 2.41 % in the fine sand fraction. Similarly, in the post monsoon season the averages are: 3.6%, 2.5% and 2.2% in the medium and 1.7%, 2.0% and 1.5% in the fine sand fractions. Among the medium sand fraction, the northern sector has the highest content of sillimanite in both pre and post monsoon seasons. In the fine sand, the southern sector has the maximum content in the pre monsoon season, but in the post monsoon period central sector has the maximum value followed by north and southern sectors.

4.3.2g Rutile

Rutile is a wide spread accessory mineral in metamorphic rocks, particularly in schists, gneisses and amphiboles. It is less significant in igneous rocks, but it occurs in hornblende rich plutonic rocks and pegmatites. Rutile occurs only on very small amounts in the medium and fine sand fraction of the Kayamkulam estuary.

The average percentage of rutile in the pre and post monsoon period is .68 and 1.1% in the medium sand fraction and in the fine fraction it is 0.27% in pre monsoon and 0.33% in the post monsoon. The sector wise distribution for the north, central and southern sectors for pre monsoon period are 0.3%, 0.88% and 0.86% in the medium sand and 0.23%, 0.38% and 0.21% for the fine sand fraction. Similarly for the post monsoon it is 0.5%, 1.3%, and 1.5% in the medium fractions and 0.5%, 0.4% and 0.1% for the fine sand fractions respectively for the north, central and southern sectors. For both the seasons most of the samples rutile is negligible.

4.3.2h Monazite

Monazite is identified only in some samples of the study area. In the pre and post monsoon periods the average content of monazite is 0.25% and 0.43% in the medium sand fraction, and that in the fine fraction is 0.24% and 0.26% respectively. Since monazite is scarcely distributed, it is not worth to discuss in terms of sectors.

Heavy mineral study as a correlation tool is a great interest in sedimentary petrographic investigations, particular for subsurface correlation in certain sedimentary basins. The mineralogy of each grain rather independent of surrounding grains because source area are mineralogically complex and weathering conditions may varying dramatically in geographically adjacent areas particularly in clastic sediments. Hence for bringing out the depositional history of sedimentary basin mineralogical study of detrital constituents is of great significance.

An attempt has been made to find out the source rock for lake sediments based on the relative abundant heavy minerals, petrological characters of the source area and regional distribution of heavy minerals in the present study.

From the table it is found that the most dominant heavy minerals all three sectors both for the pre and post monsoon and that to for the two size fractions are Opaques, Garnet, Zircon, Pyroxene, and Sillimanite, less abundant are amphibole, monazite, rutile. Among the garnet, almandine (pink) occurs more in southern part where as grossularite in occurs in the central part and northern part. In the northern sector for pre monsoon rutile and monazite are virtually absent, while it is present in post monsoon for the medium grained sand. On the contrary it is present *in all through the season in fine-grained sands. The virtual* absence of rutile and monazite in the medium sand for the pre monsoon can be attributed to the source where in much of the sediments are derived from the adjacent paleoridges and runnels of the northern sector. The same has been discussed in the Chapter 3.

Correlation matrix of the heavy minerals where tabulated to understand their interrelationship (Table 4.3 a and b) for the medium and fine sand. Opaque exhibits a marginal correlation with rutile and highly significant inverse co-relation with garnet, zircon and marginal inverse significant co-relation with pyroxene and Sillimanite. Sillimanite shows a highly significant positive correlation with

Pyroxene, Zircon where as zircon shows a significant positive correlation with garnet, monazite. A significant correlation with rutile for the medium sands of pre monsoon. In the post Monsoon opaque shows a highly significant with monazite, amphibole with that of Garnet and Zircon. Garnet with rutile shows a high significant correlation. In the case of fine fraction as an inverse relation has been exhibited by opaques with zircon, amphibole, Pyroxene and Sillimanite. A highly significant correlation has been exhibited by zircon with amphibole, pyroxene and monazite for the pre monsoon. Where as in the post monsoon highly significant inverse correlation exhibited by opaques with Sillimanite zircon, garnet, amphiboles, and rutile. A highly significant positive correlation has been shown by amphibole with garnet, pyroxene, rutile and Sillimanite, while pyroxene shows a highly significant correlation with monazite, Sillimanite, and rutile. Similarly rutile exhibits a highly positive correlation with Sillimanite.

Under a given set of hydraulic conditions medium to fine grains of heavy minerals will tend to accumulate along with quartz and other lighter minerals of larger size, due to their high specific gravity. In the Kayamkulam estuary a high concentration of heavies in the fine grade is due to the settling of both medium to fine heavies in the finer grade is due to the settling of both medium to fine heavies along with coarser quartz, wherever the competency of the river decreases. These hold good for the central as well as southern sector where the Pallikkalthodu and Krishnapuram Ar empties their sediments.

Hand (1964) and White and William (1967) observed a non-hydraulic equilibrium in modern sand and explained it primarily caused by selective sorting based on size density and shape of grains. They could also show that the heavy minerals once settled or deposited or more difficult to sweep along hydraulically equivalent quartz. Therefore heavies moving by saltation with lights could tend to be smaller than the predicted settling velocity and these heavies are shielded to from current by larger Quartz grains. Thus the heavies lag behind the larger quartz. Hence in the Kayamkulam estuarine sediment the decrease of heavy mineral both in the grades in the down stream especially in the southern and central region may be due to non entrainment by low energy currents subsequent deposition and protection by the coarse, light minerals. More over the smallest lighter minerals cannot settle in the place where a heavy mineral on the same size settle by the currents due to their density differences. The lighter minerals are transported and deposited further down stream. Also heavies did not move with the same frequency that of quartz.

Among the various factors which affect the total heavy minerals and down stream mineralogical variation, the most important factors are selective weathering, differential or selective abrasion and selective sorting of minerals according to size and density for the down stream variations of the heavy minerals of Kayamkulam estuarine sediments size was not taken into consideration since the heavy minerals were estimated only for two size grades and not in the bulk samples.

It is an accepted fact that selective removal of heavy minerals occurs as a result of sub aerial weathering or due to post depositional as evidenced by the decrease in the unstable minerals result of the present heavy mineral study shows the decrease of less stable minerals such as amphiboles. Change of heavy minerals composition in a unidirectional flow may theoretically be attributed to particle size reduction, changes in the average hydraulic condition and difference of tributary supply. The decreasing percentage direction of transport can also be explained in terms of particle reduction such selective abrasion could result in progressive and systematic illumination of softer and more durable minerals and complementary enrichment of harder and more durable minerals. The present study an increase of opaque and garnet and decrease of relative unstable minerals noticed reveals that selective abrasion has taking place. The above conclusion is drawn from the order of durability of most the abundant heavy mineral as given by Dana (1960) which have in the order, Garnet, Opaques, Amphibole and Pyroxene. The increase or decrease in heavy mineral content depends on sorting based on density and size. Such selective sorting involves the lagging behind certain constituents owing to a high specific gravity, large size or low spherucity. That is minerals of lower density, smaller size, and larger surface area may travel more rapidly than the associated minerals. In the direction of the currents increase in the content of garnet and zircon and decrease of opaques in the direction of transport indicates a selective sorting in the northern sector this can be due to the tidal effect.

From the above discussion it can be concluded that selective weathering has played a prominent role in the variation of heavy minerals assemblages followed by progressive sorting of heavy minerals.

4.4 Provenance

The probable source form, which the heavy minerals have been liberated, can be inferred from the heavy mineral assemblages and their relative abundances. From the relative abundance of the heavy mineral and their assemblages, the probable source rock for the heavy minerals in the sediments of the Kayamkulam estuary is assimilated.

The drainage basin of the Pallikkal thodu, Krishnapuram Ar and Thrikkunnapuzha empting into the Kayamkulam estuary are mainly consist of Khondalite, Charnockite, Garnetiferrous Quartzo Feldspethic gneiss of Which Khondalite and Charnockite are widely spread out. Khondalite is a garnetiferous Sillimanite gneiss with graphite rich in garnet and Sillimanite. Colourless to pale pink garnet is characteristic of Khondalite, pink of Charnockite and deep brown to deep pink garnet is characteristic of gneissic rocks. (Mallik, 1968). Prismatic character of sillimanite suggests its deviation from Khondalite. Zircon may be derived from a variety of rocks and probable source can be inferred from the morphological characters. Rounded and sub rounded zircons showing overgrowth are characteristic of derivation from Khondalite, charnockite and gneissic rock respectively. Hornblende may be derived from igneous and metamorphic rocks and bluish to bluish green hornblende is typical of high-grade metamorphic rock. Van Andel and Poole (1960) have pointed out that the bluish green hornblende is characteristic of metamorphic provenance. Monazite has been derived from charnockite and Khondalite and hypersthene from charnockite.

From the heavy minerals study it can be concluded that the major heavy mineral constituent are opaques, Garnet, zircon and pyroxene, which reveal that, the terrain comprises of Khondalite, Charnockite and gneisses. Abundance of garnet and greenish amphibole reflects the contribution from high-grade metamorphic rocks.

4.5 CLAY MINERALS

Clay minerals that constitute a major part of the fine fractions of the sediments are reactive responds of geologic materials, which characterize certain environment prevailing at a particular time. Therefore clay mineral composition of the sediment are of vital important so as to unravel the condition which they are deposit and also to elucidate the relating environment. The composition and distribution of the clay, minerals have been used as the indicators of sediment dispersion in marine environment and also the mineralogy can be used in delineating the fine grained sediment dispersal and current patterns (Biscaye 1965, Griffiths,1979). Thus the study on the clays and clay minerals are of high significance to obtain a complete understanding of the origin and the environment of the sediment.

Taggart and Kaiser (1960), Subba Rao (1963), Al-Mussawy and Basi, (1993) has stressed on the importance of the source area and its climate which controls the type of clay minerals rather than the environmental conditions of deposition, while Nelson (1959), Naidu (1968), Amorosi, et al. (2001) place emphasis on the process of the environmental digenesis of clays. The importance of the depositional environment of the clay mineral distribution has been stressed by Weaver (1959),while has brought out a comprehensive discussion on the environmental aspects of the clay minerals (Amorosi, et al. 2001).

Clay mineralogical investigations has been carried out for the sediments of Chilka, Pulicat, Kolleru lakes, Iskappalli lagoon, Vembanad estuary, Ashtamudy estuary by (Subba Rao, 1985; Sajan 1986-88; Padmalal, 1992).

4.5.1 Result and Discussion

Table 4.4 provide the results of the clay mineral analysis carried out for the Kayamkulam estuarine sediments for the three sectors. The various clay minerals identified from these segments are montmorillonite, kaolinite and illite. montmorillonite is the most abundant clay mineral present all through the estuary followed by kaolinite and illite and hence not discussed sector wise.

Many researchers consider that the clay mineral content in the sediments is detrital by origin, reflecting the characters of the source material. Where there is very little change in the depositional environment, which is due to differential flocculation and/or size segregation (physical sorting). Grim (1953) explained that the environmental digenesis is the reason for the clay mineral variation stating that once clay mineral enter into saline water, they are no longer in equilibrium with seawater and will undergo partial or complete chemical transformation to take up more stable phase.

Table: 4.4 Percentages of Clay minerals of the Kayamkulam estuary for the Pre and Post Monsoon Seasons

	Sample No.	Kaolinite	Montmorillonite (Smectite)	Illite	Sample No.	Kaolinite	Montmorillonite (Smectite)	Illite
	POST MONSOON				PRE MONSOON			
	2	31.56	63.01	5.43	2	32.14	57.87	9.99
	4	33.62	57.77	8.61	4	30.37	62.53	7.10
N	6	25.25	68.73	6.02	6	27.85	65.22	6.93
	10	11.63	81.19	7.18	10	20.16	70.84	9.00
	Average	**25.52**	**67.68**	**6.81**	**Average**	**27.63**	**64.12**	**8.26**
	13	11.42	85.33	3.23	13	18.67	76.46	4.87
	15	2.49	93.59	3.91	15	10.38	80.62	9.38
C	17	14.34	75.06	10.60	17	20.46	72.35	7.19
	20	25.11	69.34	5.55	20	27.27	69.78	2.95
	Average	**13.34**	**80.83**	**5.82**	**Average**	**19.20**	**74.80**	**6.10**
	22	32.07	60.00	7.93	22	32.07	57.87	10.06
	24	37.27	55.35	7.38	24	30.46	58.76	10.78
S	27	45.13	51.65	3.22	27	40.58	54.25	5.17
	29	53.75	44.28	1.97	29	49.21	42.86	7.93
	Average	**42.06**	**52.82**	**5.13**	**Average**	**38.08**	**53.44**	**8.49**

Higher proportions of the montmorillonite reflected all throughout the estuary could be explained in terms of relatively small drainage basin of Kaymkulam estuary with undefined canals draining the area, differences of energy in various environments, size segregation of minerals and cation absorption. Higher proportions of montmorillonite with little amount of kaolinite can also be explained due to the off shore sediments being transported in to the estuary by the tidal currents, which may be purely representative of the assemblage of immediate off shore sediments. Fluvially induced currents are only of short duration in the estuary as only few undefined canals/stream flow in to the estuary. Therefore the tidal circulation is the major process of sediment distribution in the Kayamkulam lake. A part of the offshore sediment rich in montmorillonite brought in suspension of the incoming tidal currents gets deposited in the inner part of the lake when the tidal currents lose their velocity they move into relatively deeper part of the lake reflecting the estuarine mixing process/estuarine circulation dynamics. A similar observation has been reported for Solvent estuarine system (Algan et al., 1994) and James river estuary.

The low content of illite indicate that drainage contributes some amounts of the degraded illite, which might be formed due to the preferential stripping of potassium from illite by plants. This degraded illite absorbs more and more potassium and become well crystallized so as to enrich the percentage. High liquid and particulate matter discharge during the monsoon generally enhance the illite content (Pujos et al., 1997). But such a phenomenon has not observed in the present study, which again rule out the diagenitic changes.

Kaolinite being the second dominating clay mineral in the estuarine sediments reflecting a greater intensity of lateritic weathering at the source rock. Kaolinite is the stable product of the laterisation or latrosols produced by deep tropical weathering (Biscaye 1964; Bhukhari and Nayak, 1996). Therefore the kaolinite can be considered as to be formed under tropical weathering of lateritic soil or laterite in the small drainage basin of the Kaymkulam estuary reflecting the source. The low content of kaolinite may be due to the high content of the calcium in the sediments, which favours the formation of smectite. The low content of kaolinite and presence of amphiboles in traces may be due to the unfavourable climatic and physico chemical conditions as well as to the rapid transport and deposition of freshly weathered material (Pehlivanoglou et al., 2000). Hence the high content of the montmorillonite can also be explained in the light of high content of calcium in the study area. Decrease in the kaolinite and increase in the montmorillonite towards the bar mouth (central sector) can also be explained on the differential settling velocities of clay minerals. According to the theory on the differential settling velocities of clay minerals in waters of increasing salinity are in the following order: illite, chlorite, kaolnite and montmorillonite. Therefore illite and kaolinite are flocculated earlier than montmorillonite and get deposited near shore, whereas montmorillonite will deposit seaward. The above finding is accordance with Whitehouse et al., (1960); Mohan and Damodaran, (1992). The high content of montmorillonite and low content of the kaolintie in the estuarine sediments of the Kayakulam estuary can also be explained by size segregation theory Gibbs (1977) explained the lateral clay mineral variation based upon size segregation theory, according to which montmorillonite are having smallest particle size and hence are deposited seaward. Kaolinite has the intermediate size while 10 A° micas are the greater size. Therefore it can be concluded that the high content of montmorillonite and low content of the kaolinite in the study area can be due the size segregation.

Local conditions can interfere favouring the formation of other minerals like montmorillonite even in tropics where intense weathering conditions typically favours the formation of silica and base poor minerals like kaolinite (Biscaye 1964). In an alternating wet and dry climate montmorillonite develops at the expense of kaolinite in the drainage basin. Therefore high content of montmorillonite in the study can also be explained in terms of above observation. A large seasonal oscillation in interstitial pH and Eh probably contributes to rapid clay transformation.

The digenetic change may possibly reduce the montmorillonite content as it passes from the river confluence. The montmorillonite derived from the drainage basin might have been changed to iliite as it have a expanded lattice, significant inclination for base exchange and ion absorption. Hence, the illite under the area of observation was formed by the transference of montmorillonite due the base exchange and ion absorption. Edzwalds et al., (1974) observed a decreasing trend in kaolinite from upper estuary towards the sea for the Palmeico estuary and explained this in terms of equilibrium condition with the environment, which support the view, that kaolinite stable in acidic and unstable in alkaline environment. The decrease in the content of kaolinite from northern and southern segments to the central segment can be explained in the above line of observation.

From the above discussion it is clear that clay mineral in the Kayamkulam estuary are controlled primarily by source, physical sorting, size segregation, conditions of prevailing environment and absorptions of ions besides estuarine circulation dynamics.

CHAPTER V

GEOCHEMISTRY

5.1 INTRODUCTION

Geochemistry deals with the distribution and migration of geochemical signals within the earth in space and time. The history of geochemistry naturally includes much of the history of chemistry and geology. In recent years, decisive breakthrough in the study of sediment geochemistry has been recorded, which led to a better understanding of the fluvial processes. The transport phases of elements are generally controlled by the size spectrum of clastic sediments in aqueous environments.

The estuarine environments are not simply areas in which there are direct transports of material between the continents and the oceans. The initial transfer takes place in estuaries, and it is here that the first reaction exchange of elements occurs between fresh water and seawater, and their associated solids. Both major and minor elements take part in estuarine chemical transactions involving dissolved and particulate phases. The variation of major and trace elements in the sediments are the reflections of the various factors, which ultimately govern their distribution.

Trace elements are introduced into estuaries in two principal forms, viz; those associated with solid and colloidal material and those in solution. Trace elements may be removed from solution by a number of processes, which include adsorption into inorganic and organic detritus, extraction by organisms and by precipitants like Fe and Mn oxides. The studies reveal that although some elements may be desorbed from river borne detritus on meeting with saline waters, adsorption also possible under peculiar conditions. One important adsorption mechanism operative in the removal of trace elements from solution during estuarine mixing is the formation of iron oxide coatings on clay particles, which have acted as negatively charged nuclei for the adsorption of hydrolysis products of iron. Oxides of iron and manganese are very efficient scavengers of trace elements. Goldberg (1954), Jenne (1968), and Aston and Chester (1973), Sajan (1992), Padmalal and Seralathan, (1995) have suggested that the oxide coating formed on detrital particles in estuaries may remove trace elements from over lying water column.

Geochemical data of surfical environments may reflect the influence of several factors including the source characteristics. Chemical elements in estuarine sediments may be found as constituents of primary rock-forming minerals, minerals formed during weathering, minerals typical of mineralisation, ions adsorbed onto colloidal particles and clays and in combination with organic matter (Rose, 1975). The annual riverine input of a trace element to the oceans must be equal to the output of that element associated with marine sediments. Bed load sediment discharge is deemed to represent not more than 10% of the suspended load (Meade, 1981) but the data substantiating this estimate are still fragmentary, (Milliman and Meade,1983 and Albarede and Semhi, 1995). Geochemists have extensively studied the major rivers of the world in order to estimate fluxes of continental material supplied to the oceans, (Potter, 1978; and Meybeck 1988).

Investigations on the geochemical behaviour of recently deposited sediments in various aquatic environments have become an important area of scientific studies, as these studies can give enough information on anthropogenic pollutions. Further such studies can throw light into the hidden resources and also the natural processes operating with in these environments.

5.2 REVIEW OF LITERATURE

Many studies have been carried out world over to understand the geochemical behaviour of elements moving form land to sea through various fluvial systems. Metal distributions along the Goeksu River and its delta show that there is an increase in Na, K, Co, and Ni concentrations seaward. The increase of these elements in marine sediments is due to sorption from seawater onto particulate matter. Correlation analysis applied to the composition on the river Goeksu sediments reveals Al, Fe, and K as components of the carrier substance. One, therefore, expects the major component of the carrier substance to be clay minerals known to occur in Goeksu Valley (Sanin, et al., 1992). Trace metals in the aquatic environment are generally concentrated on solid geochemical phases that eventually become incorporated into estuarine and marine sediments. The mechanism of trace metal concentration is believed to be adsorption on various geochemical phases such as hydrous metal oxides, clays and organic matter. Sediment metal (Ag, Cu, Fe, Ni, Pb, and Zn) concentrations varied widely reflecting differences in sediment grain size, with higher metal concentrations located in the fine-grained and have high spatial variability (Breslin et al.,1999; Zhang et al., 2002).

The elemental concentration of sediments not only depends on anthropogenic and lithogenic sources, but also upon the textural characteristics, organic matter content, mineralogical composition and depositional environment of sediments (Presely and Trefry,1980). It is generally believed that metals are associated with smaller grain size particles (Whitney 1975; Gibbs 1977; Biksham et al., 1991). In addition, the grain size distribution of sediments may show spatial heterogeneity, so that a wide range in heavy metal concentration may be found. Several studies have indicated that in environments, where grain size distribution varies considerably, valid comparisons of metal concentrations cannot be made without a correction for grain size effect (De Groot et al., 1982; Forstner and Wittmann 1983). Ujevic et al.,(1998) while working on the relationship between Mn, Cr, Pb and Cd concentrations, granulometric composition and organic matter content in the marine sediments from a contaminated coastal area observed a high correlation between Pb and Cr concentrations, and organic matter content and the percentage fine size fractions. Cadmium and Mn are not related either to organic matter or to granulometric composition. But Gnandi and Tobschall, (1999) observed a positive correlation for Cd, Sr and Zn with grain size and an inverse relationship with Cr, Cu and Ni for the marine coastal sediments of Togo.

Albarede and Semhi (1995) carried out geochemical investigation on three sand size fractions from the Meurthe river and its tributaries and brought out the tight control of the bedrock geology on the geochemistry of the bedload. Vital et al., (1999) successfully utilized clay as well as heavy mineral fractions to deduce provenance. Based on the results of the study on geochemistry of sediments of lowermost Amazon River, Vital and Stattegger (2000) opined that chemical weathering processes strongly modify original sediment composition and can be recognized on the basis of their geochemical signature. The natural occurrence of metals in the environment complicates assessments of potentially contaminated marine sediments because measurable quantities of metals do not automatically infer anthropogenic enrichment (Schiff and Weisberg, 1999).

Murthy and Veerayya (1972 and 1981) made a preliminary investigation on organic carbon and trace element contents in the bulk sediments of Vembanad lake. The geochemistry of sediments of the Indian rivers has received wide attention in the recent past to understand the elemental composition of the sediments, the influence of anthropogenic activities on riverine chemistry and the transport of metals from rivers to the coastal oceans (Borole et al., 1982; Subramanian et al., 1985; Seralathan, 1987; Ramesh et al., 1990; Biksham et al., 1991; Jha et al., 1990; Konhauser et al., 1997 and Singh, 1999). A comprehensive review of environmental geochemistry of Indian river basins is that of Subramanian (1987). Mass transfer studies of geochemical constituents in Indian rivers have been carried out by researchers like Subramanian (1980), Sarin and Krishnaswami (1984), Sitasawad (1984), Seralathan and

Seetharamaswamy (1987), Chakrapani and Subramanian (1990). The geochemical transfer of metals through Cauvery river has been investigated by Subramanian et al. (1985) and Seralathan (1987). The mineralogical and geochemical association of metals in the Krishna river sediments has been studied by Ramesh et al. (1989, 1990). Mallik and Suchindan (1984) and Padmalal (1992) analysed a few major and trace metal in the sediments of Vembanad estuary and Muvattupuzha river and Central Vembanad estuary respectively to ascertain the relation with granulometry. Desorption from fresh water clay minerals and control of Fe and Mn oxides over the trace elements in the estuarine region has documented by (Seralathan, 1987).

The distribution of Si, Al, Fe, Mn, Cu, Zn, Ni, and Cr in different grain size fractions and geochemical association of Fe, Mn, Cu, and Zn with less than 63μm size fraction of bed sediments of Damodar river shows, concentrations of trace metals tend to increase as the size fractions become finer. The exchangeable fraction of the Damodar river sediments contains very low amounts of trace metals suggesting poor bioavailability of metals (Singh, 1999). The main processes that determine the behaviour of heavy metals in the Scheldt estuary are tidal hydrodynamics, sediment transport, and sorption of heavy metals on suspended matter (Babi et al.,1998). Their studies on calculated profiles of dissolved and sorbed concentrations of heavy metals in the water column indicated an accumulation of heavy metals in the zone of the turbidity maximum, while closer to the sea the concentrations diminish due to mixing of the polluted fluvial sediments with unpolluted marine sediments and came out with a conclusion that only a small part of the heavy metals reaches the sea. It was not possible to predict sediment areas with the highest levels of metal contamination using visual criteria or knowledge of the erosion and sedimentation pattern of the river (Bervoets et al., 1999). The Clyde and Firth estuaries of U.K. are identified as to be the most contaminated areas, where the trace metal concentrations in these estuaries are more closely related to those of aluminium than to organic carbon or the less than 63μm size fraction (Balls, et al., 1997).

Marine geochemists frequently utilize various methods of sequential extraction to ascertain the origin and behaviour of trace metals associated with coastal marine sediments. The main objective is to test the potential mobility/stability of particulate metals in the natural environments (Latouche et al.,1993). The speciation of heavy metals in the aquatic environment has received considerable attention recently (Chen et al, 1976; Hong and Forstner, 1984 ; Rapin, 1984 and Li et al., 2000). These studies throw light on two aspects: 1) their levels in the environment and 2) their fractionation in different phases. The investigations provide information on the mobility of the metal and bioavailability factors, and also highlight the role of processes such as sorption, diffusion and mobilization in controlling the concentration of metals in sediments (Calmano and Forstner, 1983). *Rapin (1984) is of opinion that sequential* extraction procedures would provide information on the history of metal inputs, diagenetic transformation within the sediments and the reactivity of heavy metal species of both natural and anthropogenic origin. Earlier studies on heavy metals were confined to the partitioning of metals into detritus and nondetrital fractions (Gad and Lerich, 1966).

5.3 RESULTS AND DISCUSSION

5.3.1 Geochemistry of the major constituents

The result of the geochemical investigations and their relative abundance in the Kayamkulam estuarine sediments for the Pre and Post monsoon periods are in the Table. 5.1 a and b. The geochemical distribution and the elemental geochemistry of the various major elements have been discussed in relation to the prevailing physico chemical conditions of depositional environment and the clay minerals. The result of the inter elemental correlation matrix is provided in Tables 5.2 a - d. The interelemental correlation matrix is determined to ascertain the relation between elements if any and their behaviour pattern. Likewise the same results can be used as an effective tool for demarcating the souls of maximum and minimum variation. Surface plots (Fig.5.1 a and b) were drawn for the major constituents in the bulk and clay fractions for the pre and post monsoons to access their aerial distribution. Similarly scatter plots were also drawn so as to know their coexistence covariance (Fig.5.1 c - h).

5.3.1a Organic carbon

Study of organic carbon in aquatic environment is an important area of investigation, which can throw light on the biogeochemical cycling, ecosystem energy and storage, and transport of pollutants. Transport of land derived carbon

Table 5.1a CONCENTRATION OF C-ORG, CARBONATE AND MAJOR ELEMENTS (%) IN THE BULK SEDIMENTS OF KAYAMKULAM ESTUARY

		PRE MONSOON								POST MONSOON							
	Sample No.	C-org	Carbonate	Na	K	Ca	Mg	Fe	Mn (ppm)	C-org	Carbonate	Na	K	Ca	Mg	Fe	Mn (ppm)
	1	3.47	7	1.04	0.90	1.16	0.09	0.56	222	2.46	4	1.32	1.00	1.37	0.12	0.56	181
	2	3.69	6	1.16	0.78	1.16	0.10	0.54	222	2.05	6	1.08	1.06	1.26	0.16	0.46	191
	3	3.31	7	1.04	0.94	1.11	0.10	0.52	228	2.22	3	1.06	0.88	1.00	0.11	0.44	276
	4	1.40	7	0.54	0.62	0.74	0.07	0.33	185	2.05	2	1.10	0.52	0.68	0.03	0.10	91
	5	1.71	8	0.56	0.60	0.69	0.07	0.35	200	1.90	2	0.66	0.54	0.68	0.05	0.22	145
N	*6*	2.57	8	0.56	0.58	0.63	0.06	0.30	174	1.55	3	1.44	0.92	1.21	0.14	0.47	294
	7	2.30	8	0.88	0.98	1.00	0.18	0.50	307	1.25	3	0.88	0.44	0.68	0.03	0.10	97
	8	2.71	6	0.78	0.26	0.63	0.01	0.13	131	0.82	5	1.04	0.82	0.89	0.15	0.32	178
	9	1.57	9	1.02	1.20	1.05	0.18	0.46	276	1.40	3	0.94	0.88	1.05	0.11	0.30	174
	10	2.05	7	1.42	1.24	1.32	0.20	0.49	306	1.60	1	0.24	0.20	0.58	0.07	0.14	97
	Average	**2.48**	**7**	**0.90**	**0.81**	**0.95**	**0.11**	**0.42**	**225**	**1.73**	**3**	**0.98**	**0.73**	**0.94**	**0.10**	**0.31**	**172**
	11	2.10	8	1.22	1.32	1.47	0.27	0.63	295	1.07	1	1.84	1.30	2.16	0.13	0.24	284
	12	1.53	8	1.56	1.48	2.26	0.13	0.32	310	1.90	2	1.34	1.36	1.63	0.16	0.39	249
	13	1.47	11	1.58	1.36	2.50	0.14	0.33	300	2.50	6	1.52	1.38	1.82	0.19	0.41	200
	14	1.15	18	1.40	1.38	1.79	0.26	0.52	346	3.37	12	1.72	1.44	2.05	0.23	0.43	249
	15	1.50	13	1.22	0.14	3.00	0.03	0.32	400	2.45	15	1.80	0.14	2.63	0.03	0.13	173
C	*16*	3.41	4	1.30	1.18	1.37	0.20	0.49	281	3.20	7	1.62	1.48	2.32	0.25	0.47	277
	17	4.52	9	1.00	1.06	0.95	0.12	0.17	202	3.45	1	1.08	1.00	1.11	0.19	0.52	268
	18	4.98	14	1.50	1.22	1.11	0.21	0.45	238	2.60	3	0.62	0.22	0.58	0.04	0.13	107
	19	4.03	13	1.42	1.06	1.16	0.19	0.43	244	1.30	2	0.64	0.62	0.58	0.09	0.19	130
	20	3.34	12	0.78	0.88	1.00	0.08	0.39	314	0.99	3	0.70	0.62	0.68	0.05	0.15	114
	Average	**2.80**	**11**	**1.30**	**1.11**	**1.66**	**0.16**	**0.41**	**293**	**2.28**	**5**	**1.29**	**0.96**	**1.56**	**0.14**	**0.31**	**205**
	21	1.48	3	0.82	0.36	0.63	0.05	0.21	166	3.10	6	0.36	0.46	0.58	0.06	0.24	171
	22	1.33	5	0.80	0.56	0.77	0.06	0.10	200	2.80	3	0.40	0.28	0.62	0.05	0.13	170
	23	1.23	8	0.94	0.62	0.89	0.08	0.43	181	1.64	2	0.54	0.08	0.89	0.03	0.17	186
	24	1.52	7	0.52	0.70	0.84	0.08	0.42	363	1.60	2	0.92	0.90	1.16	0.06	0.52	159
	25	1.16	9	1.00	0.38	0.68	0.03	0.19	238	1.50	1	0.62	0.20	0.32	0.02	0.15	58
S	*26*	1.26	10	0.94	0.86	1.00	0.07	0.41	265	1.31	1	0.74	0.68	0.68	0.05	0.26	122
	27	1.31	9	0.62	0.26	0.47	0.06	0.54	276	1.00	1	0.82	0.60	1.00	0.04	0.25	204
	28	1.15	11	0.72	0.76	1.21	0.03	0.50	216	1.15	1	0.26	0.30	0.42	0.07	0.16	213
	29	0.79	7	0.94	0.26	0.47	0.03	0.19	277	1.05	10	1.32	0.86	1.00	0.06	0.41	185
	30	0.66	6	0.78	0.72	1.16	0.06	0.54	91	1.00	4	0.78	0.38	0.84	0.06	0.37	104
	31	1.48	7	0.88	0.80	1.00	0.10	0.48	191	0.49	3	1.32	0.86	1.37	0.12	0.48	260
	Average	**1.22**	**7**	**0.81**	**0.57**	**0.83**	**0.06**	**0.36**	**224**	**1.51**	**3.09**	**0.73**	**0.51**	**0.81**	**0.06**	**0.29**	**167**

* N - NORTHERN SECTOR, C - CENTRAL SECTOR, S - SOUTHERN SECTOR

Table: 5.1b CONCENTRATION OF C-ORG, CARBONATE AND MAJOR ELEMENTS (%) IN THE CLAY SEDIMENTS OF KAYAMKULAM ESTUARY

		PRE MONSOON							POST MONSOON						
	Sample No.	C-org	Na	K	Ca	Mg	Fe	Mn (%)	C-org	Na	K	Ca	Mg	Fe	Mn (%)
	1	4.67	0.4	0.7	1.2	0.62	4.81	83	1.63	1.0	0.96	1.6	0.56	5.56	109
	2	8.49	0.4	0.8	1.4	0.47	4.10	92	8.34	0.4	0.96	1.6	0.99	4.88	117
	3	5.43	0.4	0.8	1.4	0.48	3.71	86	4.35	0.3	0.97	2.2	0.92	4.96	100
	4	3.14	0.4	0.7	1.6	0.52	3.52	52	1.39	2.0	0.98	2.4	0.89	5.65	143
	5	3.40	0.4	0.8	1.4	0.58	3.71	91	4.17	1.6	0.94	2.0	0.62	4.55	114
N	6	1.70	0.4	1.0	2.8	0.71	5.16	118	9.95	1.0	1.08	2.4	0.75	5.96	109
	7	11.30	1.2	0.8	3.6	0.84	4.53	106	3.53	5.8	0.64	5.0	1.08	2.71	179
	8	6.24	4.0	0.6	7.6	1.19	3.49	193	5.89	2.0	1.04	2.6	1.19	4.56	108
	9	6.88	1.6	0.8	4.4	1.16	4.11	96	3.70	2.4	0.92	3.0	1.50	4.73	164
	10	1.95	3.6	0.9	6.4	1.67	4.23	150	1.99	1.0	0.84	1.8	1.88	5.83	225
	Average	**5.32**	**1.3**	**0.8**	**3.2**	**0.83**	**4.14**	**107**	**4.49**	**1.8**	**0.933**	**2.5**	**1.04**	**4.94**	**137**
	11	9.68	2.6	0.9	4.8	1.95	5.64	184	8.84	5.0	0.72	4.4	1.21	2.31	140
	12	6.96	1.6	0.9	5.4	2.41	6.50	227	5.20	1.6	0.96	2.8	1.83	5.62	181
	13	1.15	1.8	0.9	5.8	2.25	5.82	190	0.85	2.4	0.52	4.8	2.74	4.74	110
	14	5.27	2.4	0.8	6.6	2.15	5.13	170	2.25	2.8	0.88	5.2	2.34	5.11	197
	15	0.85	0.9	0.3	6.2	2.63	4.30	115	0.17	2.8	0.9	5.4	2.28	5.01	200
C	16	5.86	1.6	0.9	5.2	2.24	5.84	179	1.21	2.8	0.9	4.4	2.15	4.92	183
	17	4.67	0.2	0.9	3.6	1.10	5.32	94	2.66	1.2	0.86	2.6	0.87	5.39	123
	18	3.06	3.4	0.8	4.4	1.78	5.16	174	1.73	2.4	0.72	4.6	2.18	4.21	205
	19	1.78	2.6	0.7	5.6	1.82	4.81	190	3.55	1.4	0.86	2.4	1.98	5.62	194
	20	4.33	4.4	0.6	5.6	1.15	3.18	131	3.29	1.0	0.74	3.6	1.41	5.14	170
	Average	**4.36**	**2.1**	**0.8**	**5.3**	**1.95**	**5.17**	**165**	**2.98**	**2.34**	**0.81**	**4.02**	**1.90**	**4.81**	**170**
	21	4.33	2.0	0.8	5.0	1.25	4.31	143	3.55	2.0	0.7	2.6	1.25	4.35	130
	22	3.90	2.8	0.7	5.4	1.04	4.37	120	1.21	2.6	0.6	4.4	1.10	4.01	100
	23	3.31	4.6	0.5	7.0	0.67	3.26	118	1.47	3.6	0.52	4.8	0.99	3.47	105
	24	12.40	0.4	0.6	4.2	0.43	3.35	59	4.55	1.0	0.76	1.8	0.40	3.61	54
	25	3.06	1.4	0.5	4.0	0.71	4.40	225	0.09	6.2	0.42	5.0	0.82	2.15	217
S	26	1.51	4.0	0.4	4.4	0.38	3.68	78	4.41	1.8	0.56	5.2	0.45	3.39	58
	27	1.44	2.0	0.5	5.2	0.54	3.12	135	1.39	2.4	0.56	2.6	0.39	3.90	188
	28	1.53	2.6	0.4	6.4	0.48	4.09	84	2.17	0.4	0.52	1.8	0.56	7.11	324
	29	2.80	0.8	0.5	1.6	0.62	5.79	171	3.20	1.2	0.52	2.0	0.43	6.23	170
	30	2.75	1.6	0.5	2.0	0.42	5.20	96	4.85	0.2	0.56	1.4	0.39	5.39	90
	31	2.80	1.6	0.6	1.6	0.43	5.81	116	8.15	0.2	0.5	1.6	0.39	5.95	93
	Average	**3.62**	**2.2**	**0.5**	**4.3**	**0.63**	**4.31**	**122**	**3.19**	**1.96**	**0.57**	**3.02**	**0.65**	**4.50**	**139**

