

**MINERALOGY AND GEOCHEMISTRY OF THE  
SEDIMENTS OF MUVATTUPUZHA RIVER AND  
CENTRAL VEMBANAD ESTUARY, KERALA, INDIA**

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CERTIFICATE

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

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## Preface

*"The Story of Ganga from her source to the sea, from old times to new, is the story of India's civilization and culture" - Jawaharlal Nehru*

Rivers and estuaries have been the foci of civilization from the dawn of recorded history or long before. Much of the materials released during natural crustal weathering have been carried to the ocean by various geological agents such as rivers, wind, glaciers etc., of which rivers alone transport about 90% of the total sediment flux annually. However, all the sediments borne off by rivers seldom reach the sea as considerable quantity is detained in the estuarine and the other near shore environments. During transportation and deposition, the sediments undergo tremendous and endless changes in their mineralogy and chemistry. Textural attributes have a strong bearing on all these changes. Besides, mankind's association with rivers and estuaries has further complicated the natural pace of the above processes.

The interest in mineralogy and geochemistry of riverine and estuarine sediments is increasing at a considerable rate due to the growing awareness of environmental monitoring and management. The heavy, light and clay mineral suites in sediments unfold information about the provenance of sediments, type of weathering and climate of the drainage basin. Mineralogical assemblage in consonance with textural characteristics can also be used for evaluating the nature and energy conditions of the depositing medium. On the other hand, geochemistry of sediments provides a wealth of information about the various physicochemical processes operating during transportation/deposition and also the anthropogenic effects on the geologic cycle, the fundamental problem of our current environmental crisis.

Central Kerala is one of the most densely populated segments in the Peninsular India. This region is blessed with numerous interlacing network of rivers and estuaries. But unfortunately, this zone is severely impacted by contaminant discharges from industrial (eg. chemical, fertilizer, paper, etc.), urban and agricultural sources. Recent evidences indicate that the region is under the threat of severe ecological impairments. It is therefore highly significant to implement systematic monitoring measures for the proper maintenance and management of the ecological habitat of this region. Researches on global scale by several investigators revealed that studies on surficial sediments can provide better insights and future guide-lines to all riverine and estuarine monitoring/management programme.

In view of the above, an attempt has been made in this investigation to delineate the mineralogical and geochemical composition of the sediments of Muvattupuzha river and Central Vembanad estuary to have a better scenario of the various mineralogical and geochemical processes operating in these environments. Stress has been given to the granulometric dependence of minerals and geochemical parameters of sediments.

The present study is addressed in six chapters:

Chapter 1 deals with the general introduction. The various methods employed during sample collection and processing, analytical procedures and computational techniques are given in Chapter 2. Chapter 3 depicts the textural characteristics of the sediments including the surface texture of quartz by SEM. The mineralogical constitution of sand as well as a few silt and clay samples is discussed in Chapter 4. Chapter 5 presents the geochemical characteristics of the bulk sediments and sand, silt and clay fractions. Geochemistry of suspended sediments, rocks and soils of the drainage basin of Muvattupuzha river and the geochemical abundance of U and Th in the sand fraction of the study

area are also dealt in this chapter. Summary of the study and the salient conclusions drawn from the results thereof are given in Chapter 6.

The references cited are furnished at the end of the thesis.

The following research papers are presented/published during the course of this investigation.

1. Padmalal, D. and Seralathan, P. (1991) Interstitial Water-sediment geochemistry of P and Fe in the sediments of Vembanad lake, West Coast of India. Ind. Jour. Mar. Sci., Vol. 20, pp. 263-266
2. Seralathan, P. and Padmalal, D. (1991) Geochemistry of the Tertiary Formation at Pozhikkara Cliff Section, Kerala - Its Palaeoenvironmental significance. Jour. Geol. Soc. Ind., Vol. 38, pp. 277-281
3. Padmalal, D. and Seralathan, P. (1992) Heavy metal content in the suspended particulates and bed sediments of a Tropical Perennial river and its estuary, Kerala, India. Jour. Geol. Soc. Ind., (Under revision)

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## CHAPTER 1

## GENERAL INTRODUCTION

### 1.1 INTRODUCTION

Rivers and estuaries constitute the major pathways of natural and anthropogenic materials from land to the sea. Compared to other geological agents such as wind, glaciers, ground water etc., the total amount of materials (dissolved, suspended and bed sediments) carried by rivers is remarkably high. Several attempts have been made to assess the quality and quantity of river transported materials to the ocean realm. Lal (1977) estimated that the total mass of suspended sediments in the ocean is approximately  $10^{16}$  gram, the majority of which is contributed by the rivers through estuarine environments. Milliman and Meade (1983) computed that 12-13 tons of suspended sediments are supplied to the world oceans annually by rivers and further  $1-2 \times 10^9$  tons are supplied as bed load and flood discharges.

The characteristics of river basin such as climate, vegetation, geology and geomorphology are the important factors which control the composition and quantities of materials carried by rivers. Intense industrial developments, primarily concentrated along the banks of rivers and estuaries, large scale urbanization and agricultural activities have considerably complicated the natural pace of riverine and estuarine sedimentation processes. Further, evidences indicate that, irrational approaches to meet the quest of such developmental activities have created severe impairments to the natural settings of these environments.

The natural and man-made materials entering rivers and estuaries are subjected to a series of mineralogical and chemical changes. Textural characteristics of sediments have a considerable bearing on all the physico-chemical changes taking place in the riverine and the estuarine environments. The relationship existing between texture,

mineralogy and chemistry in sediments can be used for the reconstruction of ancient environments. Further, such studies in modern sediments can provide insights into the pollution aspects of these environments.

In view of the above, the Muvattupuzha river and the Central Vembanad estuary (ie, from Thannirmukham bund to Fort Cochin) are selected for detailed mineralogical and geochemical studies (Fig. 1). Importance is given to the textural dependences of mineralogical and geochemical constituents of sediments.

## 1.2 LOCATION

**Muvattupuzha river:** Muvattupuzha river is one of the major perennial rivers in Central Kerala. It has a length of about 121 Km and a catchment area of about 1,554 Sq.Km. (CESS, 1984). The river originates from the western ghats and drains mainly through highly lateritized crystalline rocks. It debouches into the Vembanad estuary near Vaikom. Two major tributaries namely Thodupuzha and Kaliyar join the Muvattupuzha river near Muvattupuzha town. After flowing as a single stream upto Vettukattumukku, the river branches into two distributaries namely Ittupuzha and Murinjapuzha. The river exhibits dendritic drainage pattern (Fig. 1). The entire Muvattupuzha river basin lies between Lat.  $9^{\circ}45'$  -  $10^{\circ}05'N$  and Long.  $76^{\circ}22'$  -  $76^{\circ}50'N$ . The river discharge ranges from 50 m<sup>3</sup>/sec (premonsoon) to 400 m<sup>3</sup>/sec (monsoon). Peak discharge is recorded during June to October. Considerable changes have taken place in the flow characteristics of the Muvattupuzha river after the commissioning of the Idukki hydroelectric project in 1976, across the adjoining Periyar river (Balchand, 1983). The tail-race water (19.83-78.5 m<sup>3</sup>/sec) was directed into the Thodupuzha tributary from Moolamattom power station. This tail-race water (almost constant) plus surface run off have not only altered the morphological characteristics of the river considerably but also the sediment dynamics and ecological habitat of the river basin as well.

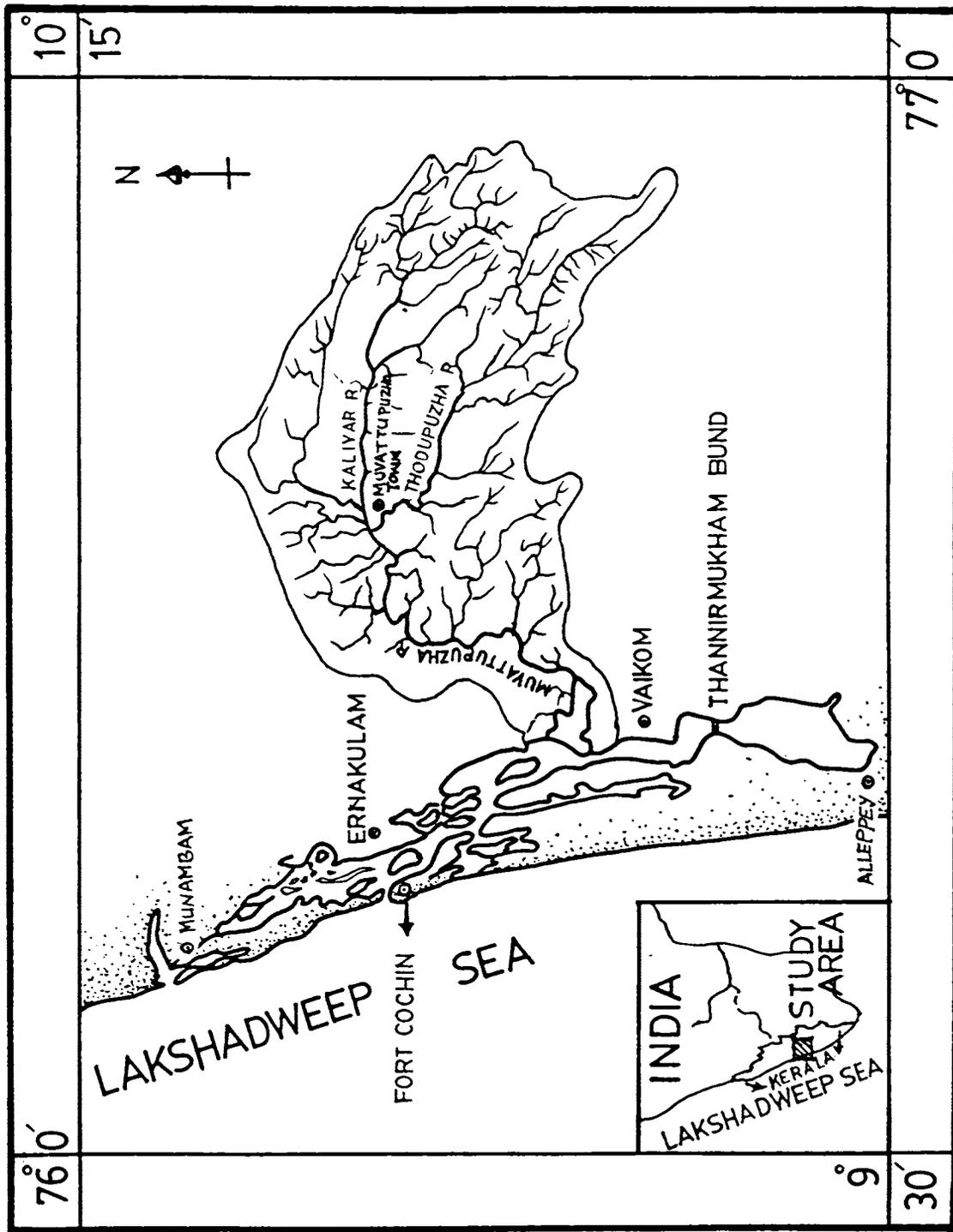


Fig. 1 Location of the study area and drainage pattern of the Muvattupuzha river

The important characteristic features of the Muvattupuzha river drainage basin are as follows: (MVIP, 1976)

Total catchment area	:	1554 Km <sup>2</sup>
Maximum altitude	:	1093.6 m
Minimum altitude	:	1.5 m
Mean altitude	:	170.7 m
Total length of the river	:	121 Km
Mean slope	:	0.813
Maximum width of the basin	:	38 Km
Minimum width of the basin	:	4 Km

**Central Vembanad estuary:** Vembanad estuary (Fig. 1) is the largest backwater system in the west coast of India, extending parallel to the coast from Alleppey in the south to Munambam in the north (Lat 9°28' - 10°10'N and Long. 76°13' - 76°25'E). It has a length of about 113 Km and the breadth varies from a few hundred meters to 14.5 Km, covering an area of about 233 Sq.Km. This estuarine system has two openings with the Lakshadweep sea; one at Fort Cochin and the other at Munambam (north of the study area). Seven major rivers (five from south of Cochin; Achankoil, Pamba, Minachil, Manimala and Muvattupuzha and two from north; Periyar and Chalakkudi) debouch into the estuary. On the southern side of the estuary, a barrage has been constructed near Thannirmukham to prevent salt water intrusion especially during extreme droughts (premonsoon). The present investigation is confined to Thannirmukham bund and Fort Cochin (Lat. 9°40' - 10°0'N, Long 76°13' - 76°25'E).

**Estuarine hydrography:** Estuarine hydrography plays an important role in the sedimentation and geochemical processes of this environment. The quantum, duration, transport and settlement of particulate sediments depend directly on estuarine hydrography. The hydrography of the Vembanad estuary has been investigated by several researchers (Qasim

and Reddy, 1967; Qasim et al., 1968; Sankaranarayanan and Qasim, 1969; Josanto, 1971a; Lakshmanan et al., 1982; Sankaranarayanan et al., 1986 and Anirudhan, 1988). The distribution of temperature in the estuary is a function of the input of fresh water from rivers as well as the intrusion of salt water from Lakshadweep sea. Processes like exchange of heat with atmosphere and other localized phenomena are also likely to influence the hydrographic conditions of the system. The temperature of water varies between 25 and 31°C. Low salinity values ranging from 0 to  $10 \times 10^{-3}$  at the surface and 0 to  $12 \times 10^{-3}$  at the bottom were observed during monsoon. This was brought about by the combined effect of land drainage from the prevailing monsoonal rains causing high fresh water discharge from the river and intrusion of salt water from the sea. As the season advances to post and premonsoon, higher salinity values ranging from 10 to  $22 \times 10^{-3}$  at surface and 12 to  $24 \times 10^{-3}$  at the bottom were observed (Anirudhan, 1988). The estuarine waters considerably get diluted near the Muvattupuzha river confluence. The pH values of the surface and bottom water vary from 6.6 to 7.4 and a slight increase is observed seasonally upto postmonsoon period.

### 1.3 REGIONAL GEOLOGY (GENERAL)

Geologically, Kerala State forms part of the Peninsular Shield bounded by western ghats on the east and the Lakshadweep sea on the west. The State is mainly occupied by four major rock units. They are: (1) Pre-Cambrian crystallines, (2) Tertiary sedimentaries, (3) Laterites developed over Pre-Cambrian crystallines and Tertiary sedimentary rocks and (4) Recent to Sub-Recent sediments.

**Pre-Cambrian Crystallines:** The Pre-Cambrian crystalline rocks occupy a considerable area of Kerala which includes charnockites, garnet-biotite gneisses, hornblende gneisses, khondalites, leptinites, cordierites and other unclassified gneisses. A large part of these crystalline rocks has

undergone polymetamorphic and polydeformational activities. High grade schists and gneisses of Wynad and Surgurs cover some regions of North Kerala. The Pre-Cambrian crystallines are traversed by several acidic (granite and pegmatite) and basic (gabbro and dolerite) intrusions. The salient features of the major rock types are given below.

a) Khondalites: A major part of Periyar and Thodupuzha river basins is occupied by Khondalite group of rocks. The group includes quartzite, calcgranulite, garnet gneiss and patchy charnockite. Age determinations of these rock types indicate a range of 670 to 2200 Ma (Santhosh, 1987 and Chacko et al., 1988).

b) Charnockites: Charnockites constitute the major part of the hinterland geology. They show wide variations in composition from acidic to basic. Charnockites are massive in appearance but on close examination, yield well developed foliation or deformational banding. Apart from this, patchy type of charnockite is also recorded (Ravindrakumar et al., 1985). They are characterised by hypersthene, feldspar, quartz, hornblende and garnet.

c) Acid intrusives: Granites, pegmatites and quartz veins are the common acid intrusives observed in Kerala. Apart from this, patches of syenitic intrusions are also reported from the State. The granite bodies generally occur as fault/lineament controlled plutons emplaced between 500 to 700 Ma ago (Santhosh and Drury, 1988). At several places, the Pre-Cambrian crystallines are also traversed by simple and complex pegmatites and quartz veins.

d) Basic intrusives: Gabbros and dolerites constitute the most common basic intrusives emplaced within the Pre-Cambrian crystallines. Two distinctive systems of basic dykes are recognised. They are (1) The NNW - SSE trending leucogabbros which are exposed intermittently for over a length of 100 Km and (2) The NW - SE trending doleritic dykes.

K-Ar isotope dating has yielded  $81 \pm 3$  Ma for the former and 65-70 Ma of age for the latter (Radhakrishna et al., 1989).

**Tertiary sedimentaries:** The Tertiary sedimentary formation of Kerala unconformably overlies the Pre-Cambrians (Poulose and Narayanaswami, 1968). It extends as a narrow belt along the major part of Kerala coast and comprises two facies of sediments: (1) The continental facies, the Warkalli beds, comprises carbonaceous clays with lignified tissues/coal seams, china clays and friable sandstones and (2) the marine facies, the Quilon beds, composes of sandstones and carbonaceous clays with thin bands of fossiliferous limestones depicting the transgressive episodes occurred during Burdigalian (Upper part of Lower Miocene) time.

**Laterites:** Laterites of Recent to Sub-Recent age form the third litho-unit and they cap over both Pre-Cambrian crystallines and Tertiary sedimentaries. It is mainly composed of hydrated oxides of Fe and Al together with minor amounts of Mn, Ti, V, and Zr. These sedantary rocks are considered to be the primary source of black minerals in the beach sands of Kerala (Gilson, 1959). These rock types cover nearly 60% of the surface area of Kerala.

**Recent to Sub-Recent sediments:** The Recent to Sub-Recent sediments stretch from Kasaragod in the north to Cape Comorin in the south. They include fringes of parallel sand bars, sandy flats, alluvial sands and lacustrine deposits. These are separated from the Tertiary sedimentaries by a polymict pebble bed. From economic point of view, this zone is the most important one due to its abundant occurrence of valuable placer mineral deposits.

#### 1.4 GEOLOGIC SETTING OF THE DRAINAGE BASIN OF THE STUDY AREA

The Muvattupuzha river drains through highly varied geological formations of Pre-Cambrian crystallines, laterites and Tertiary

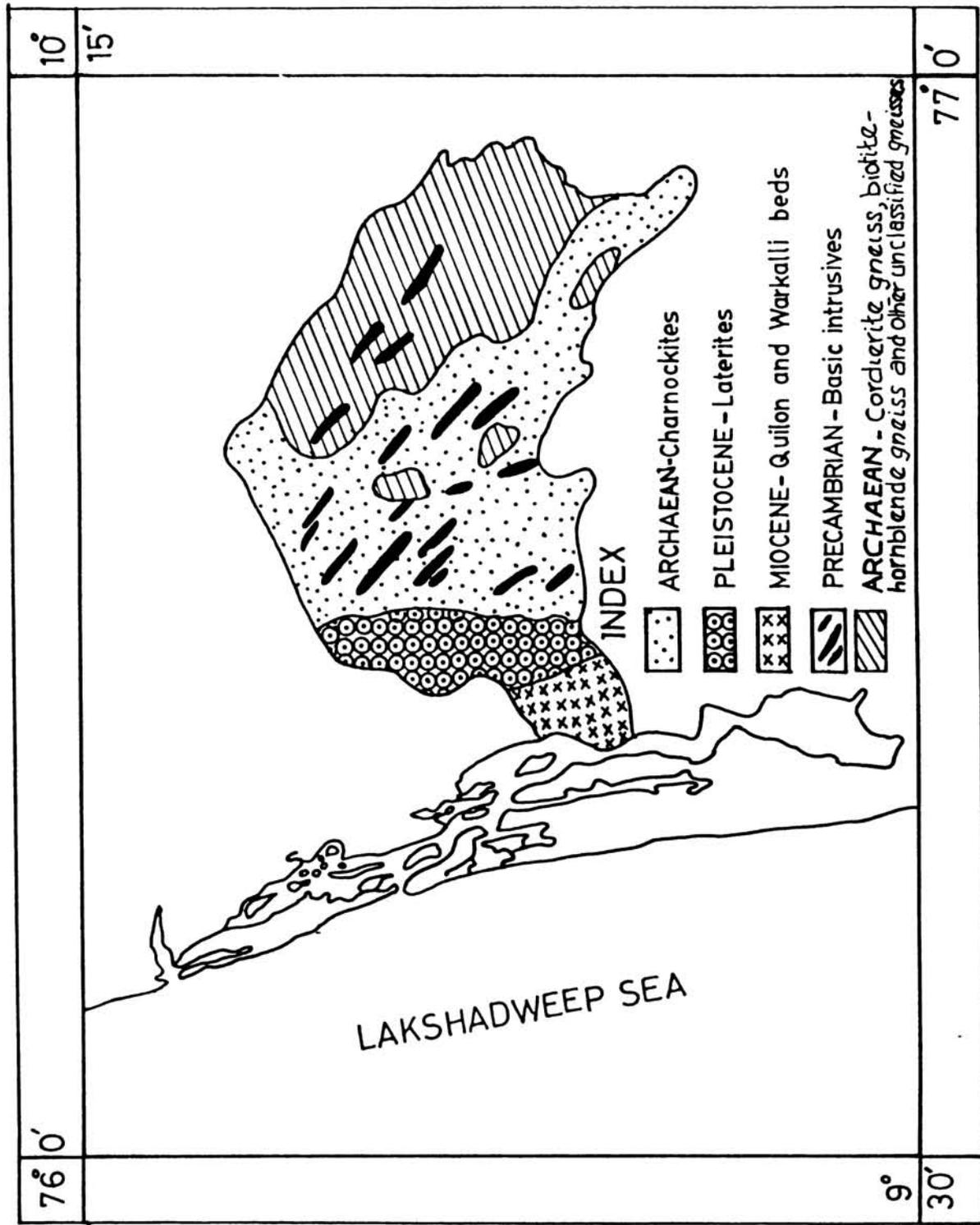


Fig. 2 Geology of the Muvattupuzha river drainage basin

sedimentary rocks. Charnockites, hornblende-biotite gneisses and other unclassified gneisses form a major portion ( $\sim 85\%$ ) of the drainage basin. They are often intruded by acid (granite, pegmatite and quartz vein) and basic (gabbro and dolerite) rocks (Fig. 2). The crystallines forming the high lands are polyphasedly deformed (Santhosh, 1988). Laterites and Warkalli beds, found near the mouth of the river, together constitute approximately 15% of the total drainage basin.

### 1.5 PHYSIOGRAPHY

Physiographically, the Muvattupuzha river basin consists of three distinct land forms. They are (1) the high lands, (2) the midlands and (3) the lowlands (CESS, 1984). The high lands ( $> 75$  m) restrict only to the upper most part of the drainage basin and form steep to very steep hill ranges of Sahyadris (a part of the Western ghats). This zone is characterised by a slope range of 70 to 100%. The midlands (75-8 m) form the major physiographic unit of the basin and cover more than 75% of the total drainage area. It generally shows gentle to moderate sloping terrain. Midlands are characterised by a slope range of 10 to 20%. The low lands exhibit nearly level to gently sloping coastal plain. This youngest planation surface is mostly depositional and is developed by fluvial as well as marine action.

Fig. 3 depicts the longitudinal profile of the river channel through Thodupuzha-Muvattupuzha-Ittupuzha river system. The profile shows gentle to moderate slope upto Muvattupuzha town. Then the gradient decreases considerably and the profile nears to Mean Sea Level (MSL).