* N - NORTHERN SECTOR, C - CENTRAL SECTOR, S - SOUTHERN SECTOR

Table 5.2a Inter-elemental correlation matrix for thebulk sediments of Kayamkulam estuary (Pre monsoon)

	C-org	Carbonate	Fe	Na	K	Ca	Mg	Mn	Zn	Cu	Cr	Co	Ni	Pb	Cd
C-org	1.000														
Carbonate	0.114	1.000													
Fe	0.109	0.190	1.000												
Na	0.306	0.388	0.195	1.000											
K	0.324	0.302	0.459	0.668	1.000										
Ca	-0.039	0.429	0.193	0.684	0.424	1.000									
Mg	0.345	0.334	0.531	0.658	0.844	0.326	1.000								
Mn	-0.049	0.478	0.221	0.414	0.304	0.561	0.388	1.000							
Zn	-0.144	-0.177	0.125	-0.310	-0.032	-0.034	-0.118	-0.108	1.000						
Cu	0.268	-0.126	0.292	-0.228	0.167	-0.234	0.084	-0.291	0.499	1.000					
Cr	0.123	0.402	0.572	0.433	0.569	0.495	0.544	0.320	-0.141	0.130	1.000				
Co	0.129	0.049	0.618	0.094	0.434	0.108	0.307	-0.114	-0.111	0.466	0.702	1.000			
Ni	0.128	0.008	0.479	-0.028	0.144	-0.081	0.234	-0.129	-0.158	0.215	0.514	0.689	1.000		
Pb	-0.080	-0.106	0.319	-0.120	-0.073	-0.128	-0.084	-0.058	0.259	0.526	0.231	0.341	0.227	1.000	
Cd	0.205	-0.206	0.363	0.147	0.374	0.029	0.373	-0.205	0.096	0.513	0.340	0.633	0.610	0.358	1.000

Table: 5.2 b Inter-elemental correlation matrix for the bulk Sediments of Kayamkulam estuary (Post Monsoon)

	C-org	Carbonate	Fe	Na	K	Ca	Mg	Mn	Zn	Cu	Cr	Co	Ni	Pb	Cd
C-org	1.000														
Carbonate	0.366	1.000													
Fe	0.197	0.170	1.000												
Na	0.179	0.546	0.518	1.000											
K	0.227	0.186	0.739	0.717	1.000										
Ca	0.317	0.609	0.432	0.893	0.626	1.000									
Mg	0.402	0.250	0.697	0.602	0.872	0.602	1.000								
Mn	0.229	0.163	0.625	0.588	0.668	0.613	0.701	1.000							
Zn	0.075	-0.006	0.357	0.118	0.095	0.013	0.016	-0.005	1.000						
Cu	0.062	-0.027	0.811	0.343	0.521	0.224	0.433	0.472	0.463	1.000					
Cr	0.113	0.280	0.825	0.714	0.789	0.699	0.758	0.781	0.187	0.732	1.000				
Co	-0.013	0.072	0.484	0.395	0.410	0.238	0.346	0.383	0.436	0.449	0.500	1.000			
Ni	0.116	0.023	0.850	0.527	0.632	0.379	0.580	0.657	0.470	0.804	0.792	0.623	1.000		
Pb	0.001	-0.031	0.383	0.456	0.396	0.239	0.223	0.274	0.399	0.511	0.434	0.175	0.538	1.000	
Cd	0.104	0.108	0.417	0.434	0.417	0.396	0.532	0.594	-0.156	0.273	0.442	0.112	0.363	0.181	1.000

Table 5.2 c Inter- elemental correlation matrix for the clay fraction (Pre Monsoon)

	C-org	Fe	Na	Ca	K	Mg	Mn	Zn	Cu	Cr	Co	Ni	Pb	Cd
C-org	1.000													
Fe	-0.008	1.000												
Na	-0.209	-0.235	1.000											
Ca	-0.095	-0.121	0.708	1.000										
K	0.343	0.413	-0.255	-0.136	1.000									
Mg	-0.021	0.490	0.194	0.573	0.314	1.000								
Mn	-0.084	0.506	0.329	0.463	0.187	0.641	1.000							
Zn	-0.163	0.009	-0.150	-0.374	-0.243	-0.415	-0.222	1.000						
Cu	0.030	-0.377	-0.086	-0.374	-0.245	-0.635	-0.429	0.692	1.000					
Cr	-0.113	0.523	0.243	0.335	0.141	0.383	0.419	-0.139	-0.374	1.000				
Co	0.039	0.063	-0.558	-0.643	-0.176	-0.640	-0.226	0.470	0.426	-0.066	1.000			
Ni	-0.051	0.176	-0.331	-0.550	-0.186	-0.503	-0.258	0.783	0.555	0.036	0.762	1.000		
Pb	0.048	0.232	-0.680	-0.553	0.103	-0.221	-0.150	0.062	0.115	-0.044	0.556	0.269	1.000	
Cd	-0.069	0.237	-0.567	-0.415	-0.063	-0.091	-0.004	0.205	0.182	-0.217	0.565	0.258	0.661	1.000

Table: 5.2 d Inter-elemental correlation matrix for the clay fraction (Post Monsoon)

	C-org	Fe	Na	K	Ca	Mg	Mn	Zn	Cu	Cr	Co	Ni	Pb	Cd
C-org	1.000													
Fe	0.062	1.000												
Na	-0.285	-0.784	1.000											
K	0.275	0.304	-0.276	1.000										
Ca	-0.391	-0.597	0.753	-0.263	1.000									
Mg	-0.325	0.036	0.234	0.246	0.514	1.000								
Mn	-0.402	0.246	0.212	-0.097	0.130	0.353	1.000							
Zn	-0.068	0.144	-0.075	-0.136	-0.128	-0.267	0.144	1.000						
Cu	0.096	0.190	-0.219	-0.117	-0.335	-0.276	-0.029	0.249	1.000					
Cr	-0.223	0.417	-0.369	0.165	-0.245	0.053	0.250	0.361	-0.287	1.000				
Co	0.157	0.525	-0.529	0.064	-0.355	0.101	-0.148	-0.290	0.215	-0.239	1.000			
Ni	0.048	0.459	-0.606	0.068	-0.518	-0.282	-0.069	0.397	-0.153	0.800	0.034	1.000		
Pb	0.169	0.337	-0.535	0.072	-0.592	-0.622	-0.207	0.246	-0.053	0.503	0.012	0.700	1.000	
Cd	0.370	-0.024	-0.053	0.008	-0.011	0.233	-0.235	-0.475	0.222	-0.670	0.647	-0.469	-0.389	1.000

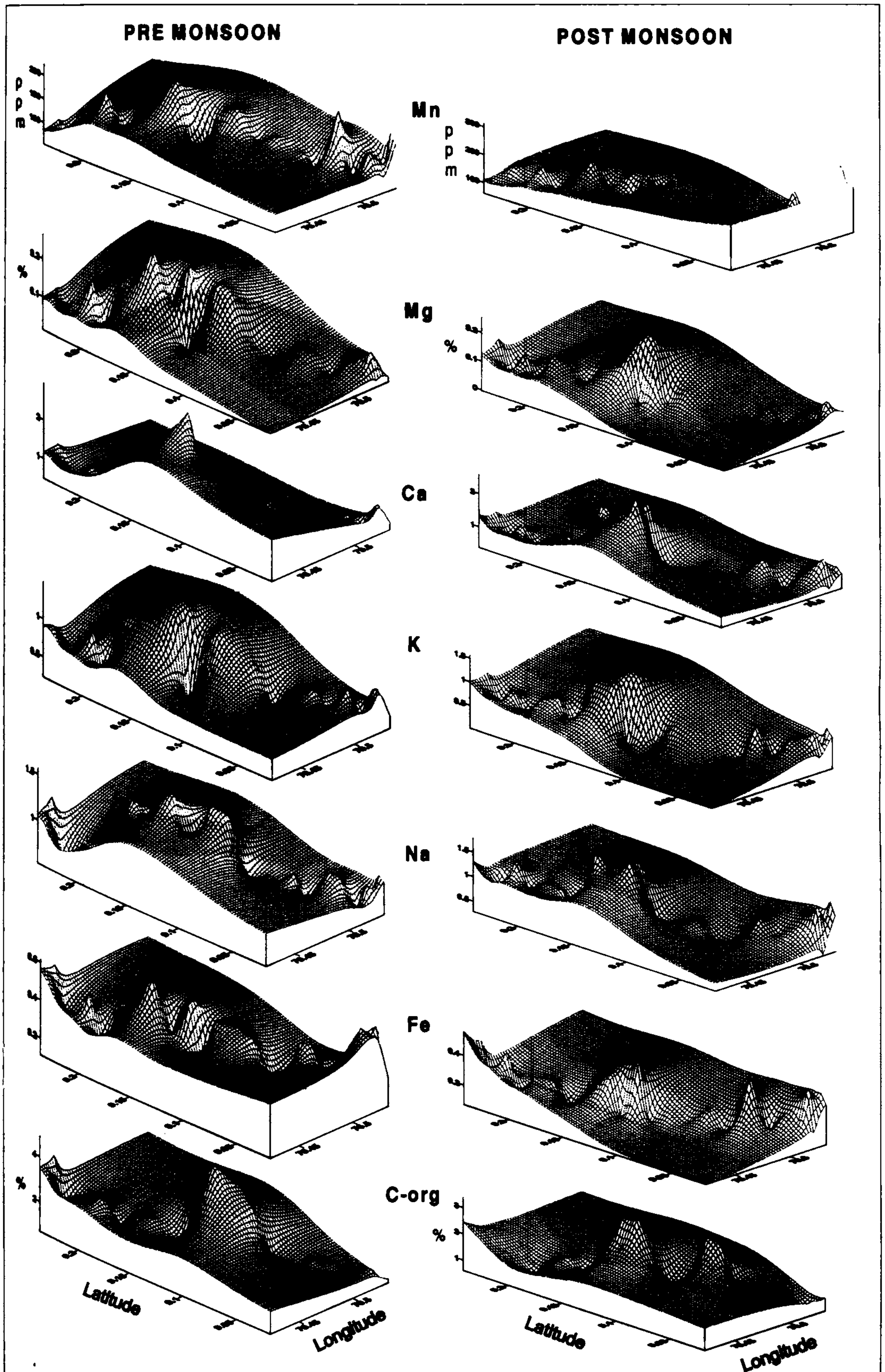


Fig.5.1a Surface plot of the major elements in the bulk sediments of the Kayamkulam estuary

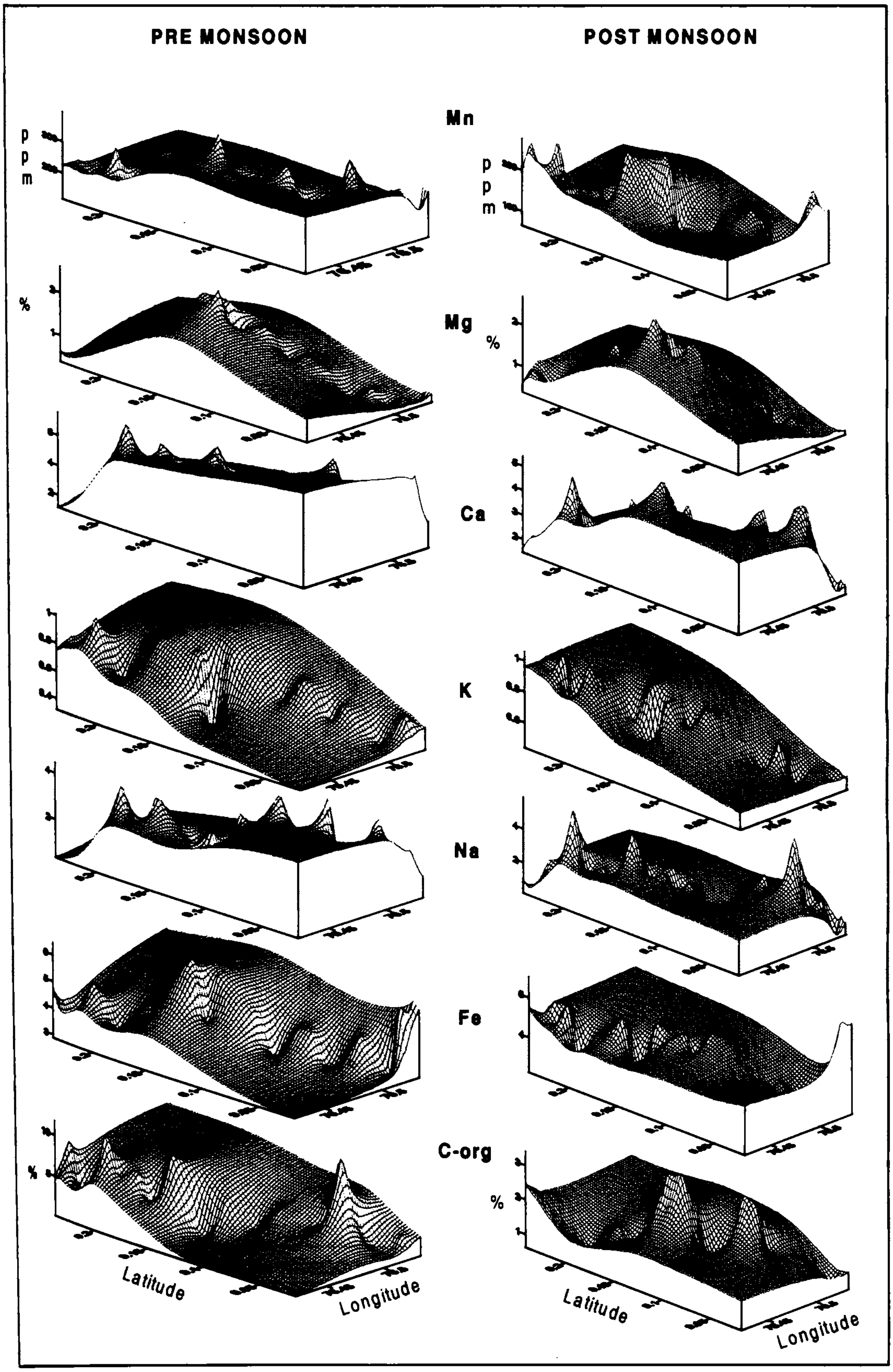
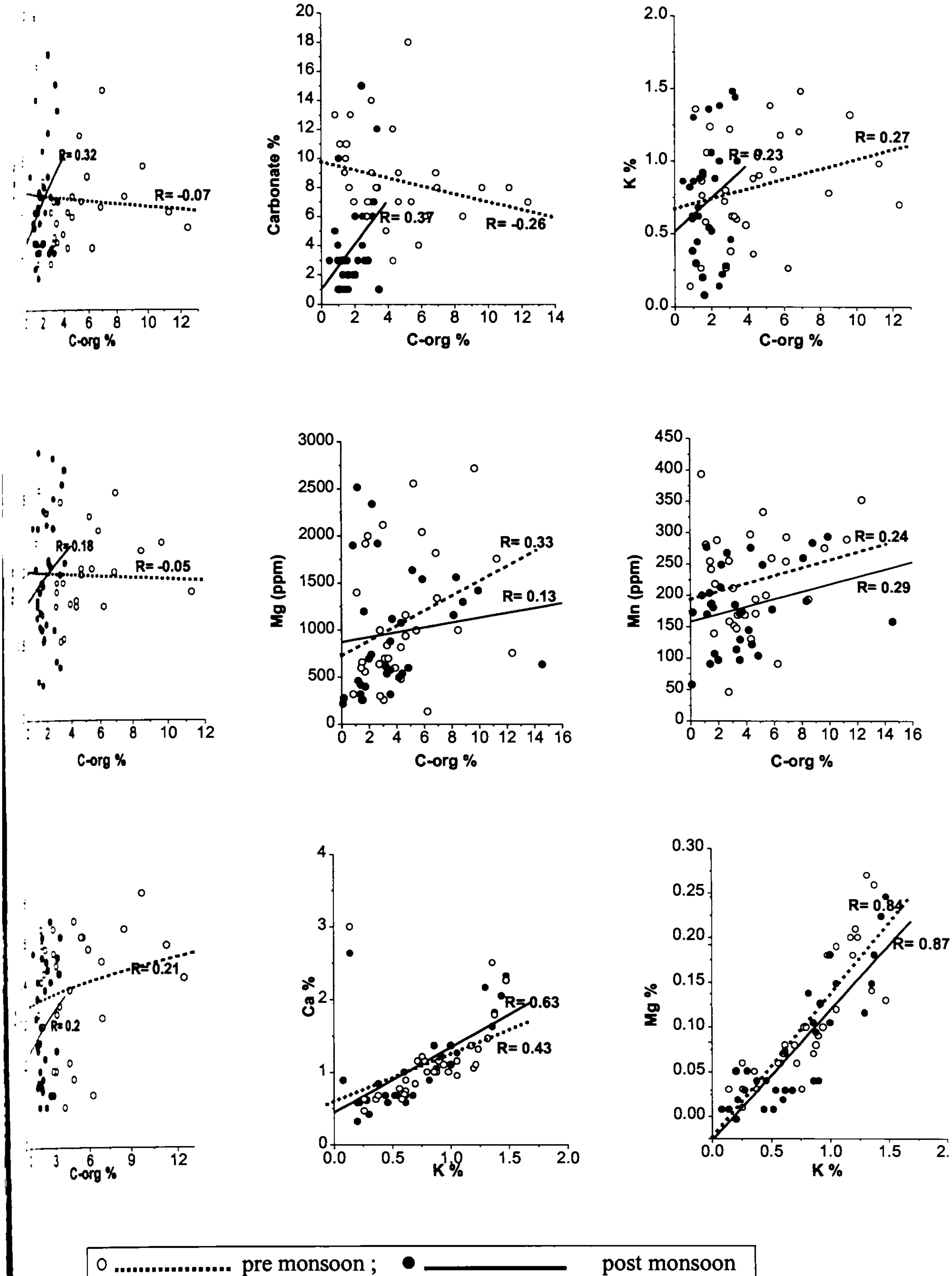
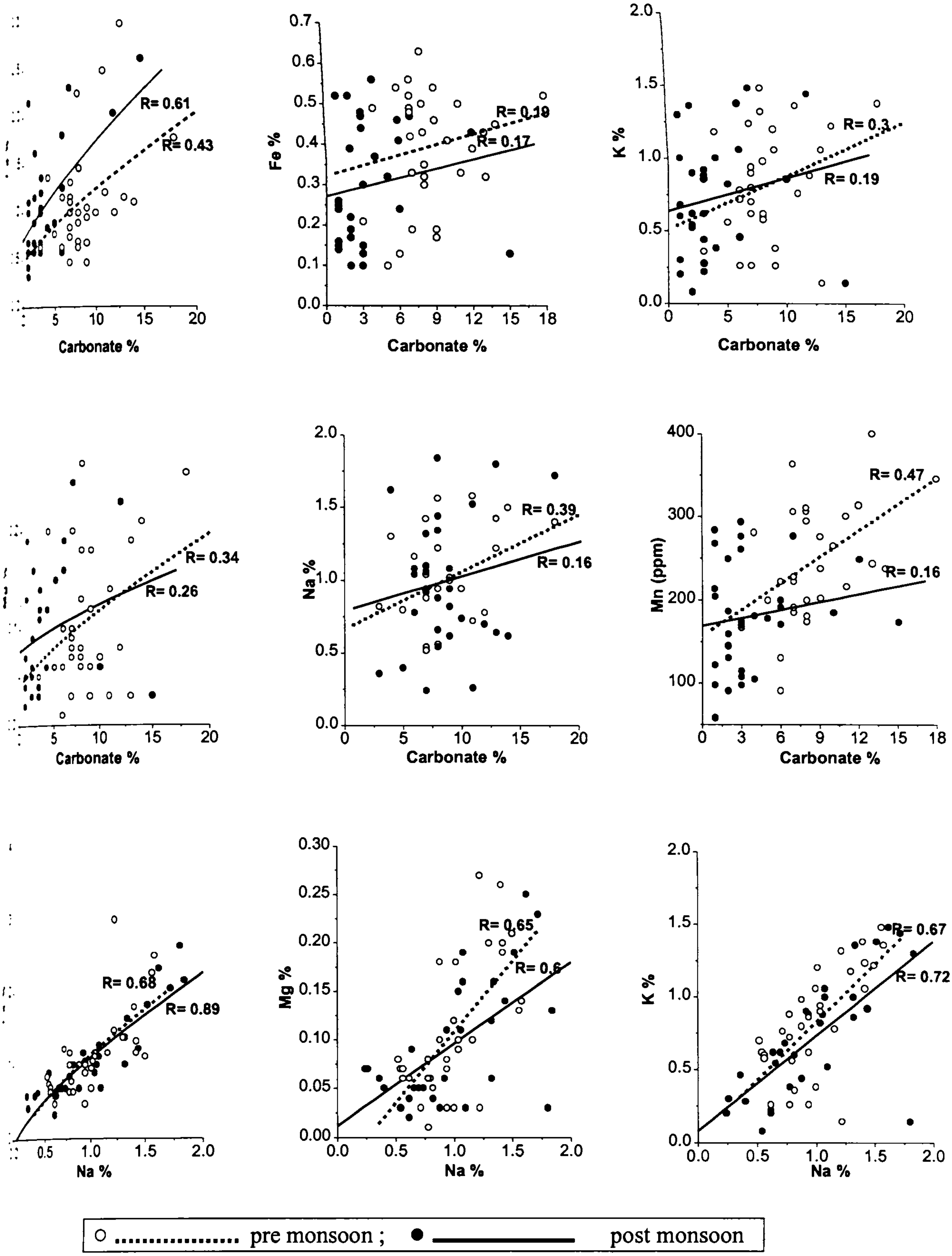


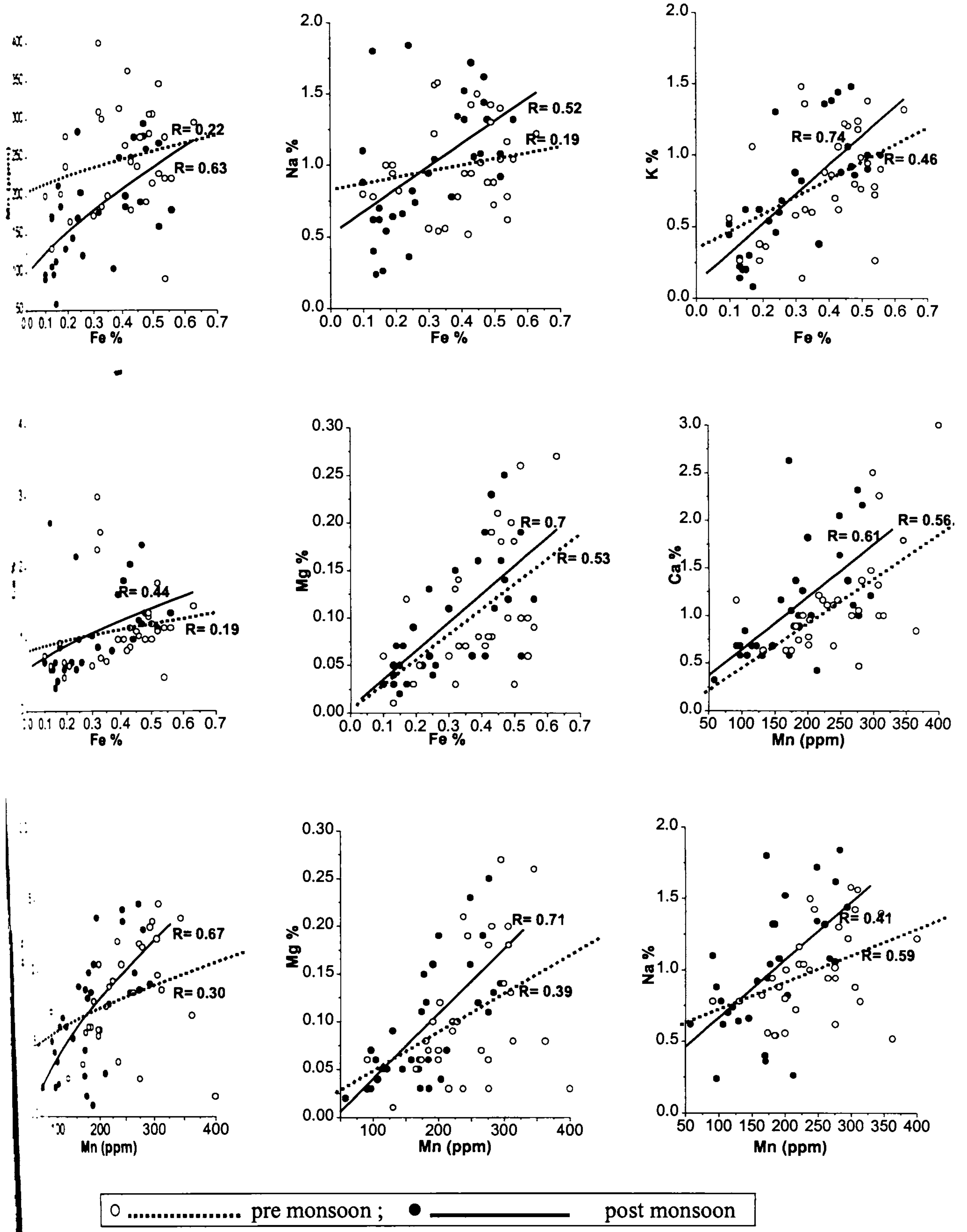
Fig.5.1b Surface plot of the major elements in the clay fraction of the Kayamkulam estuary



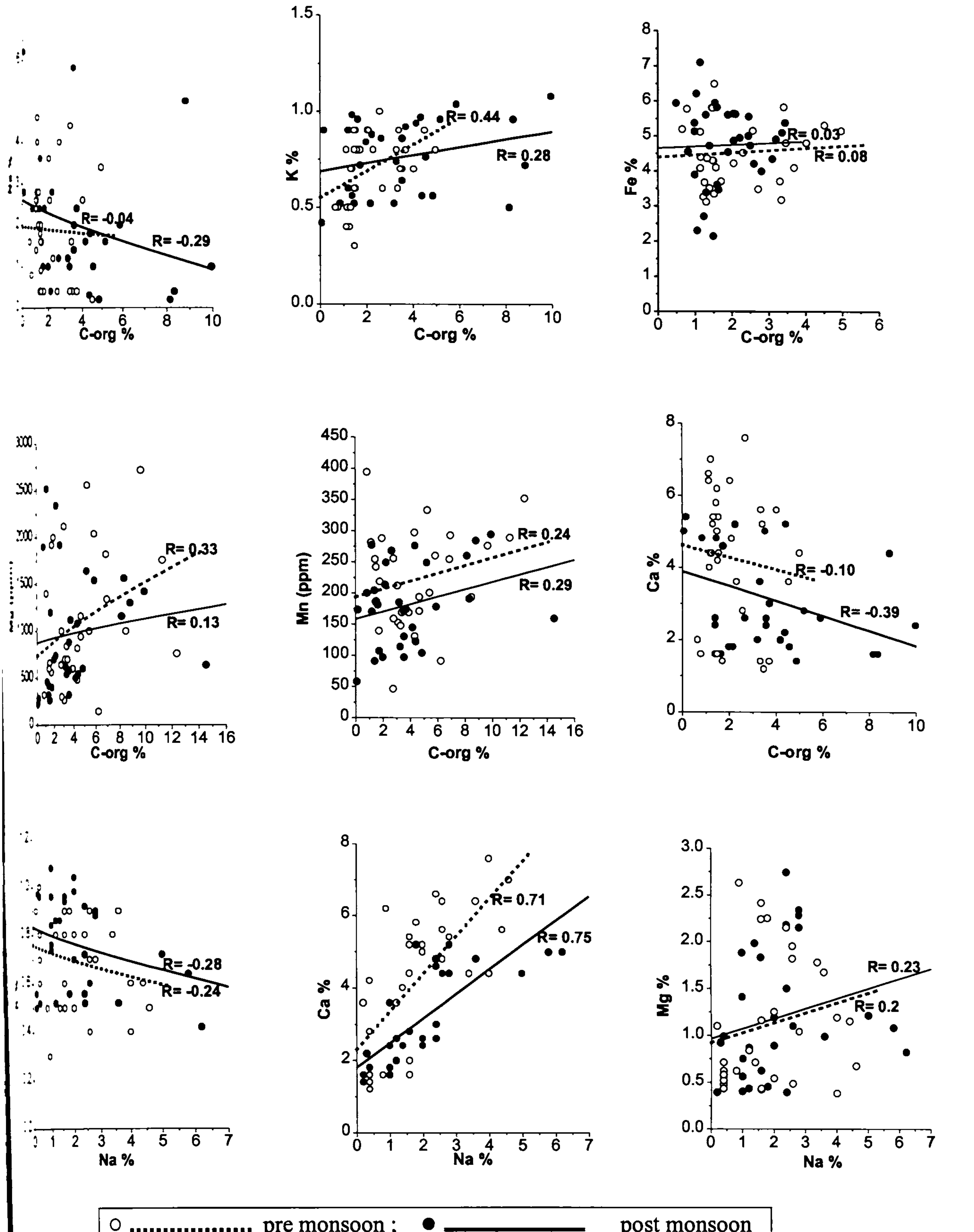
: Interrelationship between C-org Vs major constituents and K Vs major constituents in the bulk sediments.



Interrelationship between Carbonate Vs major constituents and Na Vs major constituents in the bulk sediments.



: Interrelationship between Fe Vs major constituents and Mn Vs major constituents in the bulk sediments.



.: lf Interrelationship between C-org Vs major elements and Na Vs major elements in the clayey sediments

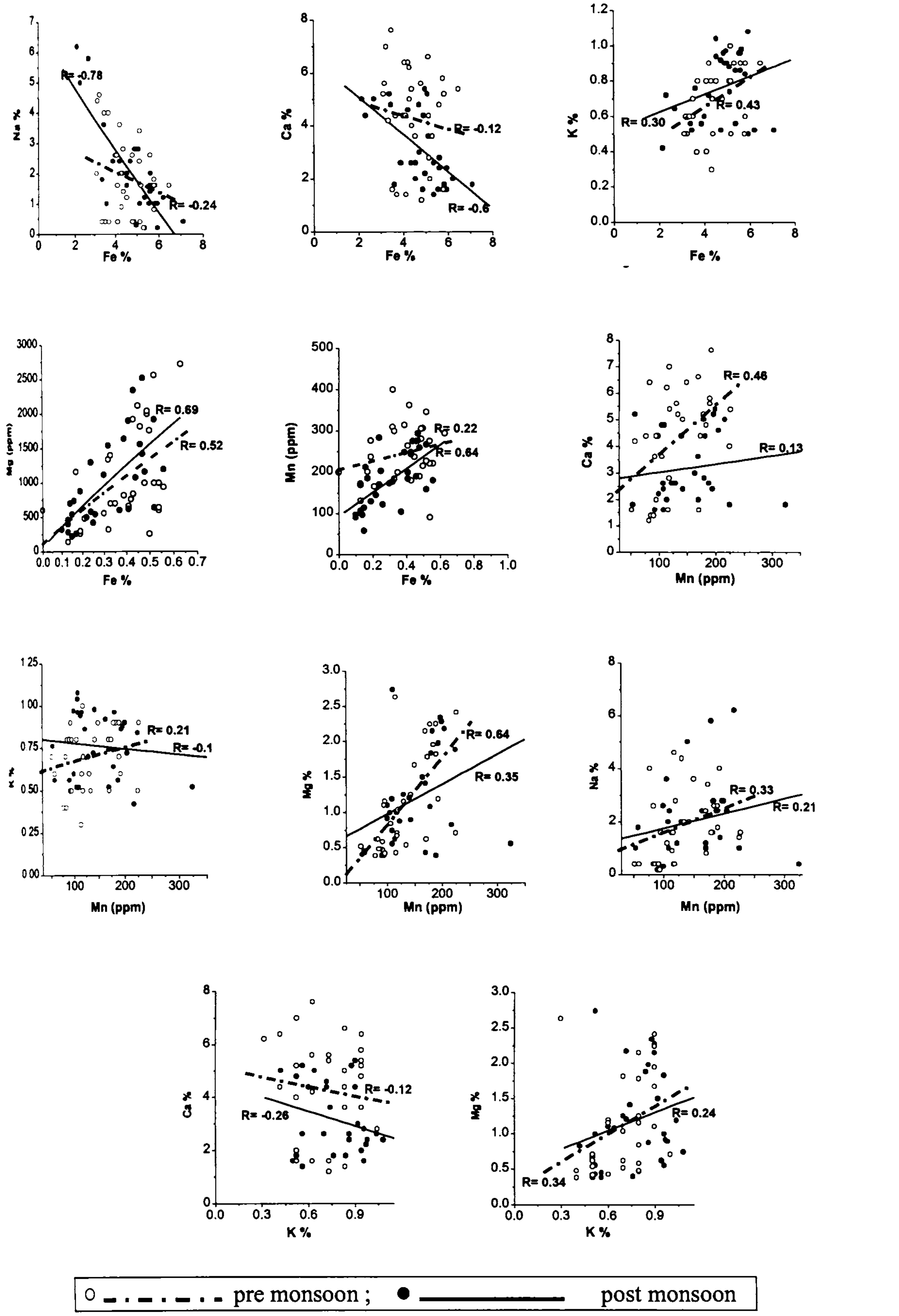


Fig. 5.1g Interrelationship between Fe, Mn and K Vs major constituents in the clayey sediments.

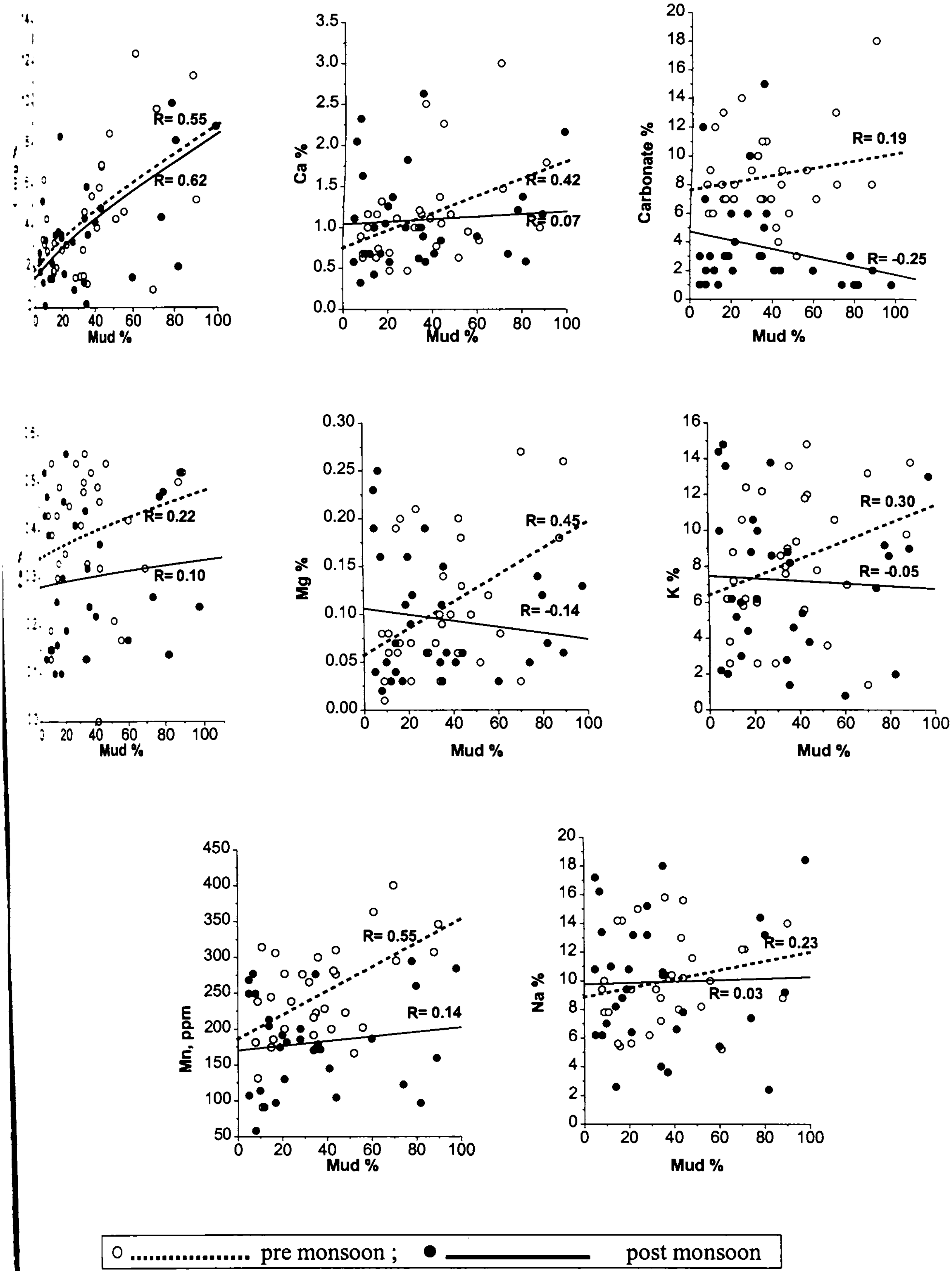


Fig. 5.1h Interrelationship between mud Vs major constituents in the Kayamkulam estuary.

through rivers, which eventually reaches to the oceans, is an important factor in balancing the global carbon budget (Kao and Liu 1996). Further the content of organic carbon is an excellent indicator of post depositional conditions. High primary biological productivity, sedimentation rate and efficient preservation make estuaries very good sinks of organic matter. Organic sedimentation in the estuarine environment results from a combined effect of allochthonouns and autochthonous inputs. An insight into these sources of organic matter in an estuary will provide the extend of biogenic processes operating in and around the system.

In the Kayamkulam estuary, organic carbon reaches from many sources. Terrestrial and marine inputs through surface drainage and flooding/tidal activities contribute a major proportion of the organic carbon. In addition to this, a substantial quantity of organic carbon reaches the system through coconut husk retting as well as biological activities within the system. In the present study, an attempt has been made to thrash out the geochemical behaviour of organic carbon associated with the pre monsoon and post monsoon sediment of Kayamkulam estuary.

Tables 5.1 a and b represent the spatial (sector-wise) and temporal (pre-monsoon and post monsoon) variations in the concentration of organic carbon in the study area. The organic carbon distribution in the sediments of Kayamkulam estuary is primarily controlled by the textural attributes of sediments. The organic carbon generally varies between 0.85% to 12.4% (av; 4.4%) in pre monsoon and from 0.2% to 14.6% (av; 3.9%) in post monsoon sediment. As discussed in the

Chapter III, this environment is floored with a spectrum of textural classes. During pre monsoon, the highest concentration (av; 9.37%) of organic carbon is recorded in sandy silts and a minimum (av; 2.52%) in clayey sand textural class. The order of abundance of organic carbon in pre monsoon in regard to the textural affinities (Table 5.1 c) is sandy silt (av; 9.68%) > sandy mud (av; 6.71%) > silty sand (av; 5.82) > silt (av; 5.27%) > sand (av; 4.2%) > muddy sand (av; 3.85%) > clayey sand (av; 2.52%). In the post monsoon season, the highest average concentration of organic carbon is recorded in the sandy mud (av; 9.27%) and minimum value in the sandy silt (av; 1.99%). The order of abundance of organic carbon in post monsoon (Table 5.1 d) is: sandy mud (av; 9.27%) > mud (8.84%) > silty sand (av; 4.6%) > muddy sand (av; 2.95%) > clayey sand (av; 2.7%) > sand (av; 2.35) > sandy silt (av; 1.99%).

In the present study the lower organic carbon content is recorded for the sand dominant sediments and higher for the mud-dominated sediments. Earlier Trask (1932) proved that the silt and clay could enrich two to four times the higher values of organic carbon than sand. This clearly indicates the role of particle size in the trapping of organic carbon in the Kayamkulam estuary. Several researchers advocate that the enhanced association of organic carbon in the finer sediments is attributed to the higher surface area of the particles, which in turn promotes the absorptive ability of organic colloids. Studies of Burns and Salomon, (1969); Sajan and Damodaran, (1981); Bednarz and Strzecka, (1993); Padmalal and Seralathan, (1995), Badarudeen et al, (1997) reiterates the above view.

Table 5.1C Abundance of chemical constituents with respect to different textural classes (pre monsoon)

SAMPLE		C-org	Carbonate	Na	K	Ca	Mg	Fe	Mn	Zn	Cu	Cr	Co	Ni	Pb	Cd
				(%)					(ppm)				(ppm)			
CLAYEY SAND																
	Max	4.33	12.0	0.94	0.88	1.16	0.10	0.54	314	284	81	136	71	108	74	3
	Min	1.44	6.0	0.54	0.26	0.47	0.06	0.30	91	80	16	66	13	23	12	1
	Aver	2.52	8.4	0.73	0.67	0.86	0.07	0.43	214	149	38	98	39	54	42	1
MUDDY SAND																
	Max	8.49	14.0	1.58	1.36	2.50	0.21	0.54	306	178	50	133	50	70	96	3
	Min	1.15	4.0	0.56	0.26	0.47	0.03	0.19	200	28	24	68	19	15	24	1
	Aver	3.85	9.0	1.12	0.93	1.16	0.13	0.40	249	110	34	104	38	48	45	2
SILTY SAND																
	Max	6.96	8.0	1.56	1.48	2.26	0.13	0.56	310	166	51	99	51	65	38	2.8
	Min	4.67	7.0	1.04	0.90	1.16	0.09	0.32	222	126	21	86	27	26	14	1.8
	Aver	5.82	7.5	1.30	1.19	1.71	0.11	0.44	266	146	36	93	39	46	26	2.3
SANDY MUD																
	Max	12.4	13.0	1.22	1.06	3.00	0.18	0.50	400	160	47	124	50	82	52	3
	Min	0.85	3.0	0.52	0.14	0.63	0.03	0.17	166	115	13	77	19	15	10	1
	Ave	6.71	8.0	0.89	0.65	1.28	0.09	0.32	288	131	33	107	37	58	31	2
SANDY SILT																
	Ave	9.68	8.0	1.22	1.32	1.47	0.27	0.63	295	154	35	134	39	78	28	3
SILT																
	Ave	5.27	18.0	1.40	1.38	1.79	0.26	0.52	346	112	32	121	43	57	24	2
SAND																
	MAX	6.24	9.0	1.00	0.62	0.89	0.08	0.43	238	144	40	103	50	64	62	3
	Min	3.06	6.0	0.78	0.26	0.63	0.01	0.13	131	74	11	41	12	52	18	1
	Ave	4.2	8.0	0.91	0.42	0.74	0.04	0.25	183	101	23	70	27	59	36	2

Table.5.1d Abundance of chemical constituents with respect to different textural classes (Post monsoon)

Sample		C-org	Carbonate	Na	K	Ca	Mg	Fe	Mn	Zn	Cu	Cr	Co	Ni	Pb	Cd
		(%)								(ppm)						
CLAYEY SAND																
	Max	3.55	15.0	1.80	0.62	2.63	0.09	0.24	173	148	30	81	86	10	32	1
	Min	0.17	2.0	0.36	0.14	0.58	0.03	0.10	97	62	15	43	20	8	4	1
	Ave	2.70	6.5	0.92	0.42	3.62	0.05	0.16	143	100	21	67	53	7	16	1
MUDDY SAND																
	Max	8.34	10.0	1.52	1.38	1.82	0.19	0.56	213	182	68	108	38	96	114	4
	Min	0.85	1.0	0.26	0.08	0.42	0.03	0.08	91	54	11	22	17	14	10	0
	Ave	2.95	3.8	0.92	0.69	0.98	0.08	0.28	176	107	29	33	25	31	33	2
SILTY SAND																
	Max	4.85	3.0	1.06	0.88	1.00	0.11	0.44	276	206	44	94	54	95	44	2
	Min	4.35	1.5	0.78	0.38	0.84	0.06	0.37	104	124	35	77	31	42	26	2
	Ave	4.60	1.5	0.92	0.63	0.92	0.08	0.41	190	165	40	86	43	69	35	2
SANDY MUD																
	Max	14.55	3.0	1.44	0.92	1.21	0.14	0.52	294	152	52	118	55	93	70	3
	Min	4.41	2.0	0.74	0.68	0.68	0.05	0.26	122	90	26	60	21	12	18	1
	Ave	9.27	1.3	1.11	0.84	1.11	0.09	0.43	209	123	40	99	44	66	47	1
SANDY SILT																
	Ave	1.99	1.0	0.24	0.20	0.58	0.07	0.14	97	130	20	44	16	3	12	1
SAND																
	Max	5.20	12.0	1.72	1.48	2.32	0.25	0.52	268	130	46	126	47	74	42	2
	Min	0.09	1.0	0.62	0.20	0.32	0.02	0.13	58	68	12	24	13	11	12	1
	Ave	2.35	4.1	1.10	0.90	1.24	0.14	0.32	189	97	24	77	29	35	19	2
MUD																
	Ave	8.84	1.0	1.84	1.30	2.16	0.13	0.24	284	78	37	127	38	69	58	2

The study of Kayamkulam lake sediments confirms the direct relationship between the texture of sediments and the organic matter content. Besides, the texture, it depends also on the supply of organic carbon to the environment of deposition, rate of deposition of organic carbon and the rate of decomposition of organic substances. The factors like depth, temperature organic productivity and oxygen content have their influence on the distribution of organic carbon.

The analysis shows variation in the distribution of organic carbon for the pre monsoon and post monsoon and even for the three sectors. The average percentage of organic carbon in the sediments of Kayamkulam estuary is much less than that of Ashtamudi lake (4.67%) and greater than that of Vembanad lake (2.55 %). The organic carbon content increases from the northern sector to central sector in the bulk sediments both for the pre and post monsoon periods, while in the clays it decreases towards the centre both for pre and post monsoons reflecting the textural variation which is already discussed in the Chapter 3. The increasing organic carbon content towards the central sector in the bulk sediments can be attributed to the transportations of the fines by the locally induced fluvial currents and the decrease towards the centre for the clay in the pre monsoon may be the removal of finer fractions by the tides.

The organic carbon decreases towards either side namely northern and southern region in pre and post monsoon for the bulk but for the clays, in the post monsoon it increases towards the northern and southern sectors, marked by the augmentation of fines. But for the southern sector the organic carbon in the bulk sediments increases towards centre for both the pre and post monsoon while in clays an increase in the content is noticed for the pre monsoon and decrease in the post monsoon. Hence in general it can be concluded that the variation in the organic carbon in the study area is due to the textural variations.

More over the northern segment is characterized by the prevailing reducing environment (odour of H_2S) and high rate of coconut leaf and husk retting compared to other two regions favoured the higher content of organic carbon. The contribution of organic carbon by the river runoff at northern sector can be ruled out as it lacks prominent perennial rivers. The higher content of organic carbon for central sector can be substantiated by the fact that the Krishnapuram Ar empting into the central sector contributes a higher content of organic carbon drained from the thick plantations of adjoining areas. The above observation can be justified with the station No.16 were in the substratum represents sand which yielded a higher organic carbon content. Comparatively higher depth rate of sedimentation and biogenic activity at the southern region plays a role in the contribution of organic carbon besides the river runoff by the Pallikkalthodu especially during monsoon.

From the above discussions, it can be concluded that, the variation of organic carbon observed in the sediment of Kayamkulam estuary, reflects its textural affinity, hydrodynamic influence and degree of anthropogenic activities in the system. Rate of sedimentation, rate of supply of organic carbon through domestic/urban sewage disposals, (particularly in areas influenced by sewage disposal from the Kayamkulam town slumps) contribution from agricultural and land run-off, etc., are some important factors determining the organic carbon in this system. The paradoxical observations of high organic carbon association in some sand dominant textural facies can be explained in terms of the urbanization and river contribution to that area. Moreover, the isolated patches of mangroves vegetation now existing in the central and southern sectors of the area could also be a substantial proportion of organic carbon to this estuarine system through littering and subsequent degradation /decomposition of the decomposition of the vegetative matter.

In short the organic carbon in the sediments of Kayamkulam estuary has a direct bearing on the texture, besides river runoff, prevalence of reducing environment, biogenic activity and hydrodynamic conditions.

5.3.1b Carbonates

Carbonate content is an integral part of estuarine and marine sediments. Carbonates reach the systems through various processes such as weathering of carbonate rocks, biologically controlled carbonate precipitations or through shells/shell fragments. The carbonate constituents are products of the environment where as the non-carbonate fractions are terrigenous and hence may be considered as a dilutant of the carbonate fraction. In the Kayamkulam estuary, the main contribution of carbonate is from shells or shell fragments.

Tables 5.1 a furnish the spatial variation of total carbonate including calcium as well as magnesium carbonates, in the bulk sediments of the Kayamkulam estuary and Table 5.1 c and d provide its percentages with respect to different textural classes. Spatial distribution of carbonate varies from 3-18% in pre monsoon sediments and 1-15% in post monsoon sediments. In general, the average carbonate percentage for pre monsoon sediments is two times higher than post monsoon counterparts. This clearly indicates the role of marine biogenic activity in enhancing the carbonate levels in the Kayamkulam estuary. The average carbonate contents in various textural classes in the decreasing order silt (av; 18%) > muddy sand (9%) > clayey sand (8.36%) > sand (8%) = sandy silt (8%) and sandy mud (8%) > silty sand (av; 7.5%) in pre monsoon sediments, whereas in post monsoon, the order is clayey sand (av; 6.5%) sand (av; 4.14%) > muddy sand (av; 3.75%) > silty sand (av; 1.5%) > sandy mud (av; 1.25%) > sandy silt (av; 1%) = mud. In general, the sand rich sediments enrich higher carbonate contents than mud/clay rich counterparts; reinforcing the fact that shells within the sediments contribute to the carbonate content in the study area.

The variations in the carbonate contents reflect the differences in the environmental conditions of deposition (Setty and Madhusudhana Rao, 1972). Its content in sediment water interface varies widely and is attributed to the prevailing conditions of the overlying water masses (Badarudeen et al., 1997). The augmented value of carbonate content in the study area is contributed mainly by shelled organisms like gastropods and pelcypods, which ultimately deposit their calcareous exoskeleton to the environment soon after their death. Further, the shell and sand mining activities in the basin can also contribute a substantial quantity of lime mud to the sediments, a feature also reported earlier by Badarudeen et al., (1996). Photosynthesis and respiration by organisms can accelerate the carbonate precipitation, (Damodaran and Sajan, 1983, Sebastian et al., 1990) from the overlying waters thereby affecting the net inorganic carbon flux. Cloud (1965), has stated that any biological production which affects the amount of CO_2 in solution, may disturb the carbonate equilibrium. It is proved that low values of carbonate in sediments are indicative of reducing environment whereas high values represent oxidation conditions (Krumbein and Garrels, 1952 and Jonge and Villerius 1989). The various physicochemical conditions prevailing in the Kayamkulam estuary especially the reducing conditions (as evinced from the odour of H_2S), urban inputs from the Kayamkulam town shallowness of the estuarine bed etc has locally affected the carbonate content in the study area,

Carbonate and non-carbonate fractions have different origin and ages of deposition. The various sources for the carbonate are from transportation of the calcareous material by rivers, organic and inorganic precipitation from the overlying waters, and the shell fragments and the tests of organisms. Binocular microscopic *observation revealed the presence of shell fragments of molluscs* and tests of organisms, whereas petrological microscopic study didn't show any carbonate minerals like calcite, or dolomite.

Higher content of carbonate at the southern region may be due to the biogenic activity. The binocular microscopic examination revealed the abundance of molluscs' shells and tests of foraminifers in the region. A similar finding is also noted for the northern region irrespective of the reducing environment, which in fact retards the biogenic activity. Moreover only undefined canals draining through the palaeo runnels and ridges reach the northern sector. Therefore lack of major rivers prevalence of reducing environment at the northern sector point to the fact that the undefined canals / streams draining through the palaeo ridges and runnels draining though the adjacent ridges and runnel form the source for carbonate to the northern region. The increasing trend of carbonate from northern and southern region to central region may be due to biogenic activity at that sector and the transportation of shell fragments towards the central both by the tides and locally induced fluvial currents with in the system. Comparatively lower content of carbonate for the post monsoon may be due to the removal or breaking down of the shells/shell fragment by the tides. Hence the main source of carbonate for the Kayamkulam estuarine sediments is from the shell fragments and tests of organisms.

5.3.1c Sodium and Potassium

Chemical analysis of sediments has been performed without removing salts present in the interstitial water of sediments because interstitial water and its ingredients are considered as integral part of sediments. Moreover, the desaltation processes removes a significant amount of exchangeable elements present in the sediments (Islam and Lotse, 1986). Generally, a major portion of Na and K will be fixed with in the lattice of clay minerals (Sajan, 1988). It is presumed that the Na and K contents in the sediments of the Kayamkulam estuary are bounded either by adsorption or cation exchange processes. The Na and K, released during weathering, may remain in ionic form in the overlying waters. By taking into account of the role of clay minerals in the fixation of Na, it seems that major part of Na may be tied up with montmorillonite or illite. Na ions compete very effectively than K ions for vacant exchange site in clay minerals. The proportionate site variation of Na and K in the pre monsoon and post monsoon sediments of Kayamkulam suggests presumably the common source of derivation.

Tables: 5.1 a and b show the concentration of Na and K along the estuarine environment of Kayamkulam lake, in the pre and post monsoon seasons, respectively. Na varies between 0.52% and 1.58% (av; 1%) in the bulk sediments of pre monsoon and between 0.24% to 1.84% in post monsoon. However, K shows an average of 0.82% (0.14% to 1.48%) in pre monsoon and 0.72% (0.08% to 1.48%) in the post monsoon sediments. Not much variation is exhibited by K for these two seasons. When consider their association in different textural classes, (Table 5.1 c) it is seen that the highest Na concentration is observed in Silt (av; 1.4%) followed by silty sand (av; 1.3%), sandy silt (av; 1.22%), muddy sand (av; 1.12%), sand (av; 0.91%), sandy mud (av; 0.89%) and clayey sand (av; 0.73%) in the sediment recovered during the pre monsoon season. But for K, for the same season exhibits their order of abundance as silt > sandy silt > silty sand > muddy sand > clayey sand > sandy mud > sand.

In the post monsoon season, the sediments of this ecosystem exhibit the lowest concentration of Na in sandy silt (av; 0.24%) and the highest concentration in mud (av; 1.84%). The abundance of Na in the other textural classes are in the order; sandy mud> sand > muddy sand = silty sand and clayey sand. Average content of K in muddy sand and silty sand do not vary in significant levels. Similar to Na, K also exhibits highest percentage in mud dominated sediments (av; 1.3%), which is six times greater, compared to the sandy silt (av; 0.2%). The clayey sand shows an average concentration of 0.42% (0.14% - 0.62%), which is two times lesser than its association in sandy mud (0.68% -0. 92 %).

The average concentrations of Na and K in the clay fraction of pre monsoon and post monsoon are given in Tables: 5.1 b. The average concentrations of Na in the pre monsoon and post monsoon seasons are 1.9% (0.2 – 4%) and 2.0 % (0.2 – 5.8%) respectively. The concentration of Na was higher in the clay fraction than bulk sediments. The sector wise distribution reveals that the highest concentration of Na in both bulk sediments and clay fraction is for the central sector. The average concentration of Na for the pre monsoon in north, central and southern sectors are 1.28%, 2.15%, 2.16%, respectively and their post monsoon concentration are 1.75%, 2.34% and 1.95%. The values obtained from the present study is higher when compared to Vellar Estuary, (Mohan, 1990); Ashtamudi Lake, (Sajan, 1988), and lower than Vembanad estuary (Padmalal, 1992).

The average concentration of K in the clay fraction of pre monsoon and post monsoon period is given in the Tables 5.1 b. A comparative evaluation of the bulk sediments and clay fraction of the pre monsoon and post monsoon period reveals that in the bulk sediments of pre monsoon has higher concentration than post monsoon. But in clay fraction, the post monsoon period has higher average concentration. This is applicable to all the sectors of both fractions in the pre and post monsoon period also. It is also observed from the table that the maximum average concentration is seen in the northern sector for clay fraction, but in the bulk sediment, the maximum average concentration is for the central sector. The sector wise average concentration in the northern, central and southern sectors of pre monsoon and post monsoon seasons are 0.8%(0.58 - 1.02%) and 0.76% (0.28 – 0.92%), 0.54% (0.38 – 0.76%) and 0.93% (0.64 – 1.1 %) 0.81% (0.72 – 0.96%) and 0.57% (0.42 – 0.76%) respectively.

The maximum variation in the average concentration is noted in the central sector. In general, the distribution pattern of these alkali elements is controlled by desaltation processes, adsorption or cation exchange processes, particle size – the more finer the sediments the higher its concentration values. The observed phenomenon is attributed to the particle controlled exchange processes operating in the system.

5.3.1d Calcium and Magnesium

Ca and Mg enter the environments through weathering of plagioclase feldspar. The uptake of Mg by clay minerals during estuarine mixing can release Ca to the overlying waters (Kastner and Gieskes, 1976 Perry et al. 1976; Lawrence et al. (1979), Drever, (1971); Sholkoritz (1973); Presley and Trefry (1980) has found that Ca rich fresh water clays preferentially adsorb Mg in brackish water. The marginal enrichments of Mg in estuaries is probably attributed to progressively larger fixation of Mg by clay minerals. Sayles and Mangelsdorf (1976) have stated that Mg is an important exchangeable cation in seawater. Russel (1970) indicates that upon prolonged soaking montmorillonite will take up Mg from seawater especially when pH values are greater than 8.

The average percentage of Ca in bulk sediment of the Kayamkulam estuary in both the periods are given in the Tables 5.1 a and b. The average percentages in the pre monsoon and post monsoon bulk sediments are: 1.15% (0.47 -3%) and 1.1% (0.32 – 2.63%). Both in the bulk and clays Ca content decreases from central part to either side namely to northern and southern sectors for both pre monsoon and post monsoon. Ca has shown a significant to highly significant correlation with Mg in the bulk and a highly significant correlation in clays for pre and post monsoons respectively while with Mn, highly significant correlation for the bulk, for both the seasons and in clays significant correlation only for the pre monsoon periods. With Na, Ca shows a highly significant positive correlation in bulk sediment and clay fraction.

From the sector-wise distribution, for the bulk sediment of pre monsoon and post monsoon, it is confirmed that in the pre monsoon the percentage of Ca is higher. The average percentage of northern, central and southern sectors for pre monsoon are, 0.95% (0.63 – 1.32%), 1.66 % (0.95 – 3%) and 0.83 % (0.47-1.21%), and in the post monsoon period are 0.94% (0.58 – 1.37%), 1.56% (0.58 - 2.63 %) and 0.81% (0.32 – 1.37%). It is clear from the Table 5.1a that in both pre monsoon and post monsoon periods the maximum average percentage of Ca is found in the central sector.

In the clay fraction, the average percentage of Ca in the pre monsoon and post monsoon are 4.27% (1.2 – 7.6%) and 3.18 % (1.4 – 4.6%). The clay fraction in northern, central and southern sectors of the pre monsoon accounts for the average concentrations of 3.2 % (1.2 – 7.6%); 5.3% (3.6 – 6.6 %) and 4.3% (1.6 - 7.0%) the post monsoon accounts for 2.46 % (1.6 – 5%), 4.02% (2.4 – 5.4%) and 3.02% (1.4 – 5.2 %), respectively. In clay fraction also the maximum average concentration in seen is the central sector. This spatial distribution of Ca concentration in the sediments and also its enhanced concentrations in sector can be explained as interlayer cation exchange by clay mineral structure. The variation of Ca contents can partially been attributed to the Ca being associated as calcium carbonate in shells/ tests.

In the study area, the Mg concentration varies from 0.4 -0.272% (av; 0.11%) in the pre monsoon and 0.02-0.25% (av; 0.10%) in the post monsoon Tables 5.1 a and b. Mg shows a highly significant correlation with Na, K, Fe for pre monsoon and post monsoon while Mn and Ca shows marginal significant correlation for pre monsoon and highly significant correlation in post monsoon. In the case of carbonate Mg shows a marginal significant correlation for pre monsoon and for post monsoon no significant correlation.

The average concentration of Mg in the bulk and clays for both the season, has not recorded any significant variations. The sector wise analysis shows that in the pre monsoon, the Mg content exhibits higher values in the central sector 0.16% (0.03 - 0.27%) which is followed by the northern sector with an average of 0.11% (0.01 - 0.2%) and southern sector (0.03% - 0.1%,) av; 0.06%. In the post monsoon the northern sector has an average percentage of 0.10% (0.03-0.16%); in the southern sectors the percentage ranges from 0.026 -

0.116% (av: 0.05%). The central sector, which is affected by constant ebbing and flooding activities, has maximum Mg values the average being 0.14% (0.04 - 0.2%).

The average percentage of Mg for the clay fraction of the pre monsoon is 1.14 % and that of post monsoon is 1.2 % Table 5.1 b. The sector wise distribution brings to the fact that the central sector exhibits high content of Mg both in the bulk sediment and clay fractions. The southern sector has the minimum percentage content both in pre and post monsoon. The textural classes of Kayamkulam estuarine sediment for the pre monsoon shows that the maximum percentage of Mg is seen in the sandy silt (av; 27%), silt (av; 0.26%), muddy sand (av; 0.13%) silty sand (av; 0.11%) sandy mud (av; 0.09%), clayey sand (av; 0.07%) and sand (av; 0.04%). In post monsoon higher concentration of Mg is seen in sand (av; 0.14%), mud (av; 0.13%), sand mud (av; 0.09%). Muddy sand (av; 0.08%) = silty sand, sandy silt (av; 0.07%) and clayey sand (av; 0.05%). From the table 5.1 c and d it is noticed that the percentage of Mg increases towards central sector from northern sector and decreases from central to southern sector.

The Mg concentrations in the clay fractions of the pre monsoon seasons are 0.83 %, 1.95% and 0.63 % for the northern, central and southern sectors respectively. Similarly in the post monsoon period, the Mg concentration are 1.04%, 1.9% and 0.65% respectively in the above three zones.

The regional variation in Ca and Mg content of the Kayamkulam estuarine sediments can be explained as interlayer cation in the clay mineral structure, as calcium carbonate in shells and as biogenous origin. From the highly significant correlation of Ca with carbonate it can be concluded that Ca is fixed as $CaCO_3$ in the skeletal material/shells. Hirst (1962) has also observed a similar variation in the modern sediments of gulf of Paria. From the Table 5.1 a and b, it is noticed that both for bulk and clay, Ca content decreases from central sector to northern and southern sectors for the pre and post monsoon. This variation can be explained in terms of clay mineral variation. Nelson (1962) observed that the significant part of Ca is tide up in montmorillonite. The central sector of the Kayamkulam estuary is characterized for the higher content of montmorillonite (Table 4.4) and decreases to northern and southern sector. Therefore above variation in the Ca content can be explained in the light of clay mineral composition. A part of Mg is biogenous origin since Mg has shown marginally significant correlation with organic carbon. The variation of Mg content in the Kayamkulam estuarine sediment is due to fixing up of Mg in clays. Availability of Mg and Ca and Paucity of K favours the formation of montmorillonite. It is found that Ca rich fresh water clays preferentially absorb Mg in brackish water. Mg is fixed up in montmorillonite and a little in illite. Mg shows marginally to highly significant correlation with Ca suggesting its concentration in the carbonates. It can be concluded from the above discussion that the regional variation of Mg in the Kayamkulam estuarine sediments are due to absorption of Mg mainly in montmorillonite and illite, incorporation of Mg in the carbonates and hence a part due to biogenous origin.

5.3.1e Iron and Manganese

The distribution and geochemical behaviour of Fe and Mn in aquatic environments have received wide attention among scientific community because understanding of these redox - sensitive elements is a prerequisite in the assessment of toxic contaminants causing disastrous effects to organic life (Forstner and Wittmann, 1983 and Sajan 1992).

The weight percentage of iron refers to total iron, which is determined as Fe_2O_3. Average content of iron in the bulk sediments of the Kayamkulam estuary for the pre monsoon is 0.39% and to that of post monsoon is 0.30% for the clays and the average content is 4.54% and 4.75% for the pre and post monsoon respectively. In the pre monsoon for the bulk sediments iron content practically shows no variation from northern to central region while a slight decrease is noticed towards southern region. In the post monsoon a decrease from northern to southern region through central part is observed. In the clays comparatively a high content of iron is realised with an average of 4.54% for pre monsoon and 4.75% for the post monsoon. The iron content of clays decreases from central sector to either sides of the estuary for the pre monsoon while a general decrease from northern to southern sector is noticed. Fe shows a significant positive correlation with organic matter and manganese.

The average content of manganese in the bulk sediments for the pre monsoon is 247ppm and for that post monsoon, it is 181ppm. For the clays the manganese content is 131ppm and 149ppm respectively for the pre and post monsoon. It is observed that the manganese content in the clays is much lower than that of bulk for all two seasons. It is also observed that the central region records maximum content of manganese both for the clays and bulk in all the seasons and in all cases the manganese content decrease from central region to either sides of the estuaries.

Concentration of Fe and Mn in the bulk as well as in clays for of pre and post monsoon are given in Tables: 5.1 a and b. The concentration of Fe in the bulk sediments ranges from 0.13% to 0.63% (av; 0.40%) in pre monsoon and 0.10% to 0.56% (av; 0.30%) in the post monsoon period. Among the three sectors of the Kayamkulam estuary, the northern sector has the maximum value followed by central sector and the least in the southern sector.

In pre monsoon, the northern segment accounts for an average value of 0.42% of Fe followed by central segment (av; 0.41%) and southern segment (av; 0.36%) respectively. The content for the Fe in northern sector is (av; 0.31%), central (av; 0.31%) and southern sector (av; 0.29%).

Among the various textural classes the maximum content of Fe is observed in the sandy silt (av; 0.63%) followed by silt (av; 0.52%), silty sand (av; 0.44%), clayey sand (av; 0.43%), muddy sand (av; 0.40%) sandy mud (av; 0.32%) and sand (av; 0.25%), in the pre monsoon season (Table 5.1 c); and in the post monsoon (Table 5.1 d) the sandy mud fraction has a highest average value of 0.43% followed by silty sand (av; 0.41%), sand (av; 0.32%), muddy sand (av; 0.28%), mud (av; 0.24%), clayey sand (av; 0.16%) and sandy silt (av; 0.14%). The reported values of Fe for the Kayamkulam estuarine sediments is markedly lower when compared to the Vembanad estuary, (Padmalal and

Seralathan 1995). The observed average Fe value in sediments of Cochin estuary is 4.39%, (Padmalal 1992). A similar level in the concentration of Fe has also been observed by Jayasree and Nair (1995). Murthy and Veerayya (1981) estimated an average of 3.74% of Fe in the bulk sediments of Vembanad estuary while Mallik and Suchindan (1984) reported an average of (4.41%). The average Fe contents in the Kayamkulam estuary is less than the reported values in Kolleru lake (Rama Murthy 1972); Iskapalli lagoon sediments, (Subha Rao, 1985). This is primarily resulted from the dominance of coarser clastics, particularly quartz rich sand, in the bulk sediment of the Kayamkulam lake.

The average concentration of Fe in the clay fraction ranges from 3.12 to 4.53% (av; 4.54%) in the pre monsoon period from 2.15 – 7.11% (av; 4.75%) in the post monsoon period. There is different view regarding the chemical state in which Fe is transported to the sedimentary basin. It is believed that iron has been transported to the depositional environment partly in solution and partly in colloidal form. When the Fe bearing sediments come into contact with oxygenated slightly alkaline waters of the estuary, iron is oxidised to ferric state and is precipitated as ferric hydroxide complexes. In the present study the increasing trend of iron content, noticed from the northern sector to the central sector, especially for the pre monsoon clays, indicates a higher oxidative precipitation if iron occurs as Fe^{3+} and $Fe(OH)_3$. Oxidative precipitation increases and is highly possible under higher aeration associated with turbulence. In an estuary when the river water mixes with sea water, the negatively charged iron bearing colloids react rapidly with sea water cations to form precipitate. Removal of iron from solution in the above manner exists in several estuaries (Yeats and Bewers, 1976; Holiday and Liss 1976, Sajan 1992). Higher content of iron in the bottom sediments of lake indicates the prevalence of such phenomenon. Comparatively higher content of Fe in the central region with respect to other two regions can be attributed to above. The positive correlation of Fe with organic matter indicates that a part of iron is incorporated in organic matter. Very fine organic residues have the ability to fix iron and other cations by adsorption, and iron forms on important micro-constituents of living tissues of animals and plants (Rankama and Sahama 1950). Three factors namely ability of organic carbon to fix Fe by adsorption, the part played by organic carbon in the precipitation of Fe as a sulphide and the concentration of Fe by living organism after their death and decomposition can be related to the close association of Fe and organic carbon in sediments. Fe can be precipitated as ferrous sulphide in a reducing environment. Prevalence of reducing environment at the northern part comply with the above since the northern part of Kayamkulam estuary is identified for the prevalence of reducing environment (odour of H_2S).

Fe might have been fixed up either within clay mineral structure as an essential ion (cation exchange) or externally to clay mineral structure (adsorption) in the sediment of Kayamkulam estuary. Illite and montmorillonite can accommodate Fe in their lattice, it is most likely that, greater part of the iron is fixed up in montmorillonite as the same has inter layer water, and unsatisfied negative charge and highest cation exchange capacity of all the clay minerals (Nelson 1962). The exchange reaction in which iron will be fixed up by montmorillonite is largely depend on the valency state of Fe, which in turn is controlled by the prevailing environmental conditions of deposition. Therefore in the southern part of the Kayamkulam estuary, Fe might be fixed up in montmorillonite.

Manganese is carried to the sea both in solution and as a constituent of sediment debris. There are controversial view regarding the origin and manner in which Mn is incorporated into hydrolysed sediment. It is generally conceded that the Mn in sedimentary cycle is reached from the drainage basin as bicarbonates $Mn(HCO_3)_2$ but deposited as oxides in the form of organic and/or inorganic colloids, finally divided detrital grains and cementation matrix. Correns (1941) considered that Mn is biologically extracted while Kuenen (1941) considered that Mn is a chemical precipitate. Mn can be incorporated into sediments through several biological and inorganic mechanisms. The bicarbonate in weathering solutions derived from the dissolution of Mn bearing minerals on attaining a slight degree of alkalinity, mostly changes to unstable $Mn(OH)_2$. The divalent Mn is readily oxidized to quadravalent state when the solutions come into contact with the atmospheric or dissolved oxygenated area and is precipitated as $Mn(OH)_2$ or finely divided MnO_2 and the precipitation often takes place in fresh water. In 1960, Garrels described in detail the importance of the physicochemical factors and the effect of pH and Eh on the precipitation of Mn.

Mn has an average value of 247ppm (91ppm - 400ppm) in the bulk sediments of the pre monsoon samples. In the post monsoon samples, the Mn accounts for as an average value of 181ppm with a range of 58 – 294ppm

(Tables 5.1 a). It is seen that the amount of manganese in the pre monsoon sediments is higher than that of post monsoon period. The metal content increases towards the northern sector. In the silt the highest amount of Mn is reported during pre monsoon and in post monsoon it is in the mud. In the pre monsoon the Mn concentration is in the decreasing order as follows silt, sandy silt, sandy mud, silty sand, muddy sand, clayey sand and sand. In post monsoon the Mn concentration is in the decreasing order mud followed by sandy mud, silty sand, muddy sand, clayey sand and least in sandy silt fraction. From the detailed regional wise distribution, it is clear that the central sector of the estuary has the maximum Mn content with an average of 293ppm for the pre monsoon, which is higher than post monsoon average of 205ppm. The northern and southern segments have more or less same level of Mn concentration. In the pre monsoon the average concentration of Mn in the northern segment is 225ppm (131 - 307ppm) and in the southern sector with an average of 224ppm (91-363ppm) while for the post monsoon the northern and southern sectors the average values are 172ppm (91-294ppm) and 167ppm (58 to 213ppm) respectively.