### 1.6 CLIMATE

Climate is a significant parameter which affects the various stages of morphogenic processes such as erosion, transportation and

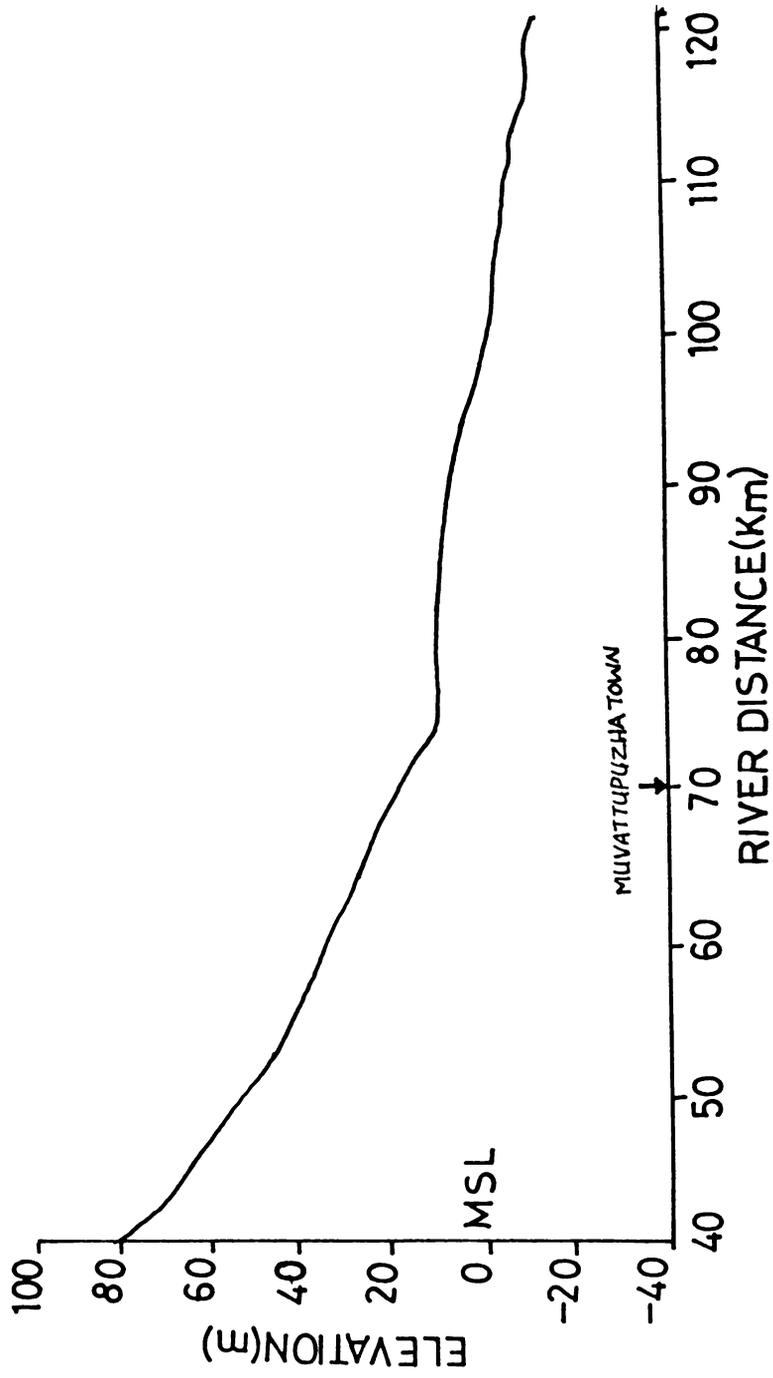


Fig. 3 Longitudinal profile (Gradient) of the Thodupuzha - Muvattupuzha - Ittupuzha river channels

deposition. It not only influences weathering but also affects considerably the quality and quantity of river transported materials. The Muvattupuzha drainage basin enjoys characteristic tropical humid climate. A dry summer season from February to May (premonsoon) is followed by southwest monsoon (June-September) of heavy rains and then postmonsoon season (October-January) with a relatively low rainfall to scanty thunder storms. However, the high altitude areas of the basin have a temperate climate. The average annual rainfall of the study area varies from 2500 mm to 5000 mm depending upon the physiography. Maximum rainfall occurs during south-west monsoon season. The temperature of the basin varies between 10°C (January-February) and 32°C (March-May). The catchment area has very high humidity of more than 80%.

#### 1.7 LAND USE

Man's intervention in the catchment area of the Muvattupuzha river basin has started a century ago. Before that the catchment area was covered by luxuriant tropical forests and grasslands. In the second half of the nineteenth century clearing of forests started in the high lands for rubber plantation. The land use types are distinctly governed by physiography and climate of the region. There are mainly 5 broad categories of land use types distributed unevenly in the drainage basin (Nair, 1987). The elevated regions are used for rubber plantation followed by forest lands, grass lands and arable lands. Extensive waste lands formed of hard crust of laterite which are generally unsuitable for cultivation are also seen in the area. In the upper regions of the river, in addition to rubber, pepper, tapioca, ginger etc. are also cultivated. The lower regions are primarily used for tapioca and paddy cultivation.

## 1.8 OBJECTIVES OF THE PRESENT INVESTIGATION

The major objectives of this thesis are the following.

- 1) To study the granulometric composition and the spatial variation of textural attributes of Muvattupuzha riverine and Central Vembanad estuarine sediments. The bearing of textural grades and statistical parameters on the hydrodynamic conditions prevailing in the study area are also delineated.
- 2) To analyse the mineralogical assemblages in various size grades of the riverine and estuarine sediments as well as to highlight its granulometric dependence.
- 3) To envisage the hydrodynamic conditions responsible for the observed mineralogical diversities.
- 4) To determine the provenance of the sediments.
- 5) To findout the geochemical variability of organic carbon, phosphorus and certain major (Na, K, Ca and Fe) and trace (Mn, Pb, Cu, Co, Ni, Cr, Cd and Zn) elements in the bulk sediment and various size fractions (sand, silt and clay) of the riverine and estuarine sediments.
- 6) To emphasise the metal levels in suspended sediments as well as rocks and soils of the drainage basin.
- 7) To trace out the level of radioactive elements (U and Th) enrichment in the sand fraction of study area.

## CHAPTER 2

## MATERIALS AND METHODS

### 2.1 INTRODUCTION

This chapter deals with the various methods employed in the collection, processing and analysis of the samples used for this investigation. The present investigation is scheduled into two phases: (1) Field survey and (2) Laboratory investigations.

### 2.2 FIELD SURVEY

A total of 44 riverine and 43 estuarine sediment samples were collected at regular intervals along the course of the Muvattupuzha river (Fig. 4) and the Central Vembanad estuary (Fig. 5). A stainless steel vanVeen grab was used to collect sediments from the estuary and also deeper parts of the river course. From shallow water regions of the river, sediment samples were obtained by penetrating a PVC pipe of 10 cm diameter into the river bed. All samples were carefully transferred to neatly labelled polyethylene bags. Five litres of water samples from 10 stations in the riverine and estuarine regions were also collected using a Casella water sampler. Bucket sampling method was adopted to obtain water samples from shallower regions of the river.

In addition, 19 rock samples and 4 soil samples from the drainage basin of Muvattupuzha river were also collected to know the background elemental levels. All the samples were brought to the laboratory and kept in an inert atmosphere till further processing/analysis. Utmost care was taken not to contaminate the samples during collection and handling. Sampling was started in April 1988 and ended in May 1988. The time interval between sampling was minimised as much as possible to get better accuracy.



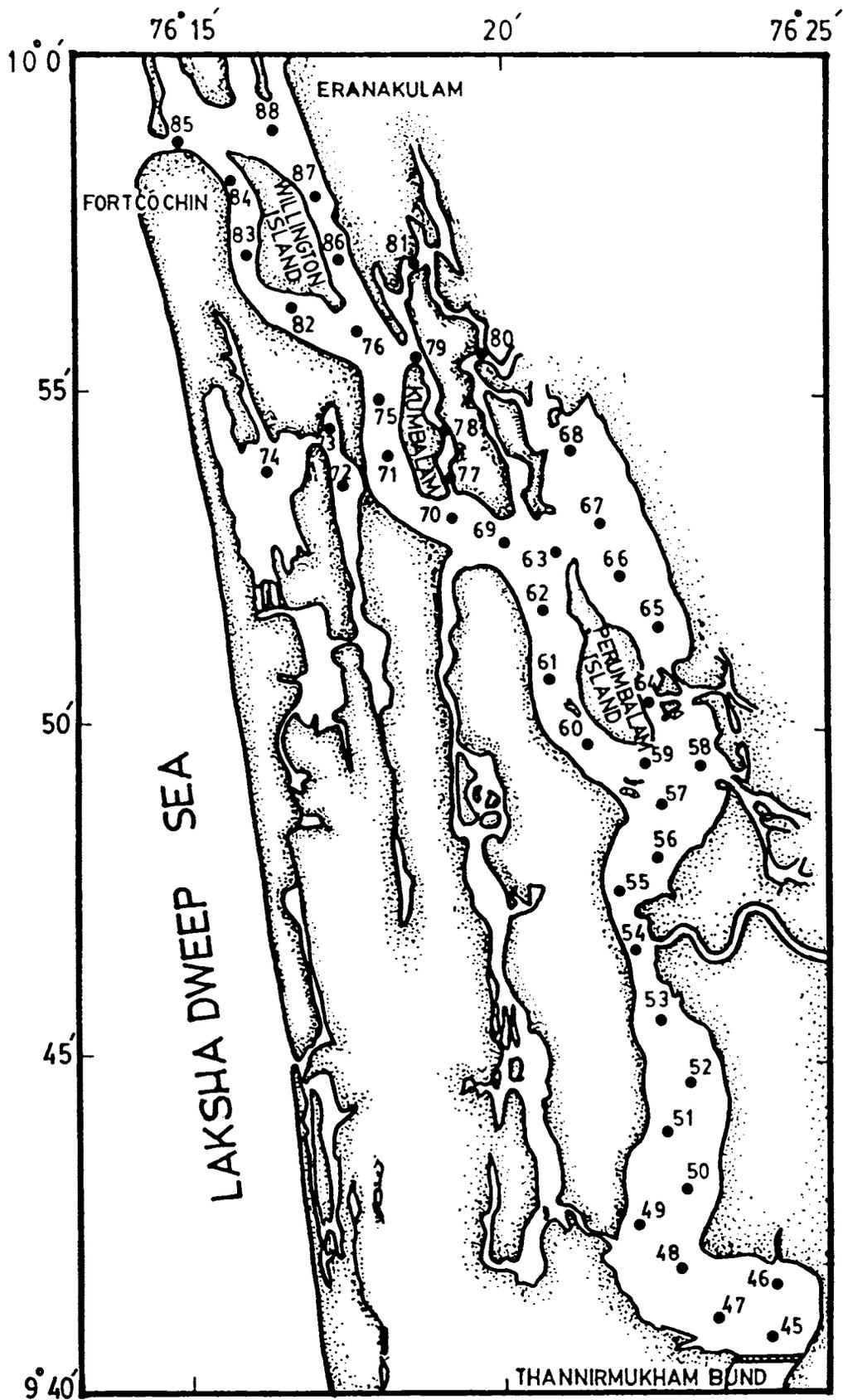


Fig. 5 Sampling locations in Central Vembanad estuary

## 2.3 LABORATORY INVESTIGATIONS

### 2.3.1 SUSPENDED SEDIMENTS

The water samples were filtered through 0.45  $\mu\text{m}$  membrane filters (previously weighed) and the suspended matter left over the filters were oven dried at  $50\pm 3$  °C along with the filter paper. It was then weighed and stored in a vacuum desiccator till analysis.

### 2.3.2 TEXTURE

Sand samples were washed, dried and subjected to coning and quartering and a representative portion (about 100 gm) was subjected to dry sieving. Each sample was sieved for 15 minutes on mechanical Ro-Tap sieve shaker using a standard set of ASTM Endecott sieves at half phi ( $\frac{1}{2} \phi$ ) intervals. The fractions left over in each sieve were carefully transferred, weighed and cumulative weight percentages were calculated. Samples which contain significant amount of silt and clay fractions were analysed by combined sieving and pipette analysis as suggested by Lewis (1984).

Known quantities of silt and clay rich sediments were dispersed overnight in 0.025 N solution of sodium hexametaphosphate. The coarse fraction was separated from the dispersed sediments by wet sieving using a 230 mesh (63  $\mu\text{m}$ ) ASTM sieve. The filtrate containing the silt and clay fractions were carefully transferred to a graduated 1 litre measuring jar and volume made up. The solution was then stirred thoroughly to obtain a homogenous suspension. A 20 ml of the filtrate was pipetted out into previously weighed 50 ml beakers at fixed time intervals from depths as suggested by Lewis (1984). All the aliquots were oven dried to constant weight at  $60\pm 3$ °C and weighed accurately after cooling at room temperature. Dry sieving was carried out on sand fraction to complete the analysis.

The cumulative weight percentages of the above analyses were plotted against the respective grain sizes in phi units on a probability chart. The cumulative frequency curve is completed and the values of 1, 5, 16, 25, 50, 75, 84 and 95 percentiles were recorded. For a few samples (with high percentage of clay), which do not attain higher percentiles, the conventional extrapolation method suggested by Folk and Ward (1957) was adopted. The grain size parameters such as mean size, median, standard deviation, skewness and kurtosis were calculated following Folk and Ward (1957).

$$\begin{aligned} \text{Mean size} &= \frac{(P_{16} + P_{50} + P_{84})}{3} \\ \text{Median} &= P_{50} \\ \text{Standard deviation} &= \frac{(P_{84} - P_{16})}{4} + \frac{(P_{95} - P_5)}{6.6} \\ \text{Skewness} &= \frac{(P_{84} + P_{16} - 2P_{50})}{2(P_{84} - P_{16})} + \frac{(P_{95} + P_5 - 2P_{50})}{2(P_{95} - P_5)} \\ \text{Kurtosis} &= \frac{(P_{95} - P_5)}{2.44 (P_{75} - P_{25})} \end{aligned}$$

The interrelationships existing between these parameters have also been worked out to elucidate the hydrodynamic conditions of the depositing medium. In addition to this, the percentages of gravel (> 2 mm), sand (0.063 - 2 mm) and mud (< 0.063 mm) for gravel bearing riverine sediments, and sand, silt (0.063 - 0.004 mm) and clay (< 0.004 mm) for gravel free riverine and estuarine sediments, were also plotted on a triangular diagram of Folk et al. (1970) to determine the sediment types. CM pattern of riverine and estuarine sediments was worked out following Passega (1964).

### Scanning Electron Microscopic (SEM) Studies

Standard procedures as suggested by Goudie and Bull (1984) were used for SEM analysis. Sub-samples containing quartz grains (from + 80 mesh) were treated with 10% hydrochloric acid, stannouschloride and sodium hexametaphosphate to remove carbonates, iron coatings, and clay particles respectively. Then the grains were washed, dried and mounted on stubs. The mounted grains were sputter-coated with gold and photomicrographs were taken using Stereoscan 180 at standard magnifications ranging from 160 X to 2400 X. The interpretations of the photomicrographs thus obtained were made following Georgieva and Stoffers (1980) and Marshall (1987).

#### 2.3.3 MINERALOGY

Different methods were adopted to study the mineralogical constitution of riverine and estuarine sediments. They are summarised below.

**Heavy minerals:** The sand fraction was washed thoroughly with deionised water and oven dried at  $50 \pm 3^\circ\text{C}$ . About 100 gm of the coned and quartered sand fraction was sieved for half phi interval. From +45, +60, +80, +120, +170 and +230 mesh size fractions, heavy and light minerals were separated using bromoform ( $\text{CH}_2\text{Br}_2$  - specific gravity : 2.85 at  $20^\circ\text{C}$  changing  $0.023/^\circ\text{C}$ ) and separating funnel. The minerals thus separated were washed with acetone, dried and weighed to find out the total heavy and light mineral contents. The heavy minerals were then boiled for a few minutes with dil. HCl and a tinge of stannous chloride crystals to removes the Fe/Mn coating over the detrital heavy grains. A total of 300-400 grains from each heavy residue was mounted on glass slides using canada balsm. The individual minerals in each slide were studied under a Leitz petrological microscope following standard methods.

**Light minerals:** Hayes and Klugman (1959) staining method was followed to estimate the quartz and feldspar contents of sand fraction. The bromoform floats from +45, +80 and +170 meshes of some selected samples were washed, dried and mounted on glass slides with canada balsm. Etching of the mounted grains was carried out using hydrofluoric acid fumes. The etched grains were subsequently treated with concentrated solution of cobaltinitrite for two-three minutes. Then the grains were rinsed, dried and stained with 0.5% eosine B. On staining soda-lime felspars turn to pink, potash feldspars to orange yellow and quartz remains unaffected. About 200-300 grains were counted and the number percentages of quartz and feldspars were estimated.

**Mineralogy of silt and clay fractions:** The mineralogy of silt and clay fractions was estimated semiquantitatively by X-ray diffraction technique. The organic matter in the samples was eliminated by treating with  $H_2O_2$ . Powder method was used to estimate the mineralogical constitution of silt fraction. Oriented smear slides as suggested by Gibbs (1968) were prepared for clay fraction ( $< 2 \mu m$ ) and run on Phillips X-ray diffractometer using  $K\alpha$  radiation and Ni filter. The slides were then glycolated and repeated the experiment. The chart drive 1 cm/min, goniometer  $1^\circ/\text{min}$  and intensity  $2 \times 10^2$  were maintained.

- (1) Quartz: Identified from its (100) Peak at  $4.26A^\circ$ . It also gives supplementary peak at  $2.46A^\circ$ .
- (2) Feldspar: Orthoclase was identified from its 6.66 peak and plagioclase from  $6.39A^\circ$  peak.
- (3) Montmorillonite is identified by its (001) peak at  $14A^\circ$  which expands to  $17A^\circ$  on glycolation.
- (4) Kaolinite will give peaks at the same spacing as that of chlorite and hence their identification becomes difficult.

However, Biscaye (1964) pointed out that kaolinite in addition to two strong peaks at  $7.16\text{\AA}$  and  $3.58\text{\AA}$  gives always very small peak at  $2.38\text{\AA}$ .

- (5) Illite exhibits a major peak at  $10\text{\AA}$  and minor peaks at  $5\text{\AA}$  and  $3.3\text{\AA}$ . The peaks remain unaffected on glycolation.
- (6) Gibbsite gives distinct peak at  $4.85\text{\AA}$ .

**Scanning Electron Microscopic studies:** Photomicrographs of heavy sands (from +120 and +230 meshes) and clay fractions ( $< 2\ \mu\text{m}$ ) of the two environments were taken using Stereoscan 180 as described earlier. The magnification ranges from  $44\times$  to  $2000\times$ .

#### 2.3.4 GEOCHEMISTRY

The riverine and estuarine sediments were washed gently (for desalting) with deionised double distilled water and sieved using 230 mesh ( $63\ \mu\text{m}$ ) ASTM sieves under wet condition. The sand fraction left over the sieve was separated. The filtrate was then transferred to 2 litre measuring jar and the volume made up. It was then separated into silt and clay fractions following settling velocity principles. The sand ( $> 63\ \mu\text{m}$ ), silt ( $63-4\ \mu\text{m}$ ) and clay ( $< 4\ \mu\text{m}$ ) fractions thus obtained were oven dried at  $50\pm 3^\circ\text{C}$  to constant weight. A known amount of well powdered, homogenised size fractions as well as the corresponding bulk sediments (without washing) were digested with  $\text{HF-HNO}_3\text{-HClO}_4$  acid mixture. Suspended sediments and powdered/homogenised rock as well as soil samples were also subjected to identical treatment. All the digested samples were used for elemental analysis following various techniques (Table 1). A brief description of the methods employed is given below.

TABLE 1 - Various analytical methods and instrument/make/model employed in the geochemical study

Serial No.	Parameters studied	Method	Instrument Make/Model	Reference
1.	Sediment organic carbon	Titrimetric	-	Elwakeel and Riley (1957)
2.	Phosphorus	Colorimetric	Hitachi Model 2000 Double Beam Spectrophotometer	Murphy and Rieley (1967)
3.	Sodium and potassium	Flame Photometric	Systronics FPM Digital model	APHA 1981
4.	Calcium	Titrimetric	--	APHA (1981)
5.	Iron	Colorimetric	Hitachi Model 2000 Double Beam Spectrophotometer	APHA (1981)
6.	Manganese and trace elements	Atomic absorption spectrophotometric	Perkin Elmer Model 2380	Rantala and Loring (1975)
7.	Radioactive elements	PC-based multi-channel gamma ray analyser	Nucleonix (with RCA 6342 counter)	Rybach et al. (1966)

**Sediment organic carbon:** The sediment organic carbon was determined by wet oxidation method of ElWakeel and Riley (1957). Organic matter was oxidized by a known quantity of chromic acid and the amount of chromic acid used was then determined by back titration with standard ferrous ammonium sulphate solution. Diphenylamine was used as an indicator. The average of triplicate measurements not differing 0.2% of the analyses was used in this study.

**Phosphorus:** Phosphorus as phosphate ( $\text{PO}_4\text{-P}$ ) form was determined based on the reaction of the ions with an acidified molybdate reagent to yield a phosphomolybdate complex (Murphy and Riley, 1962). It was then reduced to a highly blue coloured compound. The intensity of the colour developed will be proportional to the concentration of the phosphate phosphorus in the solution. This blue coloured solution exhibits maximum absorption at 880 nm. The amount of phosphate phosphorus was determined by comparison with a set of standard samples.

**Sodium and Potassium:** Sodium and potassium were determined using flame photometer, based on the procedure as described in APHA (1981). In order to avoid the inter element and anionic effects, Fe, and Al were removed from solution by precipitating with ammonia solution. It was then aspirated for the estimation of Na and K. Calibration curve for Na and K were drawn separately and concentration of the metals was estimated.

**Calcium:** Ca in the sediment sample solution was determined titrimetrically with standard EDTA solution at a pH of 12 (APHA, 1981). Murexide was used as indicator. This indicator changes its colour from pink to purple at the end point.

**Iron:** Fe was determined colorimetrically as  $\text{Fe}_2\text{O}_3$  following APHA (1981). The experiment was based on the development of a pink-red coloured orthophenanthroline complex. A 10% hydroxylammonium hydrochloride was used to reduce Fe at a pH 4.8 to 5. The intensity of the colour was measured at 510 nm by spectrophotometer. The amount of total Fe was estimated from the standard calibrated values.

**Manganese and Trace metals:** Mn and trace metals were analysed using atomic absorption spectrophotometer (Model PE 2380) following the method suggested by Rantala and Loring (1975).

**Precision and accuracy:** The precision and accuracy of the heavy metal estimation were checked against two USGS standard rock samples  $G_2$  and  $W_1$  (Table 2). All the metal values were in agreement with the published values of Rantala and Loring (1975) and Flanagan (1976).

**Radioactive element estimation:** About 200 gm of sand fraction of some selected riverine and estuarine sediments (15 nos.) was powdered to 200 mesh size. It was then fed to a PC-based multichannel gamma ray analyser. The concentration of U and Th were computed after calibration with natural standards.

TABLE 2 - Heavy metal concentration of USGS standard rocks (Fe in percentage; others in ppm)

	Fe	Mn	Cd	Zn	Cr	Ni	Co	Cu	Pb
$W_1$									
Observed	7.87 (0.02)	134 (0.002)	-	89 (1.4)	121 (1.2)	72 (0.82)	44 (0.22)	116 (0.52)	31.58 (0.32)
Published (1)	7.76	132	-	86	114	76	47	110	31.2
Published (2)	7.96	127	-	86	116	66	41	122	34
$G_2$									
Observed	1.83 (0.03)	28 (0.002)	0.031 (0.001)	84 (1.25)	9 (0.42)	9 (0.21)	8 (0.24)	13 (0.63)	10 (0.42)
Published (1)	.185	26	0.39	85	7	5	5.5	12	8
Published (2)	1.90	25	--	87	7	12	7	12	12

Paranthesis - standard deviation of triplicate analyses

1. Flanagan (1976)
2. Rantala and Loring (1975)

## CHAPTER 3

## TEXTURE

### 3.1 INTRODUCTION AND REVIEW OF LITERATURE

In the past five decades, granulometric studies of unconsolidated sediments have been a subject of intense research as it is fundamentally related to the mechanism of transport and deposition of sediments. Exhaustive studies on global scale reveal the existence of significant correlation between size frequency distribution and depositional processes. Further, proper selection and combination of statistical parameters can excellently be used to discriminate various environments of deposition of ancient as well as recent sediments (Folk, 1966; Friedman, 1967 and Hails and Hoyt, 1969). Apart from environmental implications, the particle size distribution bears considerable influence on the mineralogical (Mishra, 1969 and Patro et al., 1989) and chemical (Williams et al., 1978 and Forstner and Wittmann, 1983) constitution of sediments as well. Hence, an attempt has been made in this chapter to understand the particle size distribution of the sediments of Muvattupuzha river and Central Vembanad estuary so as to have proper insights of its influence on the mineralogy and geochemistry.

The grain size analysis of clastic sediments is very important on many ways and are as follows: (a) the grain size is a basic descriptive measure of the sediment; (b) the grain size distributions may be characteristic of sediments deposited in certain environments; (c) the grain size distributions may yield information about the physical mechanisms acted on the sediments during deposition; and (d) the grain size may be related to other properties such as permeability, mineralogy, geochemistry etc. The characteristics of grain size distribution of sediments may be related to the source materials, process of weathering, abrasion and corrosion of the grains and sorting processes

during transport and deposition.

Several studies of the size distributions of clastic sediments have revealed the existence of statistical relationships between the different size parameters such as mean size, sorting (standard deviation) skewness and kurtosis. The relation between mean size and sorting is particularly well established and many studies have shown that the best sorted sediments are generally those with mean size in the fine sand grade (Pettijohn, 1957; Griffiths, 1967 and Allen, 1970). Several attempts have been made to differentiate various environments from size spectral analysis as particle distribution is highly sensitive to the environment of deposition (Mason and Folk, 1958; Friedman, 1961, 1967; Griffiths, 1962; Moiola et al., 1974; Stapor and Tanner, 1975; Nordstrom, 1977; Goldberg, 1980; Sly et al., 1982 and Seralathan, 1988). Friedman (1961, 1967) has studied the samples of relatively fine grained sands taken from many different localities around the world from various environments such as dunes, beaches and river. The most effective distinction of sands from these three environments is shown by a scatter diagram of moment standard deviation (sorting) versus moment skewness. Visher (1969), based on the log normal distribution of grain size, has identified three types of populations such as rolling, saltation and suspension which indicate distinct modes of transportational and depositional processes. Passega (1957, 1964) has established the relationship between texture of sediments and process of deposition rather than between texture and environment as a whole. According to Passega, a clastic deposit is formed by sediments transported in different ways. In particular, the finest fraction may be transported independently of the coarser particles. Swift sedimentary agents be characterised best by parameters which give more information on the coarsest than on the finest fractions of their sediments. Hence, the logarithmic relation between the first percentile (C) and median (M) of clastic sediments is highly significant in understanding the transportational regimes.