The Mn content in the clay fraction decreases considerably from that of the bulk sediments both in the pre monsoon and post monsoon periods. In clay fraction, Mn shows higher concentration in the post monsoon than in the pre monsoon period (Table 5.1 b). The average Mn concentration in the pre monsoon clay fraction is 131ppm (52- 227ppm) and in the post monsoon clay fraction is 148ppm (54-324ppm). From the detailed sector wise analysis of both the seasons, it is noted that the central sector has the maximum concentrations of Mn, followed by the southern sector and least is the northern sector. The sector-wise average concentration of pre monsoon period are 107 ppm (52-193 ppm), 165 ppm (94-227 ppm) and 122 ppm (59-225 ppm) respectively. The clay fractions of the post monsoon period accounted 137 ppm (108-225 ppm), 170 ppm (110 – 205 ppm) and 139 ppm (54 – 324 ppm) in northern, central and southern sector respectively.

In the present study it is observed that for both pre monsoon and post monsoon the central part has recorded a higher value for the Mn content and is getting depleted to northern and southern part. The same trend is seen for the clays also. The progressive depletion of Mn from the central part to northern and southern part does not directly reflect the source rock of the catchments area where the river drains through the khondalite rocks but for the post monsoon, it is characterized by mineral containing Mn. However, at the northern part of the estuary, Mn presents as manganous sulphide because of the reducing environment and the availability of sulphide ions.

The size fractionation study reveals that Mn and Fe are enriched in fine fraction than coarser counterparts, especially in sands. The enhanced Mn levels with fine-grained sediments is axiomatic (Trefrey and Presley, 1976); Mudorch, 1984, Seralathan (1987) and Nair et al. (1990). The researchers Kemp and Thomas (1976) opined that the increase in the association of metals with fine grained sediments is due to the greater surface area of the finer particulates. Further, precipitation of Fe and Mn hydrolysates over finely dispersed particulates in aquatic sediments can also enhance the net concentration of these metals, (Lee, 1985 and Padmalal and Seralathan, 1995).

High significant positive correlation with Fe both for bulk and clays for the post monsoon indicates that these two elements are co-precipitated as insoluble ferric maganic hydrate. Co-precipitation of Mn-Fe is favoured by the negatively charged $Mn(OH)_4$ solutions and positively charged $Fe(OH)_3$ (Hirst, 1962). No significant correlation with organic matter is seen for the Mn content of the Kayamkulam estuarine sediment. Kalesh (1980) stated that Mn could be held in the lattice structure of clay minerals. Though no direct significant correlation is exhibited by Mn with clay, the possibility of Mn held in the lattice of montmorillonite cannot be ruled out as Mn shows a very high significant correlation with Ca, significant correlation with K and Mg. Hence the above observation suggest that a part of Mn is fixed in the lattice of montmorillonite in the sediments of Kayamkulam estuary. Comparatively higher content of Mn in the central part not only reflect the source and various sorption and desorption mechanisms, but also the contribution of heavy minerals as region is marked for higher content of garnet.

5.4 TRACE ELEMENT GEOCHEMISTRY

5.4.1 Results and discussion

Trace elements are transferred to the depositional sites as constituents of detrital materials, structurally bounded in various clay minerals found at a near site of weathering and as oxides coating on clay mineral surfaces. Considerable quantities of these elements are also carried into solution and get incorporated into sediments by different processes at varying rates based on physico-chemical condition prevailing in the depositional environments. Trace elements are removed from solutions by adsorption into organic and inorganic colloidal suspended material, extraction by marine organisms and by precipitants like Fe and Mn oxides or by sulphide ions.

In recent years, for distinguishing the depositional environment the chemical composition of sediments especially the distribution of trace elements are used. Generally, the amount of trace elements in modern sediments is controlled by the elemental solubility in waters, feeding capacity of the drainage basin and by the prevailing environmental conditions. Adsorption, chemisorptions and ion exchange processes, ionic radius, valency, chemical banding, ionisation potential, electronegativety, temperature, pressure etc are major the geochemical properties that control the trace element content in the clay minerals. Elemental solubility in waters and sedimentation rates in depositional basin also influence the trace element content of sediments besides the chemical factors. Precipitating manganese and ferric oxides and other precipitates also entrap some of the trace elements. Flocculating clay particles adsorbs certain amount of trace elements. Planktonic organism also extracts trace elements from seawater, which are vital for their life. The composition of rocks in the drainage basin of the rivers by and large determines the kind and content of the trace elements in the sediments. The trace elements determined for their geochemistry are Zn, Cu, Cr, Co, Ni, Pb and Cd. Concentration of these elements in ppm are given in table 5.3

a and b for the bulk and clay fraction respectively for the pre monsoon and post monsoon. The surface plots of these trace elements are provided in Fig. 5.2 a and b. so as to decipher their aerial distribution.

5.4.1a Zinc

Zinc is one among the ubiquitous elements; its mean concentration in the earth's crust is estimated as 70ppm (Levinson 1974). The metal represents 0.004% of the earth's crust and 25th in the order of abundance (Abbasi 1989). The freshwater sediments from unpolluted areas contain Zn concentration of 67 ppm (Forstner,1976). Nriagu (1980) conducted a comparative study in the aerial distribution of Zn concentration in rural and urban areas and reported that the metal is enriched substantially in the urban areas than rural areas. This clearly indicates that the major causative factor for enhanced levels of Zn in natural environments presumably the anthropogenic activities (Levinson, 1974; Abassi, 1989; Forstner, 1976 and Nriagu 1980).

The total Zn content in the sediments is mainly dependent on the composition of the parent rock, (Sillanpaa, 1972; Kabata Pendias and Pendias, 1984). In the present study, the average concentration of Zn in the bulk sediments for the pre monsoon and post monsoon periods is 126 ppm (28-284ppm) and 110ppm (54 - 206ppm), respectively. It is clear that the concentration of Zn in the pre monsoon season is comparatively higher. The sector wise examination in the distribution pattern of Zn (Table 5.3 a) reveals that the northern sector exhibits the highest concentration compared to other sectors

Table 5.3a CONCENTRATION OF TRACE ELEMENTS (ppm) IN THE BULK SEDIMENTS OF KAYAMKULAM ESTUARY

		PRE MONSOON							POST MONSOON						
	Sample No.	Zn	Cu	Cr	Co	Ni	Pb	Cd	Zn	Cu	Cr	Co	Ni	Pb	Cd
		(ppm)							(ppm)						
N	*1*	126	51	99	51	65	38	3	164	68	108	38	96	74	2
	2	142	50	95	48	65	72	3	182	36	104	34	73	48	2
	3	136	47	88	50	54	32	3	206	44	94	54	95	44	2
	4	130	27	68	33	25	12	1	144	22	43	17	14	114	1
	5	178	39	72	29	24	43	2	98	22	55	18	35	30	0
	6	284	81	66	20	23	74	2	116	46	107	54	93	60	3
	7	140	37	105	43	68	40	2	148	15	43	86	19	4	1
	8	74	11	41	12	60	18	2	68	31	98	38	56	32	2
	9	128	31	112	47	70	26	2	136	25	79	26	36	22	1
	10	140	33	129	41	60	96	3	130	20	44	16	3	12	1
	Average	**148**	**41**	**88**	**37**	**51**	**45**	**2**	**139**	**33**	**78**	**38**	**52**	**44**	**2**
C	*11*	154	35	134	39	78	28	3	78	37	127	38	69	58	2
	12	166	21	86	27	26	14	2	68	23	88	28	48	42	2
	13	115	24	112	28	15	24.2	1	94	31	89	25	24	28	4
	14	112	32	121	43	57	24	2	76	25	111	46	59	32	2
	15	115	13	124	27	45	34	1	108	15	81	20	10	16	1
	16	96	27	108	36	44	28	2	110	31	126	37	54	24	2
	17	118	41	124	47	82	20	2	114	46	111	47	74	20	2
	18	28	33	114	44	55	30	1	130	13	24	15	17	8	1
	19	94	38	126	39	68	34	2	62	22	69	25	18	12	1
	20	138	27	114	31	29	32	1	102	21	54	17	11	12	1
	Average	**114**	**29**	**116**	**36**	**50**	**27**	**2**	**94**	**26**	**88**	**30**	**39**	**25**	**2**
S	*21*	160	25	77	19	15	10	1	82	30	75	20	20	32	1
	22	56	33	85	28	46	29	2	76	11	25	20	18	8	1
	23	86	40	103	50	64	62	3	54	11	54	18	15	6	3
	24	120	47	103	50	81	52	3	152	52	111	55	79	38	0
	25	144	18	66	19	52	28	1	80	12	24	13	21	8	2
	26	80	33	110	45	49	38	BDL	90	26	60	21	12	18	1
	27	138	16	75	13	65	30	BDL	88	21	63	21	15	18	2
	28	138	33	133	49	59	66	2	78	35	66	19	12	10	2
	29	74	24	68	19	18	54	1	98	35	79	32	33	22	1
	30	154	47	136	71	108	56	3	124	35	77	31	42	26	2
	31	120	37	120	57	79	50	2	134	35	118	45	79	70	2
	Average	**115**	**32**	**98**	**38**	**58**	**43**	**2**	**96**	**27**	**68**	**27**	**31**	**23**	**1.47**

*** N - NORTHERN SECTOR, C - CENTRAL SECTOR, S - SOUTHERN SECTOR, BDL- BELOW DETECTION LEVEL**

Table: 5.3.b CONCENTRATION OF TRACE ELEMENTS (ppm) IN THE CLAY SEDIMENTS OF KAYAMKULAM ESTUARY

		PRE MONSOON							POST MONSOON						
		Zn	Cu	Cr	Co	Ni	Pb	Cd	Zn	Cu	Cr	Co	Ni	Pb	Cd
	Sample No.				(ppm)							(ppm)			
N	1	124	84	135	61	101	76	2	124	117	119	60	89	46	2
	2	120	103	137	54	99	102	2	110	80	143	59	104	66	3
	3	108	132	134	59	85	80	2	112	81	139	59	87	81	2
	4	306	188	132	52	147	76	1	116	86	135	60	85	95	2
	5	130	104	132	58	97	98	2	318	135	122	49	75	56	2
	6	166	134	156	60	96	104	3	188	153	129	65	78	70	3
	7	172	177	137	53	98	66	2	298	90	116	43	71	40	1
	8	140	88	136	39	57	56	1	96	45	131	46	78	50	2
	9	150	51	147	41	67	48	1	144	96	162	56	130	56	2
	10	118	58	159	39	65	64	2	130	61	173	61	105	32	2
	Average	**153**	**112**	**141**	**51**	**91**	**77**	**2**	**164**	**94**	**137**	**56**	**90**	**59**	**2**
C	11	120	52	177	48	82	74	2	30	96	37	43	18	1	3
	12	122	48	184	43	93	62	1	69	169	50	93	34	2	5
	13	106	38	169	41	86	69	1	53	150	68	84	28	2	4
	14	118	51	175	39	82	76	1	90	34	154	48	73	34	2
	15	125	70	140	40	64	86	3	120	48	149	47	75	33	2
	16	136	49	183	43	84	74	2	190	78	147	46	78	28	2
	17	136	120	178	53	107	82	2	258	207	143	54	89	40	1
	18	132	78	186	39	90	66	1	134	75	158	54	85	46	2
	19	150	96	178	50	100	62	2	140	101	180	57	104	44	3
	20	158	164	168	41	84	50	1	308	87	153	57	117	50	2
	Average	**130**	**77**	**174**	**44**	**87**	**70**	**2**	**139**	**104**	**124**	**58**	**70**	**28**	**2.50**
S	21	118	68	171	60	113	66	2	212	73	153	60	109	50	2
	22	142	104	214	52	101	76	1	211	82	130	53	97	47	2
	23	164	187	135	42	91	66	2	208	120	120	48	81	40	2
	24	144	125	156	69	132	90	2	94	80	129	65	116	98	2
	25	160	108	158	73	120	90	2	136	54	115	36	36	32	2
	26	122	86	150	39	95	42	1	80	47	111	58	79	46	2
	27	182	122	144	59	98	54	2	132	266	117	47	63	46	2
	28	156	80	195	57	105	72	1	278	141	147	58	106	80	2
	29	218	130	178	69	125	104	3	100	54	142	78	107	72	2
	30	162	87	162	64	122	96	2	180	144	130	59	111	80	2
	31	328	190	158	77	210	70	2	234	149	142	60	112	66	3
	Average	**172**	**117**	**166**	**60**	**119**	**75**	**2**	**170**	**110**	**131**	**56**	**92**	**60**	**2.11**

* N - NORTHERN SECTOR, C - CENTRAL SECTOR, S - SOUTHERN SECTOR

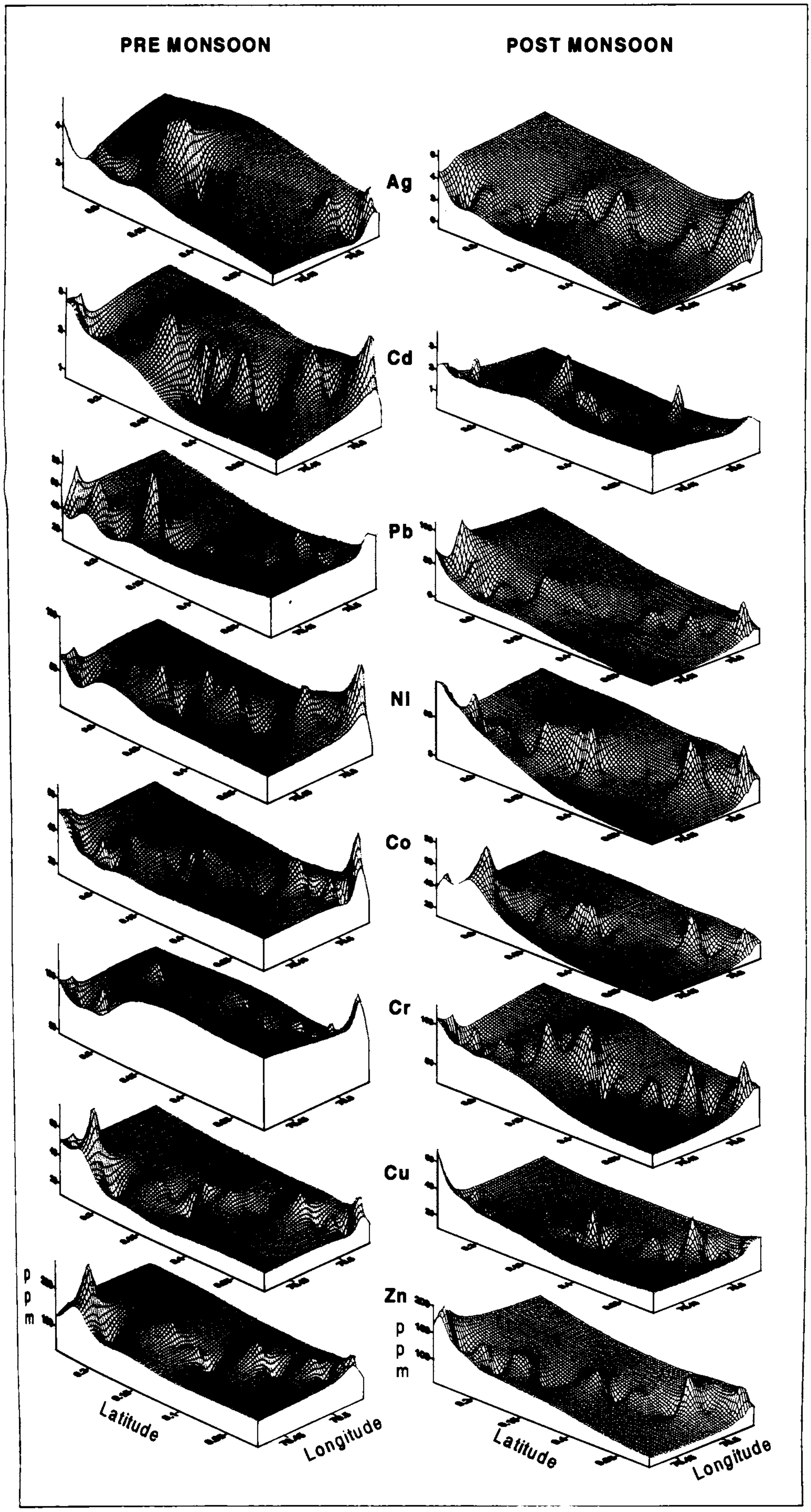


Fig.5.2a Surface plot of the of the trace elements in the bulk sediments of Kayamkulam estuary

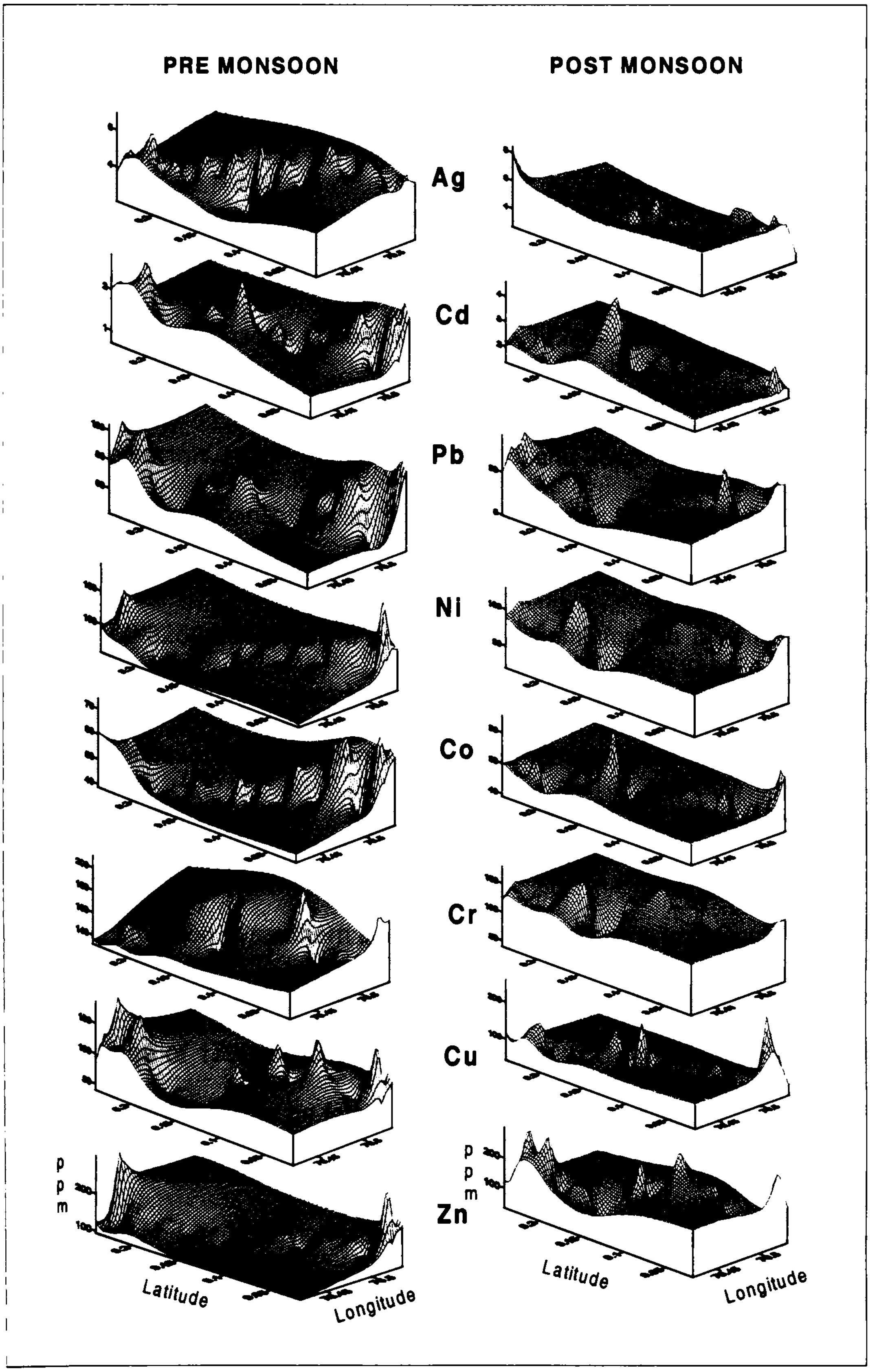


Fig.5.2b Surface plot of the trace elements in the clay fraction of the Kayamkulam estuary

in both the seasons. This may be attributed to the dominance of clay in the sediments as well as higher supply of Zn rich particulates from the hinterland areas that host the Kayamkulam thermal power plant (KTPP). The northern sector of pre monsoon has an average concentration of 148 ppm (74 – 284 ppm). In the post monsoon season the average concentration of northern sector is 139ppm (68 – 206 ppm). The average concentrations of central and southern sectors for the pre monsoon periods are 114 ppm (28 – 166ppm) and 115 pp (56 - 160ppm). In the post monsoon period the average concentrations of central and southern sectors are 94 ppm (62 – 130ppm) and 96ppm (54 – 152 ppm).

The concentration of Zn in the clay fraction is higher than that of bulk sediment. The average concentration of Zn in the pre monsoon clay fraction is 152 ppm (106-328ppm) and 158 ppm (30-318 ppm) for the post monsoon. In bulk the average concentration is greater in the pre monsoon period, which is contrary in the case of clay sediments. In pre monsoon clay fraction the lowest concentration is for the central sector with an average of 130 ppm (106-158 ppm) followed by the northern sector with an average of 153 ppm (108-306 ppm) and highest concentration in southern sector, having an average concentration of 172 ppm 118 – 328 ppm). In the case of post monsoon the southern sector has the highest average of 170ppm followed by northern (av; 164ppm) and central (av; 139ppm). Adsorption of Zn by ferrous sulphide can be one reason for the higher content of Zn in the sediment of northern sector. Due to low solubility of Zn in natural waters and its behaviour during chemical weathering, its major transport and accumulation in the sedimentary environment is to be expected in detrital matter. In the central sector the Zn is competitively less to that of northern and southern sectors. This may due to the lack of finer sediments.

On the basis of the textural attributes, the pre monsoon bulk sediments the highest average value is for sandy silt (av; 154ppm) followed by clayey sand av; 149ppm), silty sand (av; 146ppm), sandy mud (av; 131ppm), silt (av; 112ppm), muddy sand (av; 110ppm) and sand (av; 107ppm). The same for the post monsoon the silty sand has the highest average concentration of 165ppm, followed by sandy silt (av;130ppm), sandy mud (av;123ppm), muddy sand (av; 107ppm), clayey sand (av; 100ppm) sand (av: 97ppm) and mud (av; 78ppm).

Seralathan (1979) has reported an average value of 119.2ppm of Zn in the clay fraction of Cauvery river sediments and 118.6ppm in the Coleroon estuary. In some highly polluted sedimentary environments abnormally high value of Zn have been reported. The average content of Zn in the bulk sediments r clays is 258ppm and 316ppm respectively in the Astamudy lake, Sajan (1988) where as Ouseph (1987) has recorded 780ppm of Zn in the Periyar river sediments.

Organic matter has got prominent role in the concentration of Zn. But in the present study no correlation between Zn and organic matter is noticed in any sector of the lake either in bulk or clays. Hence Zn is not concentrated to any significant extent in organic matter. Zn has a greater affinity for sulphur, it is precipitated as sulphide in the zones enriched with sulphur. As mentioned earlier, the northern sector is marked for the prevalence of a reducing environment, which in turn might have favoured the higher concentration of Zn in this zone.

Hence it can be stated that, Zn is precipitated as sulphide in the from Zn $(HS)_3$. Relatively a higher pH may also have facilitated a higher content of Zn, either by precipitation or adsorption.

Zn can diadochically replace ferrous iron and magnesium in silicate mineral structures because of a similar ionic radii of iron and magnesium adsorption of Zn by ferrous sulphide or oxide is ruled out in the present case as Zn has not shown any specific correlation except for post monsoon and that too a marginal positive correlation. If at all any adsorption process has taken place, then it will be for the bulk sediments that too for the post monsoon. Relatively finer texture of sediments can be considered as the reason for the higher content of Zn in clays especially at the southern sector. It is stated that Zn travels with clays and explained it as an environmental enrichment in sulphides with finer clastics. Because of the higher exchange capacity of smectite, it can be considered that a part of Zn is fixed up in clays. Experiments showed that montmorillonite have high exchange capacity specifically for cations such as Cu^{2+} and Zn^{2+} in acid and neutral conditions. Hence it can be considered that a part of Zn is tied up in montmorillonite and this may be the season for the higher content of Zn at the southern sector where an acidic/neutral environment prevents.

Due to low solubility of Zn in natural waters and its behaviour during chemical weathering, its major transport and accumulation in the sedimentary environment in to be expected in detrital matter, Magnetite in a better carrier of Zn. Therefore the source for the Zn at the central sector is from detrital minerals, though the contribution is minor. The central sector is noticed for the higher content of heavies. Lack of finer sediments at central sector reflected in the lower content of Zn. From the above discussion, it can be stated that Zn content of the Kayamkulam estuarine sediments mainly depends on the texture of the sediment and on the clay minerals.

5.4.1b Copper

The average abundance of Cu metal in the lithosphere is 70ppm and that in the earths crust ranges from 24 - 55ppm (Baker1990). The abundance of cu in basaltic rocks is greater than that of the granitic rocks and it is very low in carbonate rocks. The metal ranks 25th in abundance among the elements present in the earths crust. The average copper concentration in sedimentary rocks is lower, 45ppm in shales, 5ppm in sandstones and 4ppm in limestone. Freshwater sediments free from industrial and sewage pollution, the copper levels up to 16.8 ppm have been reported Taylor (1964), Krauskopf, (1972).

The average concentration of Cu is 34ppm (11 – 81 ppm) in the pre monsoon and 29ppm (11 – 68 ppm) in the post monsoon for the bulk sediments (Table 5.3. a). The concentration of Cu is low when compared to the copper content of the Vellar estuary, Mohan (1990); and Ashtamudi estuary, Sajan(1988). Among the different seasons studied, the pre monsoon bulk sediment concentrated more of Cu than post monsoon. The segment wise comparison of Cu for the pre monsoon and post monsoon indicates that the central region close to the estuarine mouth has the lowest concentration whereas though the contribution is minor. The central sector is noticed for the higher content of heavies. Lack of finer sediments at central sector reflected in the lower content of Zn. From the above discussion, it can be stated that Zn content of the Kayamkulam estuarine sediments mainly depends on the texture of the sediment and on the clay minerals.

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In the present study the concentration of Cu in the clayey fraction is much higher. The higher values in clay fraction are seen throughout the entire estuary n both the periods and it is provided in the Table 5.3 b. In the pre monsoon clayey sediments, the average Cu concentration is 102ppm ranging 38-190ppm and in the post monsoon period it range from 34 -226 ppm with an average of 103ppm. Among the three segments in the pre monsoon, the southern sector has the maximum concentration followed by northern sector and the least in the central region. This also reiterates the above said dissolution mechanism when the sediments come in contact with saltwater. In the post monsoon of southern sector the concentration ranges between 47-266ppm (av; 110ppm) and in the northern region the concentration of Cu has an average of 94ppm (45-153ppm) and in the central region the average is found 104ppm (34 - 207ppm).

The aerial distribution of Cu in the clayey sediments for the pre monsoon shows that the average concentration in the northern segment is 112ppm (51-177ppm) followed by southern sector ranging from 68-190 ppm with an average of 117ppm. The lowest concentration is for the central sector being 77ppm (38-164ppm). From the study it is assumed that the higher concentration of Cu in the clay fractions of the Kayamkulam estuarine sediment is due to the adsorption and cation exchange by the same.

Murthy and Verayya,(1981) and Malik and Suchindan (1984) reported as average of 36.5ppm and 25.7ppm of Cu respectively for the bulk sediments of Vembanad estuary. The increasing trend of Cu in the fine particulates, especially clay minerals for certain heavy metals also have tremendous influence on the dissolution of Cu, Mitchell, (1964) and Soong, (1974). During estuarine mixing, the metal like Pb and Ni repel Cu and Zn from the clay minerals.

Regarding the regional variation of Cu content in the Kayamkulam estuarine sediments, from the central sector it decreases towards northern and southern sectors both for the bulk and clays in all two seasons. From the Table 5.2 a-d it is seen that in the bulk fraction Cu is showing marginally significant correlation with Zn for the pre monsoon and highly significant correlation with Fe and K and marginally significant correlation with Na, Mg, Mn and Zn for the post monsoon, while in the clays Cu shows a highly significant positive correlation with Zn, negative correlation with Mg, marginally negative correlation with Fe, Ca, and Mn for the pre monsoon.

Cu, like other trace elements is found in sediments as exchangeable ions bound in organic compounds, in the crystal lattices of alumino-silicates and other minerals. Mobility of copper in high in solution and occurs as $Cu2^{+}$ ions. It is removed from the solution as sulphide in reduzate sediments and as copper oxy-salts in high p^{H} environments. $Cu2^{+}$ can replace $Fe2^{+}$ and Mg $2^{+.}$ The various process by which Cu can be removed are as precipitate of insoluble compounds precipitates of sulphide ion in zones of low oxidation potentials, adsorption by material such as ferrous sulphate, hydrated ferric oxide, hydrated Mn oxide, and clays and removal by metabolic action of organisms. High concentration of Cu can be adsorbed on clay minerals, iron oxides and organic matter. Fixation of Cu by clay minerals by adsorption and cation exchange has been pointed out by Hirst (1962).

In the present study, it is assumed that the higher concentration of Cu in the clay fraction is due to the adsorption and cation exchange by the same. This is inferred from the fact that it has shown a marginally negative correlation with Fe. Cu can be considerably concentrated by accumulation of under reducing conditions in sulphide bearing mud. At the northern sector precipitate of sulphide ion is considered as an important factor, since the necessary reducing environment and very low oxidation potential are found there. Swain (1963) found higher content of Cu in the reduced muds of English lake. Therefore, it may be reasonably concluded that the reducing environment with low oxidative potential favoured the concentration of Cu at the northern sectors of the estuary.

The increasing trend of Cu content from the central sector to northern and southern sectors both for bulk and clays can be explained in terms of adsorption and cation exchange of smectites In the present study, the highest concentration of Cu is found associated with montmorillonite, which dominates the northern and southern sector of the estuary. Rao et al., (1974) found a high content of Cu association with montmorillonite. Hence the Cu content of the Kayamkulam estuarine sediments directly depends on the fine texture of the sediments, on clay minerals, as wrapped up from the above discussion.

5.4.1c Cobalt

Cobalt is one of the important metals, which is closely related to our industrial civilization. In nature, Co is mostly abundant in unstable Ferro magnesium minerals like pyroxene, amphiboles and biotite, Smith (1990), and hence cobalt in sediments and sedimentary rocks reflects the composition of the source rock from which they have been derived. Co is characteristically more able to migrate than other trace metals, Nriagu (1980). In sediments, it is stable in the presence of Nitrogen 'donor molecules. It can be easily be oxidised in hypergene zones and can be converted to the trivalent state. The fate of Co is strongly influenced by aqueous reactions with soluble species and with particulates. Cobalt is relatively scarce in the earth's crust, but the human body requires vitamin B12, which is a cobalt (III) complex to form haemoglobin.

Having the ability to occupy low symmetry sites in enzymes, Cobalt (II) is an enzyme activator, Rose (1983).

The concentration of Co (in ppm) in the bulk and clay fractions of the Kayamkulam estuarine sediments is given in Table 5.3 a and b. In the bulk sediments Co concentration ranges 12-71ppm with an average of 37ppm in the pre monsoon period and an average of 33 ppm (13 -86ppm) in the post monsoon period. The concentration of Co when compared to different textural classes in the post monsoon show there is an decreasing order of concentration from clayey sand (av; 52.8ppm)> sandy mud (av; 43.8ppm) > silty sand (av; 42.5ppm) > mud (av; 38ppm) > sand (av; 29ppm) > muddy sand (av; 25.5ppm) and sandy silt (av; 16ppm). In the pre monsoon season the maximum concentration is seen in the silt (av; 43ppm), following this the concentration decreases as follows, sandy silt (av; 39ppm) = clayey sand =silty sand >muddy sand (av; 38ppm) > sandy mud (av: 37ppm) and least in the sand fraction with an average of 27 ppm.

The sector wise distribution reveals that in the bulk sediments for northern sector the average concentration of Co is 37ppm followed by central 36ppm and in the southern 38ppm for pre monsoon and that of post monsoon is 38ppm, 36ppm and 27ppm for north central and southern sectors respectively. From the table it is noted that there is no relation in the distribution of Co for the two seasons.

The pre monsoon and post monsoon concentration of Co in the clay fraction is given in the Table 5.3 b. The average concentration is 52 ppm (39 – 77ppm) and 57ppm (36 – 93 ppm) in the pre and post monsoon respectively. The sector wise distribution of Co clay reveals that in the pre monsoon the maximum concentration is in the southern sector but for post monsoon the southern sector shows least concentration. Likewise in the post monsoon the maximum concentration is in the central sector but for premonsoon the central sector reports lowest concentration. The sector wise average concentration of clay for pre monsoon is 51ppm, 44ppm and 60ppm for the northern, central and southern sectors respectively and that of post monsoon are 56ppm, 58ppm and 56ppm. In the southern sector the pre monsoon has more concentration and it is also shown in the case of bulk sediments. Co shows highly significant to marginally significant correlation with Fe and marginally significant correlation with K. In clays Co shows marginally significant correlation with Fe (Table 5.2 a-d).

Kharkar et al (1968) stated that, Co, which have been adsorbed out clay minerals and clay coated particulates of river borne sediments are desorbed when the latter comes into contact with high saline waters. The pattern of variability of Co is due to the desorption of Co (Fe-Mn oxide bound and clay mineral bound) under the estuarine condition, a feature well established by many investigators. Evans et al., (1977); Borole et al., (1982); Seralathan (1979) and Murthy and Veerayya, (1981).

The higher content Co is noticed for the northern and southern sector, in the pre monsoon both for the bulk and clay fractions. The Co content of the Kayamkulam estuarine sediments increases towards northern and southern sector from the central sector for the pre monsoon and post monsoon except in the clays for the post monsoon. In the post monsoon it decreases towards other side of the central sector. Marginal to highly significant positive correlation as exhibited by Co with Fe is suggestive of adsorption of Co by hydrated Fe_2O_3. Cobalt is considerably less efficiently desorbed from oxides of iron and manganese than it is clay mineral particles. In the sediments of Kayamkulam estuary, Co is fixed by the adsorption of hydrated Fe_2O_3 and with clay minerals, besides *the fine texture of the substratum.*

5.4.1d Chromium

Cr is seventh most abundant elements on earth but 21^{st} in abundance in the crustal rocks with an average concentration of 100 ppm. Chromium (Cr) is virtually omnipresent in the environment. It is more abundant in the earth's crust than Co, Cu, Zn, Pb and Ni. The Cr concentration in some unpolluted freshwater sediments rises upto 44ppm (Abbasi et al., 1998) The Cr concentration in the pre monsoon and post monsoon periods of bulk sediments and clay fraction of the Kayamkulam estuary is given in the Table 5.3 a and b.

The average concentration of Cr in the bulk sediments of pre monsoon period is 100 ppm (41-136ppm) and in the post monsoon period it decreases with an average of 78ppm (24-127ppm). It is clear from the table 5.3 b that the concentration of Cr is higher in the estuarine bar mouth region i.e., in the central sector with an average of 116ppm in the pre monsoon period (86-134ppm). In the post monsoon period also the central sector has the highest average value of 88 ppm (24-127ppm), which is lesser when compared to the pre monsoon bulk sediments samples. It is seen that in both the seasons the maximum average values differs in the case of northern and southern segments. In pre monsoon period, the southern segments have the average concentration next to central region, average 98ppm (66-136ppm). In the northern sector the range of Cr concentration lies between 41-129ppm with an average value of 88 ppm. But in the post monsoon season, next to the central region, the concentration is greater in the northern sector with an average concentration value of 78ppm and least average value in the southern sector with an average of 68ppm. The observed levels of Cr in the bulk sediments of the estuary are higher than the earlier reports of Mallik (1981). But the values obtained in this study is lesser than that reported by Mohan (1990) for Vellar estuary (271.7 ppm) but much less than that of Ashtamudi Lake (Sajan, 1988).