In India, textural attributes of sediments from different environments have been attempted by many researchers (Sahu, 1964; Mishra, 1969; Veerayya and Varadachari, 1975; Rajamanickam, and Gujar, 1985; Samsuddin, 1986; Seralathan, 1988 and Jahan et al., 1990). Subba Rao (1967) has made a detailed investigation on the composition and texture of the shelf sediments of the east coast of India. Grain size characteristics of sediments deposited at the mouth of Hoogly river were carried out by Mallik (1975). Rajamanickam (1983) and Rajamanickam and Gujar (1985) have investigated the grain size distribution of the surficial sediments of west coast of India. The sediment characteristics of the continental shelf of Karnataka coast have been carried out by Hashmi and Nair (1981). Murthy and Rao (1989) have investigated the textural characteristics of the sediments of Visakhapatnam coast. Like the shelves, considerable information exist on the textural aspects of beach sands as well (Kidwai, 1971; Veerayya and Varadachari, 1975; Samsuddin, 1986; Purandara et al., 1987; Unnikrishnan, 1987 and Sasidharan and Damodaran, 1988) . But studies on the textural characteristics of major river systems are meagre. Naidu (1968) has studied the textural variations of Godavari river sediments. Sediment texture of Krishna and Mahanadi drainage systems has been covered by Seetharamaswamy (1970) and Satyanarayana (1973) respectively. Dora (1978) has investigated the textural characteristics of Vasishta - Godavari drainage system. A detailed granulometric investigation of the sediments of the major and subenvironments of the modern deltaic sediments of Cauvery river has been carried out by Seralathan (1979). Mohan (1990) has studied grain size parameters and its significance of Vellar river and estuary. A few accounts also exist on the grain size characteristic of Vembanad lake as well ( Josanto, 1971b; Murthy and Veerayya, 1972a and Purandara and Dora, 1987). Recently, Sundaresan Pillai (1989) has studied the sediment input mechanisms in the Vembanad lake around Willington island.

## 3.2 RESULTS AND DISCUSSION

### 3.2.1 GRAIN SIZE VARIATION

Table 3 and Figs. 6 and 7 summarise the variation of different textural grades along the riverine and estuarine course. In river environment, the sediments in the upper reaches (Kaliyar and Thodupuzha tributaries) are characterised by high amount of pebbles, which transcend into low values as the river enters in the mid and low lands. Sample number 1 (Thodupuzha tributary) records the highest amount of pebbles (55.91%) which gradually decrease towards Muvattupuzha town, where Thodupuzha tributary meets the Kaliyar tributary. Likewise, the Kaliyar tributary also shows reduction in the amount of pebbles downstream but with high fluctuation (Table 3). The variation of pebble content after 90 Km downstream is almost negligible (Fig. 6).

Variation of granules indicates nearly a complimentary pattern to that of pebbles. This is very much so in the upper reaches of the river. Most strikingly, in general, the subsequent locations of pebble highs are the sites of granule enrichments. It is probably due to the progressive decrease in the competency of the river water downstream. Though the decrease in the content of pebbles in the initial stages of the river is compensated by an increase in the granule content, the downstream section (Murinjapuzha and Ittupuzha) records a considerable depletion in the content of pebbles owing to the differential flow pattern. Unlike in the upstream, the significant similarities in the percent variation of pebbles and granules (Fig. 6) downstream from 70 Km is an indication of close range of its size. In this context it is important to note that the pebbles of the lower reaches of the river especially below 70 Km are very fine in nature which are almost hydraulically equivalent to granules. The marked change in the flow regime (vigour) between downstream and upstream also imparts considerable effect on the grain size distribution. The variation of very

TABLE 3 - Percentage of various size grades in the sediments of Muvattupuzha river and Central Vembanad estuary

a) MUVATTUPUZHA RIVER

Sample No.	Pebble (a)	Granule (b)	Very Coarse Sand (c)	Coarse Sand (d)	Medium Sand (e)	Fine Sand (f)	Very Fine Sand (g)	100 %				Textural terminology (Folk et al., 1970)
								Mud (Silt+Clay) (c+d+e+f+g)	Sand	Gravel	Gravel (a+b)	
1	2	3	4	5	6	7	8	9	10	11	12	
1	55.91	11.05	2.35	2.92	17.17	8.06	0.92	1.62	31.42	66.96		Sandy gravel
2	24.60	13.40	8.88	12.97	22.52	14.60	1.77	1.21	60.79	38.00		Sandy gravel
3	11.49	17.38	14.49	21.10	22.05	9.79	1.29	2.41	68.72	28.87		Gravelly sand
4	12.47	38.24	25.27	16.29	5.73	0.82	0.66	0.57	48.72	50.71		Sandy gravel
5	46.78	0.87	1.58	13.51	23.8	10.42	2.17	0.67	51.68	47.65		Sandy gravel
6	7.81	32.81	28.1	20.28	6.11	3.00	1.39	0.32	59.06	40.62		Sandy gravel
7	9.79	49.71	17.98	3.70	4.24	9.51	4.42	1.18	39.32	59.50		Sandy gravel
8	-	-	0.24	6.08	65.70	25.27	1.87	0.84	99.16	-		Sand
9	9.79	49.56	17.40	3.70	4.24	9.51	4.42	1.20	39.18	59.62		Sandy gravel
10	1.13	8.14	14.57	30.70	31.68	11.27	1.59	0.92	89.81	9.27		Gravelly sand
11	33.96	8.85	7.88	17.20	20.46	9.72	1.19	0.74	56.45	42.81		Sandy gravel
12	36.70	13.29	4.28	5.70	16.64	19.61	3.03	0.75	49.26	49.99		Sandy gravel
13	10.07	18.83	11.46	12.67	29.82	14.30	2.10	0.75	70.35	28.90		Gravelly sand
14	36.64	12.32	6.87	15.00	16.23	9.51	2.10	1.33	49.71	48.96		Sandy gravel
15	20.98	16.67	12.43	12.95	21.28	11.98	1.92	1.79	39.44	37.65		Sandy gravel
15A	5.92	30.32	30.20	19.80	4.84	2.89	3.54	2.51	61.25	36.26		Sandy gravel
16	17.03	6.10	5.63	12.13	31.20	25.24	1.47	1.20	75.67	23.13		Gravelly sand
17	-	1.65	17.98	71.66	4.37	0.99	1.18	2.17	96.18	1.65		Slightly gravelly sand
18	18.63	19.17	11.68	17.11	26.50	5.82	0.66	0.43	61.77	37.80		Sandy gravel
19	31.34	21.86	17.42	14.08	10.93	2.45	0.30	1.62	45.18	53.20		Sandy gravel
20	3.34	16.33	11.94	17.44	28.58	19.62	2.39	0.36	79.97	19.67		Gravelly sand
21	2.73	19.45	34.11	32.90	9.53	0.57	0.26	0.45	78.27	22.18		Gravelly sand
23	5.72	7.44	5.56	9.16	31.11	33.07	5.72	2.22	84.62	13.16		Gravelly sand
24	1.18	15.32	29.61	33.72	16.40	2.40	0.78	0.59	82.91	16.50		Gravelly sand
25	8.86	22.37	26.37	30.32	3.33	1.07	0.45	2.25	66.52	31.23		Sandy gravel
26	0.73	4.87	11.85	34.06	41.58	5.20	0.75	0.96	93.44	5.60		Gravelly sand

1	2	3	4	5	6	7	8	9	10	11	12
27	16.60	47.21	13.31	10.73	8.51	2.03	0.64	0.97	35.22	63.81	Sandy gravel
28	1.42	23.69	25.33	17.60	23.95	7.79	0.22	0.86	74.03	25.11	Gravelly sand
29	-	3.63	7.64	15.16	33.65	35.57	3.00	1.34	96.03	3.63	Slightly gravelly sand
30	-	4.01	5.06	12.73	62.88	14.24	0.17	0.87	95.12	4.01	Slightly gravelly sand
31	-	5.34	16.36	39.78	30.53	6.04	0.33	1.62	93.04	5.34	Gravelly sand
32	0.25	2.99	6.42	20.16	37.00	29.35	1.28	0.47	96.29	3.24	Slightly gravelly sand
33	-	0.33	3.06	15.63	56.43	22.54	0.46	1.55	98.12	0.33	Slightly gravelly sand
34	-	0.19	1.31	13.94	51.40	29.94	2.24	0.98	98.83	0.19	Slightly gravelly sand
35	15.89	21.75	17.95	17.75	20.88	5.28	0.22	0.28	62.08	37.64	Gravelly sand
36	-	1.11	2.54	10.29	47.07	35.03	0.75	3.21	95.68	1.11	Slightly gravelly sand
37	-	-	0.46	18.56	62.85	16.39	0.36	1.30	98.70	-	Sand
38	-	-	-	3.47	59.57	33.89	0.79	2.28	97.72	-	Sand
39	-	-	0.75	5.15	54.55	36.84	0.89	1.82	98.18	-	Sand
40	-	3.63	7.47	31.56	50.66	6.07	0.15	0.56	96.08	3.63	Slightly gravelly sand
41	-	-	0.50	5.67	16.72	32.03	10.77	34.00	66.00	-	Muddy sand
42	-	-	-	-	-	-	-	10.9	89.10	-	Muddy sand
43	-	-	-	-	-	-	-	28.88	71.12	-	Muddy sand
44	-	-	-	-	-	-	-	47.88	52.12	-	Muddy sand

b) CENTRAL VEMBANAD ESTUARY

Sample No.	Coarse Sand		Medium Sand		Fine Sand		Very Fine Sand		Coarse Silt		Medium Silt		Fine Very Fine Silt		Coarse Medium Clay		Fine Very Fine Clay		Sand (a+b+c+d)		Clay (h+i)	Textural terminology (Folk et al., 1970)
	(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)	(i)	(j)	(k)	(l)	(m)	(n)	(o)	(p)	(q)	(r)	(s)	(t)		
1	2	3	4	5	6	7	8	9	10	11	12	13	14	100%								
45	0.79	23.08	59.04	5.21	0.36	0.93	2.35	5.78	1.18	87.79	8.23	3.98	Muddy sand									
46	3.69	5.69	23.75	12.28	22.59	0.89	4.85	6.18	20.57	56.85	12.19	30.96	Clayey sand									
47	-	-	1.39	4.43	24.88	8.05	21.00	12.55	27.70	5.82	53.93	40.25	Mud									
48	0.82	8.41	22.32	14.55	11.34	5.32	14.90	9.85	11.48	46.66	32.01	21.33	Sandy mud									
49	-	4.05	16.87	15.57	15.79	11.60	15.18	7.65	13.65	36.13	42.37	21.50	Sandy mud									
50	-	0.98	10.33	23.28	25.41	2.90	17.74	5.33	14.28	34.34	46.06	19.60	Sandy silt									
51	-	-	4.18	18.13	19.35	21.80	9.87	18.15	8.63	22.18	51.04	26.78	Sandy mud									
52	2.22	15.81	44.56	16.25	7.56	1.88	6.00	4.91	0.83	78.84	15.43	5.73	Silty sand									
53	3.80	20.76	40.81	9.79	5.71	2.32	4.57	6.42	6.60	75.58	12.39	12.03	Muddy sand									
54	15.44	51.40	29.94	2.24	0.98	0.12	0.24	0.20	0.32	99.02	0.36	0.52	Sand									
55	2.70	16.69	49.40	20.14	0.09	2.65	0.85	4.88	2.60	88.90	3.60	7.50	Clayey sand									
56	1.08	20.54	54.25	8.09	2.42	2.45	4.60	3.13	3.52	83.88	9.62	6.50	Muddy sand									
57	4.11	29.62	34.31	8.01	5.62	4.15	4.96	4.87	4.65	75.76	18.76	5.48	Silty sand									
58	-	-	10.09	36.07	14.47	5.35	3.20	10.03	21.73	45.23	23.02	31.76	Sandy mud									
59	2.10	8.86	12.84	62.63	1.44	2.83	2.50	2.28	5.05	85.60	7.08	7.32	Muddy sand									
60	0.79	13.40	57.93	11.86	5.13	2.35	1.68	2.11	5.91	83.59	9.11	7.30	Muddy sand									
61	-	-	2.30	13.03	25.65	4.13	7.37	10.4	36.90	15.55	44.05	40.40	Sandy mud									
62	-	-	-	4.87	10.26	12.60	27.06	12.35	32.88	4.87	49.90	45.23	Mud									
63	1.80	12.24	64.89	12.11	0.50	1.50	2.95	2.39	2.03	90.64	4.93	4.43	Sand									
64	12.40	47.60	31.77	3.10	0.88	0.50	1.17	2.55	0.15	94.74	2.46	2.80	Sand									
65	4.94	44.49	31.05	3.56	1.92	1.60	3.08	4.36	4.60	86.31	6.74	6.95	Muddy sand									
66	-	0.63	2.81	9.72	39.68	2.42	18.87	6.48	18.77	13.26	60.99	25.75	Sandy silt									
67	3.02	30.02	42.05	8.04	6.59	0.83	1.79	7.65	0.35	82.81	9.19	8.00	Muddy sand									
68	-	-	0.43	6.26	13.85	30.30	14.63	17.92	16.18	6.75	61.20	32.05	Mud									
69	-	-	4.1	6.37	6.69	13.83	26.73	14.38	25.43	6.37	47.26	46.37	Mud									
70	-	-	-	1.58	8.75	16.52	34.42	8.88	29.73	1.58	59.82	38.60	Mud									

	1	2	3	4	5	6	7	8	9	10	11	12	13	14
71	5.00	14.99	5.71	0.38	10.22	6.83	15.83	15.63	25.38	26.08	32.92	41.00	Sandy mud	
72	1.05	11.36	44.46	13.88	3.46	6.12	5.05	2.55	10.35	70.75	14.63	14.62	Muddy sand	
73	1.22	8.68	30.07	6.60	6.45	9.88	10.05	3.93	23.43	46.24	26.41	27.35	Sandy	
74	7.19	41.74	46.37	1.49	0.01	0.33	1.96	0.73	0.32	97.22	1.73	1.05	Sand	
75	1.20	6.28	3.07	3.49	21.20	9.50	11.20	16.98	22.07	18.98	42.34	38.68	Sandy mud	
76	1.60	15.27	53.14	7.50	2.88	1.75	4.40	2.95	10.51	77.37	9.03	13.60	Muddy sand	
77	0.91	11.06	52.49	20.87	2.00	2.98	1.55	1.98	6.54	84.97	6.53	8.50	Muddy sand	
78	0.38	12.79	41.65	31.85	2.67	2.68	1.10	1.90	5.85	85.81	6.44	7.75	Muddy sand	
79	0.39	5.35	59.43	26.40	0.06	2.80	0.60	0.61	4.75	91.19	3.46	5.35	Sand	
80	-	1.82	10.12	20.22	8.78	17.70	11.20	10.85	19.17	34.29	37.68	28.03	Sandy mud	
82	-	-	-	0.22	9.05	14.65	20.97	16.45	38.65	0.22	44.68	55.10	Mud	
83	-	-	-	4.56	20.10	4.78	17.07	18.62	30.30	9.13	41.94	48.93	Mud	
84	-	-	-	0.78	11.34	9.48	31.50	14.71	32.65	0.78	51.87	47.35	Mud	
85	-	1.26	44.28	22.05	4.94	3.45	7.36	6.68	9.98	67.59	15.74	16.68	Muddy sand	
86	3.55	19.46	15.74	3.37	11.81	6.85	6.72	11.65	19.71	42.62	27.03	30.55	Sandy mud	
87	-	-	-	1.61	16.67	4.88	36.63	32.26	7.98	1.61	58.17	40.23	Mud	
88	4.17	3.41	2.74	2.47	17.40	0.47	22.89	21.32	25.10	12.80	40.77	46.43	Sandy mud	

coarse sand is also similar to that of granules along the profile of the river (Fig. 6). A general increase in the content of coarse sand downstream is noted, but the increase is only marginal in the distributaries (Ittupuzha and Murinjapuzha). Variation of medium sand clearly indicates deviation from coarser entities by showing an increase towards river mouth. This is in consonance with the flow pattern controlled by the gradient of the terrain (Fig. 3). Thus it can be seen that coarse sand marks the transition phase of spectral changes in the sub-populations of size distribution. Fine sand also depicts a similar kind of variation as that of medium sands. However the contents of very fine sand and mud (silt + clay) are negligible and do not characterise significant variation as the flow condition does not facilitate its deposition.

Thus the overall spectral analysis of various size grades shows marked variations in the Muvattupuzha fluvial regime: (1) The enhanced amount of pebbles, granules and very coarse sands in the two tributaries indicate the existence of high energy conditions owing to the high gradient of the tributaries and (2) a sand dominant domain of Muvattupuzha river proper (main channel) with a progressive downstream increase of medium and fine sands indicates a low energy regime. This manifests the difference in the transportational pattern of bed load with the former characterising rolling processes and the latter saltation.

Unlike the river, the estuarine hydrodynamics are characterised by flow patterns coinciding with semidiurnal ebb and flood tides. The granulometric variations exemplify the complexity of the flow patterns prevailing within the Central Vembanad basin. However, coarser entities, which are encountered in the river sediments, are totally missing or present only in subtle quantities. High proportions of fine and medium sands in the immediate vicinity of Thannirmukham bund are obviously due to the scouring action of the water jet infiltration which winnows silt and clay resulting in the deposition of fine and

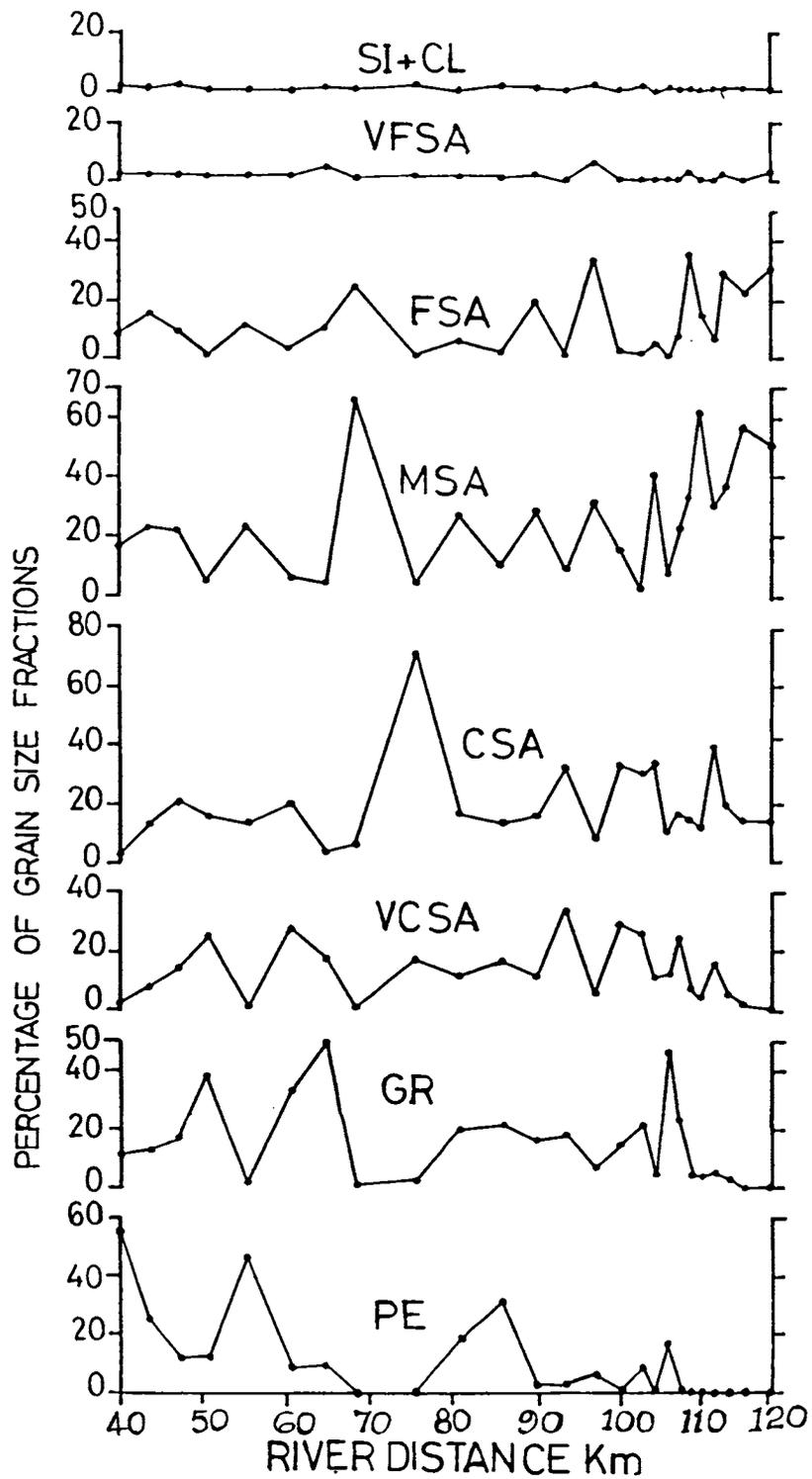


Fig. 6 Downstream variation of grain size fractions through Thodupuzha - Muvattupuzha - Ittupuzha river channels (PE Pebble, GR Granule, VCSA Very coarse sand, CSA Coarse sand, MSA Medium sand, FSA Fine sand, VFSA Veryfine sand and SI+CL Silt + Clay)

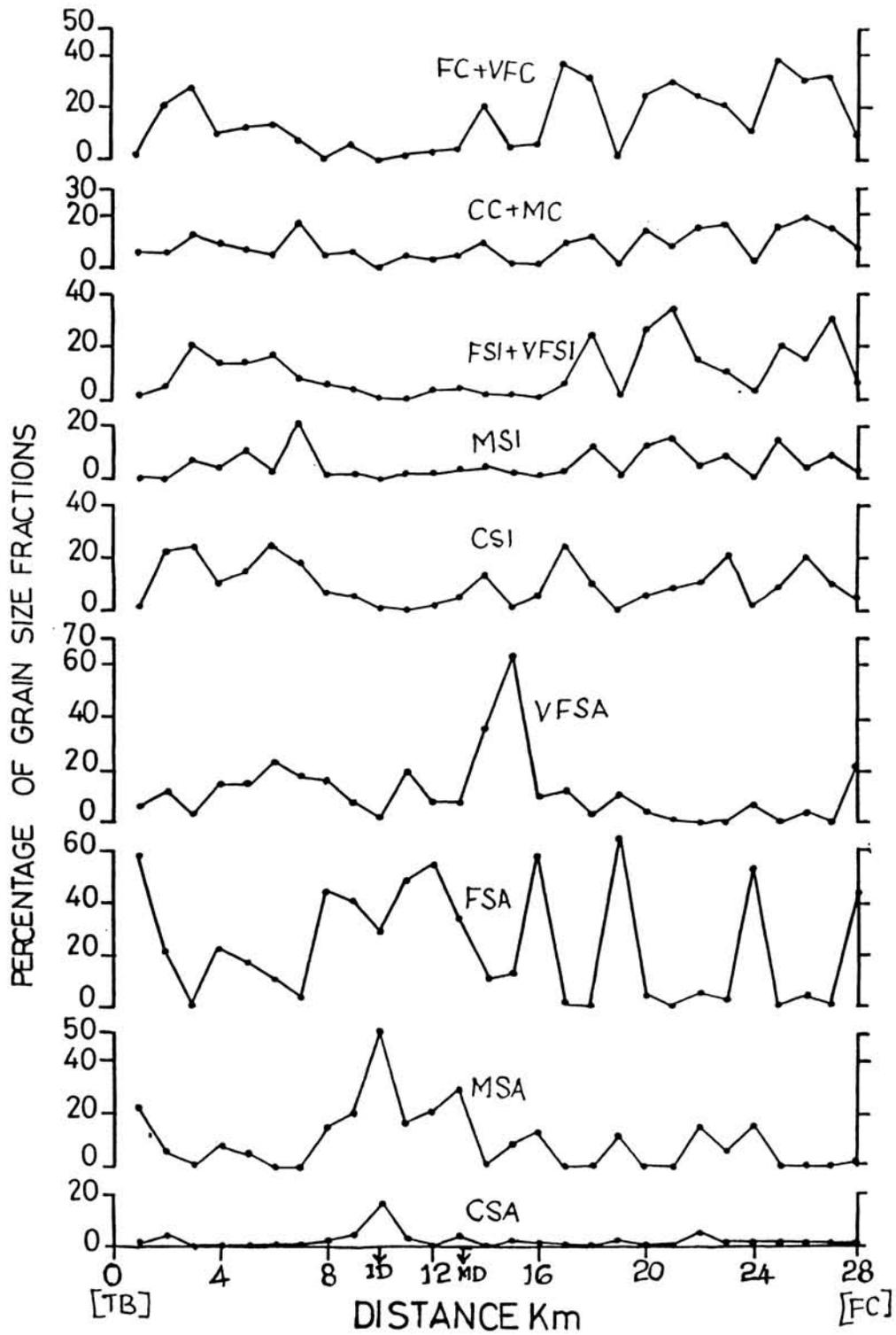


Fig. 7 Variation of grain size fractions in the sediments of Central Vembanad estuary i.e. from Thannirmukham Bund [TB] to Fort Cochin [FC]. (CSA Coarse sand, MSA Medium sand, FSA Fine sand, VFSA Veryfine sand, CSI Coarse silt, MSI Medium silt, FSI+VFSI Fine silt + Veryfine silt, CC+MC Coarse clay + Medium clay); ID Itupuzha distributary, MD Murinjapuzha distributary

medium sands. From thereon, fine particles (silt and clay) show marked enrichment towards the estuarine mouth with some sporadic cases of sand dominance (Table 3). These anomalous high values of medium and fine sand fractions may be resulted from the seasonal maintenance dredging activities by the Port authorities. The Muvattupuzha river mouth area contains substantial amount of coarse and medium sands (Fig. 7) chiefly reflecting the influx of sand load from Muvattupuzha river.