Table 5.3 b provide the Cr concentration in the clay fractions of Kayamkulam estuary. Similar to that of bulk sediments in clay fraction also pre monsoon fraction has higher concentration. The average concentrations of pre and post monsoon clay fraction are 160 ppm (132- 214 ppm) and 131ppm (37 – 180 ppm) respectively. In sector wise analysis the central sector has the maximum, average concentration except for post monsoon clay fraction. In pre monsoon clay fraction the average concentration of three sectors are 141 ppm (132-159 ppm) for northern sector, central sector has 174 ppm (140 – 186 ppm) and southern sector has an average concentration of 166 ppm (144 – 214 ppm) and that for post monsoon are 137ppm 124ppm and 131ppm for northern, central and southern sectors respectively. In the pre monsoon period the least concentration is reported in the northern sector in both bulk sediments and clay fractions. In pre monsoon period Cr shows positive correlation with all the metals expect in Zn for the bulk sediments and for the post monsoon bulk sediment shows positive correlation with all the metals. In the clay fraction for pre monsoon it shows positive correlation except in Cu, Co Pb and Cd. But in post monsoon it shows negative correlation with Na, Ca, Cu, Pb and Zinc (Table 5.2 a-d). It shows highly significant positive correlation with Fe and K and marginally to highly significant positive correlation with Mn in the bulk. While in clays highly significant positive correlation with Fe and marginally significant correlation with Ca, Mg and Mn for the pre monsoon and marginally significant positive correlation with Fe for the post monsoon.

On the basis of textural classification in the pre monsoon period the highest average value is in the sandy silt (av; 134 ppm) and is the rest of the classes in the decreasing order of concentration as silt (av; 121ppm) > sandy mud (av; 107ppm) > muddy sand (av; 104ppm) >Clayey sand (av; 98 ppm) > silty sand (av; 93ppm) and sand (av; 70ppm). On the post monsoon the highest average is in the mud (av; 127ppm) but only one sample will come under in this class. Next to that is sandy mud and the value rages from 60 -118 ppm (av;99 ppm) > silty sand (av;86ppm) > sand (av;77 ppm) and its range (24 -126 ppm) > clayey sand (67 ppm), sandy mud (av; 44 ppm) > and in the muddy sand (av; 33ppm).

In silicate minerals, $Cr3^{++}$ shows diadochus replacement with Fe^{3+} and Al $3^{+}$and in some cases in spite of the valency differences; Cr replaces ferrous iron and magnesium in many minerals. Cr^{3+} would be expected to proxy more readily for Fe^{3+} than Al $^{3+}$ on the basis of ionic radius, electronetgativity and ionisation potential. Cr^{2+} exhibits diadochy with Mg^{2+} in magnesium rich minerals. Chromium sometimes replaces Al in kaolinites and Fe, and Mg in smectites. In 1984, Mukherjee and Sahu showed that the adsorption and desorption maximum sequence as Cr>Hg>Pb>Cu>Cd>Zn> and Cd>Zn>Cu>Cr>Pb>Hg respectively for a pH of 4.

The variation in the concentration of Cr in the sediments of Kayamkulam estuary can be explained as follows. Cr may be concentrated due to adsorption by the hydrated ferric oxide as evidenced from the highly significant positive correlation. The higher concentration of Cr at the central sector is mainly because of the heavies, besides the replacement of Fe and Mg in montmorillonite. At the southern sector Cr may be the replacement of Al in Kaolinite. Cr shows no significant correlation with organic matter, which implies that concentration of Cr in organic matter is insignificant in the different sectors of the estuary. Therefore from the above it can be deduced that Cr in the Kayamkulam estuarine sediments are mainly due to the adsorption of Cr by ferric oxides and replacement of Al in kaolinite and Fe and Mg in smectites.

5.4.1e Nickel

Nickel is one of the ubiquitous elements and ranks 23rd in order abundance. Its average concentration in the earth's crust being 75ppm (Levinson 1974). In uncontaminated sediments of rivers and lakes, the Ni concentration generally is around 20ppm and reflects its concentration in the soil of the region

(Abbasi et al 1998). Nriagu (1980) computed that the world's major rivers transport about 1.1×10^{10} of dissolved and 135×10^{10} gm of particular Ni annually.

The concentration of Ni is given in the Tables 5.3 a and b shows that the Ni contents of the Kayamkulam estuarine bulk sediments are higher in the pre monsoon sediments when compared to that of post monsoon bulk sediments. This trend was also seen in the case of the clayey fractions. An average of 53ppm (15 -108) is estimated in the pre monsoon bulk sediment samples and in the post monsoon period the average concentration is 41ppm (3-96 ppm). On the pre monsoon period the average values of the three segments are almost equal i.e. in the northern segments its has an average concentration of 51ppm (23-70 ppm), in the central region the concentration ranges from 15-82ppm (av; 50 ppm) and in the southern segment it has an average concentration of 58ppm (15 - 108ppm). The total all concentration of post monsoon is lesser when compared with pre monsoon average concentrations. The average concentration of northern segment for the post monsoon is 52ppm (3-96ppm), the central sector the average concentration decreases to 39ppm and followed by southern sector with 30 ppm (12- 79 ppm).

The average concentration of Ni in the clay fraction of the pre monsoon and the post monsoon period is given in the Table 5.3 b. The average concentration in the pre monsoon is 99 ppm (57 –210 ppm) and in the post monsoon period is 84ppm (18 – 130 ppm). The pre monsoon clay fraction has the higher concentration when compared to the respective post monsoon period. The sector wise examinations found that the central sector has the least average concentration in the pre monsoon and post monsoon period ie 87 ppm and 70ppm respectively. The average concentration in the northern and southern sectors of pre monsoon and post monsoon periods are 91 ppm (57 –147 ppm), 119 ppm (91 –210) and 90 ppm (711 – 130); 92 ppm (36 –116 ppm respectively.

Considering the concentration of Ni in different textural classes the maximum average concentration in the post monsoon bulk sediments is seen in mud (av; 69ppm) > silty sand (av; 68.5ppm)>sandy mud (av; 65.8ppm) > sand (av; 35.1ppm) > muddy sand (av; 30.5ppm) > clayey sand (av; 6.25ppm) and least in sandy silts with an average value of 3 ppm. In pre monsoon the maximum average concentration is in sandy silt (av; 78ppm) > sand (av; 59ppm) > sandy mud (av; 58ppm) > silt (av; 57ppm) > clayey sand (av; 54ppm) > muddy sand (av; 48ppm) and silty sand 46ppm.

The observed ranges of Ni contents of the estuarine bulk sediments are comparable with the earlier reports (14 - 85ppm) of Mallik (1981). Comparing with the Cauvery River, the value of present study is little higher in the bulk sediments (Subrmanian et al 1985b).

The fixation of Ni in soils and sediments in caused by the hydrous iron oxide. Nickel is able to replace Mg isomorphically. Besides Fe and Mg, it can also substitute Na^+ in silicate minerals. Ni with Mg and Si can travel long distances in water and gets precipitated as complex hydrous silicates with layer lattices, when the water is neutralised. Unlike Fe and Mn, Ni tends to be in solution and is carried to longer distances and is deposited in the hydrolysate sediments. More over in estuarine sediments, it is seen that Ni has similar concentrations in both oxidising and anoxic sediments (Burton and Liss, 1976)

The variation in Ni-content of Kayamkulam estuarine sediments can be explained in term of adsorption by Fe, organic matter and by either adsorption or cation exchange in clay minerals at the northern part of the Kayamkulam estuary. Ni precipitation has taken place due to adsorption by ferrous sulphide. This inference is drawn from the marginally to highly significant positive correlation exhibited by Ni in the bulk sediments, which contain comparatively high amount of Fe (Table 5.2 a-d). At the central region, Ni fixed due to adsorption of Ni by hydrous iron oxides and clay minerals in clays.

There is an enrichment of Ni towards the southern and northern sector. This can be explained by the presence of clay minerals, which fixes Ni in them, either by adsorption as ion exchange property. Ni remains largely in the solid products of disintegration during weathering and is deposited in the hydrolysate sediments. Hence it can be considered that a significant part of Ni might have been held up in clay minerals either by adsorption or cation exchange mechanism. During weathering, Mg is leached relative to Ni and under conditions required for the formation of Smectite, Ni will be retained whenever Mg is retained in it (Hirst, 1962). Therefore it can be considered that a part of Ni is fixed in smectite, which is the predominant clay minerals at the northern and southern sectors, It is observed higher concentrations of Ni in montmorillonite relative to other clay minerals and concluded that Ni strongly favours octahedral co-ordination. Therefore it can be expected that Ni substitute Mg in the octahedral layers of montmorillonite lattice. So, from the above discussion, it can be concluded that Ni in clays is mainly due to cation exchange in montmorillonite.

5.4.1f Lead

The average concentration of Pb on the surface of the earth is 16ppm, Davis (1990). Pb discharged mainly into the surface by mining, smelting, refining as well as from the production and uses of Pb based products. It has the ability to readily incorporated with sediments will develop low mobility and hence sediment is liable to remain polluted and finally reaches to the aquatic sediments. In that aquatic environment, its chemical forms will closely control its mobility and distribution and it interacts determinately with aquatic life. Its toxicity in sediments is affected by pH, hardness, organic material and presence of other metals. The toxic effects of Pb on humans have been well documented, as man is using Pb for thousands of years, Branica and Konrad, (1980).

The concentration of Pb in the bulk sediments of both the pre monsoon and post monsoon is given in the Tables 5.3 a for the Kayamkulam estuary. The average concentration of Pb in the pre monsoon is 38ppm (10-96ppm) and in the post monsoon it ranges from 4 - 114ppm with an average of 31ppm. It is noted from the table, that the concentration of Pb is greater in the pre monsoon period when it compares to the post monsoon bulk sediments. In the bulk sediments for pre monsoon the central sector of the estuary has low concentration of Pb where there is mixing of seawater and fresh water is going on. The maximum average concentration in the post monsoon bulk sediments is in the northern sector

44ppm (4-114ppm). But the southern segment is showing least concentration of Pb ranging from 6 -70ppm (av; 23ppm). In the central part the average concentration is 25ppm(8-58ppm).

The concentration of lead in the clay fraction of both pre monsoon and post monsoon periods is 74ppm (42 – 104ppm) and 49ppm (1 – 98 ppm)(Table 5.3 b). The average concentration is higher in the pre monsoon period for both bulk sediments and clay fraction. In the pre monsoon the north, central and southern sectors have an average concentration of 77ppm (48 – 104), 70 ppm (50 -86%) and 75 ppm (42 –104). *Similarly in the post monsoon clay fraction it is* 59 ppm, (: 32 – 95 ppm), 28 ppm (18 – 50 ppm) and 60 ppm (32 –98 ppm) respectively. The northern sector has maximum average concentration in both the periods and in both bulk sediments and clay fractions. Regarding the inter relationship, Pb shows marginally significant correlation with Fe, Na and high level of correlation with K for the post monsoon in the bulk sediments. No significant level of correlation is seen for the clay fraction (Table 5.2 a-d).

Based on the textural classes the maximum average of Pb in the pre monsoon and the descending order of concentration are as follows muddy sand (av; 45ppm) > clayey sand (av; 42ppm) > sand (av; 36ppm) > sandy mud (av; 31ppm) > sandy silt (av; 28ppm) > silty sand (av; 26ppm) and silt (av; 24ppm). In the same way the concentration of Pb can be described in the post monsoon also with maximum average of mud (av; 58ppm) > sandy mud (av; 47ppm) > silty sand (av; 35ppm) > muddy sand (av; 33ppm) > sand (av; 19ppm) > clayey sand (av; 16ppm) and sandy silt (av; 12ppm).

Pb from weathering of magmatic and metamorphic rock is expected tot be mainly accumulated in detrital sediments in their K bearing minerals, micas, and feldspars. Pb replaces K in its structural position. Some of amount of Pb, transported in to the sedimentary environments is being adsorbed on clay minerals and ferric hydroxides. Lead may be carried to solution in slightly acidic conditions. In neutral or somewhat alkaline water, the Pb ion become hydrolysed and is readily co-precipitated with the hydroxides of more abundant elements or adsorbed by clay minerals. Lead can replace Ca^{2+} and K^{+} diadocically in minerals. Some mobilized Pb is adsorbed on newly formed clay minerals - Kaolinite (Wedepohl, 1978). Among all the clay minerals, Kaolinite fixes maximum amount of Pb and then montmorillonite. The clay minerals contain most of the lead in sediments.

In the Kayamkulam estuarine sediments, Pb does not show any specific correlation with organic matter but shows marginally significant correlation with Na and K for the post monsoon. So it can be inferred that Pb is not concentrated considerably by Fe oxide. Therefore it can be concluded that, in the Kayamkulam estuarine sediments, most of the Pb is associated with the clays.

5.4.1g Cadmium

Cadmium next to mercury is the most toxic of heavy metal pollutants. It is responsible for Itai-Itai disease to human being-causing deterioration of bones, weakening of joints, and extreme pain. This metal is not essential for plants and animals; therefore cadmium in the environment can cause no gain but harm

(Abbassi et al;.,1998). Cd is 64th in order of abundance in the earth's crust with an average concentration of 0.2ppm (Taylor, 1964). In uncontaminated sediments, the level of Cd will generally be less than 0.5ppm (Abbasi,1998). Hutton (1982) reported that more than half of the Cd ever used in industries was produced in the last two decades. Mining and smelting of Cd, atmospheric pollution from metallurgical industries, the disposal of wastes containing Cd, burning of fossil fuels are the main sources through which Cd reaches the aquatic environments, Hutton (1982).

On comparing Cd with other trace elements it is the least distributed metal in the present study area. It is also clear that the distribution of Cd is almost equal throughout the estuary ranging from 1-3ppm (av; 2ppm) in the pre monsoon and in the post monsoon with an average of 2ppm (1-4ppm) (Table 5.3 a).

The sector wise distribution shows almost similar pattern in their average concentration both in pre monsoon and post monsoon period. But maximum concentration is in the central sector of the estuary. This average concentration of Cd in the Kayamkulam estuary is due to the adsorption mechanism operative in the removal of trace elements from solution during estuarine mixing may be the formation of iron oxide coating on clay particles which have acted as negatively charged nuclei for the adsorption of hydrolysis products of iron.

The average concentration of Cd in the clay fraction is given in the Table 5.3 b. In the pre monsoon period the average concentration is 2 ppm (1-3 ppm) and in the post monsoon period it has an average 2-ppm (1-5 ppm). The sector wise distribution shows almost similar pattern in their average concentration both in pre monsoon and post monsoon period. But maximum concentration is in the central sector of the estuary. This average concentration of Cd in the Kayamkulam estuary is due to the adsorption mechanism operative in the removal of trace elements from solution during estuarine mixing as referred above.

The detailed study in comparison with the textural class reveals that maximum average concentration of Cd is seen in the pre monsoon sandy silt (av; 3ppm) > muddy sand (av; 2ppm) = silty sand = sandy mud = silt = sand > clayey sand (av; 1ppm) and that for post monsoon is for mud (av; 2ppm) = silty sand = muddy sand = sand > sandy mud (av; 1ppm) = clayey sand and sand silt. Few samples did not yield any value and part in pre monsoon period as the concentration is below detectable range. The silty sand (av; 3ppm) shows maximum average followed by the rest of the fractions with almost equal in strength. The average Cd in the bulk is lesser when compared to that of Vembanad estuary (Mallik and Suchindan, 1984) and the Vellar estuary (Mohan, 1990). Natural variation in concentrations of Cd, Co, Cu, Ni, Pb, and Zn in sediments of Cleveland Bay is modelled by linear regression by using the concentration of Al recovered by strong acid digestion as an independent variable. In contrast, at least 60%, and generally greater than 80% of Cd is recovered by weak HCl digestion irrespective of modelled enhancement, and suggests that the statistically modelled enhancement of Cd may be more meaningful than weak HCl soluble concentrations Doherty et al., (2000).

Very substantial amounts of Cd are incorporated with sulphide phases of sediments under stagnant summer conditions, which lead the bottom waters becoming anoxic, and when the water is renewed and free oxygen is again present, Cd is partly released. (Burton and Liss, 1976). One important adsorption mechanism operative in the removal of trace elements from solution during estuarine mixing may be the formation of iron oxide coatings on clay particles, which have acted as negatively charged nuclei for the adsorption of hydrolysis products of iron. Aston and Chester (1973) have suggested that the oxide coatings formed a detrital particles in the estuaries may remove trace elements from solution and may also prevent the trace element desorption from ion exchange sites. The sorption behaviour of some elements is very sensitive to the pH of the fresh water or seawater. Thus a change in pH may result in large differences in distribution coefficients. The most sensitive change in behaviour for Cd is with in the range of 6 to 8. The pH of seawater is generally close to 8; the range in fresh water is frequently between 6 & 8, thus highly influencing the sorption behaviour. Another influence on the sorption behaviour of elements in estuarine system is the presence of particulate and dissolved organic matter. At a pH of 8.1, the adsorption of Cd is suppressed while desorption is enhanced. From the Eh-pH diagram of Cd (Burton and Liss, 1976), it is seen that the most stable solid phases are $CdCo_3$ and CdS where as the dominant stable dissolved species are Cd^{2+} and $Cd(OH)_2$.

From the above discussion, it can be concluded that the northern part of the lake Cd is held as CdS since the region is noted for the prevalence of reducing environment and as $CdCO_3$ as the central and southern sectors yielded the maximum CO_3 concentration.

5.5 TRACE METAL SPECIATION

Trace metal speciation studies in the aquatic environments are of paramount importance for the last few decades. Using these studies trace metal levels in the environment and their fractionation in different chemical phases can be delineated. Such investigations provide information about the mobility, bio availability, and factors controlling the concentration of toxic metals in sediments as well as in water column besides the origin, mode of occurrence and transport of trace metals (Calmano and Fostner, 1983). The sequential extraction procedures also throw enough light on the history of metal inputs, diagenetic transformations within the sediments and the reactivity of heavy metal species of both natural and anthropogenic origin (Rapin, 1984). Gad and Lerach (1966) investigation on sediment associated trace metals, were confined to the partitioning of metals into detrital and non-detrital fractions only. Chemical extraction procedures for the separation of metals associated with the ferro magnesium minerals, carbonates and adsorbed trace metals are the further developments in that direction (Chester and Hughes,1967). Sequential extraction was extended by Nair et al., (1991) to categorize the various forms of Cd, Cu, Pb and Zn the sediments of the Cochin estuary. Trace metal speciation studies provide knowledge on the relative phase distribution of trace metals in aquatic sediments. Tessier et al., (1979), introduced a five step sequential extraction technique. This technique facilitated the distinction between exchangeable, easily reduceable, moderately reduceable, organically bound and residual metal fractions These chemical techniques were based on the three groups of components occurring in fluvial system, which are potentially able to enrich the metals in sediments. Here an attempt has been made to understand the various chemical species of some selected trace metals viz. Zn, Cd, Cu, Co, Cr, Ni, Pb in estuarine environment of the Kayamkulam estuary.

The concentration of Zn, Cd, Cu, Co, Cr, Ni, and Pb in the various phases of the Kayamkulam sediments is given in table 5.5 Speciation studies of the trace metals in the Kayamkulam estuary both for the pre and post monsoon revealed that Cd is the most exchangeable cation fraction followed by Cr and Cu. Zn and Co has shown a very low exchangeable fractions and that too for the northern sector in the pre monsoon while Co registered only in southern sector. Ni and Pb did not show any exchangeable cation fraction. For the post monsoon, the exchangeable fractions of Cd and Cr has gone up by a few percentage while a marginal decrease is noticed in the case of Cu and considerable decrease for Zn. The variation as registered by the trace metals for pre and post monsoon can be attributed to the changes in the textural and physico-chemical conditions of the environment.

The second stage represents the carbonate bound fractions. Cd records the highest percentage (av; 34.97%) followed by Cr, Cu, Co for the pre monsoon while for the post monsoon Cd shows a considerable decrease, the average value being 24.52% followed by Cr, with a slight hike in the percentage (av;

Table 5.5 Concentration of heavy metals in various chemical phases of sediment samples for both pre and post monsoon

EXCHANGEABLE

PREMONSOON (PERCENTAGE)

	Sample No.	**Zn**	**Cd**	**Cu**	**Co**	**Cr**	**Ni**	**Pb**
	1	1.46	27.27	5.98	2.06	11.89	0.00	0.00
	2	2.20	25.00	3.53	0.00	11.25	0.00	0.00
	4	0.00	39.29	5.28	0.00	12.42	0.00	0.00
N	5	0.00	25.00	7.17	0.00	12.24	0.00	0.00
	7	4.63	37.50	6.91	8.33	11.78	0.00	0.00
	9	0.00	17.24	4.66	0.00	10.84	0.00	0.00
	Average	**1.38**	**28.55**	**5.59**	**1.73**	**11.74**	**0.00**	**0.00**
	11	0.00	18.18	3.41	0.00	10.35	0.00	0.00
	12	0.00	33.33	5.48	0.00	13.20	0.00	0.00
	14	0.00	26.09	4.86	0.00	9.77	0.00	0.00
C	17	0.00	34.78	5.03	0.00	11.75	0.00	0.00
	18	0.00	36.84	3.16	0.00	12.51	0.00	0.00
	20	0.00	23.08	4.11	0.00	10.99	0.00	0.00
	Average	0.00	**28.72**	**4.34**	0.00	**11.43**	0.00	0.00
	23	0.00	31.03	5.23	0.00	11.26	0.00	0.00
	24	0.00	27.27	5.05	0.00	11.97	0.00	0.00
	25	0.00	28.57	5.52	0.00	11.37	0.00	0.00
	26	0.00	33.33	5.12	0.00	11.57	0.00	0.00
S	27	0.00	30.77	5.35	0.00	11.17	0.00	0.00
	28	0.00	33.33	4.76	0.00	11.78	0.00	0.00
	29	0.00	50.00	6.49	0.00	13.42	0.00	0.00
	31	0.00	24.14	4.50	0.00	11.54	0.00	0.00
	Average	0.00	**32.31**	**5.25**	0.00	**11.76**	**0.00**	**0.00**

POST MONSOON (PERCENTAGE)

	Sample No.	**Zn**	**Cd**	**Cu**	**Co**	**Cr**	**Ni**	**Pb**
	1	0.00	20.83	3.53	0.00	11.03	0.00	0.00
	2	2.92	28.57	3.93	0.00	10.54	0.00	0.00
	4	0.00	40.00	7.59	0.00	13.46	0.00	0.00
N	5	0.00	46.67	6.41	0.00	12.97	0.00	0.00
	7	0.00	28.00	4.23	0.00	11.32	0.00	0.00
	9	0.00	43.48	3.33	0.00	12.08	0.00	0.00
	Average	**0.49**	**34.59**	**4.83**	**0.00**	**11.90**	**0.00**	**0.00**
	11	0.00	76.19	2.89	0.00	9.85	0.00	0.00
	12	0.00	30.00	6.25	0.00	13.89	0.00	0.00
	14	0.00	34.48	5.18	0.00	11.74	0.00	0.00
C	15	0.00	36.36	6.00	0.00	11.61	0.00	0.00
	17	1.88	36.36	3.71	0.00	11.84	0.00	0.00
	18	0.00	31.58	4.87	0.00	12.48	0.00	0.00
	19	0.00	21.43	5.83	0.00	13.05	0.00	0.00
	20	0.00	23.53	5.45	0.00	13.92	0.00	0.00
	Average	**0.23**	**36.24**	**5.02**	**0.00**	**12.30**	**0.00**	**0.00**
	24	0.00	21.21	3.25	0.00	11.33	0.00	0.00
	26	0.00	36.84	5.49	12.35	12.62	0.00	0.00
S	27	0.00	38.10	7.58	10.71	13.04	0.00	0.00
	28	0.00	40.00	6.22	8.04	13.28	0.00	0.00
	29	0.00	26.67	4.61	9.05	12.71	0.00	0.00
	31	0.00	33.33	4.13	0.00	12.03	0.00	0.00
	Average	**0.00**	**32.69**	**5.22**	**6.69**	**12.50**	**0.00**	**0.00**

Contd...

BOUND TO CARBONATES

PREMONSOON

	Sample No.	Zn	Cd	Cu	Co	Cr	Ni	Pb
					PERCENTAGE			
	1	0.00	36.36	7.64	2.47	14.65	0.00	0.00
	2	0.00	35.71	5.19	5.57	13.70	0.00	0.00
	4	0.00	32.14	8.80	7.69	15.09	0.00	0.00
N	5	0.00	45.00	11.21	2.04	15.06	0.00	0.00
	7	0.00	37.50	9.68	7.78	14.47	0.00	0.00
	9	0.00	37.93	5.64	0.00	13.53	0.00	0.00
Average	**4.67**	0.00	**37.44**	**8.03**	**4.26**	**14.42**	0.00	0.00
	11	0.00	33.33	6.30	4.94	12.68	0.00	0.00
	12	0.00	50.00	10.50	0.00	16.36	0.00	0.00
	14	0.00	21.74	5.88	5.21	12.20	0.00	0.00
C	17	0.00	34.78	7.55	10.64	14.05	0.00	0.00
	18	0.00	31.58	7.59	10.08	15.20	0.00	0.00
	20	0.00	50.00	9.59	16.13	13.41	0.00	0.00
Average	**15.33**	0.00	**36.91**	**7.90**	**7.83**	**13.98**	0.00	0.00
	23	0.00	37.93	8.00	6.22	14.02	0.00	0.00
	24	0.00	27.27	9.39	6.85	14.85	0.00	0.00
	25	0.00	38.10	8.97	8.43	14.07	0.00	0.00
	26	0.00	33.33	9.84	7.14	14.12	0.00	0.00
S	27	0.00	30.77	8.70	11.34	13.91	0.00	0.00
	28	0.00	27.78	8.84	3.66	14.34	0.00	0.00
	29	0.00	37.50	9.54	0.00	16.84	0.00	0.00
	31	0.00	20.69	7.00	1.76	14.18	0.00	0.00
Average	**26.63**	**0.00**	**31.67**	**8.78**	**5.68**	**14.54**	0.00	0.00

POST MONSOON

	Sample No.	Zn	Cd	Cu	Co	Cr	Ni	Pb
					PERCENTAGE			
	1	3.85	12.50	3.15	0.00	12.91	0.00	0.00
	2	0.00	14.29	6.00	0.00	12.52	0.00	0.00
	4	0.00	15.00	12.95	0.00	15.97	0.00	0.00
N	5	0.00	40.00	10.68	0.00	16.26	0.00	0.00
	7	0.00	24.00	6.48	0.00	14.27	0.00	0.00
	9	0.46	13.04	7.54	0.00	15.19	0.00	0.00
Average	**4.67**	**0.72**	**19.80**	**7.80**	**0.00**	**14.52**	**0.00**	**0.00**
	11	0.00	4.76	5.56	1.89	11.77	0.00	0.00
	12	0.00	35.00	11.72	0.00	17.00	0.00	0.00
	14	0.00	24.14	7.08	0.00	14.24	0.00	0.00
C	15	0.00	27.27	10.40	0.00	13.81	0.00	0.00
	17	0.00	27.27	7.16	0.00	14.21	0.00	0.00
	18	0.00	31.58	10.06	0.00	14.74	0.00	0.00
	19	0.00	35.71	12.08	0.00	15.93	0.00	0.00
	20	0.00	47.06	9.82	0.00	16.46	0.00	0.00
Average	**15.75**	**0.00**	**29.10**	**9.24**	**0.24**	**14.77**	**0.00**	**0.00**
	24	0.00	18.18	5.24	3.27	13.41	0.00	0.00
	26	0.00	26.32	7.69	0.00	15.11	0.00	0.00
S	27	0.00	33.33	10.61	0.00	15.58	0.00	0.00
	28	0.00	40.00	12.45	0.00	15.84	0.00	0.00
	29	0.00	26.67	8.07	0.00	15.54	0.00	0.00
	31	0.00	14.29	7.49	0.00	14.30	0.00	0.00
Average	**27.50**	**0.00**	**26.46**	**8.59**	**0.55**	**14.96**	**0.00**	**0.00**

Contd...

BOUND TO Fe/Mn OXIDES

PREMONSOON

PERCENTAGE

	Sample No.	Zn	Cd	Cu	Co	Cr	Ni	Pb
	1	5.83	0.00	14.95	6.17	21.26	0.00	0.00
	2	0.00	0.00	8.30	3.28	21.72	0.00	0.00
	4	0.00	10.71	10.21	5.92	17.61	0.00	0.00
N	5	0.00	0.00	10.31	0.00	17.54	0.00	0.00
	7	3.47	8.33	13.36	3.33	17.01	0.00	0.00
	9	0.00	0.00	6.62	0.00	15.19	0.00	0.00
Average	**4.67**	**1.55**	**3.17**	**10.63**	**3.12**	**18.39**	**0.00**	**0.00**
	11	0.00	6.06	7.09	0.00	14.41	0.00	0.00
	12	0.00	0.00	13.70	5.56	18.74	0.00	0.00
	14	0.00	0.00	7.42	0.00	14.13	0.00	0.00
C	17	0.00	0.00	9.43	2.66	16.30	0.00	0.00
	18	0.00	0.00	9.81	0.00	17.35	0.00	0.00
	20	0.00	0.00	8.90	0.00	15.53	0.00	0.00
Average	**15.33**	**0.00**	**1.01**	**9.39**	**1.37**	**16.08**	**0.00**	**0.00**
	23	0.88	0.00	8.00	0.00	16.24	0.00	0.00
	24	0.00	0.00	10.47	0.00	16.54	0.00	0.00
	25	0.00	4.76	11.72	0.00	16.06	0.00	0.00
	26	0.00	0.00	12.99	0.00	15.87	0.00	0.00
S	27	0.00	0.00	10.37	0.00	15.70	0.00	0.00
	28	0.00	5.56	9.18	0.00	16.41	0.00	0.00
	29	0.00	6.25	13.36	0.00	18.27	0.00	0.00
	31	0.00	0.00	7.75	0.00	15.78	0.00	0.00
Average	**26.63**	**0.11**	**2.07**	**10.48**	**0.00**	**16.36**	**0.00**	**0.00**

POST MONSOON

PERCENTAGE

	Sample No.	Zn	Cd	Cu	Co	Cr	Ni	Pb
	1	1.33	0.00	9.28	3.10	20.40	0.00	0.00
	2	2.79	0.00	9.24	4.26	19.47	0.00	0.00
	4	0.00	0.00	14.29	0.00	18.28	0.00	0.00
N	5	0.48	0.00	13.68	0.00	18.30	0.00	0.00
	7	1.02	0.00	9.01	1.01	15.75	0.00	0.00
	9	1.85	0.00	7.76	7.43	17.81	0.00	0.00
Average	**4.67**	**1.25**	**0.00**	**10.54**	**2.63**	**18.34**	**0.00**	**0.00**
	11	0.00	0.00	9.78	0.00	14.27	0.00	0.00
	12	0.00	0.00	13.67	0.00	19.03	0.00	0.00
	14	0.00	6.90	8.17	0.42	15.98	0.00	0.00
C	15	0.00	0.00	11.60	0.00	15.14	0.00	0.00
	17	0.00	0.00	12.47	0.00	17.00	0.00	0.00
	18	0.00	0.00	10.39	0.00	16.65	0.00	0.00
	19	0.00	7.14	13.75	0.00	17.99	0.00	0.00
	20	0.00	5.88	12.36	0.00	17.88	0.00	0.00
Average	**15.75**	**0.00**	**2.49**	**11.52**	**0.05**	**16.74**	**0.00**	**0.00**
	24	0.00	0.00	5.42	1.26	15.12	0.00	0.00
	26	2.36	0.00	9.62	0.00	16.61	0.00	0.00
S	27	0.00	0.00	17.42	0.00	17.51	0.00	0.00
	28	0.00	0.00	13.69	0.00	17.43	0.00	0.00
	29	0.00	0.00	10.37	0.00	16.68	0.00	0.00
	31	0.00	0.00	8.53	0.00	15.93	0.00	0.00
Average	**27.50**	**0.39**	**0.00**	**10.84**	**0.21**	**16.55**	**0.00**	**0.00**

Contd...

BOUND TO ORGANIC MATTER

PREMONSOON

	Sample No.	Zn	Cd	Cu	Co	Cr	Ni	Pb
					PERCENTAGE			
	1	5.54	3.03	12.29	8.23	17.97	0.00	0.00
	2	0.00	0.00	7.88	2.62	17.78	0.00	0.00
	4	0.00	0.00	12.32	1.78	18.44	0.00	0.00
N	5	0.00	0.00	16.14	0.00	17.98	0.00	0.00
	7	2.31	0.00	16.13	1.67	17.95	0.00	0.00
	9	1.29	0.00	11.27	3.72	19.50	0.00	0.00
Average	**4.67**	**1.52**	**0.51**	**12.67**	**3.00**	**18.27**	0.00	0.00
	11	0.00	9.09	9.71	5.23	15.62	0.00	0.00
	12	24.71	0.00	19.18	21.11	19.41	0.00	0.00
	14	0.00	2.17	9.72	0.00	15.41	0.00	0.00
C	17	0.00	0.00	12.89	5.85	17.69	0.00	0.00
	18	38.84	0.00	28.80	15.97	19.70	0.00	0.00
	20	0.00	3.85	17.81	2.58	18.42	0.00	0.00
Average	**15.33**	**10.59**	**2.52**	**16.35**	**8.46**	**17.71**	0.00	0.00
	23	0.00	0.00	16.00	0.00	18.20	0.00	0.00
	24	0.00	9.09	15.16	4.44	18.05	0.00	0.00
	25	7.68	0.00	16.21	0.00	16.90	0.00	0.00
	26	2.88	0.00	14.57	5.36	16.62	0.00	0.00
S	27	0.00	0.00	13.71	0.00	19.55	0.00	0.00
	28	0.72	0.00	13.61	0.61	16.95	0.00	0.00
	29	0.00	6.25	15.65	10.29	19.54	0.00	0.00
	31	0.00	0.00	8.75	1.76	15.78	0.00	0.00
Average	**26.63**	**1.41**	**1.92**	**14.21**	**2.81**	**17.70**	0.00	0.00

POST MONSOON

	Sample No.	Zn	Cd	Cu	Co	Cr	Ni	Pb
					PERCENTAGE			
	1	0.74	4.17	6.49	9.82	15.53	0.00	0.00
	2	6.13	0.00	7.39	9.38	14.43	0.00	0.00
	4	3.78	0.00	15.18	15.22	18.43	0.00	0.00
N	5	0.00	0.00	14.10	19.15	18.95	0.00	0.00
	7	44.74	0.00	32.11	28.28	23.23	0.00	0.00
	9	0.00	0.00	7.76	10.14	17.29	0.00	0.00
Average	**4.67**	**9.23**	**0.69**	**13.84**	**15.33**	**17.98**	0.00	0.00
	11	0.00	0.00	8.22	2.16	13.65	0.00	0.00
	12	1.79	0.00	13.67	6.58	18.63	0.00	0.00
	14	0.00	0.00	9.81	0.00	16.32	0.00	0.00
C	15	22.09	0.00	16.80	11.90	16.34	0.00	0.00
	17	5.42	4.55	10.61	12.21	16.57	0.00	0.00
	18	0.00	5.26	12.01	18.56	17.90	0.00	0.00
	19	2.34	0.00	15.00	0.00	17.99	0.00	0.00
	20	13.87	0.00	18.91	31.52	20.03	0.00	0.00
Average	**15.75**	**5.69**	**1.23**	**13.13**	**10.37**	**17.18**	**0.00**	**0.00**
	24	0.00	3.03	14.29	5.29	18.92	0.00	0.00
	26	0.00	0.00	12.09	3.09	19.50	0.00	0.00
S	27	2.47	0.00	14.02	11.43	17.70	0.00	0.00
	28	0.00	0.00	16.60	3.57	18.03	0.00	0.00
	29	0.00	13.33	12.97	12.86	18.46	0.00	0.00
	31	0.00	0.00	10.85	13.24	18.03	0.00	0.00
Average	**27.50**	**0.41**	**2.73**	**13.47**	**8.25**	**18.44**	0.00	0.00

Contd...

RESIDUAL

PREMONSOON

	Sample No.	Zn	Cd	Cu	Co	Cr	Ni	Pb
					PERCENTAGE			
	1	87.17	33.33	59.14	81.07	34.24	100.00	100.00
	2	97.80	39.29	75.10	88.52	35.55	100.00	100.00
	4	100.00	17.86	63.38	84.62	36.44	100.00	100.00
N	5	100.00	30.00	55.16	97.96	37.17	100.00	100.00
	7	89.58	16.67	53.92	78.89	38.78	100.00	100.00
	9	98.71	44.83	71.81	96.28	40.93	100.00	100.00
Average	**4.67**	**95.54**	**30.33**	**63.08**	**87.89**	**37.19**	**100.00**	**100.00**
	11	100.00	33.33	73.49	89.83	46.94	100.00	100.00
	12	75.29	16.67	51.14	73.33	32.30	100.00	BDL
	14	100.00	50.00	72.12	94.79	48.49	100.00	100.00
C	17	100.00	30.43	65.09	80.85	40.21	100.00	100.00
	18	61.16	31.58	50.63	73.95	35.23	100.00	100.00
	20	100.00	23.08	59.59	81.29	41.64	100.00	100.00
Average	**15.33**	**89.41**	**30.85**	**62.01**	**82.34**	**40.80**	**100.00**	**83.33**
	23	99.12	31.03	62.77	93.78	40.28	100.00	100.00
	24	100.00	36.36	59.93	88.71	38.57	100.00	100.00
	25	92.32	28.57	57.59	91.57	41.59	100.00	100.00
	26	97.12	33.33	57.48	87.50	41.82	100.00	100.00
S	27	100.00	38.46	61.87	88.66	39.67	100.00	100.00
	28	99.28	33.33	63.61	95.73	40.51	100.00	100.00
	29	100.00	0.00	54.96	89.71	31.94	100.00	BDL
	31	100.00	55.17	72.00	96.48	42.72	100.00	100.00
Average	**26.63**	**98.48**	**32.03**	**61.28**	**91.52**	**39.64**	**100.00**	**87.50**

POST MONSOON

	Sample No.	Zn	Cd	Cu	Co	Cr	Ni	Pb
					PERCENTAGE			
	1	94.07	62.50	77.55	87.08	40.13	100.00	100.00
	2	88.16	57.14	73.44	86.36	43.03	100.00	100.00
	4	96.22	45.00	50.00	84.78	33.86	100.00	100.00
N	5	99.52	13.33	55.13	80.85	33.52	100.00	BDL
	7	54.24	48.00	48.17	70.71	35.43	100.00	100.00
	9	97.69	43.48	73.61	82.43	37.64	100.00	100.00
Average	**4.67**	**88.32**	**44.91**	**62.98**	**82.04**	**37.27**	**100.00**	**83.33**
	11	100.00	19.05	73.56	95.96	50.47	100.00	100.00
	12	98.21	35.00	54.69	93.42	31.45	100.00	BDL
	14	100.00	34.48	69.75	99.58	41.71	100.00	100.00
C	15	77.91	36.36	55.20	88.10	43.09	100.00	100.00
	17	92.71	31.82	66.05	87.79	40.38	100.00	100.00
	18	100.00	31.58	62.66	81.44	38.23	100.00	100.00
	19	97.66	35.71	53.33	100.00	35.03	100.00	100.00
	20	86.13	23.53	53.45	68.48	31.70	100.00	BDL
Average	**15.75**	**94.08**	**30.94**	**61.09**	**89.34**	**39.01**	**100.00**	**75.00**
	24	100.00	57.58	71.79	90.18	41.21	100.00	100.00
	26	97.64	36.84	65.11	84.57	36.15	100.00	100.00
S	27	97.53	28.57	50.38	77.86	36.18	100.00	100.00
	28	100.00	20.00	51.04	88.39	35.41	100.00	100.00
	29	100.00	33.33	63.98	78.10	36.61	100.00	100.00
	31	100.00	52.38	68.99	86.76	39.70	100.00	100.00
Average	**27.50**	**99.19**	**38.12**	**61.88**	**84.31**	**37.54**	**100.00**	**100.00**

N - NORTERN SECTOR, C - CENTRAL SECTOR, S - SOUTHERN SECTOR

14.75%), Cu, again an increase (av; 8.61%) while Co exhibited an almost non-availability. Pb and Ni, as in the case of exchangeable fraction did not register any carbonate bound phase whereas Zn shows a marginal carbonate bound fraction only for the post monsoon in the northern sector.

In the Fe/Mn oxide bound phase representing the third stage of the sequential extraction, Cr yielded the highest percentage (av; 16.88%) followed by Cu (av;10.20%), Cd (av; 2.08%) and Co (av; 1.35%) for the pre monsoon. Zn recorded only for 3 stations with an average concentration of 0.51%. All for the season, Co and Cu show Fe/Mn oxide bound fraction for all the three sectors. Ni, Pb has not represented any Fe/Mn oxide bound phase for pre and post monsoon. For the post monsoon Cu and Cr recorded a very marginal hike in their percentages while Cd and Co shows a decrease in their values. Cd has virtually no Fe/ Mn oxide bound fraction for the post monsoon except for central sector.

The fourth stage of trace metal speciation is the organic matter bound, in that Cr yielded a value of av.17.87%, Cu (av; 14.39%), Co (av; 4.56%), Zn (av; 4.20%) and Cd (av; 1.67%) for the pre monsoon while for the post monsoon Cr recorded an average of 17.80%, Cu (av;13.44%), Co (av;1.22%), Zn (av; 5.17%) and Cd (av 1.52%). A substantial increase is noted for Co for the post monsoon. . As in the previous cases Pb and Ni has not recorded an organic matter bound phase. In the pre monsoon, Cr has yielded more or less a same value for all three sectors. Co, Cu, Cd and Zn show more of organic matter bound phase at central sectors. In the post monsoon all the trace metals registered a reversal of what is observed for the pre monsoon except for Zn where the northern sector yielded a higher value.

Residual bound representing the fifth stage, Pb and Ni shows 100%. In the case of Pb, for 2 stations, the concentration of Pb was below detectable range, otherwise Pb would be 100% lattice bound. Hence the only two trace elements that are 100% lattice bound and doesn't have any other extraction phase is Pb and Ni.

The conclusion drawn from the trace metal sequential extraction is as follows, Ni and Pb has only lattice bound phase.

- Zinc - 94.88% residual bound, 4% organic matter bound, 0.51%, Fe/Mn oxide bound.
- Cadmium - 30 to 35% exchangeable, 31 – 37% residual bound, 25 – 35% carbonate bound and Fe/Mn oxide and organic matter bound about 2%.
- Cobalt - 86 to 88% residual bound, 5 – 11% organic matter bound, about 1% Fe/Mn oxide bound and up to 6% in the carbonate bound.
- Chromium – 38 to 39% residual bound, 18% organic bound, 17% Fe/Mn bound, 15% carbonate bound and 11.5 to 12.5% exchangeable.
- Copper - 62% residual, 13.5 to 14.5% organic matter bound, 10 –11% Fe/Mn oxide bound, 8 – 8.6% carbonate bound and 5% exchangeable.

5.6 Pollution Status of Kayamkulam Estuary

5.6.1 Introduction

The global definition for pollution as has been put for Tully (1966) reveals as follows: pollution can be considered as an alteration of natural environment, water, soil, which renders them offensive or deleterious to the esthetical sense. For mans uses or for the animal, fish or crops, which man wishes to preserve. It is to recognize that some degrees of alteration of the environments are necessary consequence of human activity. But such alteration is not considered as pollution until they reach a limit of tolerance. For soil pollution Rennies (1966) definition stands good. He defined it as "any substance that is common or foreign to soil system, which by its presence causes adverse effect, directly or indirectly, on their productivity of soil is called soil pollution". Pollution is due to two principal factors namely urbanization and technology. The four general categories of pollution are inorganic compound occurring from industrial activity, organic material, radioactivity and minerals.

There are basically three reservoirs for metals in the aquatic environments: water, sediment and biota. Metals in these reservoirs are determined by a complex equilibrium governed by various physical, chemical and biological factors. It is a matter of observation that nearly all the metal content of aquatic ecosystems resides in sediments and water and that, the fraction in biota is small. Therefore, sediments are major compartment in the estuarine environment for heavy metal and other toxic materials. Thus an understanding of the distribution of the toxic materials is of environmental interest. Moreover sediments are extremely important in the aquatic environments since they can act as heavy metal 'traps' or 'sinks'. Recent studies in coastal marine environment had indicated that the increased geochemical cycling of trace metals by man could be well documented through sedimentological studies. Besides, knowledge of concentration and distribution of heavy metal in sediments can play a key role in detecting sources of pollution in the aquatic environments.

Lakes, estuaries and lagoons on a global basis are very important in the supply of dissolved and solid materials to the oceans. It has been estimated that 250 X 10^{14} gm/year of material enters the ocean from the continents of which 210 X 10^{14} gm/year materials is transported by rivers, that is, almost 85% of all soluble and particulate weathering products pass through the estuarine environment before entering coastal waters. Therefore the lake, estuaries and lagoons, which form the transition zones between fluvial and marine environments, constitute an important stage in the transport of sediments from the continent to oceans. They also serve as traps for a portion of the solid continental weathering products. Further they represent a situation in which sedimentary detritus, during its transport to oceans can undergo modifications through several processes operating in their systems resulting in enrichment or depletion of various heavy metals in the bottom sediments.

Metal pollution in estuarine and coastal environment is usually caused by land runoff, mining activities, shipping and dredging activities and anthropogenic inputs. Sediments in such affected domains not only record its history but also indicate the degree of pollution (Sahu and Bhosale, 1991). Almost all industrial processes and urban activities involve the release of at least trace quantities of half a dozen metals in different forms. The estuaries are particularly exposed to metal pollution more than any other body of water, since the banks of estuaries are often the hubs of increased industrial activities. A knowledge on the concentrations of the metals are highly essential for assessing metal toxicity on aquatic organisms, biological availability, detoxification, accumulation, and active or passive release from the three components of the aquatic environment. Contaminations may exist in various forms and reside in different fractions of sediment namely the soluble form, exchangeable form, easily reducible form, interactions with organic and sulfide fractions etc.

In the past few decades, there has been a great spurt of renewed activity to identify the sources and sinks of trace metals in rivers, estuaries and other near shore environments owing to the increasing awareness of environmental pollution by trace metals and its impacts on the environments (Vale, 1986; Mance, 1987; and Klomp, 1990). As a part of the growing concern over the environmental contamination and its impact on ecosystem, considerable attempts have been initiated by Governments and Private agencies to monitor the level of trace metals in solid and liquid phase of major rivers, estuaries, lagoons etc.

From the above discussion the significance of monitoring of aquatic sediments for pollution studies is very vivid. Keeping this in view, the pollution aspects of Kayamkulam estuarine sediments is discussed. For the pollution study the data of trace elements for the bulk and clay fractions of the Kayamkulam estuarine sediments is considered. Of late the term trace elements has been replaced by heavy metal, especially in the pollution studies even though both are same.

5.6.2 Result and Discussions

The concentration of trace metals both in the clay and bulk sediments of Kayamkulam estuarine sediments as given in the table 5.2.1a and b are taken as the relative abundance of heavy metals in the sediments.

The contamination factor as proposed by Tomlinson et al., (1980) is extended for the present study so as to assess the contamination levels of the heavy metals.

Contamination factor (CF) = Metal concentration in sediment/Background value of the metals. For computing the contamination factor of sediments, world average concentration of the elements reported for shale (Turekian & Wedepohl, 1961) was taken as the background values. A value of unity denotes no contamination. If the lake is not contaminated with the heavy metals, then definitely the contamination factor will be equal or lower than unity and on the contrary if the lake is contaminated with heavy metals, then the bottom sediments will have enhanced value reflecting contamination.

The contamination factor Cu, Co, Ni, Zn, Pb, Cd and Cr for the bulk fraction of the sediments for the pre monsoon are 0.75, 1.96, 0.78, 1.32, 1.92, 6.34 and 1.12, and that of post monsoon are 0.64, 1.66, 0.59, 1.16, 1.54, 5.37

and 0.87 respectively. Similarly the contamination for the clay fractions for the pre monsoon are 2.26, 2.72, 1.46, 1.6, 3.7, 5.78, and 1.78 while for the post monsoon it is 2.29, 2.99, 1.24, 1.66, 2.45, 7.4 and 1.45 respectively. From the Table 5.6, it is very clear that clay's of Kayamkulam estuarine sediments are contaminated much more than the bulk fraction for both the seasons, and is contaminated with all the heavy metals studied. Cd is the most highly contaminated heavy metal in the sediments of Kayamkulam estuary for both the seasons followed by Pb and Co for the pre monsoon and Co and Pb in the post monsoon, or in other words the heavy metal that have contaminated the Kayamkulam estuarine sediments are Cd, Pb and Co. All the three sectors of Kayamkulam estuarine sediments are contaminated with Zn except for the central sector of the post monsoon.

The non-contaminated heavy metals in the bulk fraction for both the seasons are Cu and Ni, while Cr is contaminated only for the southern and central sectors for the pre monsoon.

Work on heavy metals along the south west coast of India are few and are mostly directed towards the levels in biota except that for sediments of west coast by Murty and Veerayya (1981) Sajan (1988) and Padmalal (1992). In the present study the heavy metal content of Kayamkulam estuarine sediments is compared with the Vembanad lake and Ashtamudi lake, the adjacent estuaries (Table. 5.7)

The table reveals that Co is more and Ni and Cr is less than that of Ashtamudi and Vembanad lakes. Pb and Zn is more contaminated than that of

Table 5.6 Contamination factor of Elements in the Kayamkulam Estuary (Representing both Range and Average)

	C F BULK PRE		C F BULK POST		C F CLAY PRE		C F CLAY POST	
Elements	RANGE	AVERAGE	RANGE	AVERAGE	RANGE	AVERAGE	RANGE	AVERAGE
Fe	0.03 _ 0.14	0.08	0.02 _ 0.12	6.52	0.68 _ 1.41	0.98	0.47 _ 1.55	1.03
Mn	0.11 _ 0.50	0.31	0.07 _ 0.37	0.23	0.07 _ 0.28	0.16	0.07 _ 0.41	0.19
Cu	0.24 _ 1.80	0.76	0.24 _ 1.51	0.64	0.84 _ 4.22	2.27	0.67 _ 5.91	2.11
Co	0.63 _ 3.74	1.95	0.68 _ 4.53	1.63	2.05 _ 4.05	2.74	1.89 _ 4.11	2.89
Ni	0.22 _ 1.59	0.78	0.04 _ 1.41	0.59	0.84 _ 3.09	1.47	0.53 _ 1.91	1.31
Zn	0.29 _ 2.99	1.32	0.57 _ 2.17	1.15	1.12 _ 3.45	1.93	0.57 _ 3.35	1.75
Pb	0.50 _ 4.80	1.95	0.20 _ 5.70	1.55	2.10 _ 5.20	3.70	0.90 _ 4.90	2.60
Cd	3.33 _ 10.00	6.67	3.33 _ 13.33	6.67	3.33 _ 10.00	6.67	3.33 _ 10.00	6.67
Cr	0.46 _ 1.49	1.11	0.27 _ 1.41	0.87	1.47 _ 2.38	1.78	1.07 _ 2.00	1.54

Table 5.7 Contamination factor of Vembanad estuary, Ashtamudy estuary and Cochin backwaters.

	VEMBANAD ESTUARY						ASHTAMUDY ESTUARY						COCHIN BACKWATERS	
	Bulk fraction			Clay fraction			Bulk fraction			Clay fraction			Pre monsoon	
Element	Range		Average	Range		Average	Range		Average	Range		Average	Range	
Fe	0.09	1.79	0.95	1.33	2.27	1.79	0.36	1.70	1.26	1.02	1.39	1.39	6.52	41.30
Mn	1500	12125	4575	1500	18125	6000	0	1	0	0	1	1	50	500
Cu	0.20	1.40	0.69	0.87	1.62	1.18	0.00	4.31	1.27	0.04	1.98	1.98	0.04	0.11
Co	0.21	2.42	1.05	0.95	3.21	1.68								
Ni	0.57	2.66	1.60	1.91	3.24	2.57	0.32	3.19	1.62	1.19	2.09	2.09	0.04	0.53
Zn	0.17	1.81	0.95	1.45	2.28	1.82	0.86	17.74	2.73	1.36	3.33	3.33	0.05	0.18
Pb	0.55	1.60	0.70	1.05	2.10	1.60	15.75	67.25	33.35	27.25	45.00	45.00	1.20	3.05
Cd	6.67	26.67	13.33	10.00	36.67	20.00	0.00	36.67	6.67	0.00	6.67	6.67	33.33	80.00
Cr	0.44	2.59	1.39	1.16	2.42	1.99	1.01	5.58	2.54	1.80	3.21	3.21	0.00	0.00

Vembanad and less than Ashtamudi estuarine sediments. The contamination factor of Cd is less than Vembanad lake but in par with Ashtamudi lake. Cu registered a less contamination factor less than that of Ashtamudi but more or less equal to Vembanad estuarine sediments.

The probable sources for the heavy metals can be due to urbanisation and industrialisation. The industries located in and around the drainage basin are forest based industries, boat building yards, chemical and soap factories, machinery and electrical goods, refractories, clay and glass works, tiles and other clay products, printing and other allied industries, cotton, rayon and coir products etc. Minor industries are food-processing, aluminium and other metal based industries, rubber and rubber products (Resource Atlas of Kerala 1984). The main sources of the various heavy metal pollutants are: Pb mainly from agricultural chemicals in which pesticides contain lead arsenate as the major constituent. The crop combination of Alleppey and Quilon district directly points towards the profuse use of agricultural chemicals, besides from printing and canning industries, boat building yards, gasoline motors and burning of fuels etc. Cr and Ni are from the platting industries and Zn is form the galvanising works, Cu again from the agricultural run off and Cd mainly form aluminium and other metal burned industries refractories, tiles and glass factories, machinery and electrical goods factories.

CHAPTER VI

REMOTE SENSING AND GEOGRAPHIC INFORMATION SYSTEM

6.1 Introduction

Remote sensing can be defined as the acquisition of data about an object or scene by a sensor that is far from the object (Colwel, 1983). This name is attributed to the recent technology in which satellites and spacecrafts are used for collecting information about the surface of earth. This was an outcome of development in various technological fields from 1960 onward. Broadly, remote sensing can be interpreted as the science and art of obtaining information about an object, area or phenomena through the analysis of data acquired by a device that is not in contact with the object, area or phenomena under investigation (Lillesand and Keifer, 1994). Hence the term remote sensing is commonly used to identify earth features by detecting the characteristics of electromagnetic radiation that is reflected / emitted by the earth surface.

Remote sensing techniques promised a great deal in mid seventies of the last century. In the last century, the routine satellite monitoring of marine and coastal parameters had been limited primarily to sea surface temperature monitoring (Advanced Very High Resolution Radiometer-AVHRR) and to a lesser degree, chlorophyll (Coastal Zone Colour Scanner-CZCS) and Seasat (Synthetic Aperture Radar-SAR). High-resolution satellite images are now increasingly being used to identify areas of coral reef, seagrass, mangroves, estuary, geomorphological classes and coastal vegetation types in their particular areas of jurisdiction. This work is often complemented by digitized high-resolution aerial photography and the use of Landsat and IRS archive now available.

The remote sensing data has been proved to be useful in providing information on various components of the estuarine environment, wetland conditions, mangrove development and degradation, estuarine changes and suspended sediment dynamics etc. Rivers / streams are the major means of transport of material including suspended sediments, organic matter and nutrient salts, to the estuary and coastal zone. Depending on riverine geochemical and hydrological characteristics, the delivery of dissolved materials including inorganic nutrients and contaminants to marine environment varies. The geochemistry of river varies with the types of lithology, topography, hydrology, agricultural and urban development and vegetation cover of the river system. Due to intensive human activity on coastal plains and because rivers serve as natural conduits in transporting materials to the seas, estuary and coastal zones have become repositories of wastes / dumping grounds. Because of the high spatial and spectral resolution, remote sensing data helps to study the morphology and dynamics of the estuarine environment.

The remote sensing data is primarily in digital format. This digital data is processed further and hard copy images are generated.

6.2 DIGITAL IMAGE DATA

Remotely sensed image data are digital representation of objects on the earth. Image data are stored in data files, called as image files, on a magnetic tape, computer disks or other media. The data consists of only numbers, which are called as pixels. Each pixel represents an area of the earth at a specific location. The location of a pixel in a file is expressed using a two-dimensional coordinate system formed of rows and columns. Image data organized into such a grid are known as raster data. Image data may include several bands of information sometimes called as layers. Digital data can be arranged in several ways. The most common storage formats are: BIL (Band Interleaved by Line), BSQ (Band Sequential) and BIP (Band Interleaved by Pixel)

6.3 DIGITAL IMAGE PROCESSING (DIP)

Digital Image Processing is a collection of techniques for the manipulation of digital images by computers. The computer is programmed to insert the data into an equation, or series of equations, and then store results of the computation for each pixel. These results form new digital images that may be displayed or recorded in pictorial format.

The raw data received from the imaging sensors on the satellite platforms contains flaws and deficiencies. To overcome these flaws and deficiencies in order to get the originality of the data, it needs to undergo several steps of processing. This will vary from image to image depending on the type of image format, initial condition of the image and the information of interest and the composition of the image scene. Digital Image Processing consists of three general steps:

- Pre-processing /Image restoration;
- Display and enhancement and
- Information extraction

6.3.1 Pre-Processing / Restoration of the Remotely Sensed Images

The operations carried out in the preprocessing are follows:

- Atmospheric Correction;
- Radiometric Corrections;
- Geometric Corrections and
- Feature Extraction

Some techniques has to be applied so as to remove the unwanted and distracting elements such as image/system noise, atmospheric interference and sensor motion from an image data occurred due to limitations in the sensing of signal digitization, or data recording or transmission process. Thus image restoration includes the efforts to correct for both radiometric and geometric errors.

6.3.2 Image Enhancement Techniques

These processes aim to correct distorted or degraded image data and to create a more faithful representation of the original scene. Image enhancement techniques are employed for making satellite imageries more informative and to achieve the goal of image interpretation. The term enhancement is used to mean the alteration of the appearance of an image in such a way that the information contained in that image is more readily interpreted visually in terms of a particular need. The image enhancement techniques are applied either to single-band images or separately to the individual bands of a multiband image set. These techniques can be broadly categorized into two:

- **Spectral Enhancement Techniques:** Density Slicing, Contrast Stretching, Linear Contrast Stretch, Histogram Equalization and Gaussian Stretch.
- **Multi-Spectral Enhancement Techniques:** Band Ratioing, Principal Component Analysis, Canonical Components, Hue, Saturation and Intensity (HIS) Transform and Fourier Transformation.

6.3.3 Image Classification

Fundamentally, spectral classification forms the basis to map objectively the areas of the image that have similar spectral reflectance/emissivity characteristics. Depending on the type of information required, spectral classes may be associated with identified features in the image (supervised classification) or may be chosen statistically (unsupervised classification). Classification is also seen as a means to compress image data by reducing the large range of Digital Number (DN) in several spectral bands to a few classes in a single image and this obviously results in loss of numerical information from the original image. There is no theoretical limit to the dimensionality used for the classification, though obviously the more bands involved, the more computationally intensive the process becomes. It is often wise to remove redundant bands before classification.

The overall objective of image classification procedure is to automatically categorize all pixels in an image into landcover classes or themes. The image classification is of two types

- Supervised
- Unsupervised

6.3.3a Supervised Classification

In this system of classification, each pixel is supervised for the categorization of the data by specifying to the computer algorithm, numerical descriptors of various class types. Classification generally consists of identifying the training area and thereby developing a numerical description of the spectral attributes of the class or land cover type, by the analyst himself. Each pixel is categorized into landcover class to which it closely resembles. If the pixel is not similar to the training data, then it is labeled as unknown.

6.3.3b Unsupervised Classification

This system of classification does not utilize training data as the basis of classification. This classifier involves algorithms that examine the unknown pixels in the image and aggregate them into a number of classes based on the natural groupings or cluster present in the image. The classes that result from this type of classification are spectral classes. Unsupervised classification is the identification, labeling and mapping of these natural classes and this method is usually used when there is less information about the area.

6.4 VISUAL ANALYSIS OF DATA

Visual interpretation methods have been followed for extracting information on various natural resources. The elements of image interpretation include colour, tone, texture, shape, size, drainage pattern and association. Success in visual image interpretation varies with the training and experience of the interpreter, the nature of objects or phenomena being interpreted and quality of the images being utilized

6.5 REMOTE SENSING AND GEOGRAPHIC INFORMATION SYSTEM

Remote sensing systems produce large volumes of spatial data, which can be processed further only by efficient geographic handling and processing systems that will transform these data into usable information.

6.6 GEOGRAPHIC INFORMATION SYSTEM (GIS)

Geographic information system has been defined as a set of tools for collecting, storing, transforming and displaying geographically referenced spatial data with its corresponding attribute information to meet a specific requirement (Geeta Varadan, 1992). Its origin can be traced back to 1960s in North America. Advancement in computer graphics and high speed and low cost microcomputers has dramatic impact on the development of Geographic information systems in1980s (Taylor, 1991).

Geographic information system is normally considered to include spatially referenced computer data base and appropriate application softwares. Major components of GIS are (i) data input system, (2) data storage system and (3) data analyzing system (Stenfavonic, 1989).

Geographically referenced data in the spatial form collected by space imager are presented in the form of photographs, paper prints and digital images. Non-spatial data are soil properties, vegetation types, climate data population, socio-economic data, geochemical data etc. It is possible to transform and integrate this information into thematic map and process in the GIS. Geographical data describe objects in terms of (a) their position with respect to a co-ordinate system; (b) their attributes that are unrelated to position (such as colour, cost, pH, incidence of disease and crime) and (c) their spatial inter relationships with each other.

Geographic information system is normally categorized as either raster-based or vector-based. Raster-based systems are typically associated with image-based GIS, while vector-based systems are usually more cartographically oriented. With the evolution of computer technology and computing facilities, it is possible to deal with large volumes and complexities of spatial data sets.

6.7 APPLICATIONS OF GEOGRAPHIC INFORMATION SYSTEM

Geographic information systems are being used widely for natural resources management, environmental monitoring and planning and socio-economic and demographic research. The use of GIS provides wide scope for designing strategies for sustainable development and monitoring of environmental resources. One of the most important areas of GIS applications is micro-level regional planning for balanced regional development. Geological research often calls for combination, comparison, and correlation of different kinds of data. This is known as analysis. Such data sets are best handled in the form of GIS. A GIS is, undoubtedly, a versatile system that can aid in decision making for better planning and management of natural resources.

6.8 INTEGRATION OF REMOTE SENSING AND GEOGRAPHIC INFORMATION SYSTEM

Whereas remote sensing systems are powerful tools for the collection of the classified spatial data, the GIS are powerful tools for the management and analysis of spatial data. Most of the GIS utilize maps as their primary source of spatial data and remote sensing systems produce such spatial data in the form of maps. The interpreter generally utilizes these complex maps for visual search and retrieval but when the same data are digitized, GIS is best for their integration.

Maps produced with conventional field surveys and through remote sensing techniques can provide basic geometrical data. Combining the different sources of data either in the production phase or in the analysis phase could increase the value of the information that can be derived from these data. By combining the analysis functions of the GIS system with the image manipulation functions of the remote sensing, new possibilities in information can be generated.

There are two points of view for integration, one from the remote sensing side and one from the GIS side. For remote sensing, a GIS offers possibilities for use and distribution of the output. Remote sensing images themselves are mostly useful for the specialists and not for users such as managers and decision-makers. Moreover, display of data and production of output can easier be customized with the GIS techniques. However, remote sensing gives advantages in the updating of geo-database and for the monitoring of processes. Also for some specific requirements remote sensing data can give locally more detail than a map can.

6.9 SATELLITE REMOTE SENSING AND GEOGRAPHIC INFORMATION SYSTEM (GIS) IN ESTUARINE STUDIES.

The dynamic features that affect the estuarine zones are tides, currents, rainfall, sediment movement, freshwater outflow, saline water inflow, topography, bathymetry, physiography, land-use practices and other human activities. Most of these dynamic forces that bring about important geomorphologic changes in the estuary are fairly easily identifiable with reasonable accuracy through remote sensing techniques.

The dynamics and circulation patterns of estuarine waters that provide useful information about the productivity of waters can be used for harnessing fish resources. The study of the ecology of estuarine waters requires a fair amount of statistical data pertaining to estuaries. Regular updating of the data is an essential element in carrying out any kind of planning activity. The collection of these data through conventional means is not efficient enough for modern day planning requirements. The use of satellite remote sensing data in conjunction with GIS provides an opportunity to acquire, update and monitor the changes in a timely manner, with a reasonable degree of accuracy. Satellite remote sensing data also provides a means of locating, mapping and monitoring estuarine pollution, such as sediment and oil slicks and their movement and transport.

Repetitive and multispectral satellite remote sensing data, especially at high spatial resolutions, provides much information on the changing landuse patterns and urban growth in cities and settlements situated near the estuary and coast. Such temporal information is indispensable for any coastal zone development or management plan. Satellite remote sensing data, in both digital and analogue forms, can play a vital role in the identification and delineation of various coastal land forms and features such as bays, estuaries, lagoons, deltas, creeks, beaches, sand bars, mud flats, tidal flats and accretion ridges. The repetitiveness of the data enables monitoring of different dynamic coastal processes and phenomena such as erosion, deposition and accretion, sedimentation, marine inundation and inland migration of sand dunes over a period of time.

6.10 REVIEW OF LITERATURE

Remote sensing is increasingly being considered as one of the elements of an integrated GIS environment rather than simply as an important source of the multispectral data to be moved from the remote sensing domain into the GIS domain (Jackson & Mason, 1986; Star and Estes, 1990; Parker 1996). For the application of remote sensing and GIS to planning, there are two hosts of consideration necessary to ensure that multispectral data can be successfully converted to information useful for planning. Included in this consideration are issues of temporal facility, scale and resolution, quantitative versus qualitative model integration and linkage, operational linkage, costs, training, competency computational overhead and standards.

Temporal characteristics play a role in detecting changes in surfaces over time together with spatial, spectral, radiometric properties of sensors (Townshend and Justice, 1989). The use of data from multiple sensor system for change detection has the additional complications of differences in pixel size properties (Duggin and Robinove, 1990). Scale and resolution of photography and remote sensing imagery have passive influence on the types of information that a given user can extract. Mason et al,(1999) studied the area of Morecambe Bay in north-west England over the period 1992-97 and estimated the volume of accretion and erosion. Through analysis of satellite images, the morphometry of the coastline along the Egyptian Mediterranean has been studied by Smith and Abel-Kader (1998). Landsat images acquired in 1973, 1978 and 1984 were compared with topographic maps of 1930's and other historical references to the shoreline to identify areas of which coastal erosion is a serious problem along the Egyptian Mediterranean coast. These areas have undergone slow to moderate erosion since the turn of this century as a result of natural decrease of the River Nile flow and as a result of increased number of structures across the Nile. Airborne remote sensing with CASI (Compact Airborne Spectrographic Imager) was used to map sediment types and biotic associations for the intertidal zone from the Humber Estuary to North Norfolk within the LOIS BIOTA (Biological Influences On inter-Tidal Areas) programme (Thomson et al,1998). This will allow field-based biotic and sedimentary information to be extrapolated to provide data for modeling the coastal processes of erosion and accretion. .

Landsat images were analyzed to examine direction, amount and behavior of long-shore drift and to ascertain areas vulnerable to coastal erosion and accretion along the coast of Kerala (Kunte, 1994). Nayak et.al 1992 carried out the shoreline change mapping using Landsat MSS/TM and IRS LISS II data for the period 1967-68, 1985-89 and 1990-92 for the entire Indian coast on 1:250,000 and 1:50,000 scale. Based on the study they have concluded that most of the estuarine and lagoonal systems of the east coast of Indian are being filled up and severe erosion was noticed in Mali estuary in Gulf of Khambat. It has been estimated that in Kerala, out of the 575 km length of shoreline, about 275 km are undergoing severe erosion, 240 km are experiencing deposition and 60 km are under equilibrium. Kumar et.al.,(1989), using Landsat TM and IRS-1A imagery assessed the morphological changes going on at the Orissa coast, India. Detailed analyses were made for the coastline changes in the Dhamra and Mahanadi estuarine region. The zones of accretion and erosion together with the drifting of beach, and the sediment movement in the near shore bay and estuary region were studied.

Marchand, (1997) conducted a sedimentological and morphological mapping of the Bay of Mont-Saint-Michel (west France) by remote sensing methods. He processed optical satellite images in order to obtain morphologic and sedimentological maps of coastal areas. The experimental work is based on the Bay of Mont-Saint-Michel. An outline of the bay's geomorphology and dynamics were illustrated by a description of the optical characteristics of its sedimentary environments. Van-Wijngaarden (1999) studied the southern branch of the Rhine-Meuse estuary, The Netherlands, and a two-dimensional horizontal suspended sediment transport model was constructed in order to evaluate the complicated water quality management of the area using air-borne remote sensing video. AVHRR/NOAA-11 satellite images of the C1

(580-680 nm) and C2 (725-1100 nm) channels were used to quantify the suspended particulate matter discharged into the ocean by the Gironde estuary in France by Froidefond et al ,(1999) . The calibration method is based on a comparison between satellite values (AVHRR reflectance) and suspended particulate matter (SPM) concentrations at the sea surface, measured in-situ.

Robinson et. al, (1998) used airborne remote sensing data for the assessment of coastal and estuarine environments in general and the Humber Estuary in particular to monitor flux of Suspended Particulate Matter (SPM). A multi-year series of remote sensing images of the Neva inlet and the eastern part of the Gulf of Finland were analyzed to determine the spatial-temporal variability of the distribution of suspended matter at different scales. Synoptic, seasonal, and inter-annual variability in the distribution of suspended matter is analyzed, taking into consideration of the distinctive characteristics of the waters of the Neva Inlet reflecting the variability of sea level and seasonal stratification of water masses (Sukhacheva1997). Advanced Very High Resolution Radiometer satellite data were used to investigate the variability of the Mississippi River sediment plume and the environmental forcing factors responsible for its variability. Plume variability was determined by extracting information on plume area and plume length from 112 cloud-free satellite images (Walker, 1996). Based on the time series of NOAA AVHRR satellite remote sensing data and the geographical information system (Li,-Yan et.al, 1992), studied the development of the plume front and the turbidity maximum in the Hangzhou Bay, reflected by the distributions of temperature and suspended sediment concentration respectively, were studied in the views of either long-term behavior or the seasonal and tidal cycles.

Sasmal (1993) monitored suspended load in the estuarine environment using satellite remote sensing data with a special reference to Indian Remote Sensing Satellites (IRS). Since the periodic variation of estuarine parameters differ from that of satellite data, standard methods are adopted for establishing suitable relationship between the data sets. The satellite data collected over the estuarine environment synoptically in multi-spectral and multi-temporal mode are found suitable for estimation of suspended sediment concentration in the water column. This is expected to help in better management of the estuarine sedimentation through information and expert. Barua (1990) studied topographical, flow volume and suspended sediment concentration (SSC) in the estuary of the Ganges-Brahmaputra-Meghna river system in Bangladesh. The zone of turbidity maximum is indicated by the satellite imagery taken during the low river discharge period. Topographical and flow volume measurements, the aspect ratio and the flow ratio indicate that the system is divided into flood- and ebb-dominated channels. Suspended sediment movement in the estuary appears to be associated with the horizontal stratification of flow and with the residual movement induced by the asymmetry of the tidal wave.

Using MSS-IRS 1A LISSII and Landsat TM data, the coastal habitats of entire Indian coast have been mapped on scales of 1:250,000 and 1:50,000 scale by Space Applications Center. Some of the major findings of this study are those concerned with the health of mangrove vegetation and health of coral reefs, the extent of reclaimed area in the coastal zone for agricultural and settlements purpose and the extent of wet land areas. The extent of lagoons and the time series analysis to find the changes have also been carried out. Remote Sensing can detect turbidity and colour, which are the indicators of coastal water quality. Knowledge about suspended sediment movement helps in predicting the waste effluent transportation patch. Tides play an important role in the movement of suspended sediments and fronts. Nayak (1996) used IRS-1C WiFS data of Hugely estuary during high and low tide time and concluded that during high tide, a large amount of sediments are in suspension compared to low tide time. This is because of high turbulence prevalent during high tide.