### 3.2.2 TEXTURAL PARAMETERS

a) **Mean size:** The mean size of clastic sediments is the statistical average of grain size population expressed in phi ( $\phi$ ) units. Figs. 8a and 9a show the spatial variation of the phi mean size in riverine and estuarine environments respectively. In river, the phi mean size ranges from -0.90 to 2.58 (very coarse sand to very fine sand) and exhibits a marked increase downstream (Table 4). Grain size spectral studies reveal that pebbles and granules dominate upstream where as coarse, medium and fine sands are progressively abundant in the mid lands with an increase towards the river mouth. Allen (1970) stated that the downstream decrease in phi mean and the progressive enrichment of finer spectral classes would be ascribed by two processes; a) abrasion and b) progressive sorting. Laboratory studies of Thiel (1940) and Berthois and Portier (1957) have revealed that abrasion plays a significant role in the transformation of textural classes downstream. But this view was later countered by Kuenen (1959, 1960) who opined that abrasion is not so significant in a fluvial set up with sandy sediments. Instead, progressive sorting will be prominent in causing the textural diversities. Since the upper reaches of the Muvattupuzha river system show abundance of pebbles and granules, abrasion plays a significant role in the reduction of their sizes. However, in the downstream section, especially the Muvattupuzha river bed (occupied primarily by sand) progressive sorting seems to be more important in the size segregation of sediments than abrasion.

TABLE 4 - Grain size parameters of the Muvattupuzha riverine and Central Vembanad estuarine sediments.

Sample No.	Phi Mean	Standard Deviation	Skewness	Kurtosis
1	2	3	4	5
a) MUVATTUPUZHA RIVER				
1	-0.87	1.80	0.93	0.73
2	0.15	1.97	-0.094	0.61
3	0.17	1.62	-0.004	0.80
4	-0.80	0.98	0.36	0.32
5	-0.05	1.86	-0.15	0.61
6	1.83	0.61	-0.28	1.02
7	0.25	1.72	0.67	1.54
8	-0.47	1.19	0.28	1.08
9	0.03	1.69	-0.24	0.58
10	0.78	1.22	-0.16	0.99
11	-0.10	1.73	0.01	0.60
12	-0.23	2.04	0.46	0.65
13	-0.52	1.69	-0.23	0.72
14	-0.43	1.86	0.31	0.66
15	-0.03	1.83	0.06	0.75
15A	0.33	1.20	0.36	1.31
16	0.62	1.95	-0.44	0.35
17	0.37	0.82	0.42	2.26
18	-0.17	1.69	-0.034	0.84
19	-0.83	1.42	0.23	0.78
20	0.82	1.58	-0.15	0.74
21	-0.18	1.47	0.06	0.93
22	2.58	1.09	-0.24	0.97
23	1.35	1.61	-0.43	1.01
24	0.13	1.30	-0.045	1.50
25	-0.32	1.06	-0.22	1.12
26	-0.81	0.94	-0.18	1.16
27	-0.90	1.25	0.76	1.31

1	2	3	4	5
28	0.20	1.31	0.32	0.69
29	1.63	1.15	-0.24	0.89
30	1.37	0.65	-0.052	1.06
31	2.14	0.98	-0.03	1.10
32	1.52	1.08	-0.11	0.89
33	1.73	0.74	0.096	1.45
34	1.76	0.77	0.24	0.77
35	0.30	1.53	-0.26	0.74
36	1.82	0.76	-0.16	1.10
37	1.50	0.65	0.065	0.567
38	1.93	0.55	0.21	0.82
39	1.97	0.62	0.165	0.96
40	1.02	0.83	-0.14	1.05
41	1.70	0.79	-0.12	0.72
42	1.98	0.83	-0.14	0.98
43	2.07	0.68	0.12	1.13
44	1.98	0.72	0.42	0.86

b) C.VEMBANAD ESTUARY

45	2.85	1.65	0.30	2.02
46	5.57	3.91	0.54	1.12
47	7.4	2.78	0.29	0.64
48	5.3	3.24	0.43	0.81
49	5.63	3.12	0.44	1.09
50	5.61	2.84	0.57	1.04
51	5.67	1.93	0.30	0.83
52	3.07	1.84	0.83	1.81
53	3.40	2.37	0.58	1.82
54	1.76	0.77	0.24	0.77
55	2.51	1.53	0.33	2.76
56	2.77	1.67	0.63	3.11

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1	2	3	4	5
57	3.08	2.25	0.66	1.83
58	5.93	3.24	0.70	0.62
59	3.30	1.59	0.064	4.12
60	2.82	1.68	0.46	3.19
61	7.10	3.21	0.36	0.69
62	8.08	3.16	0.19	0.85
63	2.65	1.18	0.36	2.94
64	1.85	0.87	0.24	1.25
65	2.87	2.42	0.72	3.48
66	5.03	2.43	0.57	0.83
67	2.70	1.74	0.46	2.58
68	6.98	2.68	0.52	1.08
69	7.86	2.51	-0.04	0.77
70	7.93	2.75	0.39	0.80
71	6.67	4.17	-0.10	0.76
72	3.72	2.39	0.67	2.47
73	5.80	3.98	0.56	0.77
74	1.95	1.62	0.30	3.64
75	6.52	3.09	0.03	0.52
76	3.90	2.99	0.73	3.37
77	2.93	1.77	0.39	3.39
78	2.93	1.67	0.39	2.92
79	2.89	1.19	0.40	1.95
80	6.56	3.45	0.18	0.75
81	7.48	3.38	0.34	0.80
82	8.70	2.92	0.05	0.74
83	8.13	3.37	-0.05	0.78
84	8.32	2.82	0.23	0.85
85	4.63	2.90	0.81	1.39
86	5.50	3.86	0.37	0.69
87	7.28	1.74	-0.05	1.22
88	7.36	3.36	0.11	1.10

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When the competency of the river water declines, the coarser sediments will be deposited where as the finer will be transported further downstream. However, from Fig. 8a, it is evident that the competency of the river water fluctuates at many locations due to natural and man made obstacles. The abrupt decrease in phi mean (increase in grain size) at stations 21 and 26, (Table 4, Fig. 8) might be resulted from the local turbulence induced by Piravom and Vettukattil bridges respectively. Other similar fluctuations in Fig. 8a are presumably due to similar effects from natural turbulences.

In the estuary, the phi mean exhibits wide range of values from 1.76 to 8.70  $\phi$  (medium sand to coarse clay). Contrary to the river, the spatial variation of phi mean (Fig. 9a) shows greater fluctuations in the estuarine environment. Near the river influenced regions (8-13 Km) of the estuary, the phi mean decreases considerably. It is due to the influx of medium and fine sands from the Muvattupuzha river. From 13 Km to 28 Km, the phi mean shows a marked increase except at stations 60, 64, 74 and 85 located at 16, 19, 24 and 28 Km from Thannirmukham bund. The anomalous decrease in phi mean at these stations is due to dredging activities as said earlier. The increase in the content of phi mean towards the high saline zones of the estuary is resulted from the floc formation followed by the faster settling of fine colloidal aggregates during estuarine mixing as observed elsewhere (Krank, 1975; Carden and Mayers, 1979; Seralathan, 1979; Syvitski and Murray, 1981 and Schubel, 1982).

b) **Standard deviation:** Standard deviation or sediment sorting is the particle spread on either side of the average. The sediment sorting is good if the spread sizes are relatively narrow. Investigations show that mean size and sorting correlate well in sand and pebble grades and the correlation worsens as the grain size increases. It is also claimed that silt and clay show improved sorting as grain size increases.

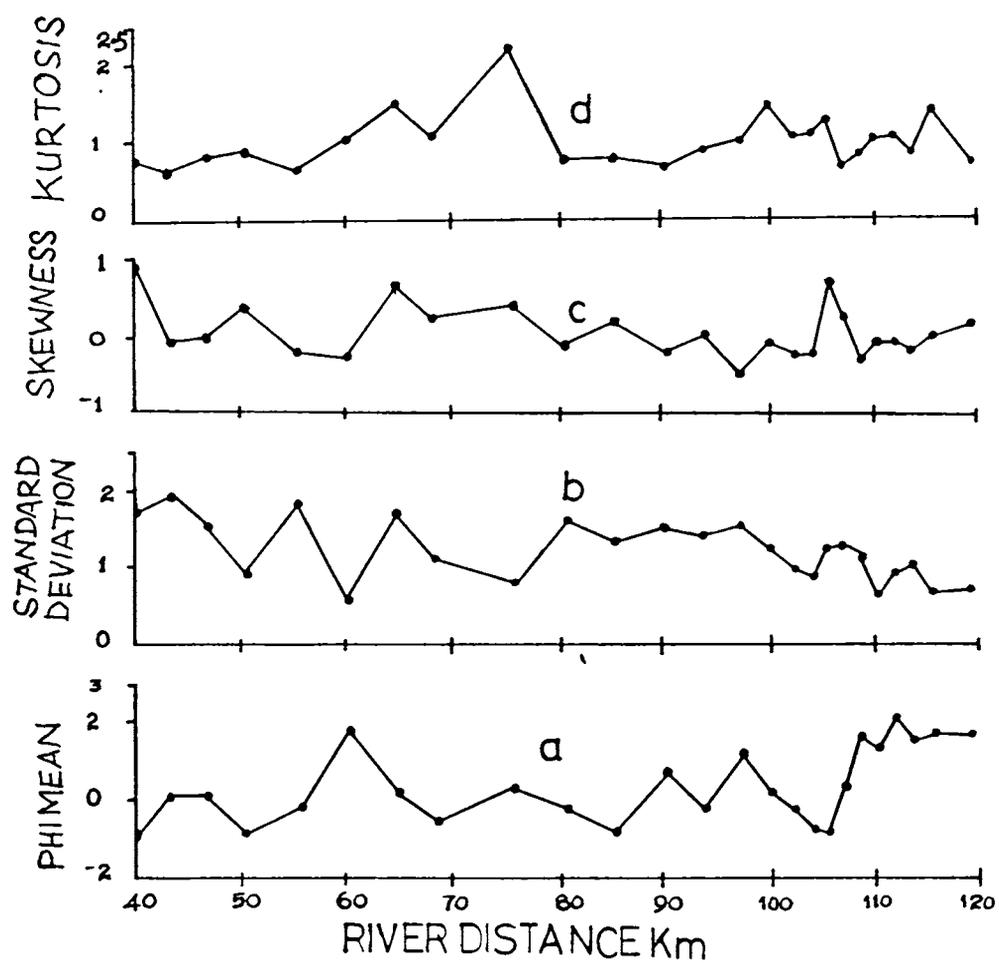


Fig. 8 Downstream variation of statistical parameters

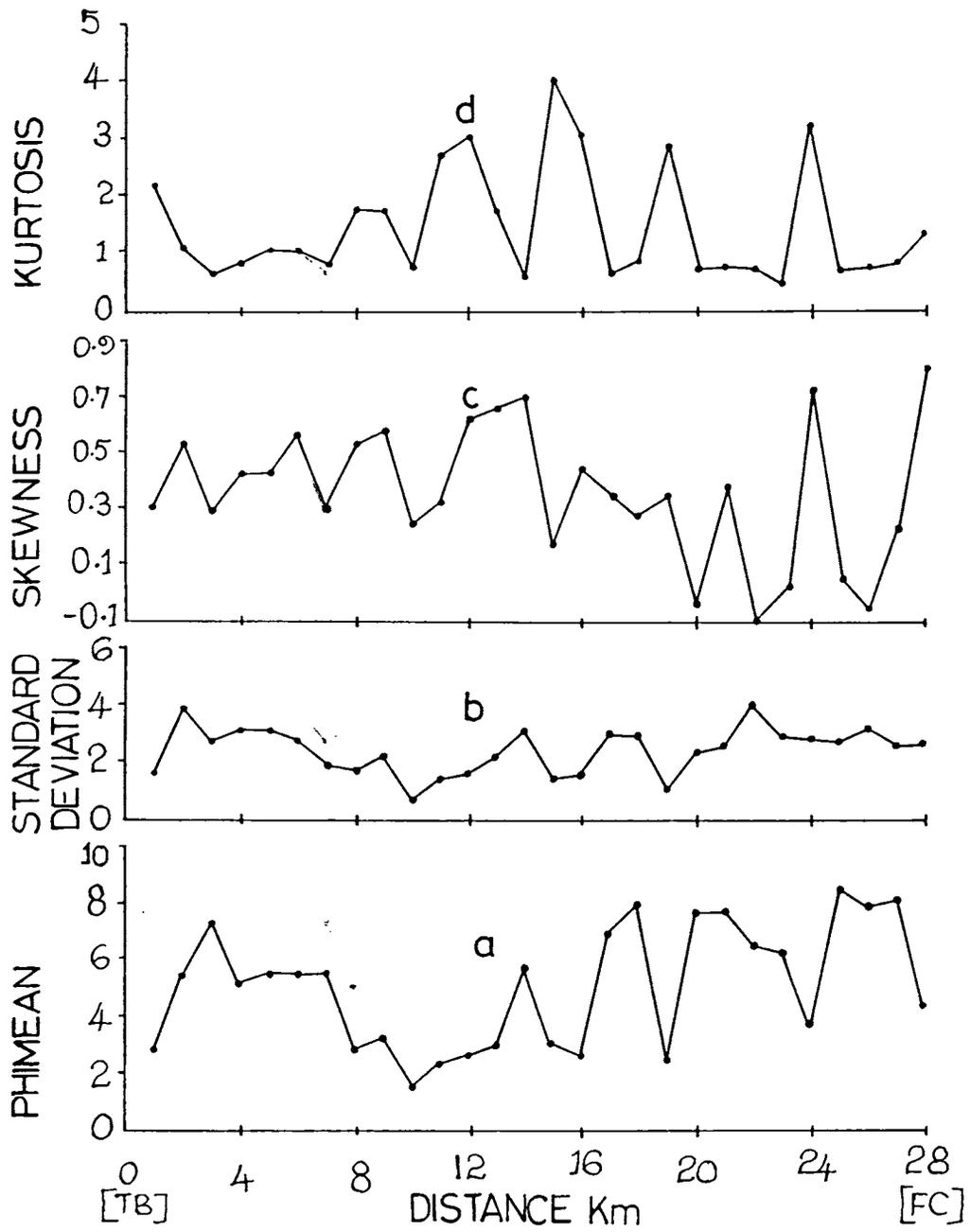


Fig. 9 Variation of statistical parameters in the sediments of Central Vembanad estuary

In the Muvattupuzha river, the standard deviation varies between  $0.55 \phi$  and  $2.04 \phi$  where as in estuary the range is between  $0.77 \phi$  and  $4.17 \phi$ . The spatial variation of standard deviation in riverine and estuarine environments is presented in Figs. 8b and 9b respectively. In river environment as the particle size decreases downstream, the sorting improves. The observed increase in sorting is presumably due to the differential transport of sediments downstream. Inmann (1949) opined that once a sediment attains maximum sorting values, any further fall in the competency of the transporting medium results in the increase of fine particles in the sediments which will again impart immaturity to the sediments. A comparative study of the sediment sorting between river and estuary reveals that the best sorting occurs in medium and fine sand grades. The existence of such a relationship has also been reported earlier by Inmann (1949), Griffiths (1951), Pettijohn (1957), Folk and Ward (1957) and Dyer (1987).

In estuary, more than 95% of the samples are of poorly and very poorly sorted nature. The abundance of finer particles especially silt and clay imparts broad particle dispersion which inturn causes very poor sorting of sediments (Allen, 1970). In the estuary only two samples (Nos. 54 and 64), which are collected at the mouth of the Ittupuzha-Murinjapuzha distributaries exhibit moderately sorted particle dispersion.

c) **Skewness:** Skewness of sediments is a measure of the asymmetry of grain size population and reflects the environment of deposition. In textural analysis skewness is considered as an important parameter because of its extreme sensitivity in subpopulation mixing. Well sorted unimodal sediments are usually symmetrical with zero skewness. In a fine skewed sediment population, the distribution of grains will be from coarser to finer and the frequency curve chops at the coarser end and tails at the finer. The reverse condition is characteristic of coarse skewed sediments. Martins (1965) has suggested

that coarse skewness in sediments could be due to two possible reasons.

- 1) Addition of materials to the coarser terminal or
- 2) Selective removal of fine particles from a normal population by winnowing action.

In the Muvattupuzha river, the skewness varies from -0.44 to 0.93 (very coarse skewness to very fine skewness) and in Central Vembanad estuary from -0.10 to 0.81 (nearly symmetrical to very fine skewed). The respective variations of skewness in riverine and estuarine environments are depicted in Figs. 8c and 9c. In river, about 60% of the sediment samples are nearly symmetrical to coarse skewed, 36% are fine to very fine skewed and the remaining samples are very coarse skewed. The river sections particularly the upstream, which consists of abundance of coarse fraction with less amounts of fine modes, yield coarse skewness. A similar type of changes has also been noticed by Folk and Ward (1957), Cadigan (1961) and Martins (1965) in their respective study areas. In the downstream the fine mode generally increases and the skewness of sediments shifts to fine entities. The skewness variation is more complex in the estuarine environment (Fig. 9c). Here, about 70% of the samples exhibit very fine skewed particle dispersion (1.6 to 0.3), while the remaining samples are nearly symmetrical and fine skewed. The very fine skewness of estuarine sediments is attributed to the addition of silt and clay modes to the sand modes (Cronan, 1972). The presence of nearly symmetrical skewed samples in the estuary indicates an equal proportion of different modes.

d) **Kurtosis:** Kurtosis, the peakedness of the frequency curve, is a measure of the contrast between sorting at the central part of the size distribution curve and that of the tails. Figs. 8d and 9d show the spatial variation of Kurtosis along the profile of the river and estuary respectively. Kurtosis of the river sediment ranges from very

leptokurtic to platykurtic (0.32 - 2.26). In the estuary, the sediments are very leptokurtic to extremely leptokurtic (0.52-4.12). In natural environments, the kurtosis values reflect the fluctuations in the velocity of the depositing medium. A value greater than unity suggests greater fluctuations (Verma and Prasad, 1981). From Figs. 8d and 9d, it is evident that the estuarine environment is characterised more by severe fluctuation in sediment kurtosis than river environment.

### 3.2.3 BIVARIATE PLOTS

Significant trends were observed by several investigators (Folk and Ward, 1957; Sahu, 1964; Friedman, 1967; Abed, 1982 and Khan, 1984) when they plotted the grain size parameters among each other. Figs. 10 and 11 depict the scatter plots of various statistical parameters of the riverine and estuarine sediments. The phi mean versus standard deviation shows an almost linear relation. The sorting worsens as the phi mean size decreases. This is true in the case of the pebble rich tributary sediments. The medium and fine sands ( $1 \phi - 3 \phi$ ) show moderate to moderately well sorted nature. The plots of mean size versus skewness is curvilinear in both the environments. In river, the curve faces upwards where as in the estuary, it is downwards. Combining these two, yields a perfect sinusoidal curve. In this way, the sediment distributional behaviour of the study area agrees to the classic work of Folk and Ward (1957) and Friedman (1961). The scatter plots between  $\phi$  mean size and Kurtosis are unevenly distributed in river environment. On the other hand, in estuary, the plots exhibit a perfect curvilinear pattern characteristic of lacustrine deposits with an admixture of coarser and finer particles. The observed pattern is similar to that of the one reported by Hakanson and Jansson (1983) for the Experimental lake sediments. The interrelationships between standard deviation and skewness, standard deviation and kurtosis, and skewness and kurtosis do not yield much information.

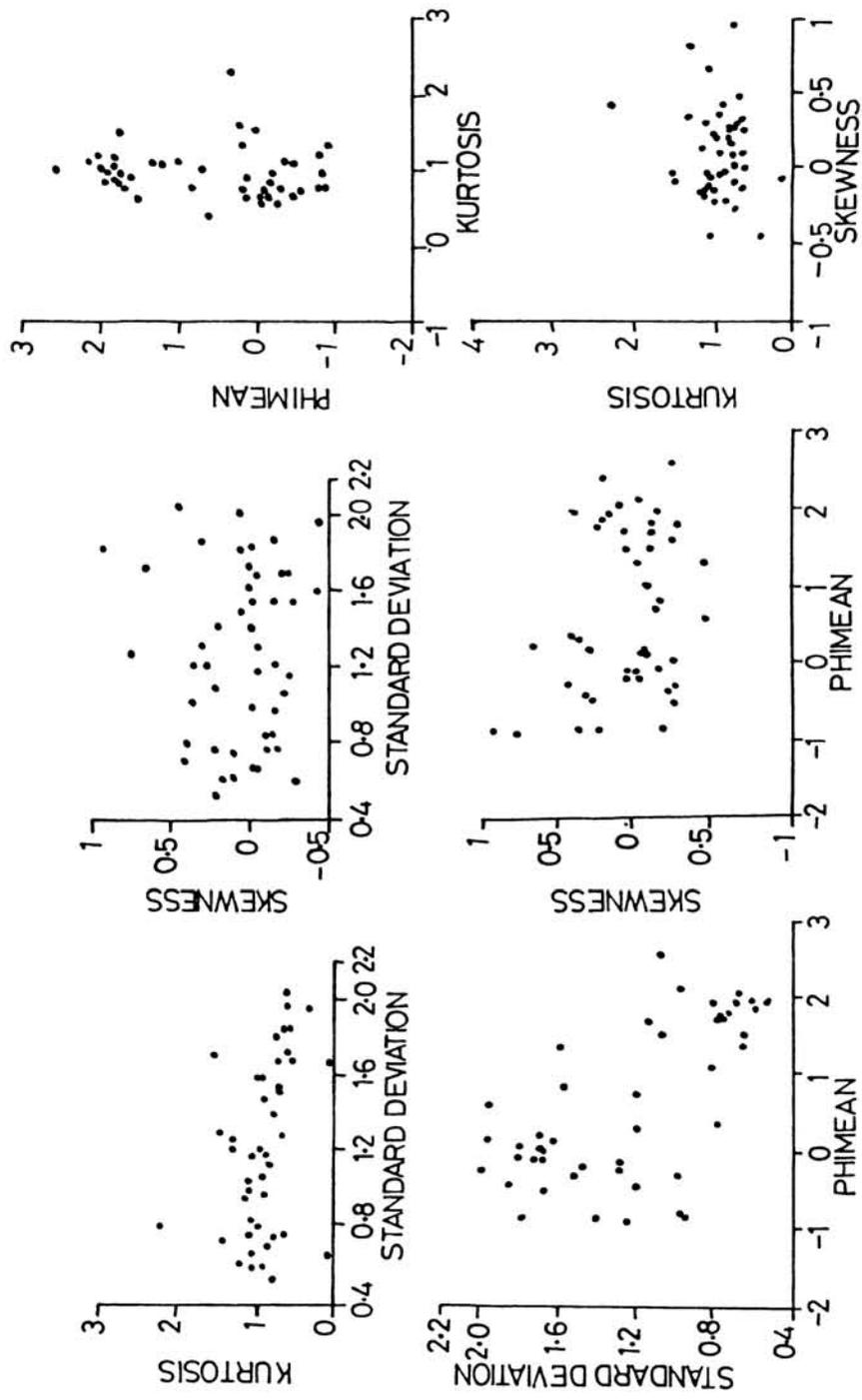


Fig. 10 Interrelationship between various statistical parameters in the sediments of Muvattupuzha river

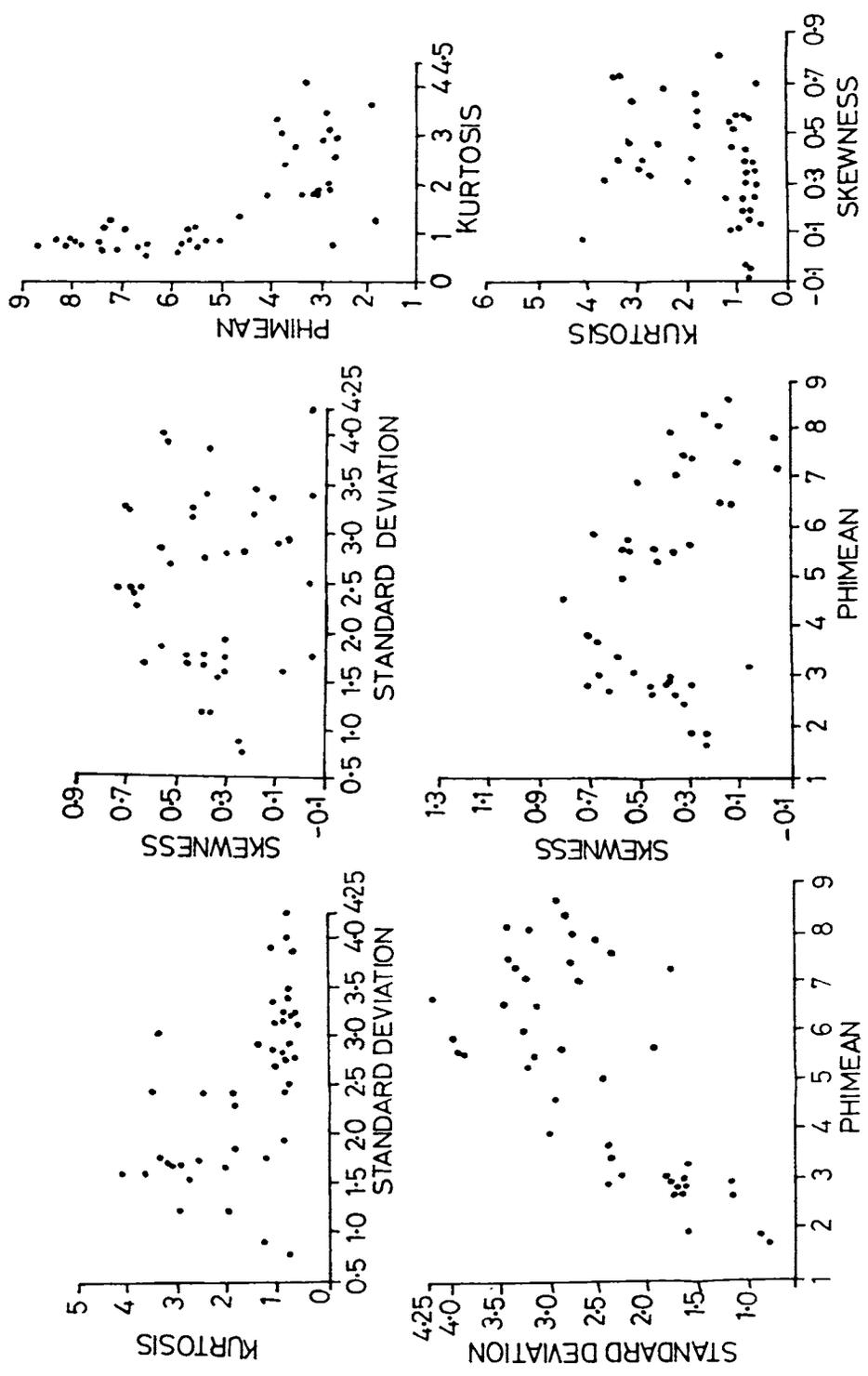


Fig. 11 Interrelationship between various statistical parameters in the sediments of Central Vembanad estuary

### 3.2.4 TEXTURAL CLASSIFICATION OF SEDIMENTS

a) **River:** Table 3 summarises the weight percentages of gravel, sand and mud in the sediments of the Muvattupuzha river. Since majority of the river sediments contain a substantial amount of gravel, the textural classification of Folk et al. (1970) for gravel bearing sand is followed to decipher the sediment types of the river basin. From Fig. 12a, it is evident that the river sediments show a wide range of sediment texture. Sandy gravel, gravelly sand, slightly gravelly sand, sand, and muddy sand are the dominant sediment types of the Muvattupuzha river bed. Sandy gravel predominates upstream. Gravelly sand and sand are progressively enriched downstream. The muddy sand types are found only in the Murinjapuzha tributary (stations 41, 42, 43 and 44).

b) **Estuary:** Fig. 13 furnishes the spatial distribution of various sediment types (Folk et al., 1970) in the Central Vembanad estuary. Sand, muddy sand, sandy mud, mud, clayey sand and sandy silt are the sediment types observed in the estuary (Fig. 12b). Of the various sediment types, sandy mud, mud and muddy sand predominate the estuarine substratum. In the southern region extensive distribution of muddy sand and sandy mud is observed from Thannirmukham bund to Perumbalam island. The area opposite to Thannirmukham bund as well as the Ittupuzha river mouth, two separate zones of clayey sand have been identified. Two patches of silty sand have also been found in the study area of which one is midway between Thannirmukham bund and Ittupuzha and the other is south of Perumbalam island. The central and northern sectors of this estuary are mainly covered by mud and sandy mud. The region around Willington island is a composite mixture of varying proportions of muddy sand, mud and sandy mud. The highly complex distributional pattern of sediments in the estuarine substratum is the result of the highly variable hydrodynamic set up prevailing in the estuary as well as the seasonal maintenance dredging operations by the Port authorities.

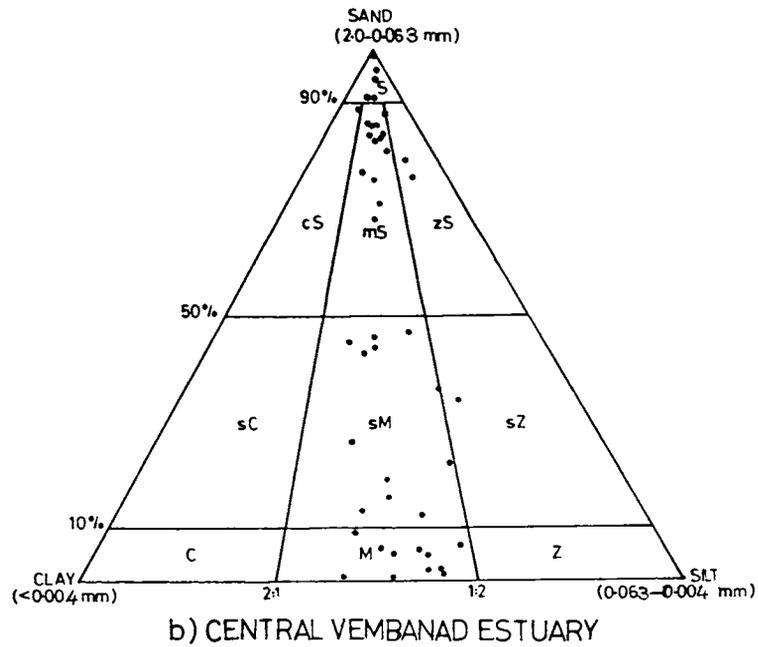
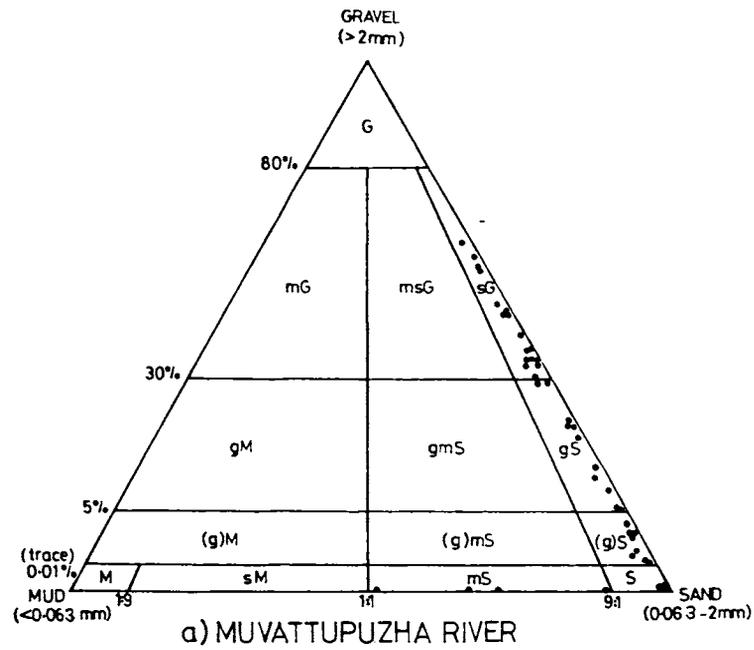


Fig. 12 Ternary diagram illustrating the nature of sediments in the riverine and estuarine environments

## ABBREVIATIONS USED

### IN FIG. 12

G = gravel  
sG = sandy gravel  
msG = muddy sandy gravel  
mG = muddy gravel  
gS = gravelly sand  
gmS = gravelly muddy sand  
gM = gravelly mud  
(g)S = slightly gravelly sand  
(g)mS = slightly gravelly muddy sand  
(g)M = slightly gravelly mud  
S = sand  
mS = muddy sand  
sM = sandy mud  
M = mud

S = sand  
zS = silty sand  
mS = muddy sand  
cS = clayey sand  
sZ = sandy silt  
sM = sandy mud  
sC = sandy clay  
Z = silt  
M = mud  
C = clay

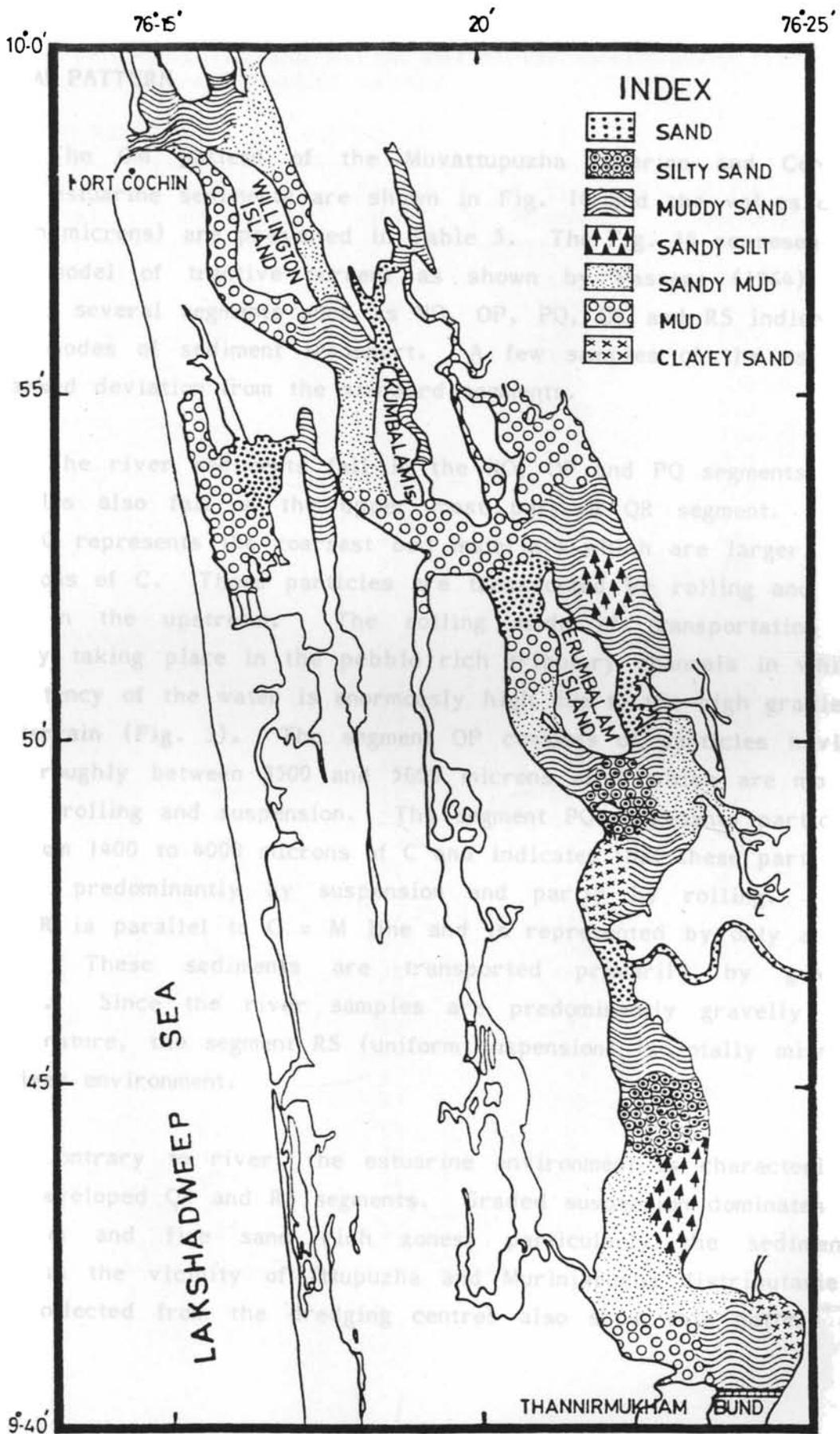


Fig. 13 Spatial distribution of sediments in the estuarine substratum

### 3.2.5 CM PATTERN

The CM pattern of the Muvattupuzha riverine and Central Vembanad estuarine sediments are shown in Fig. 14 and the values of C and M (in microns) are presented in Table 5. The Fig. 14 represents a complete model of tractive current as shown by Passega (1964) and consists of several segments such as NO, OP, PQ, QR and RS indicating different modes of sediment transport. A few samples of the estuary show marked deviation from the standard segments.

The river sediments fall in the NO, OP and PQ segments. A few samples also fall in the upper most part of QR segment. The segment NO represents the coarsest bed materials which are larger than 5000 microns of C. These particles are transported by rolling and are enriched in the upstream. The rolling mode of transportation is intensively taking place in the pebble rich tributary channels in which the competency of the water is enormously high due to the high gradient of the terrain (Fig. 3). The segment OP consists of particles having diameter roughly between 3500 and 5000 microns of C which are moved by mainly rolling and suspension. The segment PQ represents particles ranging from 1400 to 4000 microns of C and indicates that these particles are moved predominantly by suspension and partly by rolling. The segment QR is parallel to  $C = M$  line and is represented by only a few samples. These sediments are transported primarily by graded suspension. Since the river samples are predominantly gravelly and sandy in nature, the segment RS (uniform suspension) is totally missing in the river environment.

Contrary to river, the estuarine environment is characterised by well developed QR and RS segments. Graded suspension dominates in the medium and fine sand rich zones, particularly the sediments collected in the vicinity of Ittupuzha and Murinjapuzha distributaries. Samples collected from the dredging centres also show this pattern of

TABLE 5 - One percentile (C) and Median (M) of (a) Muvattupuzha river and (b) Central Vemaband estuary

a) MUVATTUPUZHA RIVER

Sample No.	C (in microns)	M (in microns)	Sample No.	C (in microns)	M (in microns)
5	8000	300	29	400	300
9	9900	700	30	1500	360
10	4400	580	31	2500	600
13	8300	580	32	2800	350
15A	7000	1325	33	1425	330
17	4600	770	34	1050	310
18	9200	1000	36	3250	280
20	6500	500	37	880	350
21	5300	1150	38	660	275
23	9200	280	39	940	275
24	1750	150	40	350	465
26	3500	540	41	1350	380
28	4600	1000	42	1250	250

b) CENTRAL VEMBANAD ESTUARY

45	460	135	67	620	180
46	1150	59	68	110	16
47	150	9	69	205	4.1
48	460	50	70	72	6.8
49	380	49	71	880	7.3
50	500	41	72	500	150
51	205	23	73	500	55
52	620	165	74	810	250
53	780	155	75	540	13
54	500	28	76	580	160
55	620	165	77	500	145
56	500	190	78	460	135
57	750	200	79	410	145
58	250	55	80	285	15
59	575	82	81	205	9.8
60	460	185	82	55	2.4
61	170	13	83	350	2.9
62	165	4.6	84	63	4.1
63	620	165	85	270	110
64	880	285	86	750	45
65	750	235	87	72	5.9
66	205	63	88	1600	7.8

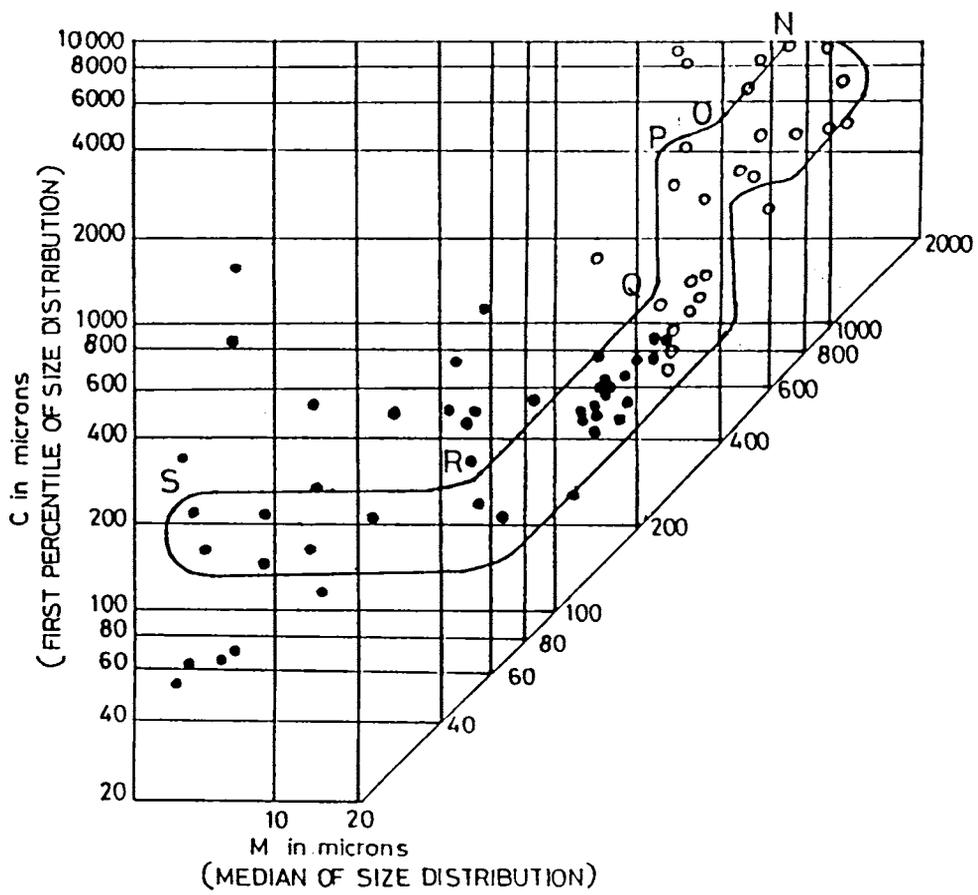


Fig. 14 CM pattern of the sediments of Muvattupuzha river (o) and Central Vembanad estuary (●)

sediment transport. The silt and clay rich samples fall in the RS segment which indicate the role of uniform suspension in transporting these sediments. The samples scattered above the ideal pattern indicate the complexity in the transportational regime which also reflects from the poorly sorted nature of these deposits.

### 3.2.6 SURFACE TEXTURES

Surface textures of clastic particles are repositories of information about the physical and chemical processes to which the particles have been subjected (Krinsley and Doornkamp, 1973). A grain of quartz sand taken from the beach bears characteristic textural signature on its surface which strongly reflects wave action. This signature is quite distinct from those produced by the action of rivers, wind or glaciers. Surface textures can be grouped into two categories. One class deals with the dullness or polish of the fragment and the other concerns the marking on the surface. Many investigators opined that a systematic study of the above two classes provides an insight into the history of transportation and deposition of clastic particles (Krinsley and Doornkamp, 1973; Baker, 1976 and Marshall, 1987). Waugh (1965, 1970) used the surface textural studies to unravel the extent of diagenesis in ancient deposits.

In view of the above, an attempt has been made in this investigation to study the surface textural patterns of quartz grains (from + 80 mesh) collected from Muvattupuzha river (Sample No. 2) and Central Vembanad estuary (Samples No. 76). The study reveals a marked variation in the surface textural patterns of these grains. The riverine quartz sand (Plate 1a) shows sharp edges and planar surfaces. High magnification (2400 X) photograph exhibits 'V' shaped impact pits (Plate 1b) which are only in the primitive stage. These 'V's indicate that the grain under examination is subjected to only small amount of wear and tear. On the other hand the estuarine quartz grain is rounded

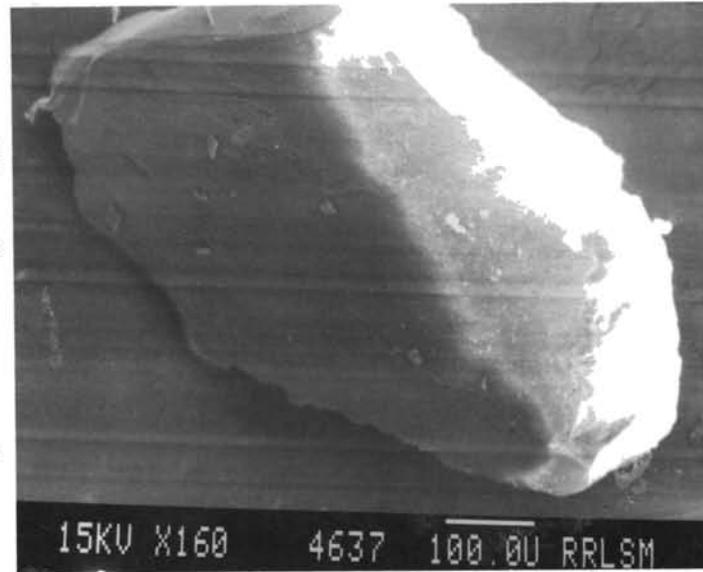


Plate 1a A quartz grain of the Muvattupuzha river (upstream) showing sharp edges and planar surfaces

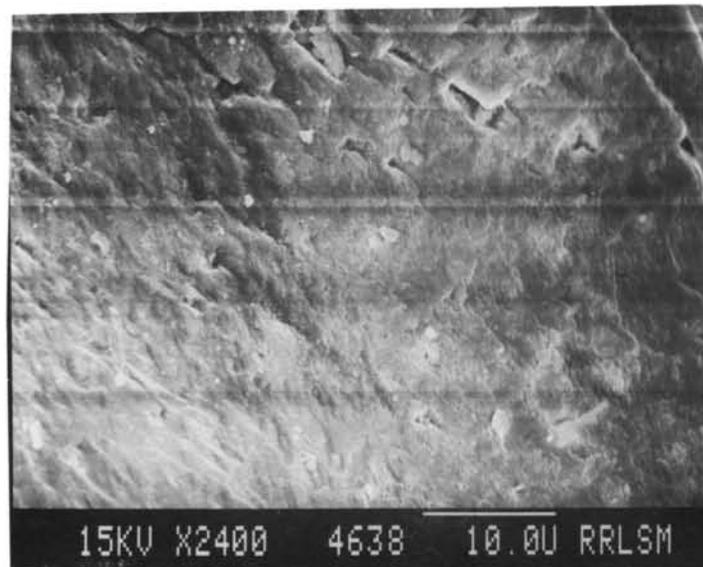


Plate 1b Quartz grain surface (riverine) showing V-pits in initial stages

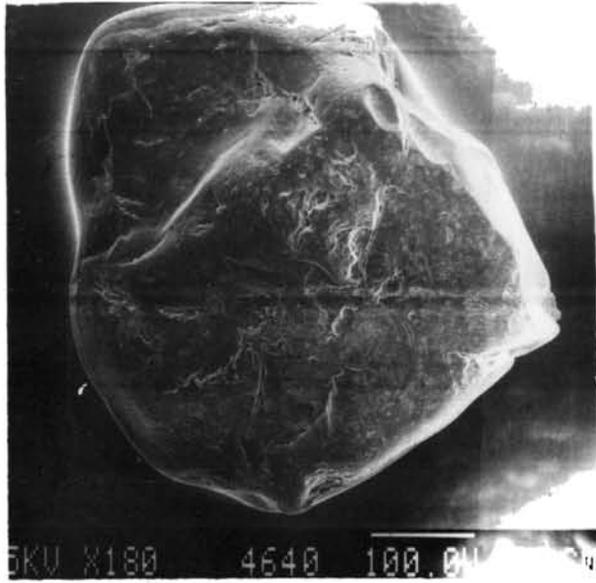


Plate 2b A well rounded quartz grain of the Central Vembanad estuary showing bulbous edges

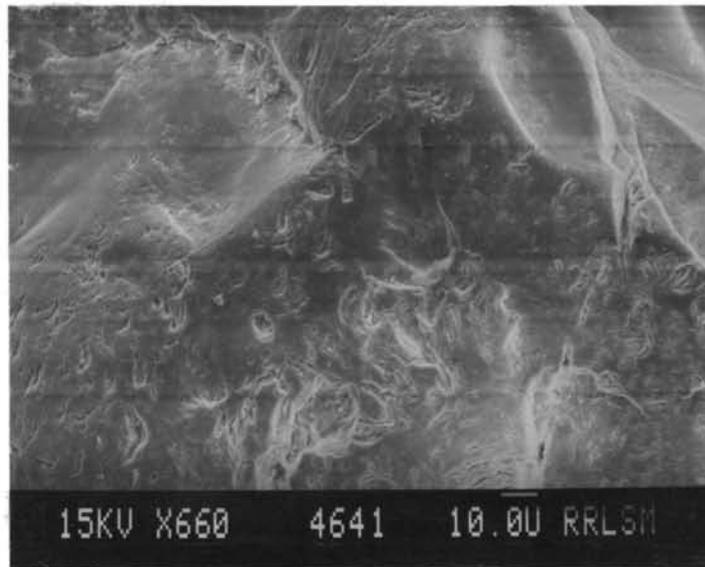


Plate 2b Photomicrograph of estuarine quartz showing pitted surface and diagenetically derived surface textures

and possesses bulbous edges (Plate 2a) which is characteristic of high energy subaqueous action (Marshall, 1987). Pitted surfaces are present on these bulbous projection. These pits are smooth and sharply cut and appear as if scooped with a small spoon (Plate 2b). Quartz grains with similar microstructures are recorded abundantly in the sandy beaches of Kerala (Samsuddin, 1990). In addition to the above surface textures, the estuarine quartz grains also register a wide spectrum of chemical dissolution structures. The complexity of these mechanical and chemical structures is also evidenced from the surface morphometry of heavy minerals especially zircon (Chapter 4; Plate 5a). Perfect rounding of the estuarine quartz grain with bulbous projections, pitted surfaces and other unoriented etch pits results from mechanical and chemical activities, distinctly indicate subaqueous impact and agitation of water with prolonged chemical activity and long residence time under which the grains are subjected to. All these structures depict a polycyclic nature of estuarine sands and a high energy environment (presumably beach environment) under which the sands are moulded prior to the deposition in the estuarine bed. From satellite imagery trace of the Landsat Frames, Mallik and Suchindan (1984) revealed that the southern and central parts of Vembanad estuary are marked by a number of beach ridges nearly parallel to the coast and form boundary of the lake margin in some places (Fig. 15). These beach ridges are resulted from the repeated transgression and regression of shore during Pleistocene time and their orientations have been controlled by the changes in deviation of the waves. During southwest monsoon, considerable amounts of sediments are reworked from these beach ridges and deposited into the estuarine basin. The surface morphometry of estuarine sillimanite, zircon as well as the heavy mineralogical studies discussed in the subsequent sections (Chapter 4) also confirm the above view.