Normalized Difference Vegetation Index (NDVI) is a computation of ratio images using data in infrared and visible bands of the electromagnetic spectrum and typically ranges from 0.1 up to 0.6, with higher values associated with greater density and greenness of the plant canopy. Vegetation indices derived from the NOAA, Advanced Very High Resolution Radiometer (AVHR R) sensor have been employed for both qualitative and quantitative studies (Tucker et al., 1991). Sellers et al., in 1995 calculated the biophysical parameters for climate models. An overview of NDVI and NDVI based studies in the Sahel is given by Holben 1986, Tucker et al., 1985, Justice 1986, Prince and Justice1991.The potential of the AVHRR for vegetation monitoring was realized after the satellite became operational (NOAA-7 was launched in 1981).

6.11 RESULT AND DISCUSSION

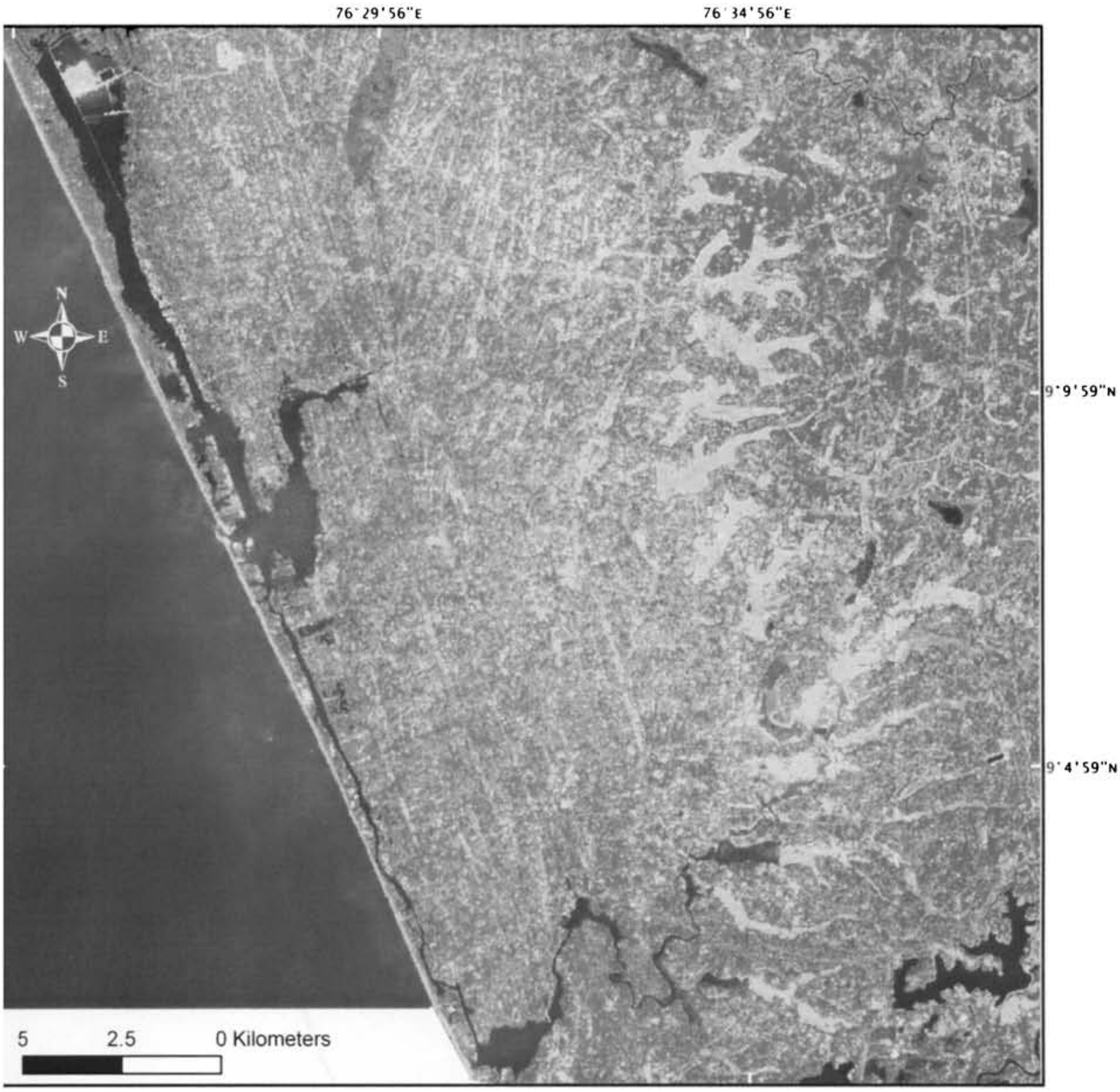
The capabilities of remote sensing and GIS have been utilized in the present study for:

- The detection of changes in area of Kayamkulam estuary;
- The classification of landuse;
- The qualitative mapping of suspended sediments;
- The delineation of health status of vegetation (Normalized Difference Vegetation Index) and
- The integration of spatial and non-spatial data;

Remote sensing data, due to its synoptic and repetitive nature is the most suitable for study like this such as short and long term areal change, inventories on erosion /accretion, qualitative study of suspended sediment concentration etc. Geographic Information System with its capability to handle large quantity of spatial and non-spatial data, is an excellent tool to analyse and integrate data produced by remote sensing method as well as those generated by conventional methods. Thus, the following paragraphs illustrate the results of the present study.

6.11.1 Change detection of Kayamkulam estuary

The false colour composite (IRS-1A, LISS III) of Kayamkulam estuary and adjoining area is shown in the figure 6.1. A comparison of the area of the Kayamkulam estuary (Fig.6.2a) of 1967 (topomap) to that of 1999 (IRS-1A, LISS III) shows that (Fig.6.2b) an area of 5.49 sq.km has been eroded and an area of 13.174 sq.km has been accreted. So, the net change in the estuarine



(SOURCE: IRS-IC, LISS III)

Fig.6.1 FALSE COLOUR COMPOSITE (IRS-IC, LISS III) OF KAYAMKULAM ESTUARY AND THE ADJOINING AREAS

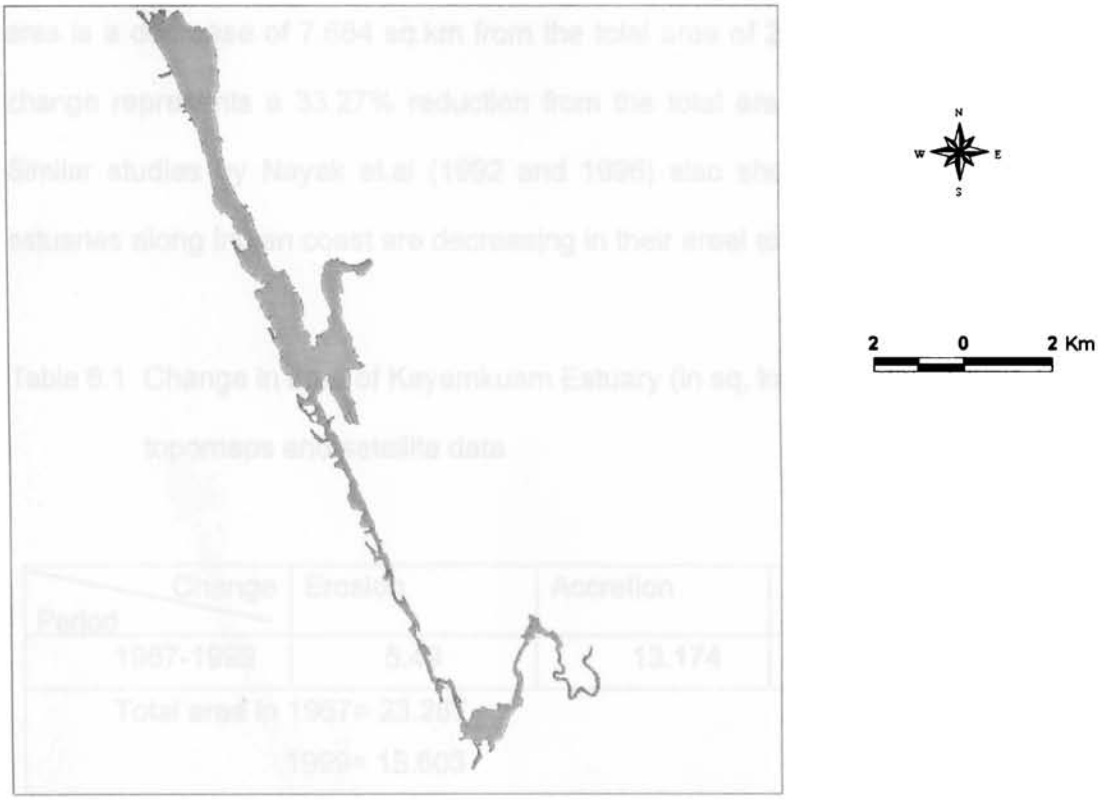


Fig. 6.2a KAYAMKULAM ESTUARY IN 1967

(Source: SOI Toposheet 1967)

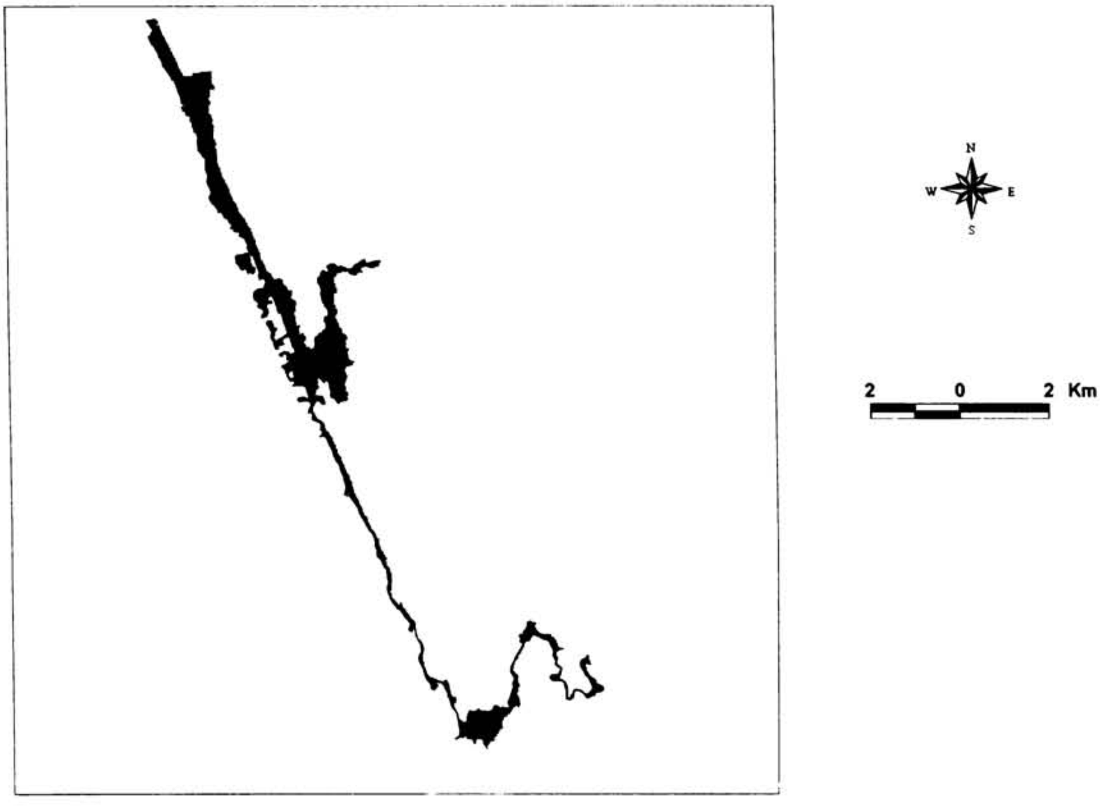


Fig. 6.2b KAYAMKULAM ESTUARY IN 1999

(Source: IRS 1C - LISS III)

area is a decrease of 7.684 sq.km from the total area of 23.287 in 1967. This change represents a 33.27% reduction from the total area in 1967 (Fig.6.3). Similar studies by Nayak et.al (1992 and 1996) also show that most of the estuaries along Indian coast are decreasing in their areal extent

Table 6.1 Change in area of Kayamkuam Estuary (in sq. km) based on topomaps and satellite data

Change / Period	Erosion	Accretion	Net change
1967-1999	5.49	13.174	7.684
Total area in 1967= 23.287 1999= 15.603			

Between 1967 and 1999, deposition took place mainly in the northern and the central part of the study area. The deposition in the northern part is due the reclamation of land by National Thermal Power Corporation (NTPC). This anthropogenic deposition is clearly visible in the satellite image by its well-defined and straight boundaries. The deposition seen on the central part is near the mouth of the estuary where it meets the Arabian Sea on the west. The long-term complex estuarine and marine forces operating on this area might have resulted in the deposition, which consists mainly of sand. Deposition seen on the other parts is rather less and this might be due to both man made and natural causes. Erosion along the side of the estuary is noticed in the southern part of the study area. This could be due to the

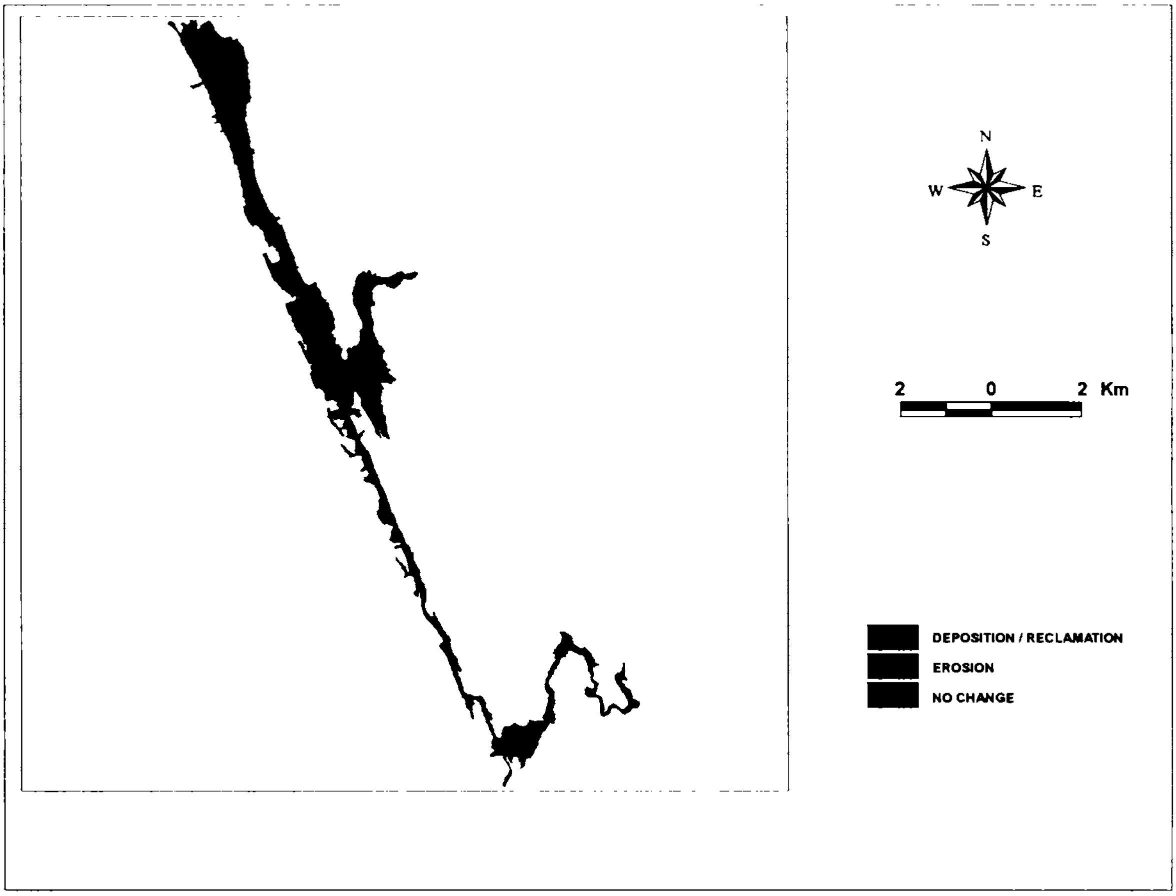


Fig. 6.3 MORPHOLOGICAL CHANGES IN KAYAMKULAM ESTUARY (1967-1999)

widening of channel for the increased inland water transportation in connection with tourism.

6.11.2 Landuse Classifications

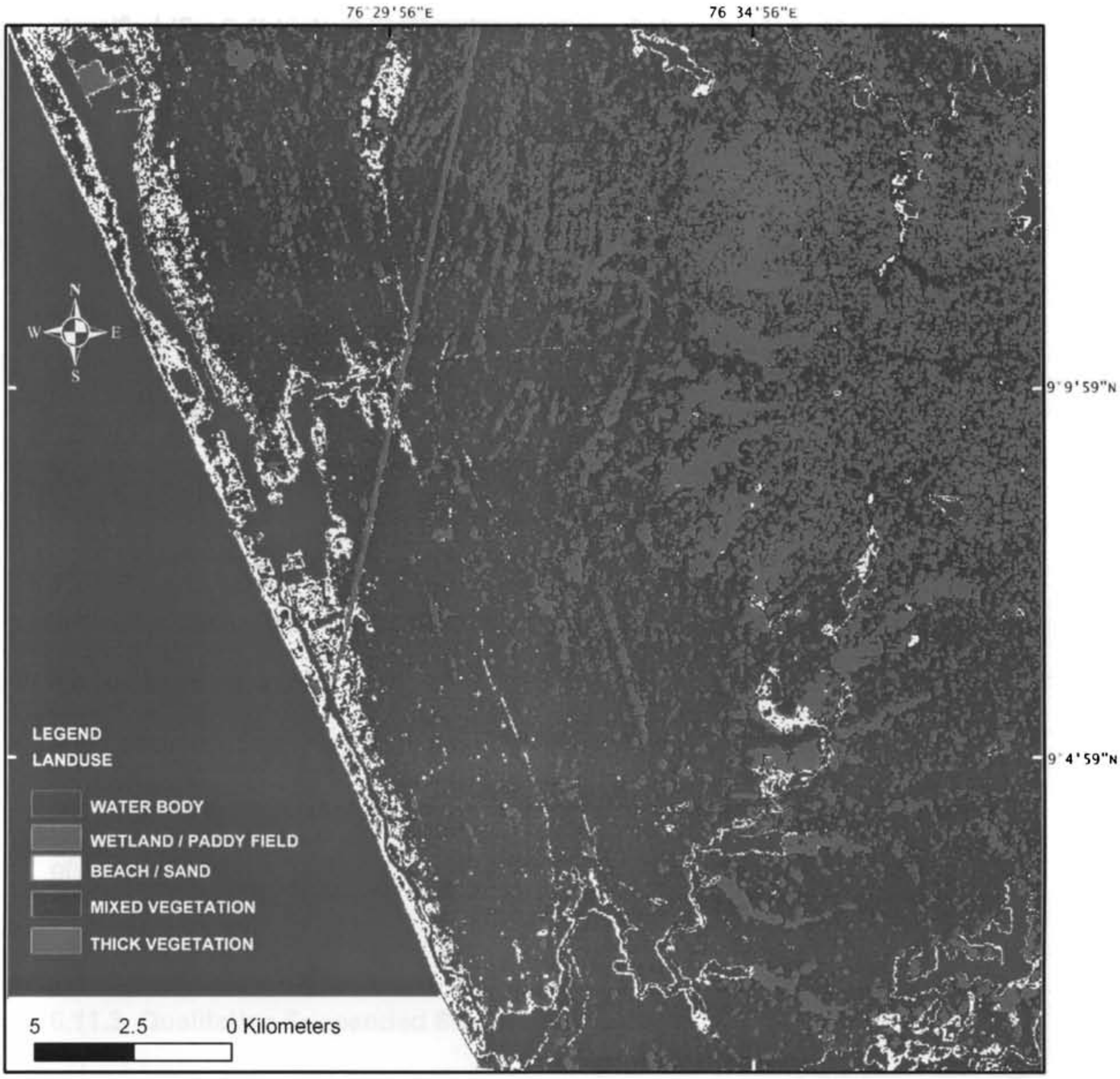
The landuse of the study area has been delineated using satellite image (IRS-IC, LISS III, 1999) by unsupervised and supervised way of classifications.

6.11.2a Unsupervised Classification

Figure 6.4a shows the landuse pattern of the area around Kayamkulam estuary. Five types of landuse are noticed according to unsupervised classification. These are:

1) Water body;
2) Wet land / Paddy field;
3) Beach / Sand;
4) Mixed vegetation and
5) Thick vegetation

Among these five types, mixed vegetation is the predominant one, which consists of coconut, arecanut, plantation crops etc. The wetlands are noticed on the eastern side of the Kayamkulam estuary. A noise in the satellite image is also seen as a straight line in NNE-SSW direction, across the image.



(SOURCE: IRS-IC, LISS III)

Fig.6.4 a LANDUSE OF THE KAYAMKULAM ESTUARY AND THE ADJOINING AREAS (UNSUPERVISED CLASSIFICATION)

6.11.2b Supervised Classification

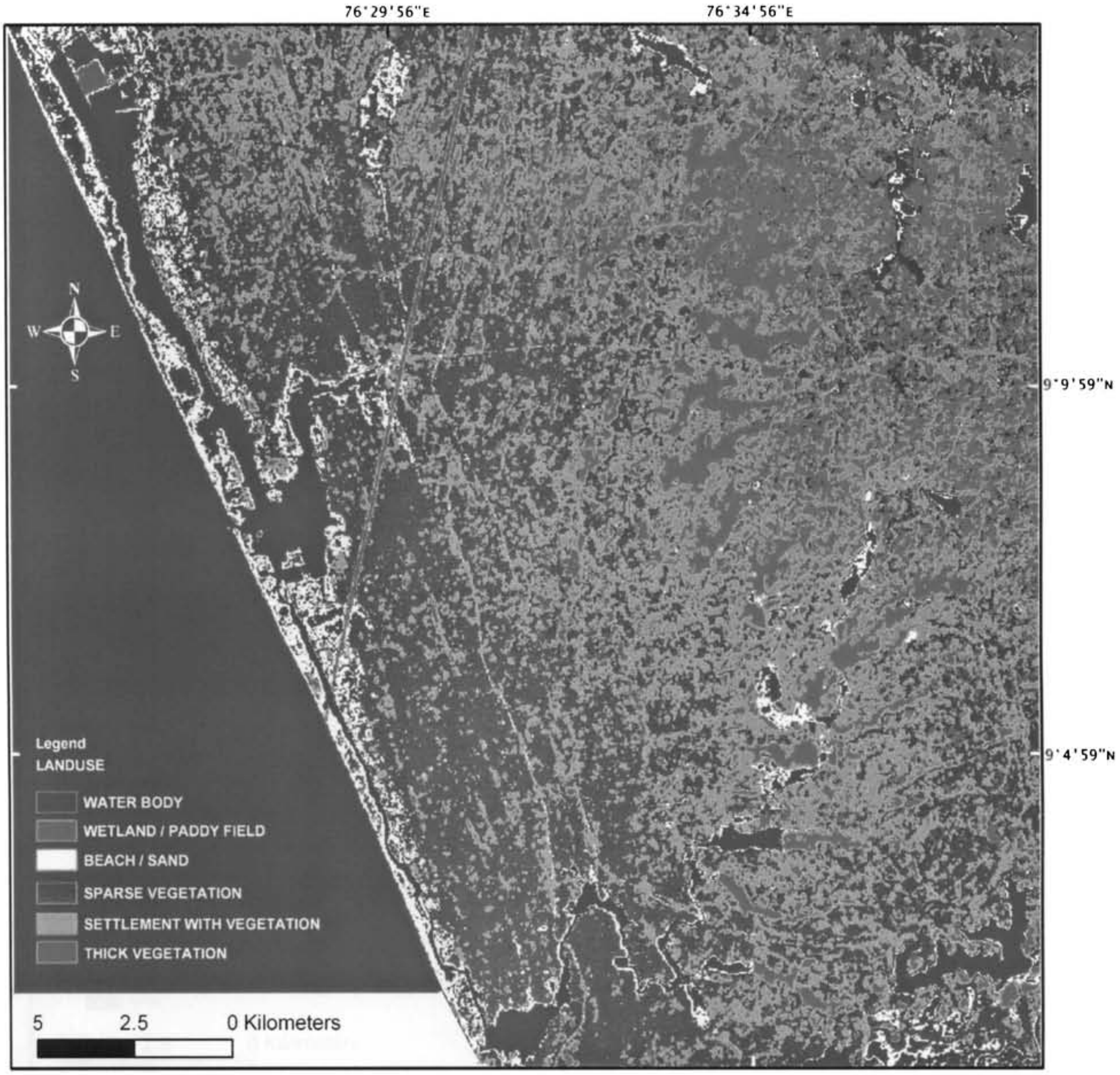
Based on the ground truth verification, the landuse of the study area has been classified (Fig.6.4b) into six categories as shown below

1) Water body;
2) Wet land / Paddy field;
3) Beach / Sand;
4) Sparse vegetation;
5) Settlement with vegetation and
6) Thick vegetation

Beach/sand deposits are noticed along the sides of the estuary and along the coast. Some sand deposits are also observed further in land along the banks of the water bodies, which drain into the estuary. Sparse vegetation and settlement with vegetation are seen in almost the entire area. In the map showing supervised classification of landuse also there is a noise in the form of a straight line.

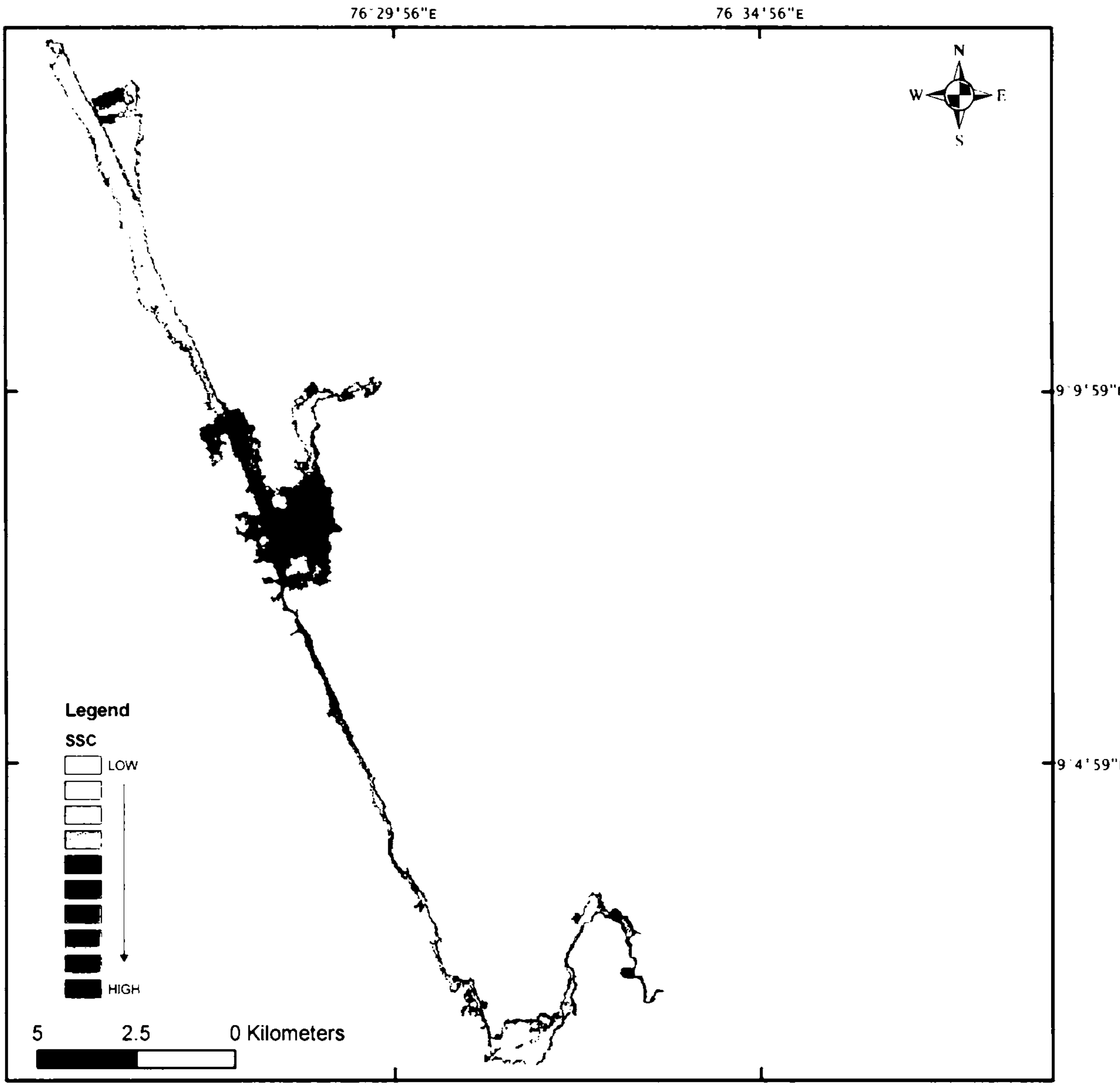
6.11.3 Qualitative Suspended Sediment Mapping

In the present study suspended sediment concentration has been classified into ten categories using unsupervised classification of band 3 of LISS III, IRS IC image. This unsupervised classification clearly shows spatial distribution (Fig.6.5) of suspended sediments in the Kayamkulam estuary. It



(SOURCE: IRS-IC, LISS III)

Fig 6.4 b LANDUSE OF THE KAYAMKULAM ESTUARY AND THE ADJOINING AREAS (SUPERVISED CLASSIFICATION)



(SOURCE: IRS-IC, LISS III)

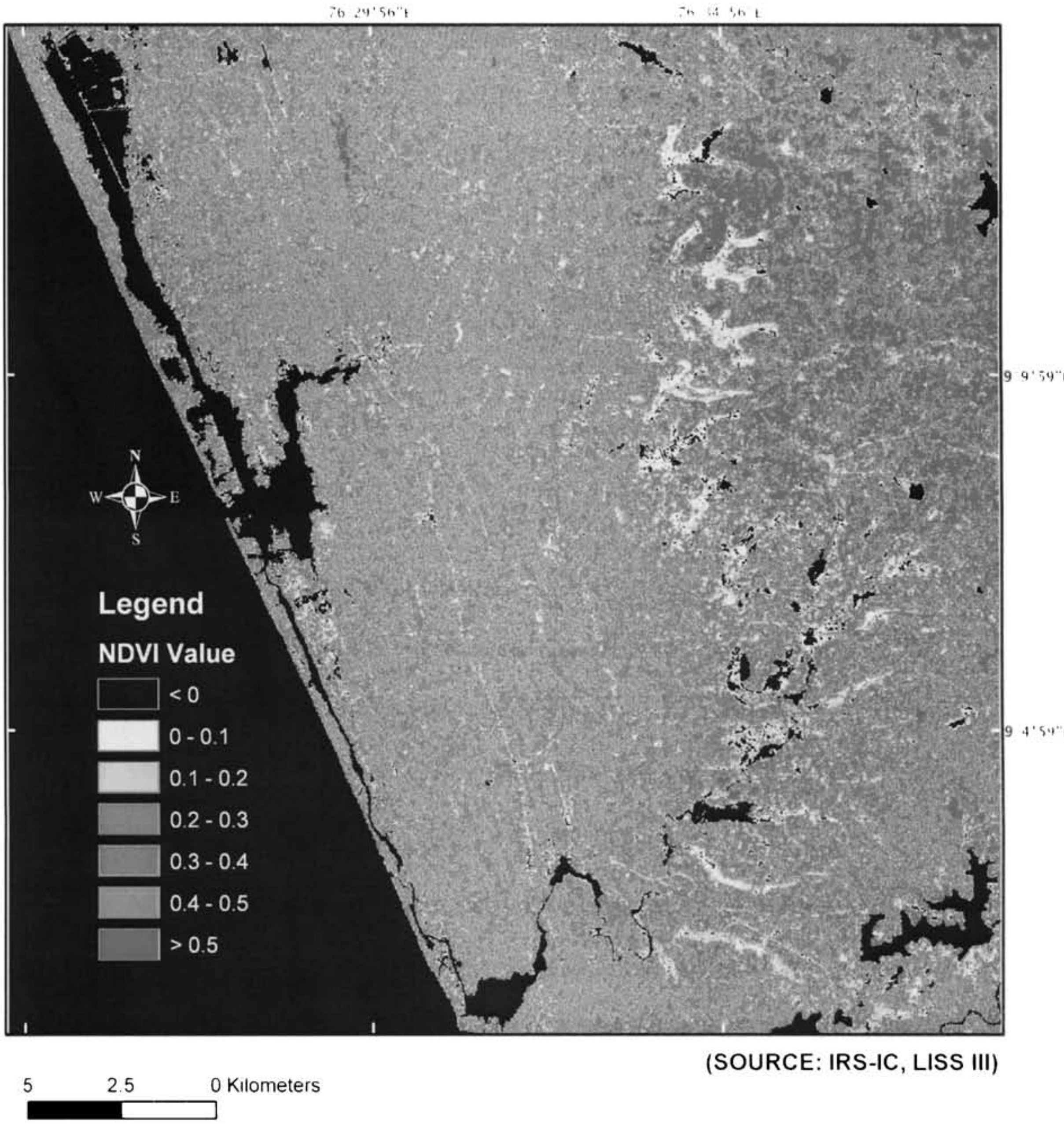
Fig.6.5 SUSPENDED SEDIMENT CONCENTRATION OF KAYAMKULAM ESTUARY

can be noted that the central portion, where the estuary has connection with the sea, has high-suspended sediment concentration. This observation very well justifies the findings as explained for the depositional process as discussed in chapter three.

The high concentration of suspended sediments in the central portion of the estuary is due to the dynamic condition prevailing over the area. The constant action of tidal waters and that of currents keep the sediments, in this portion of estuary, in suspension. The usefulness of remote sensing image for the qualitative and quantitative mapping of suspended sediment has already been discussed by Chauhan et al.,(1997). High concentration of suspended sediments observed in northern part can be attributed to the ongoing activities of NTPC. Ouseph (1987) has already shown that 200 medium and large-scale industries release 267x 10^3 m^3 of waste water per day either directly to sea or to inshore waters like estuaries and backwaters in Kerala.

6.11.4 Normalised Difference Vegetation Index (NDVI)

NDVI is determined to find out the health status of vegetation around the Kayamkulam estuary. According to this index there are seven classes in the present study area (Fig.6.6).



(SOURCE: IRS-IC, LISS III)

Fig. 6.6 NORMALISED DIFFERENCE VEGITATION INDEX FOR THE ADJOINING AREAS OF KAYAMKULAM ESTUARY

Table 6.2 Normalized Difference Vegetation Index of adjoining areas of Kayamkulam estuary

NDVI- Index	Health status
<0	No vegetated surface (Water bodies)
00-0.1	Poor
0.1-0.2	Very low
0.2-0.3	Low
0.3-0.4	Moderate
0.4-0.5	Good
>0.5	Very Good

'Good' and 'Moderate' vegetation are observed near the estuary with small patches of 'Low' vegetation. Areas with 'Poor' vegetation and 'Very good' vegetation are noticed away from the estuary on the eastern side. Water bodies typically show a negative index value.

NDVI typically ranges from 0.1 upto 0.6, with higher values associated with greater density and greenness of plant canopy (Lillisand and Kiffer, 1994). The NDVI of 0.2 to 0.5, observed on western part of the study area is due to the mixed vegetation containing coconut, arecanut and plantation crops. The high NDVI value, that is more than 0.5, is observed on the eastern portion due to the predominant thick and healthy vegetation.

6.11.5 Integration of spatial and non-spatial data

In a study involving GIS, both spatial and non-spatial data can be integrated for further analyses and information extraction. In the present study large volumes of non-spatial data have been generated by textural, mineralogical and geochemical studies of sediment samples collected from 31 locations in the estuary. In GIS these kind of non-spatial data can be input to the feature attribute tables of respective coverage (spatial data). In this case the coverage is a point coverage containing 31 sample locations as points. The value of parameters (textural, mineralogical and geochemical) for each point could be input to the attribute table as a record of that particular point.

By inputting all the parameters in a GIS it is possible to display the same by selecting any or all points. It is also possible to display (Fig.6.7a & 6.7b) the values of selected parameters (textural, bulk sediment geochemistry and heavy minerals of coarse fraction) of all the 31 stations.

In this way the GIS with all attribute values could be used to conduct the contamination studies of heavy metals and its spatial distribution is shown in figure 6.8a and 6.8b. Contamination by nickal and its spatial distribution in Kayamkulam estuary is shown in figure 6.9a and 6.9b. this study, cumulative contamination of Cu, Co and Ni has been identified by selecting points, which have values of Cu,Co and Ni greater than one. Arc/Info GIS used in the present study allows selecting points based on logical expressions. Thus the GIS provide maps showing (Fig. 6.10a & 6.10b) regions contaminated by these elements.

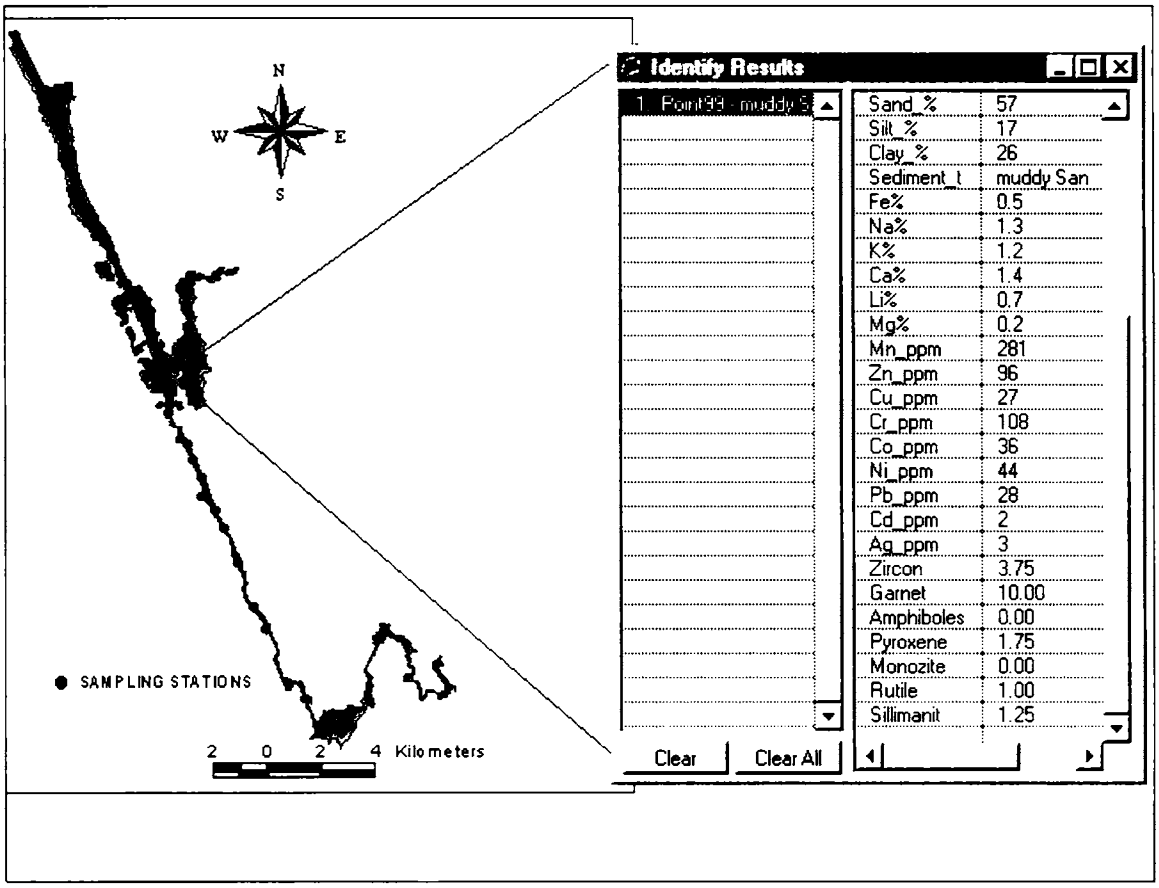


Fig. 6.7a SPATIAL DISTRIBUTION OF TEXTURAL, BULK SEDIMENT GEOCHEMISTRY AND HEAVY MINERALS OF COARSE FRACTION DURING PRE MONSOON

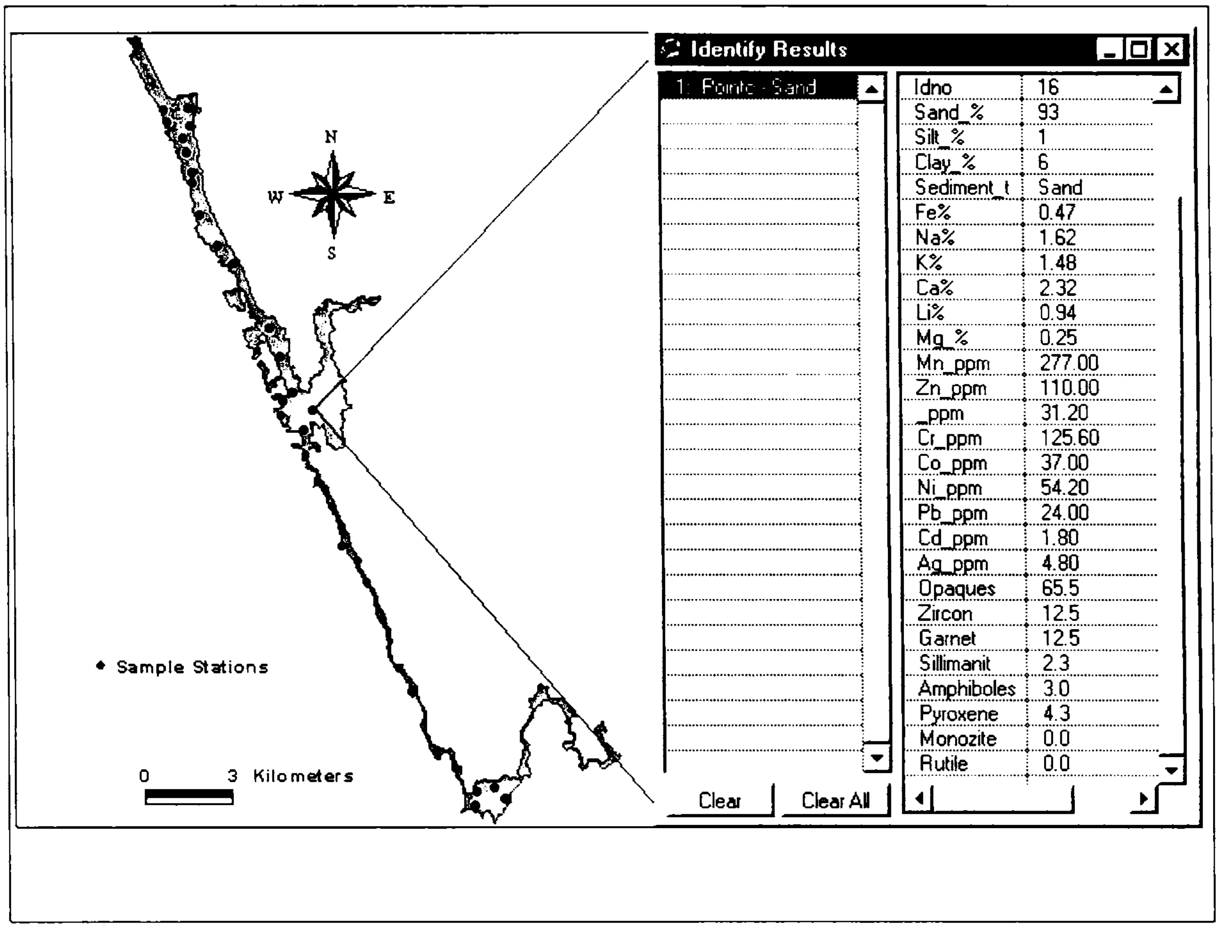


Fig. 6.7b SPATIAL DISTRIBUTION OF TEXTURAL, BULK SEDIMENT GEOCHEMISTRY AND HEAVY MINERALS OF COARSE FRACTION DURING POST MONSOON

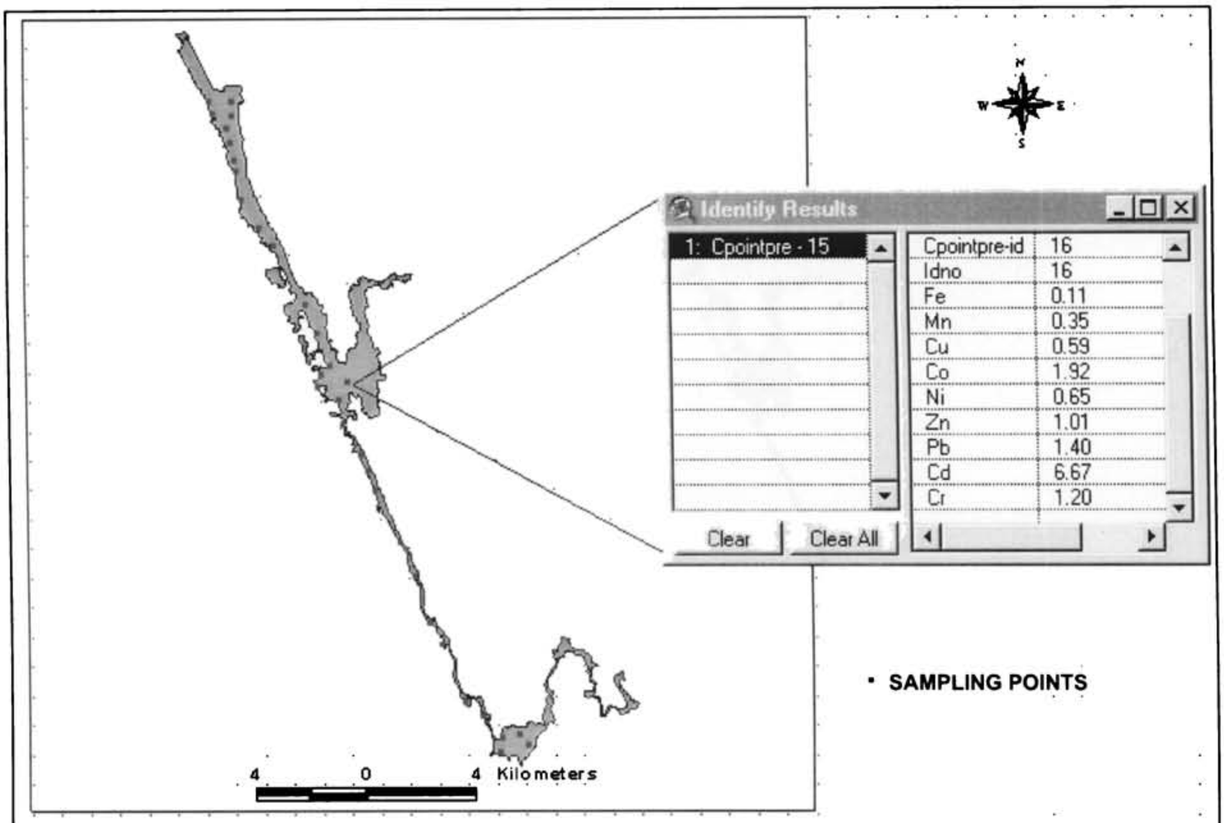


Fig. 6.8a SPATIAL DISTRIBUTION OF HEAVY METALS IN KAYAMKULAM ESTUARY (PRE MONSOON)

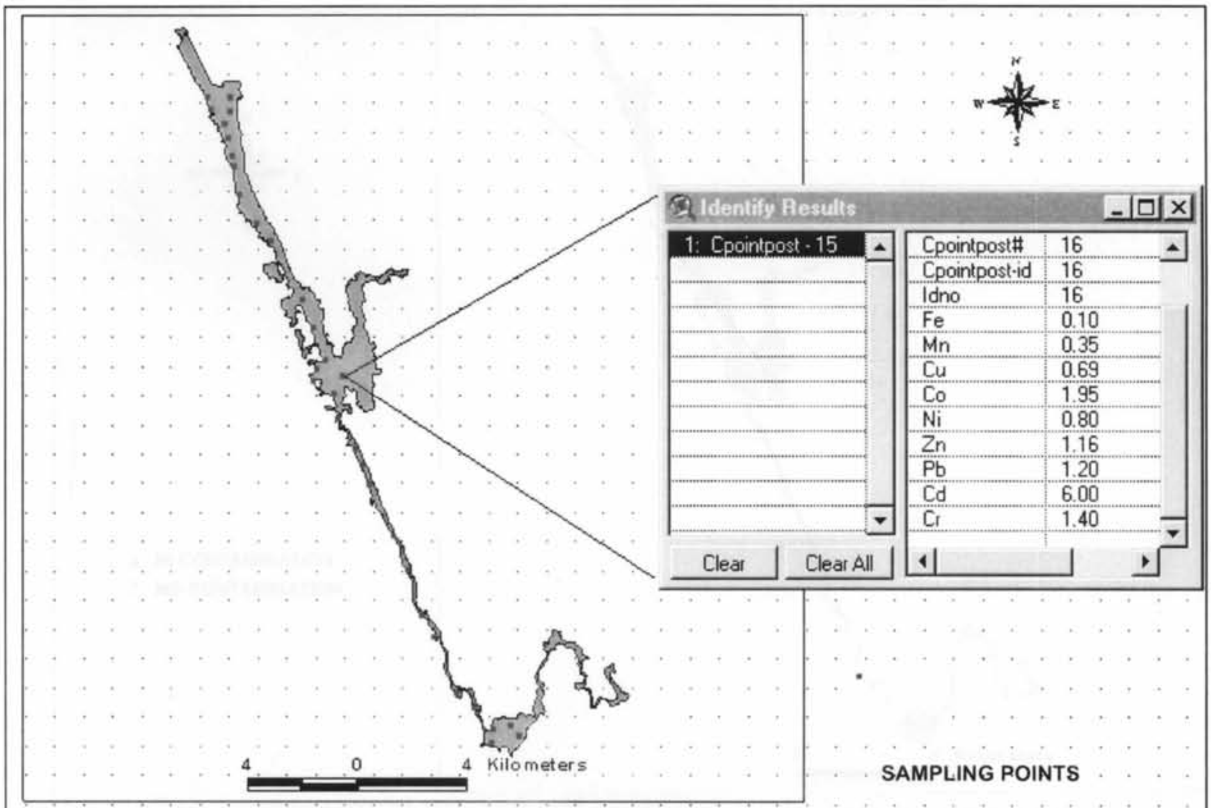


Fig. 6.8b SPATIAL DISTRIBUTION OF HEAVY METALS IN KAYAMKULAM ESTUARY (POST MONSOON)

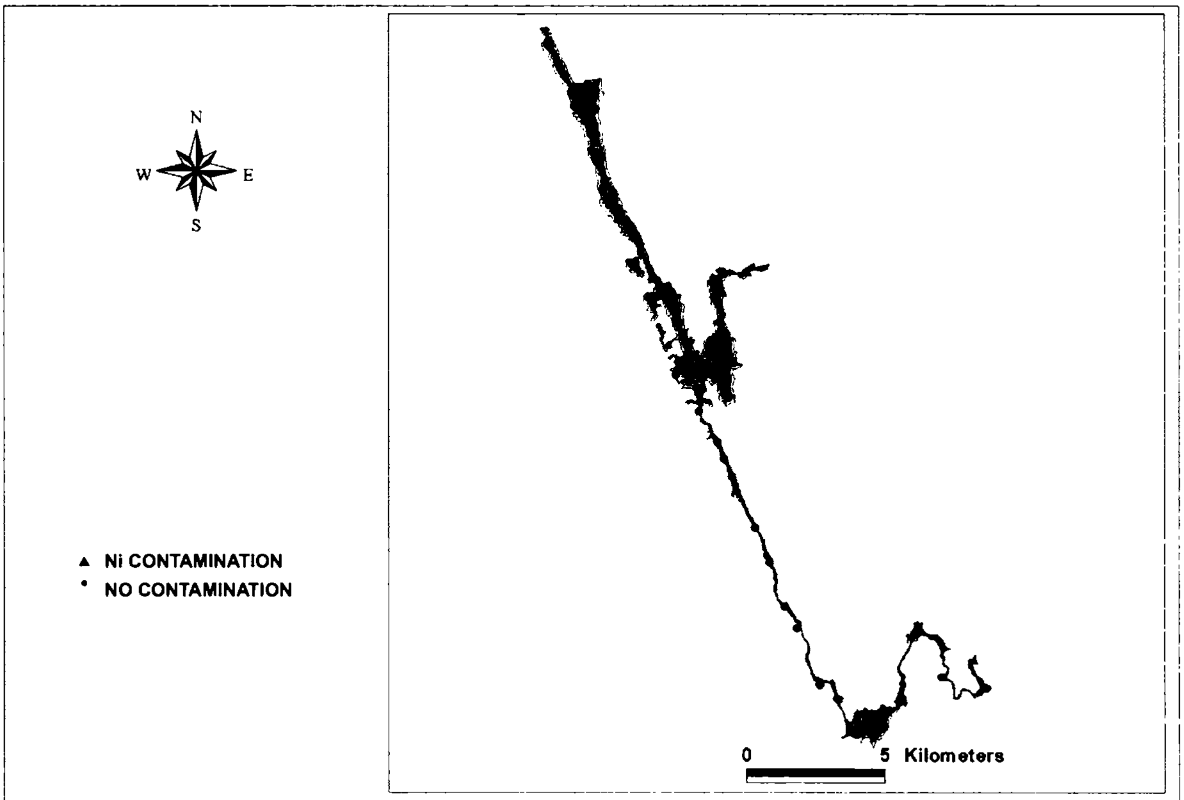


Fig.6.9a CONTAMINATION INDEX OF Ni IN KAYAMKULAM ESTUARY (PRE MONSOON)

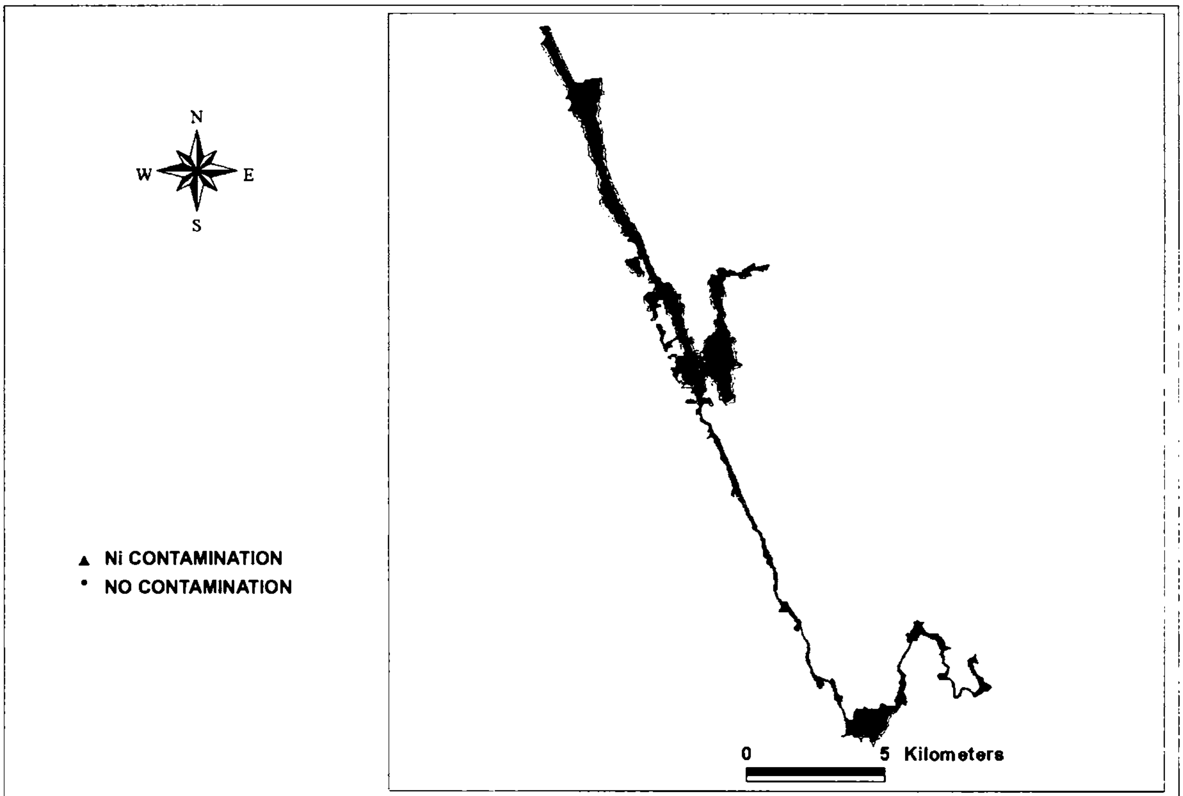


Fig.6.9b CONTAMINATION INDEX OF Ni IN KAYAMKULAM ESTUARY (POST MONSOON)

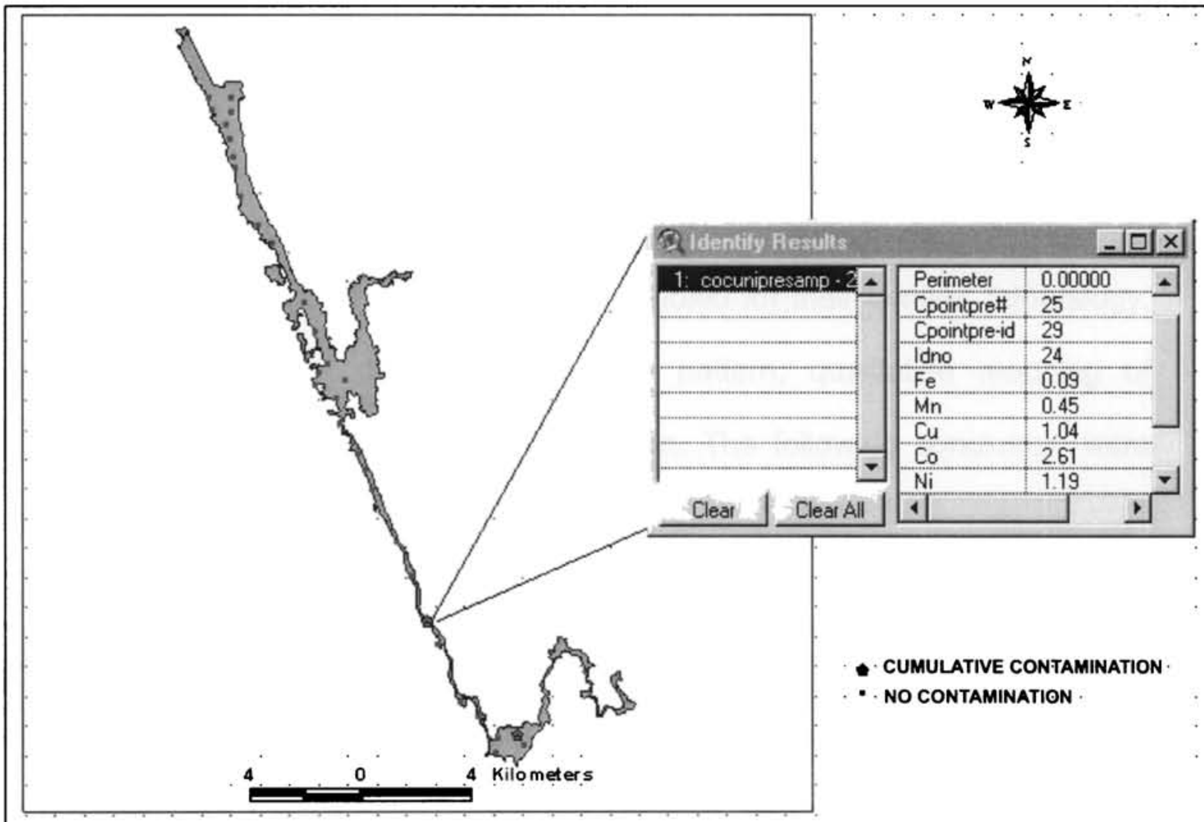


Fig. 6.10a CUMULATIVE CONTAMINATION OF Cu, Co & Ni IN KAYAMKULAM ESTUARY (PRE MONSOON)

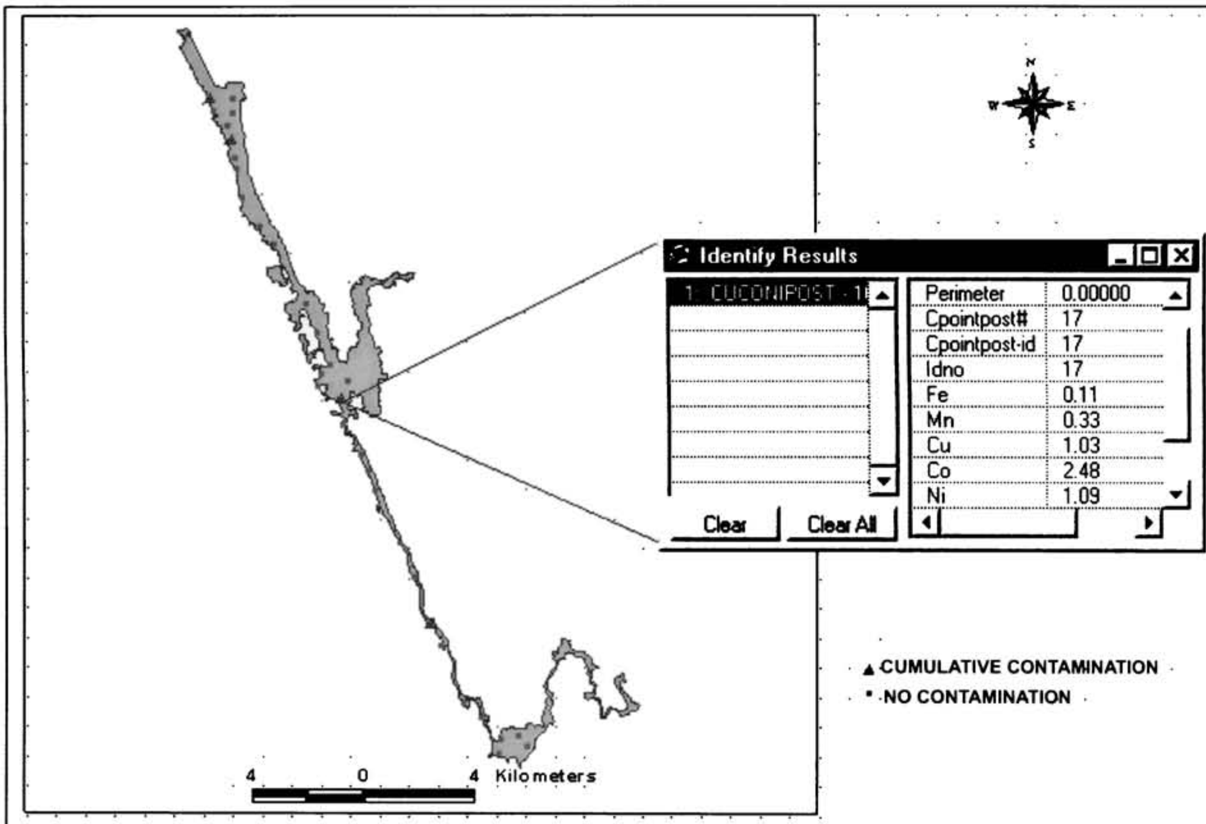


Fig. 6.10b CUMULATIVE CONTAMINATION OF Cu, Co & Ni IN KAYAMKULAM ESTUARY (POST MONSOON)

CHAPTER VII

SUMMARY AND CONCLUSION

The Kayamkulam estuary has been studied for their texture, mineralogy, geochemistry, change detection, land use pattern, qualitative mapping of sediment and health status of the vegetation. The following conclusion were drawn there of from the results and discussion.

The textural analysis carried out for the sediments in the different environments of the Kayamkulam estuary reveal that the northern sector is dominated by muddy sand both for the pre and post monsoon. The central sector is dominated by muddy sand for the pre monsoon while, the sand become the most prominent textural class in the post monsoon. It is seen that the entire Kayamkulam estuarine sediments are floored mainly of fine to very fine sand. The variation in sand, silt, clay for the pre and post monsoon reflects the source as well as the transporting agent. The presence of numerous paleoridges and runnels in the adjoining areas of northern sector has been identified from the false colour composite (IRS IC LISS -III) of the study area.

Thrikkunnapuzha a man made canal and a network of undefined minor streams which drain in to the northern sector of the estuary are not competent agents to transport substantial amount of sediments during pre monsoon, but can contribute considerable amount of coarser clastics from the paleoridges and runnels during the monsoon. The Krishnapuram Ar and the Pallikkal Thodu, the two low order perennial streams emptying into the central and southern sectors are not contributing much sediments to the respective sectors in the pre monsoon but, contributes considerable amount of sediments in the monsoon period. The locally induced fluvial current in turn reworks the sediment at the southern sector while the tides control the sediment distribution at central sector.

From the CM pattern of the sediments constructed for the Kayamkulam estuary reveals that the sediments are transported mainly by suspension and rolling as well as graded suspension.

The surface textural features of quartz grains as delineated by scanning electron microscopic studies for the southern sector reveals features of river transported sediment while for the central and northern parts exhibits high degree of polishness, sphericity, roundness etc characteristic of sub aqueous impact pits. The mixed nature of the quartz grains indicates its derivation from the present to paleo ridges.

From the heavy mineral analysis it is very clear that the heavy minerals are concentrated several fold higher in the fine sand fractions. The observed heavy mineral diversity in Kayamkulam estuary is indicative of the in put of heavies from hinterland by the Pallikkal Thodu which drains in to the southern part of the estuary. The intense marine activities in and near by areas concentrated the heavy minerals removing the lighter particles in the sediment. The sediments were further modified by constant ebbing and flooding activities at the bar mouth. Therefore the density-based segregation is the major causative factor for the observed higher mineral content in the finer sands. The decrease of heavies down stream especially in the southern and central sectors may be due to non-entrainment of the heavies by low energy currents subsequent to deposition. An increase of more durable minerals like opaque and garnet and decrease of relatively less stable minerals noticed in the Kayamkulam estuarine sediments reveals the selective abrasion as an important cause for the heavy mineral variation. An increase in the content of garnet and zircon and a decrease of opaque in the direction of transport indicated the selective sorting in the northern sector. In short selective weathering has a prominent role followed by progressive sorting in the variation of heavy mineral assemblages.

It is concluded form the relative abundance of the heavy minerals and their assemblages that khondalite and charnockite are the main contributors to the heavy minerals in the Kayamkulam estuary besides quartzo-feldspathic gneisses.

Montmorillonite is the most abundant clay mineral present all through out the lake followed by kaolinite and illite. Higher proportion of montmorillonite can be due to the relatively small drainage basin, different energy levels at different sectors of the estuary, size segregation of minerals and cation adsorption. A part of the offshore sediment rich in montmorillonite brought in suspension of the incoming tidal currents gets deposited in the inner part of the lake when the tidal currents looses its velocity, they move in to relatively deeper part of the lake reflecting the estuarine mixing processes or estuarine circulation dynamics.

Low content of illite indicates the drainage contributes. Comparatively higher content of kaolinite reflects greater intensity of laterite weathering at the source rock, as kaolinite is the stable product of the laterisation. Hence kaolinte can be considered to be formed under tropical weathering. The clay minerals in the Kayamkulam estuary are controlled primarily by source, physical sorting, size segregation, conditions of prevailing environment and absorptions of ions besides estuarine circulation dynamics.

Studies on the organic carbon content reveal the direct bearing between the texture of the sediment and organic carbon content. High content of organic carbon at the northern sector is due to the prevalence of reducing environment, the fine texture of the sediment and the coconut leaf and husk retting. Higher content of organic carbon at the central and southern sectors reflects the river contribution especially in the monsoon periods besides the fine texture at the southern sector.

Higher content of carbonate at the southern and central sectors are primarily of biogenic origin, which comes from the shells and tests of organisms. Prevalence of reducing environment at the northern sector resulted in a lower carbonate content. The main source of carbonate for the Kayamkulam estuarine sediments is from the shell fragments and tests of organisms.

The geochemical distributions of Na, K, Ca, Mg, Fe and Mn from the bulk and clay fractions are discussed in relation to physicochemical conditions of the depositional environment, organic carbon and carbonate contents. The relative differences observed for Na and K in the estuarine sediments especially in clays are due to clay mineral composition, initial composition of the source material, progressive changes in the salinity and salts from the pore solution. Major parts of the Na ions are tied up with montmorillonite. The regional variation in the Ca and Mg content is due to the fixing up of Ca in montmorillonite as inter layer cations in the clay mineral structure and as calcium carbonate in the shells and test of organisms. Major part of the Mg is fixed in montmorillonite. A part of Ca and Mg is of biogenous origin.

The variation in the Fe content is due to the precipitation of Fe under oxidising and reducing environments, fixing up of Fe in clay mineral structure either by cation exchange or by adsorption and close association with organic matter. Fe is fixed up in montmorillonite. Mn is co-precipitated with Fe especially in fine fractions. A part of Mn is also fixed up with the lattice of montmorillonite.

The following aspects of trace elements were revealed from their studies. Zn is precipitated as sulfides in the reducing environments and a part is fixed up in montmorillonite. Cu is associated very much with the clays either by adsorption or by cation exchange. Cu gets concentrated more in the reducing environment with low oxidative potential. Variation in the cobalt concentration depends on fine texture, clay mineralogy and fixing up of cobalt by adsorption of hydrated Fe_2O_3. Cr is concentrated in the sediments of Kayamkulam estuary as absorption by the hydrated ferric oxide and by the replacement of Al in kaoloinite and Fe-Mg in smectite. Significant part of Ni is held up in the clay minerals due to cation exchange in montmorillonite. Pb is associated with clays and depends only on the texture of the sediments. Cd precipitaes as CdS and $CdCO_3$.

Trace metal speciation studies for the sediments of the Kayamkulam estuary revealed that Cd is the most exchangeable fraction followed by Cr and Cu fraction. In the carbonate fraction Cd recorded the highest percentage followed by Cr and Cu, while in the Fe and Mn oxide phase Cr yielded the highest value followed by Cu. Cd and Co registered only a low percentage. Cd has virtually no Fe/Mn oxide bound fraction.

Cr registered the highest percentage for organic matter bound fraction, next to it is Cu. Pb and Ni yielded hundred percent residual phase and the only trace metal does not have any other extraction phase is Pb and Ni.

The pollution status of the Kayamkulam estuary was evaluated making use of the contamination factor as determined for each heavy metal. From the study, it is concluded that the Kayamkulam estuarine sediments are contaminated with Cu and Ni. Kayamkulam estuary is least polluted when compared with the adjacent estuaries namely Vembanad and Ashtamudi.

Remote sensing which is proved, time and again to be a useful tool in various fields of earth science, has been useful in the present study for change detection, landuse pattern, qualitative mapping of sediment and health status of vegetation (NDVI). GIS, which is a powerful tool in integrating large quantities of spatial data, has been used in conjunction with remote sensing data pertaining to this study area.

Change detection study has brought out that the area of Kayamkulam estuary has been reduced considerably from 1967 to 1999 (33.27%). One of the major causes of reduction in the area is the reclamation of the land by NTPC for the thermal power plant. Erosion, which is noted along the southern portion of the estuary, is due to the widening of channel for inland navigation. The central portion of the estuary has also experienced reduction in the area in the form of sand deposits formed by complex estuarine and marine forces in this area.

For determining landuse around the study area, unsupervised and supervised classifications of satellite image are carried out. Both these classifications show moderate to good cover of mixed vegetation with settlement areas in between around the estuary.

Another unsupervised classification of satellite image shows high concentration of suspended sediments in the central and northern most portion of the estuary, showing both natural and anthropogenic activities respectively.

NDVI, which is a measure of health status of vegetation has been determined and colour coded map prepared for the study area, shows that 'moderate' to 'good' status of health of vegetation around the estuary. Finally Arc/Info GIS has been utilized to integrate spatial data (Sample location and areal extent of the estuary) and non-spatial data (textural, bulk sediment geochemistry and heavy minerals of coarse fraction) to develop a strong database on the Kayamkulam estuary, which could be used for information extraction and contamination status.

To sum up, the different environments of Kayamkulam estuary has been brought out by the textural, mineralogical and sedimentological studies. Remote sensing has proved beyond doubt as an efficient tool for delineating the various aspects of Earth science and GIS as a powerful tool for integrating large quantities of spatial and non spatial data generated for the Kayamkulam estuary. The present study has provided excellent base line information for computing/ evaluating post industrial pollutions.

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