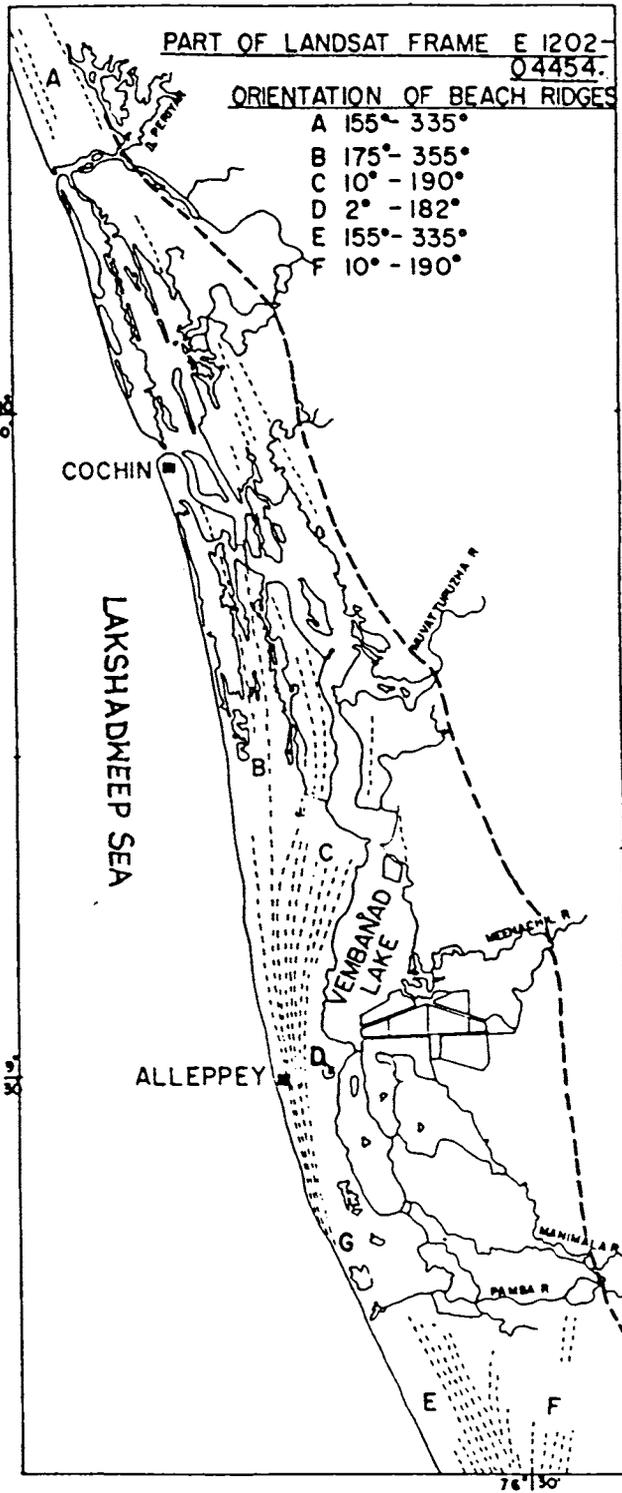


Fig. 15 Orientation of palaeo-beach ridges reconstructed from landsat imagery (Source: Mallik and Suchindan, 1984)

## CHAPTER 4

## 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. Assemblage of minerals in sedimentary deposits has been used for many years to unravel the sources and transportational pathways of sediments. Apart from this, the mineralogical make up 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 mineral fractions in riverine and estuarine sediments renders valuable information on the nature of contribution and energy conditions of the depositing medium.

Study of the mineralogical make up of sediments should always accompany the study on textural characteristics, as the texture has a direct bearing on the mineralogical constitution of sediments. In many published accounts, one or two size fractions have only been examined to represent the entire heavy mineralogical assemblage of sediments. 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 (Rubey, 1933; Rittenhouse, 1943; Friedman, 1961; Mishra, 1969; Blatt et al., 1972 and Patro et al., 1989). Moreover, knowledge of size frequency distribution of individual minerals is essential to understand the interaction between physical properties of minerals and the physical processes operated during their transportation and deposition. Further, 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. On the other hand, study

of light minerals can give insight into the source rock characteristics and the maturity of sediments. The principal interests related to the study of clay minerals are its sensitivity to the source area fluctuation and diagenetic changes of sediments.

#### 4.2 REVIEW OF LITERATURE

Studies on detrital heavy minerals received wide attention in the last five-six decades due to their strong bearing on the provenance of the sediments as well as their wide use as a correlation tool in solving various sedimentological problems. The era of modern heavy mineralogy begins with the classic work of Rubey (1933). He was the first to explain precisely about the size distribution of heavy minerals in sedimentary deposits using settling velocity equation. The work of Rittenhouse (1943) stressed the complex interrelationship between source rock characteristics and transport processes that determine the heavy mineral distribution in fluvial set up. Eversince the introduction of hydraulic equivalent concept by Rubey (1933), it has been widely recognised that the hydraulic behaviour of heavy minerals is jointly influenced by their physical properties (size, shape and density), availability of the minerals and dynamics of the transporting medium. The interrelationship between various heavy minerals and the influence of size, shape and density on hydraulic sorting have been further investigated by Briggs (1965). Blatt and Sutherland (1969) have shown that the rate of chemical alteration is greater in coarse grained sediments than in less permeable fine grained sediments due to the availability of enough intrastratal solution in the former. Bradley (1952), Van Andel and Poole (1960), Lowright et al. (1972), Stapor (1973), Stingerland (1977), Flores and Shideler (1978), Morton (1986) and Stattegger (1987) have used the heavy mineral assemblages in unravelling the transportation and depositional history of sediments.

The effects of physical and chemical weathering on minerals are often difficult to distinguish (Edelman and Doeglas, 1931; Dryden and Dryden, 1946 and Raeside, 1959). Pettijohn (1941) suggested that the diversities in heavy mineral assemblages are more in the youngest sediments than ancient ones, and further, the number of heavy mineral species may gradually decrease as the age of the sediment increases. Such a decrease in the heavy mineral species could be due to the action of intrastratal solution (Pettijohn, 1941). But contrary to this, Krynine (1942) stressed provenance as the key factor for the above said mineralogical diversities.

Several investigators have made systematic approach to study the mineralogical diversities observed along the course of rivers. Pollack (1961) surmised that selective sorting based on shape factor is not an important factor for downstream variation of heavy minerals. However, Briggs et al. (1962) have pointed out that both density and shape of minerals are important in imparting sorting of minerals downstream. The role of progressive sorting based on size and specific gravity differences has also been studied by investigators like Allen (1970), Carver (1971), Blatt et al. (1972), Komar and Wang (1984) and Komar et al. (1989).

In India, detailed studies on heavy mineral variations have been restricted to some major river systems which include Godavari (Naidu, 1968), Krishna (Seetharamaswamy, 1970), Mahanadi (Sathyanarayana, 1973), Vasishta-Godavari (Dora, 1978) and Cauvery (Seralathan, 1979). Unlike river systems, considerable amount of information exists on the heavy mineral occurrences of the beach environments. Jacob (1956) made a detailed study on the heavy mineral concentrate of the beach sands of Thirunelveli, Ramnad and Tanjore districts of Tamil Nadu. Heavy mineral suites of Visakhapatnam - Bhimunipatnam areas have been investigated by Roy (1958). Mahadevan and Rao (1960) discussed the heavy mineral concentrates of Vishakapatnam

beach. The heavy mineral deposits between Quilon and Cape Comerin on the south west coast of India have been studied by Tipper (1914) and Brown and Dey (1955). Investigators like Aswathanarayana (1964), Prabhakara Rao (1968), Purandara et al. (1987), Mallik (1986), Mallik et al. (1987), Unnikrishnan (1987), Sasidharan and Damodaran (1988), and Purandara (1990) have studied the heavy mineral suite of the beach sands of Kerala. The heavy mineral deposits of the shelf region of the west coast of India have also been studied by several investigators (Mallik, 1974; Siddique et al., 1979; Siddique and Rajamanickan, 1979 and Rajamanickam, 1983). Mallik (1981) made a detailed study on the distribution pattern of heavy minerals of the continental shelf of Kakinada. Kidwai et al. (1981) investigated the distribution of heavy minerals in the outer continental shelf sediments between Vengurla and Mangalore. They have suggested that heavy mineral assemblages of sediments indicate mixed igneous and metamorphic provenance. Detailed geological and geophysical surveys conducted along the Konkan coast by Gujar et al. (1989) reveal the occurrences of several promising isolated placer deposits.

The composition of light minerals (bromoform floats) of clastic sediments has been studied for a better understanding of the mineralogical maturity and fluvial processes. In 1957, Pettijohn has pointed out that the mineralogical maturity of sediments can be expressed by the quartz/feldspar ratio. Though there is not much difference in the specific gravities between quartz (2.65) and feldspar (2.70), there exists considerable difference in the stability index between the two, because feldspars are comparatively less stable than quartz. Many researchers opined that the increase of quartz/feldspar ratio downstream is the result of selective abrasion of the easily weatherable feldspars (Russel, 1937; Pettijohn, 1957; Pollack, 1961; Seibold, 1963; Seetharamaswamy, 1970 and Seralathan, 1979). The relative proportions of these minerals in sediments have also been extensively used for reconstructing climatic as well as tectonic history of ancient sedimentary

deposits (Blatt et al. 1972 and Hashmi and Nair, 1986).

A cursory glance of literature reveals that studies on the mineralogical constitution of silt fraction are meagre owing to the difficulties in their separation and examination. However, mineralogical studies of this fraction are of considerable importance to have a better understanding about the granulometric dependence of minerals.

Clay minerals are an integral component of fine sediments. Investigations regarding the distribution and origin of clay minerals have proved to be an important tool for elucidating pathways of fine grained sediments (Weaver, 1959; Biscaye, 1965; Scafe and Kunze, 1971; Shaw, 1973; Kolla et al., 1981 and Nair et al., 1982). Tagaart and Keiser (1960), Subba Rao (1963), Seetharamaswamy (1970), Seralathan (1979) and Mohan (1990) have opined that source area and climate have tremendous influence on the quality and quantity of clay minerals. The effect of diagenesis on the dispersal pattern of clay minerals has been emphasised by Grim et al. (1949), Grim and Johns (1954), Nelson (1959) and Carroll (1969). In recent years clay mineral studies are being carried out to assess the fate and dispersal pattern of many major and trace elements in the sediments of rivers, estuaries and nearshore environments (Reinson, 1975 and Prithviraj and Praksh, 1990).

#### 4.3 RESULTS AND DISCUSSION

##### 4.3.1 MINERALOGY OF SAND

The sand fraction of the Muvattupuzha riverine and the Central Vembanad estuarine sediments has been analysed for various heavy and light minerals. The results obtained are discussed below.

#### 4.3.1A HEAVY MINERALS

**Total heavy minerals:** Table 6 shows the weight percentages of total heavies in different sizes namely +45 (0.50 - 0.35 mm), +60 (0.35 - 0.25 mm), +80 (0.25 - 0.177 mm), +120 (0.177 - 0.125 mm), +170 (0.125 - 0.088 mm) and +230 (0.088 - 0.063 mm) mesh fractions of riverine and estuarine environments. In river sands (Figs. 16, 18A and 19A), heavy mineral occurrences are recorded in all the six fractions whereas in the estuary (Figs. 17, 18B and 19B), heavy minerals are confined only to the last 4 size fractions. In the following sections, the size fractions of heavy minerals are mentioned (combining two successive meshes) as medium (0.50 - 0.25 mm), fine (0.25 - 0.125) and very fine (0.125 - 0.063 mm) sands. The respective ranges of heavy minerals in medium, fine and very fine sand fractions of the river sediments are from 0.48 to 32.26%, 0.87 to 72.55% and 2.98 to 69.66%. In estuary, the variations of heavy minerals in fine and very fine sand fractions are from 0 to 15.45% and 0.75 to 44.67% respectively.

Figs. 18A and 18B reveal the downstream variations of total heavy mineral contents in different size grades of the riverine and estuarine sands. From Table 6 and Fig. 16, it is evident that, in general, the upper reaches of the Muvattupuzha river system (i.e. the tributaries namely, Thodupuzha and Kaliyar) exhibit higher amount of heavy minerals than the lower reaches. Stations 1, 2, 9, 14 and 15 show significant enrichment of heavy minerals particularly in the fine and very fine sand fractions. Among the tributaries, Kaliyar registers high concentration of total heavies than Thodupuzha.

In the Muvattupuzha river proper (i.e. downstream from the Muvattupuzha town to Vettikattumukku), the total heavy mineral percentages are markedly lower, but the heavy mineral modes are slightly shifted towards finer grades. Station 23 (located downstream of Piravam bridge) records the highest heavy mineral content in this

TABLE 6 - Heavy mineral percentages (Individual and total) in various size fractions of Muvattupuzha riverine and Central Vembanad estuarine sands

a) MUVATTUPUZHA RIVER		HMs (100%)														
Sample No.	Grain size	HMs (100%)														
		LMS (100%)	HMS (100%)	OP (100%)	Non-OP (100%)	Am	Py	Ga	Zi	Bi	Ru	Mo	Si	Al		
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15		
1	a	89.73	10.27	19.17	80.83	53.33	13.33	6.67	0.83	6.67	-	-	-	-		
	b	67.74	32.26	45.89	54.11	21.92	6.16	10.27	1.37	13.69	-	0.68	-	-		
	c	42.54	57.46	69.83	30.17	11.86	6.44	4.75	2.71	3.05	-	1.02	-	0.34		
	d	32.53	67.47	63.93	36.07	10.71	7.14	2.86	9.28	3.56	-	1.78	-	0.74		
	e	31.38	68.62	53.76	46.24	16.96	9.95	2.69	15.57	-	-	0.54	-	0.54		
	f	52.23	47.77	38.81	61.19	23.57	9.76	2.14	22.14	-	-	2.14	0.48	0.95		
2	a	96.62	3.28	1.80	98.20	60.36	14.41	10.81	-	11.71	-	-	-	0.90		
	b	95.16	4.84	2.11	97.89	59.86	10.56	14.79	-	12.68	-	-	-	-		
	c	93.42	6.58	2.51	97.49	59.79	19.09	9.55	2.01	5.53	-	0.50	-	1.00		
	d	84.08	15.92	16.47	83.53	53.81	18.88	5.22	2.81	2.01	-	0.40	-	0.40		
	e	53.64	46.36	48.66	51.34	22.85	10.22	-	11.02	0.54	-	1.34	-	0.81		
	f	51.46	48.54	50.94	49.06	10.72	6.97	3.49	24.66	0.80	-	1.34	-	1.07		
4	a	96.51	3.49	2.59	97.41	51.95	19.58	12.98	1.29	10.39	-	-	-	1.20		
	b	97.76	2.24	2.91	97.09	64.08	15.53	5.83	2.91	6.79	-	-	-	1.94		
	c	96.11	3.89	2.35	97.65	52.94	23.53	7.06	5.88	5.88	-	-	-	2.35		
	d	94.84	5.16	7.28	92.72	58.94	20.53	5.29	1.98	1.98	0.66	1.32	-	1.98		
	e	94.45	5.55	4.68	95.32	43.75	31.28	7.81	9.38	-	-	-	-	3.12		
	f	85.34	14.66	12.81	87.19	42.72	28.21	4.62	10.31	-	-	0.62	-	0.71		
7	a	95.97	4.03	9.21	90.79	61.84	7.89	-	-	19.74	-	-	-	1.32		
	b	93.47	6.53	23.26	76.74	40.69	19.76	3.49	2.33	10.46	-	-	-	-		
	c	96.77	3.23	14.08	85.92	71.83	11.27	2.82	-	-	-	-	-	-		
	d	96.94	3.06	12.75	87.25	66.14	18.73	0.79	21.19	-	-	-	-	0.39		
	e	<del>96.46</del>	3.54	23.10	76.90	49.54	19.76	1.82	4.56	-	-	-	-	1.22		
	f	85.70	14.30	42.11	57.89	26.08	11.00	2.15	17.46	-	-	0.48	-	0.72		

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
8	a	95.97	4.03	9.89	90.11	52.75	19.78	10.99	-	5.49	1.09	-	-	-
	b	93.89	6.11	11.58	88.42	59.15	7.93	15.24	1.22	4.88	-	-	-	-
	c	88.29	11.71	61.69	38.31	16.42	5.47	12.44	-	3.98	-	-	-	0.99
	d	94.32	5.68	56.46	43.54	18.66	7.66	6.69	1.91	7.66	-	0.48	-	0.48
	e	97.02	2.98	23.87	76.13	44.59	12.16	6.76	9.01	2.70	-	-	-	0.90
	f	90.27	9.73	28.93	71.07	38.68	11.32	6.92	11.01	-	-	0.63	-	0.79
9	a	91.66	8.34	6.35	93.65	75.39	12.69	3.17	1.59	-	0.79	-	-	-
	b	71.03	28.97	11.05	88.95	71.05	11.05	3.68	2.63	-	0.53	-	-	-
	c	42.80	57.20	50.98	49.02	32.35	8.82	2.45	4.41	-	-	-	-	0.98
	d	27.45	72.55	69.12	3.88	19.29	5.26	0.70	4.56	-	-	0.35	-	0.76
	e	30.34	69.66	60.86	39.14	17.42	4.07	-	16.29	-	0.23	-	-	1.13
	f	49.46	50.54	42.35	57.65	29.59	5.34	-	21.43	-	-	0.26	-	1.02
14	a	96.58	3.42	19.35	80.65	61.29	9.68	4.84	-	4.84	-	-	-	-
	b	90.31	9.69	37.34	62.66	47.64	10.73	1.72	1.29	-	-	0.43	-	0.86
	c	79.81	20.69	49.75	50.25	33.83	7.96	2.49	2.48	1.49	-	0.50	-	1.49
	d	77.33	22.67	34.27	65.73	46.66	17.83	1.39	2.45	0.70	-	-	-	0.70
	e	69.64	30.36	15.85	84.15	63.62	10.49	0.89	7.81	-	-	0.67	-	0.67
	f	68.42	31.58	23.02	76.98	41.27	11.91	1.85	18.78	-	-	1.06	0.79	1.32
15	a	91.95	8.05	0.83	99.17	67.50	17.50	9.17	-	-	-	-	-	1.67
	b	91.32	8.68	0.75	99.50	72.00	20.50	5.00	-	1.50	-	-	-	0.50
	c	89.00	11.00	3.28	96.72	74.68	16.74	2.68	0.50	-	-	-	-	1.11
	d	79.90	20.01	1.74	98.26	73.62	17.97	1.16	1.45	0.87	-	0.87	-	2.32
	e	59.48	40.52	8.00	92.00	54.44	25.00	2.33	6.67	1.33	-	1.00	-	1.12
	f	51.30	48.70	16.63	83.37	48.66	13.35	1.03	16.43	0.82	-	1.02	-	1.23
15A	a	92.65	7.35	3.25	96.75	63.41	9.76	19.51	0.81	3.25	-	-	-	-
	b	83.42	16.58	5.56	94.44	57.64	15.97	15.97	0.69	4.17	-	-	-	-
	c	94.04	5.96	15.56	84.44	44.44	11.11	13.33	-	13.33	-	-	-	2.22
	d	94.09	5.91	15.61	84.39	53.17	17.07	5.37	1.46	6.34	-	-	0.47	0.49
	e	93.00	7.00	12.39	87.61	55.98	21.37	2.14	2.14	4.70	-	-	-	1.28
	f	92.21	7.79	11.52	88.48	57.35	21.81	6.13	1.96	-	-	-	-	1.23
17	a	90.31	9.69	2.14	97.86	80.00	12.14	2.86	-	1.43	-	-	-	1.43
	b	94.36	5.64	4.16	95.84	70.83	16.67	4.16	-	4.14	-	-	-	-
	c	97.25	2.75	-	-	-	-	-	-	-	-	-	-	-
	d	96.94	3.06	2.29	97.71	64.22	25.23	2.75	1.37	2.75	-	-	0.45	0.92
	e	93.21	6.79	8.06	91.94	66.13	22.58	1.61	1.61	-	-	-	-	1.61
	f	94.23	5.77	6.88	93.12	61.61	24.59	1.64	1.96	1.64	-	0.98	0.32	3.60

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
20	a	97.76	2.24	3.01	96.99	58.65	17.29	11.28	-	6.02	-	-	-	3.76
	b	94.46	5.54	2.54	97.46	60.00	24.36	4.06	-	5.08	-	-	-	4.07
	c	91.42	8.58	4.87	95.13	66.21	15.80	3.27	-	4.63	-	0.25	0.50	3.27
	d	83.54	16.45	25.87	74.13	47.77	11.86	4.55	2.98	2.49	-	-	-	4.48
	e	89.78	10.22	32.63	67.37	48.68	6.32	1.05	5.79	1.32	0.53	-	-	-
	f	82.04	17.96	28.78	71.22	50.18	6.64	0.74	8.12	1.11	-	1.11	2.95	-
23	a	98.66	1.34	6.94	93.06	62.50	12.50	11.11	-	4.17	1.39	-	-	1.39
	b	98.98	1.02	17.16	82.84	54.43	13.61	6.51	1.78	6.51	-	-	-	-
	c	99.13	0.87	15.09	84.91	63.02	12.83	4.15	3.02	3.02	-	-	-	1.13
	d	92.92	7.08	30.67	69.33	49.07	13.60	2.67	2.67	0.53	-	-	-	0.80
	e	60.40	39.60	40.21	59.79	36.87	11.34	1.03	8.76	-	-	0.26	-	1.29
	f	41.26	58.74	55.76	44.24	15.54	4.75	0.90	21.39	-	-	0.91	-	0.73
25	a	95.72	4.28	4.39	95.61	67.03	20.88	5.49	-	2.19	-	-	-	-
	b	91.57	8.43	6.96	93.04	68.99	13.29	9.49	1.27	-	-	-	-	-
	c	94.62	5.38	11.24	88.76	64.04	14.61	7.86	2.24	-	-	-	-	-
	d	94.04	5.96	7.55	92.45	66.98	17.92	1.26	5.66	0.63	-	-	-	-
	e	94.89	5.11	21.20	78.80	62.18	12.89	0.57	2.29	-	-	-	-	0.86
	f	89.14	10.86	17.47	82.53	58.87	12.90	8.33	1.08	-	-	-	-	1.34
26	a	98.29	1.71	2.58	97.42	72.41	10.34	10.34	1.72	2.59	-	-	-	-
	b	93.51	6.49	4.96	95.04	70.25	15.70	4.13	1.65	3.31	-	-	-	-
	c	90.24	9.76	2.61	97.39	74.63	13.06	5.97	1.12	1.12	0.75	-	-	0.75
	d	88.99	11.01	4.88	95.12	76.09	12.85	-	1.03	1.54	-	0.26	-	1.03
	e	88.00	12.00	19.66	80.34	49.15	22.37	2.03	3.39	2.03	-	0.68	-	0.68
	f	85.82	14.18	12.41	87.59	60.99	18.79	-	2.48	2.48	-	1.42	-	1.42
30	a	98.96	1.04	2.29	97.71	78.16	12.64	3.45	-	3.45	-	-	-	-
	b	96.01	3.99	4.22	95.78	65.40	23.63	2.95	1.27	2.11	-	-	-	0.42
	c	90.55	9.45	7.48	92.52	71.03	18.07	1.87	1.25	-	-	-	-	0.31
	d	84.24	15.76	11.11	88.89	67.13	15.74	1.39	3.24	-	-	-	-	1.39
	e	76.89	23.11	18.06	81.94	58.86	16.38	0.67	3.68	-	-	0.33	0.33	1.67
	f	93.51	6.49	29.46	70.54	43.75	13.99	0.59	9.23	-	-	1.19	0.59	1.19
33	a	98.70	1.30	13.33	86.67	65.83	10.83	6.67	1.67	1.67	-	-	-	-
	b	93.78	6.22	10.33	89.67	66.85	14.13	4.35	1.09	2.72	-	-	-	0.54
	c	94.60	5.40	19.40	80.60	61.19	10.45	2.49	3.98	-	0.49	-	-	1.99
	d	87.95	12.05	17.11	82.89	60.43	11.77	0.80	9.09	-	-	0.27	-	0.54
	e	62.77	37.23	33.78	66.22	42.73	9.39	1.34	12.08	-	-	-	-	0.67
	f	67.89	32.11	45.92	54.08	26.28	6.89	0.76	18.37	-	-	0.51	-	1.28

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
36	a	98.81	1.19	6.00	94.00	50.00	11.00	3.00	2.00	28.00	-	-	-	-
	b	97.32	2.68	11.90	88.10	64.88	16.07	3.57	1.19	2.38	-	-	-	-
	c	97.57	2.43	13.18	86.82	60.45	17.04	1.13	1.61	5.47	-	-	-	0.32
	d	89.16	10.84	20.17	79.83	61.76	13.02	1.26	2.94	-	-	-	-	0.84
	e	91.56	8.44	28.79	71.21	50.00	12.97	1.26	5.69	-	-	0.32	0.32	0.63
	f	78.41	21.59	25.57	74.43	50.00	11.99	0.67	10.41	-	-	0.67	-	0.67
41	a	99.52	0.48	4.76	95.24	61.91	16.67	4.76	-	11.90	-	-	-	-
	b	98.32	1.68	52.38	47.62	37.38	6.67	-	0.71	0.95	-	0.23	-	-
	c	97.10	2.90	10.19	89.81	64.48	12.96	2.31	6.94	1.39	0.46	-	-	0.93
	d	92.37	7.63	15.82	84.18	50.15	13.85	1.85	7.21	1.89	-	-	-	1.23
	e	81.06	18.94	24.88	75.12	49.02	11.71	0.49	8.80	3.17	-	-	-	1.95
	f	85.83	14.17	17.37	82.63	60.22	8.68	1.68	11.76	-	0.28	-	-	-
43	a	96.50	3.50	11.86	88.14	59.32	10.17	1.69	-	16.95	-	-	-	-
	b	95.66	4.34	14.29	85.71	58.40	9.67	1.26	2.10	14.29	-	-	-	-
	c	95.70	4.30	13.86	86.14	64.11	9.90	3.22	6.68	2.23	-	-	-	-
	d	93.80	6.20	13.62	86.38	56.04	10.03	1.28	9.51	7.46	-	0.51	-	1.54
	e	80.71	19.29	21.38	78.62	55.11	8.99	0.47	9.26	2.61	-	-	-	1.19
	f	67.24	32.76	36.02	63.98	44.54	11.27	2.62	8.85	1.10	-	-	-	0.60
44	a	99.24	0.76	4.65	95.35	74.42	13.95	4.95	-	-	-	-	-	2.33
	b	98.36	1.64	3.28	96.72	72.13	18.03	1.64	-	3.28	-	-	-	1.64
	c	95.12	4.88	1.98	98.02	74.21	18.25	1.19	1.98	1.19	0.39	-	-	0.79
	d	89.48	10.52	6.49	93.51	64.26	18.09	2.17	6.14	1.08	-	-	0.36	1.44
	e	95.54	4.46	15.91	84.09	54.16	17.81	1.66	6.65	1.90	-	0.95	-	0.95
	f	94.88	5.12	8.89	91.11	60.63	20.95	0.32	5.71	-	-	1.91	-	1.59

b) VEMBANAD ESTUARY

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
49	c	98.61	1.39	9.69	90.31	63.87	9.69	-	11.45	3.52	-	-	-	-
	d	99.25	0.75	15.69	84.31	63.37	10.46	-	4.65	6.97	-	0.58	-	1.76
	e	98.93	1.07	6.32	93.68	64.68	17.31	2.57	5.74	-	-	-	-	2.79
	f	99.00	1.00	-	-	-	-	-	-	-	-	-	-	3.05
52	c	96.43	3.57	18.18	81.82	15.45	5.91	-	57.27	0.45	-	1.36	0.45	0.91
	d	95.06	4.94	27.41	72.59	19.31	4.63	-	44.79	1.16	-	0.38	1.16	1.16
	e	89.68	10.32	25.07	74.93	39.94	7.16	-	25.62	0.55	0.27	0.83	0.27	0.55
54	b	97.74	2.26	4.86	95.14	68.06	11.81	0.69	9.03	4.17	-	-	-	2.08
	c	97.26	2.74	4.40	95.60	62.26	20.13	-	8.81	3.14	-	-	-	1.25
	d	94.62	5.38	3.93	96.07	65.73	15.73	-	12.36	1.12	-	-	-	1.12
	e	95.57	4.43	2.47	97.53	75.58	7.41	1.23	9.88	1.23	-	-	-	2.20
	f	94.47	5.53	2.21	97.79	62.83	21.24	-	10.62	0.88	-	0.88	-	1.33
58	c	99.08	0.92	4.88	95.12	43.90	9.76	2.44	39.02	-	-	-	-	2.44
	d	98.92	1.08	9.31	90.69	38.23	9.31	-	33.82	5.88	0.98	0.98	-	1.47
	e	98.79	1.21	7.96	92.04	33.56	5.19	-	48.44	2.08	-	2.08	-	0.69
	f	94.01	5.99	28.38	71.62	27.03	6.31	-	36.04	0.90	0.45	-	0.45	0.45
64	c	99.83	0.17	7.77	92.23	9.71	1.94	-	78.64	-	-	-	-	1.94
	d	94.33	5.60	60.97	39.03	1.04	0.35	-	36.59	0.35	-	0.35	-	0.35
	e	85.66	14.34	67.03	32.97	3.78	1.62	-	24.86	0.54	-	0.54	-	1.08
	f	85.41	14.59	49.81	50.19	14.56	3.45	-	27.97	-	0.77	1.92	-	1.53
67	c	99.29	0.70	13.60	86.40	10.00	8.18	1.82	63.64	-	-	-	-	2.73
	d	97.37	2.63	37.28	62.72	6.51	2.37	1.78	50.29	-	-	0.59	-	1.18
	e	81.30	19.70	61.11	38.89	5.98	3.42	-	28.63	-	-	0.85	-	-
	f	74.26	25.74	57.01	42.99	9.95	3.17	0.45	25.79	-	-	1.81	0.91	0.91
78	c	99.44	0.66	2.47	97.53	75.58	7.41	1.23	9.88	1.23	-	-	-	2.20
	d	95.57	4.43	2.21	97.79	62.83	21.24	-	10.62	0.88	-	0.88	-	1.33
	e	95.25	4.75	4.49	95.51	57.55	16.33	-	17.55	1.22	-	0.82	0.41	1.63
	f	90.48	9.52	24.04	75.96	36.47	13.65	0.59	21.66	0.59	0.59	0.89	0.29	1.21
75	c	97.01	2.99	1.65	98.35	68.59	15.70	1.65	10.74	-	-	-	-	1.65
	d	96.48	3.52	24.65	75.35	42.61	9.86	0.35	20.42	-	-	-	-	2.11
	e	92.56	7.44	16.49	83.51	55.33	7.56	-	17.87	1.03	-	0.68	0.34	0.68
	f	89.05	10.95	15.38	84.62	54.19	8.04	-	19.93	1.05	0.35	1.05	-	1.39

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
74		c	99.56	0.44	6.31	93.69	54.05	24.32	2.70	3.60	-	-	-	-	-
		d	98.35	1.65	10.69	89.31	59.94	17.56	5.34	6.11	-	-	-	-	0.76
		e	91.53	8.47	23.43	76.57	37.76	18.53	-	17.48	-	-	1.75	-	1.05
		f	91.57	8.43	11.65	88.35	45.63	22.33	-	13.59	-	-	2.91	-	3.88
80		c	84.51	15.49	64.28	35.72	21.43	7.14	-	7.14	-	-	-	-	-
		d	98.85	1.15	13.73	86.27	44.71	13.73	-	23.53	2.35	1.18	-	-	0.78
		e	98.55	1.50	8.89	91.11	50.85	12.71	0.85	25.00	-	0.42	-	0.42	0.85
		f	94.42	5.58	17.23	82.77	41.85	10.15	-	27.69	-	-	0.92	0.62	1.54
76		c	99.50	0.50	5.63	94.37	54.37	11.25	-	25.63	1.25	-	1.87	-	-
		d	95.98	4.02	17.71	82.29	5.90	5.90	0.74	48.04	-	0.37	0.74	-	1.47
		e	72.84	27.16	26.57	73.43	23.19	5.79	0.48	41.55	0.97	-	0.97	-	0.48
		f	55.33	44.67	54.00	46.00	15.14	3.14	0.57	20.28	0.86	1.71	2.86	-	1.43
86		c	99.02	0.98	5.23	94.77	59.30	12.21	1.16	21.51	0.58	-	-	-	-
		d	92.09	7.91	21.88	78.12	39.29	8.04	0.45	28.57	-	-	0.89	-	0.89
		e	80.13	19.87	48.66	51.34	16.96	3.57	0.89	26.78	0.45	-	1.34	0.45	0.89
		f	93.81	6.19	39.15	60.85	24.26	6.81	0.85	24.68	-	0.42	-	0.42	1.27
85		c	98.82	1.18	7.41	92.59	55.56	14.41	-	14.41	3.70	3.70	-	-	-
		d	98.22	1.78	3.59	96.41	53.78	17.93	-	22.31	0.39	0.79	0.39	-	0.79
		e	90.95	9.05	4.69	95.31	59.57	17.33	-	15.88	0.72	-	-	-	1.80
		f	70.47	29.53	12.95	87.05	55.04	12.23	1.08	16.91	0.72	-	0.36	0.72	0.72

a = 0.50 - 0.35 mm (+45 mesh)    b = 0.35 - 0.25 mm (+60 mesh)    c = 0.25 - 0.18 mm (+80 mesh)  
d = 0.18 - 0.125 mm (+120 mesh)    e = 0.125 - 0.088 mm (+170 mesh)    f = 0.088 - 0.063 mm (+230 mesh)

LMS = Light minerals    Non-Op = Non-Opaque

HMS = Heavy minerals    Op = Opaque

Ga = Garnet    Zl = Zircon    Bi = Biotite    Am = Amphibole    Py = Pyroxene

Si = Sillimanite    Al = Altered    Ru = Rutile    Mo = Monazite

channel.

From Fig. 18A it is evident that the medium and fine heavy sand fractions show an almost similar variation downstream. The frequency distribution of sands in the six size fractions selected for heavy mineral separation and the heavy percentage in the respective fractions (for some selected samples) are plotted after applying normalization procedure to make it to a sum total of hundred. The curves (Fig. 20) depict distinct variations of both size frequency and heavy mineral content with the former registering decreased values towards finer ends. A marked inverse relationship is exhibited by the heavy mineral curves with the size frequency curves indicating their abundance in the finer size grades.

The heavy mineral content in the fine sand fraction of the estuary (Fig. 18B) does not show any marked variation along its profile, whereas the heavies of the very fine sand fraction exhibit an increase towards the estuarine mouth. Further, the content of heavies in the very fine sand fraction is several folds higher than that of the fine sand fraction. The behaviour of the size frequency curves with heavy mineral curves is similar to that observed in river environment (Fig. 21).

**Causes of total heavy mineral variation:** The salient features observed from the variation of total heavy minerals in the river sediments are: (1) the upstream area, especially the two tributaries (Thodupuzha and Kaliyar), registers significantly high amount of total heavies and further, the content of total heavies, in general, shows a progressive decrease downstream; and (2) there is a gradual enrichment of heavy minerals with fining size. Pollack (1961) observed a similar variation of total heavies in the South Canadian rivers and he explained this phenomenon on the basis of hydraulic equivalent concept proposed by Rubey (1933). Rubey's hypothesis states that the grains of different

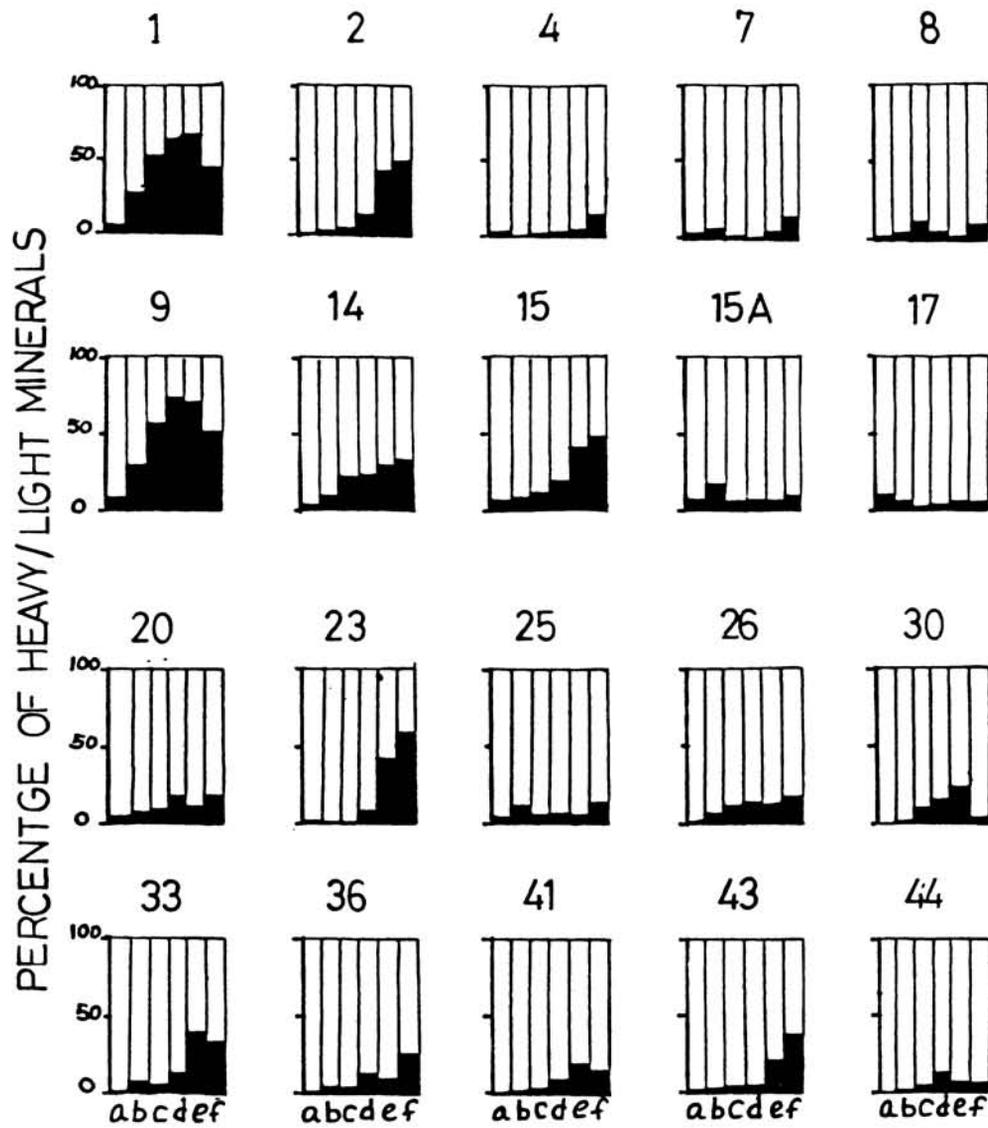


Fig. 16 Distribution of heavy(●)and light(□)minerals in various size grades of Muvattupuzha river sands (Symbols are similar to that of Table 6)

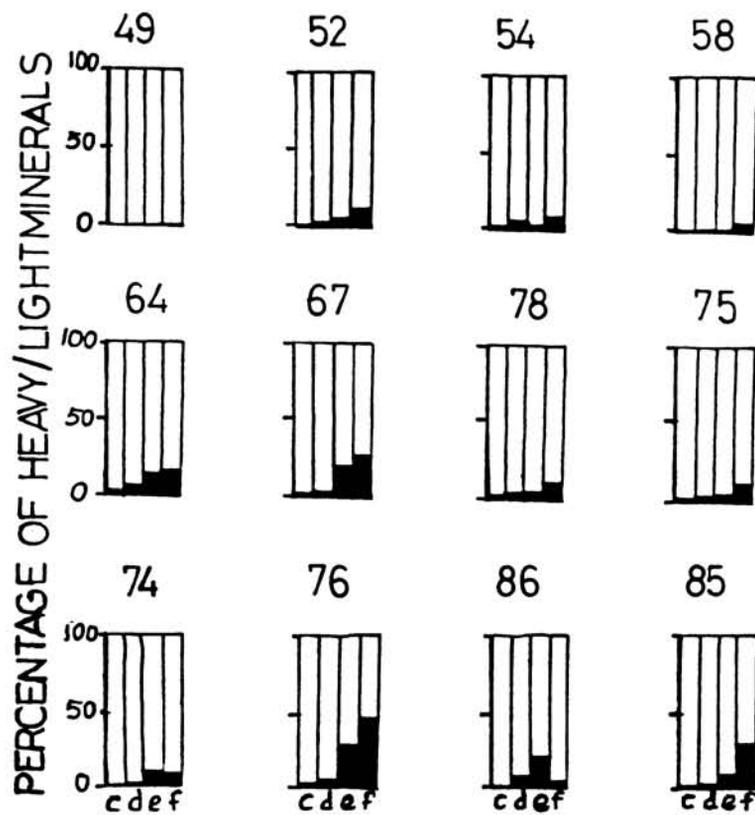


Fig. 17 Distribution of heavy and light mineral in various size grades of Central Vembanad estuary (Symbols are similar to that of Table 6)

densities if deposited together should have the same settling velocities or the denser minerals should be smaller by an amount predictable on the basis of settling velocity equation. Based on theoretical observation he also emphasized that the grain size distribution of heavy minerals would be displaced towards the finer size grades with respect to the mineral quartz. However, subsequent investigations by a number of other researchers show that the heavy and light minerals in natural sands and sandstones are seldom in hydraulic equilibrium (Briggs, 1965; Lowright et al. 1972 and Stingerland, 1977). Thus, the working hypothesis proposed by Rubey is considered to be somewhat imperfect. Hand (1964) also observed the non-hydraulic equilibrium conditions in modern sands and explained the heavy and light mineral variations primarily on the basis of selective sorting. White and Williams (1967) have found that the heavy minerals once deposited are less easily entrained and transported by currents than grains of light minerals of the same size and shape. Therefore, heavies moving by saltation with lights would tend to be smaller than the predicted size by settling velocity equation. The heavies are further shielded from currents by larger quartz grains and thus remain behind while larger quartz grains are moved.

The upstream regions of the Muvattupuzha river system (i.e. the tributaries) are characterised by a high gradient geomorphological setup (Fig. 3) which favours higher flow velocity particularly during monsoon season. This is evidently attested by the granulometric investigation (Chapter 3) with an abundance of coarser fractions (pebbles and granules) in the upstream as channel lags. The observed enrichment of total heavies in this part is in consonance with the high energy based transportation pattern by depositing simultaneously the coarser (lighter) and heavier grains in the upstream. Consequent upon the drop in the gradient of the river profile when it enters in mid and low lands, the heavies register a depletion in percentage in sediments.

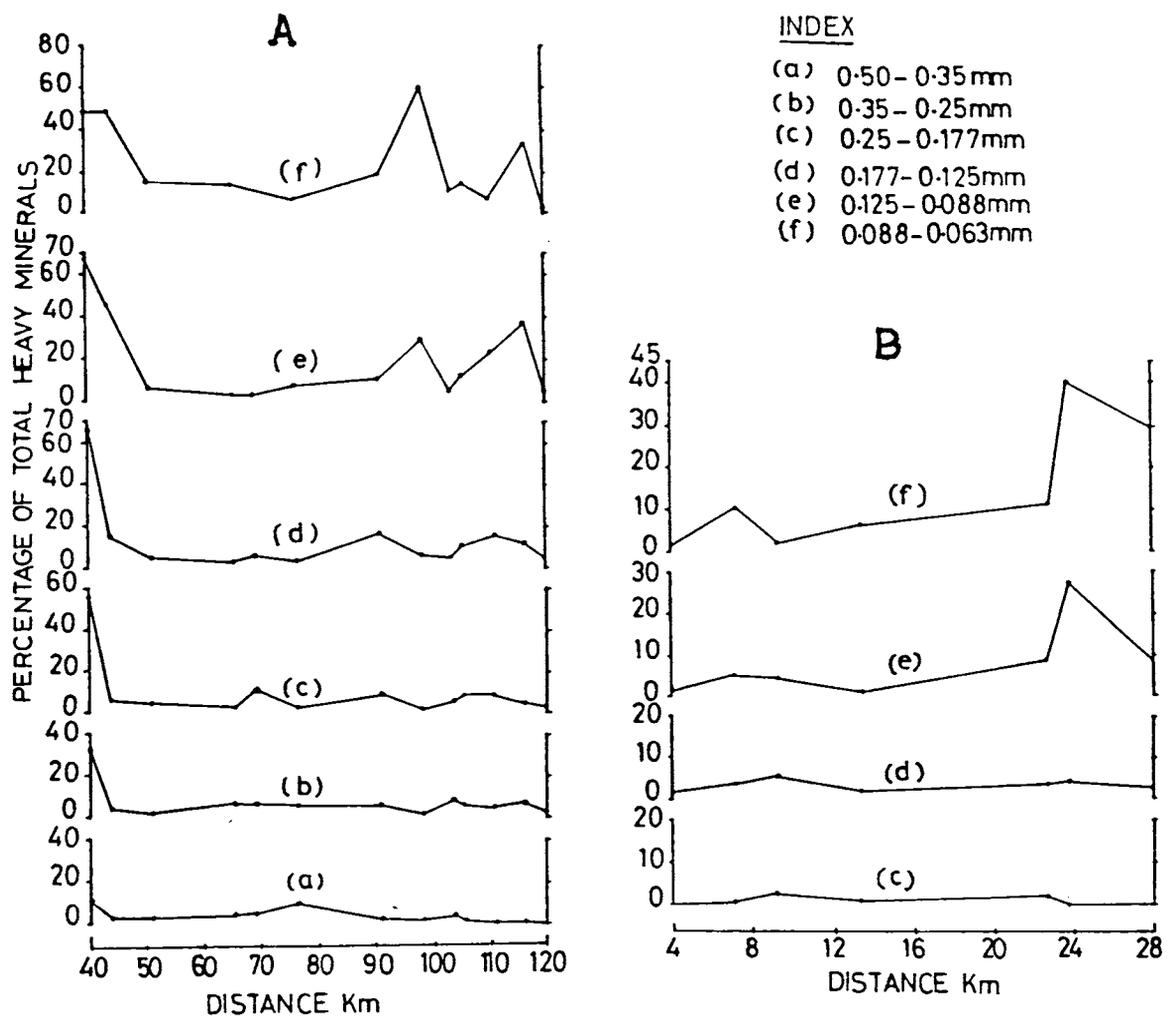


Fig. 18 Downstream variation of total heavy minerals in various size fractions of riverine (A) and estuarine (B) sands

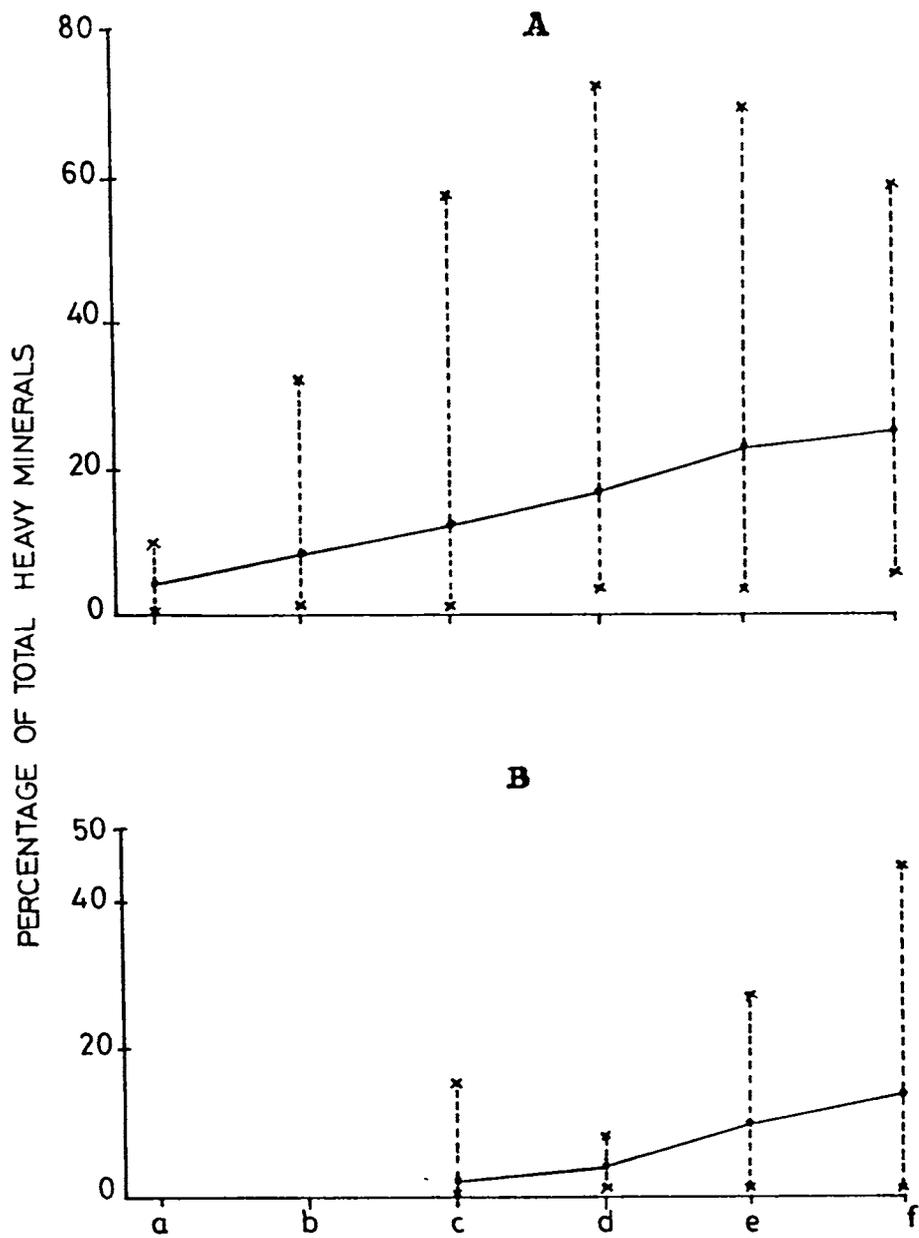


Fig. 19 Granulometric variation of total heavy minerals in the sand fractions of Muvattupuzha river (A) and Central Vembanad estuary (B): a 0.50-0.35 mm, b 0.35-0.25 mm, c 0.25-0.177 mm, d 0.177-0.125 mm, e 0.125-0.088 mm, f 0.088-0.063 mm; x = range

Selective sorting of the heavies based on their size, shape and density plays a pivotal role in their entrainment and transportation resulting in their progressive enrichment with fining size. Studies made by Komar et al. (1989) also re-affirmed the general impression that selective sorting process significantly effects the heavy mineral composition in sediments. Apart from this, certain amount of variation can be brought about by the inability of the low energy currents to entrain the heavies after its deposition and also by the shielding action of coarser light minerals which prevents further movements of heavies (White and Williams, 1967).

The minor fluctuations observed in the heavy mineral contents downstream might be due to the local turbulences resulted from natural and man made obstacles - a feature also reported earlier from the Rio-Grande river of South Western Texas by Shideler and Flores (1980). The locally increased heavy mineral content at stations 23 and 33 (the stations are located slightly downstream of the bridges) can be explained by the presence of bridges (Piravam and Vettukkattumukku bridges) constructed across the river. The flow pattern undergoes considerable changes due to the presence of intervening pillars of the bridges. The jetting of water through the gaps creates local turbulences which inturn cause the flushing away of lighter grains and favour concentration of the heavier and coarser lighter grains. The variations observed at other stations are presumably resulted from similar effects due to natural turbulences.

In the estuary, the content of total heavies is slightly lower when compared to the river environment. But the heavy mineral modes are displaced towards the finer fractions particularly in sandy sediments (Fig. 21). Heavy mineral content of the sand fraction separated out from muddy samples deviates considerably from the above said granulometric relation. This is due to inefficiency of sorting processes owing to the cohesive nature of the mud. Further, the low energy conditions

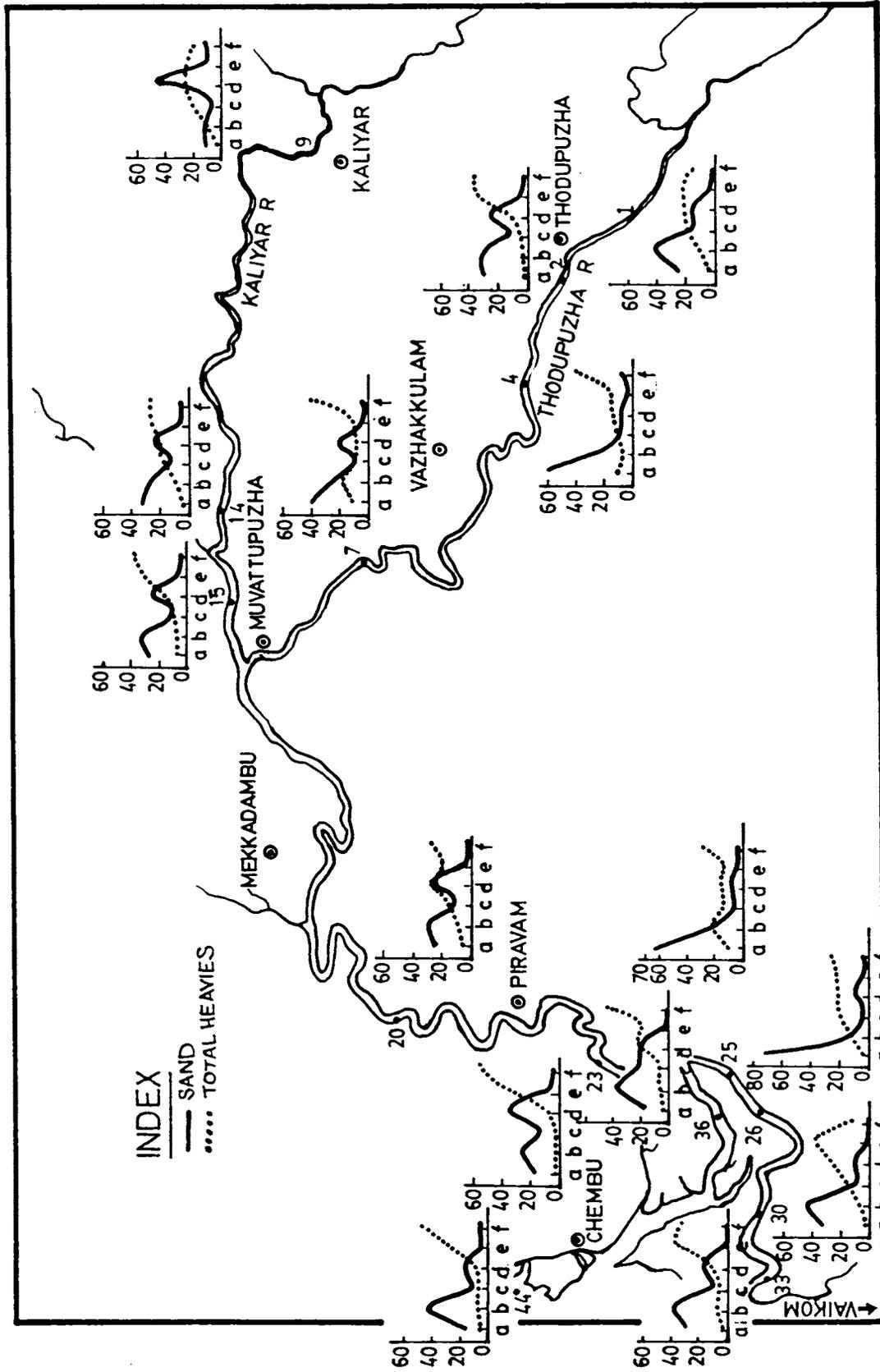


Fig. 20 Normalized frequency distribution of sand and total heavies in the sediments of Muvattupuzha river. X axis : heavy content/sand content; Y axis : a +45, b +60, c + 80, d + 120, e + 170 and f +230 mesh sizes

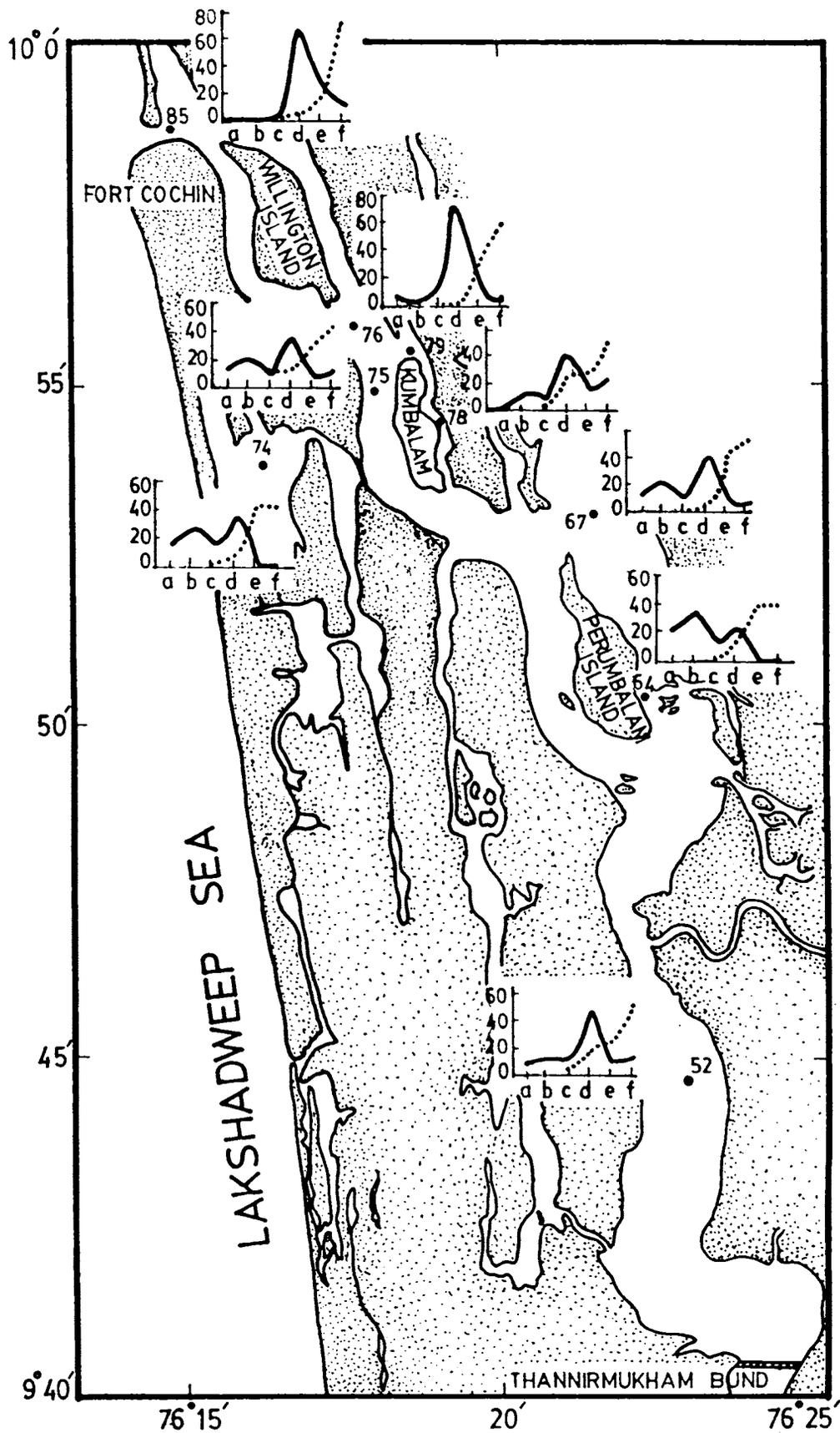


Fig. 21 Normalized frequency distribution of sand and total heavies in the sediments of Central Vembanad estuary (Explanations are similar to that of Fig. 20)

prevailing in these zones are not sufficient for sorting processes. The high content of total heavies towards the estuarine mouth is presumably attributed to the tidal currents.

**Heavy mineral assemblage:** The heavy mineral suite of the Muvattupuzha riverine and the Central Vembanad estuarine sands contains a wide spectrum of minerals. The various minerals identified with their characteristic features are described below.

(a) **Opagues:** Opagues are abundant in all size grades (Table 6). The average concentrations of opagues in medium, fine and very fine sand fractions of the Muvattupuzha river are 10.13%, 20.35% and 26.68% respectively. In the estuary the contents of opagues in fine and very fine sands are 12.79% and 25.31%. The content of opagues in the riverine and estuarine sands shows considerable variation with distance in all the size grades. The variability is antipathetic to that of the comparatively lighter heavy minerals like amphiboles and pyroxenes (Figs. 22a-c; 23a,b). The opaque minerals are subrounded to well rounded (Plate 7a,b) and are progressively enriched in finer grades (Figs. 24a,b; 25). Opaque minerals studied under reflected light show that ilmenite (Plate 3) constitutes a major part of the opagues population. Some of the ilmenite grains are altered to leucoxene. Apart from ilmenite, minor amount of magnetite and hematite are also present in the opaque population.

(b) **Amphiboles:** The most abundant heavy mineral group in the riverine and estuarine sands is the amphiboles. It constitutes more than 50% of the total heavies (Fig. 25). The content of amphiboles shows 2-3 and 3-4 fold enrichments than pyroxenes in riverine and estuarine environments. Hornblende is the dominant amphibole mineral identified in the study area. Apart from hornblende, traces of tremolite/actinolite are also present. Hornblende shows brown, green or bluishgreen colour and prismatic nature (Plates 8a,b; 9a,b). In the coarser grades many

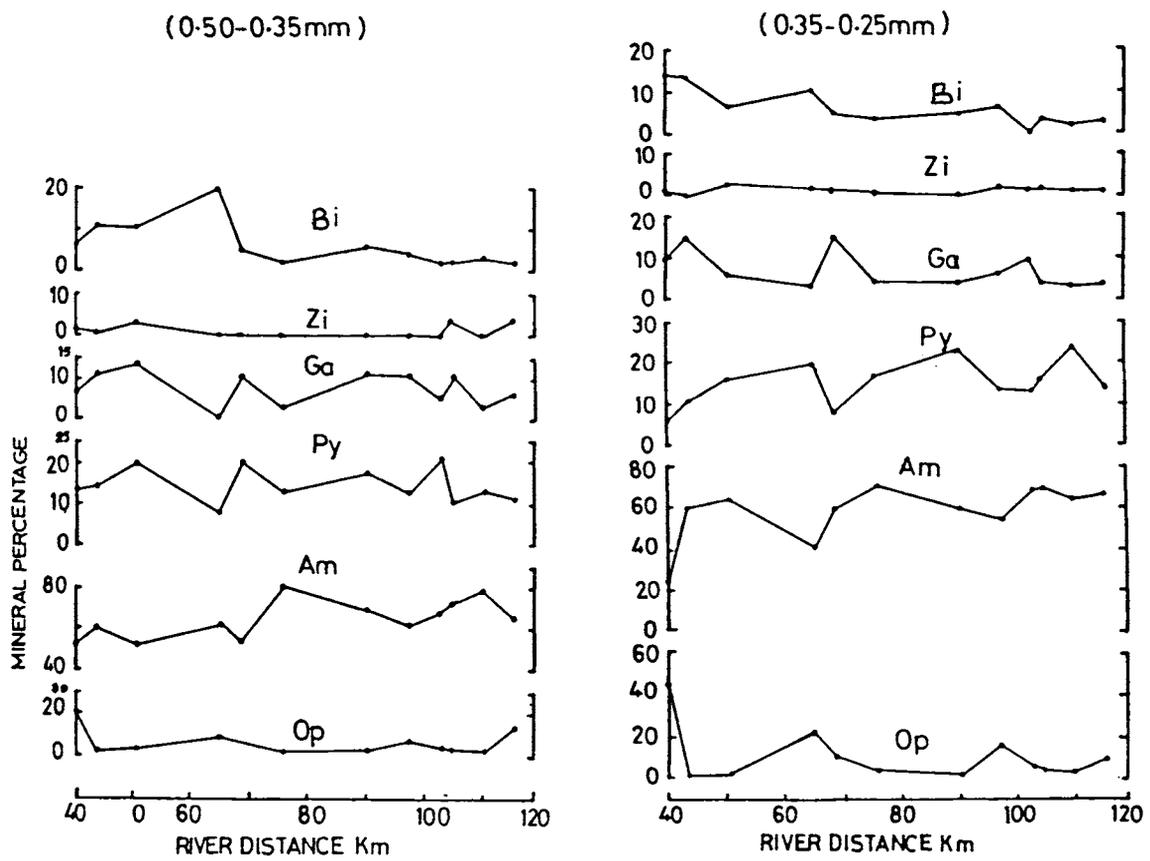


Fig. 22a Downstream variation of heavy minerals in two size fractions (0.50-0.35 mm and 0.35-0.25 mm) of river sands (symbols are same as that of Table 6)

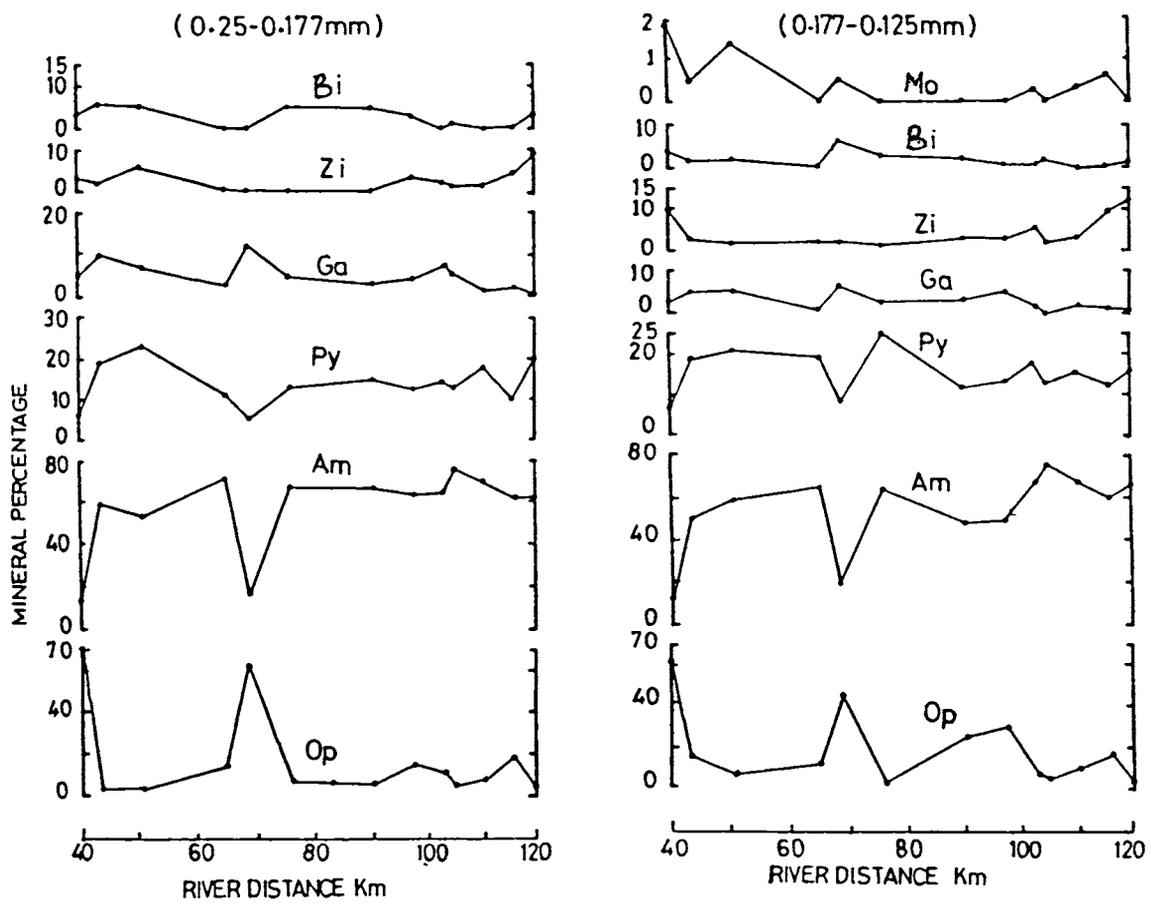


Fig.22b Downstream variation of heavy minerals in two size fractions (0.25-0.177 mm and 0.177-0.125 mm) of river sands (symbols are same as that of Table 6)

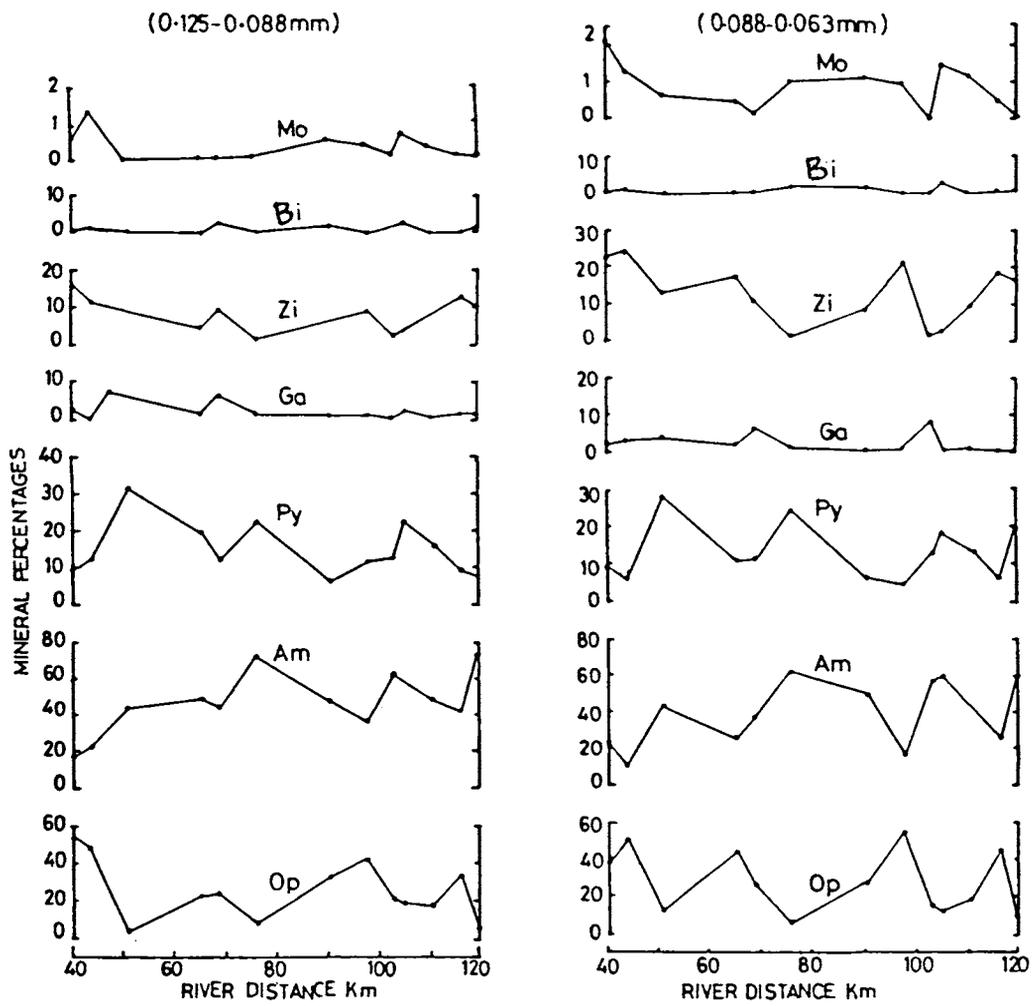


Fig.22c Downstream variation of heavy minerals in two size fractions (0.125-0.088 mm and 0.088-0.063 mm) of river sands (symbols are same as that of Table 6)

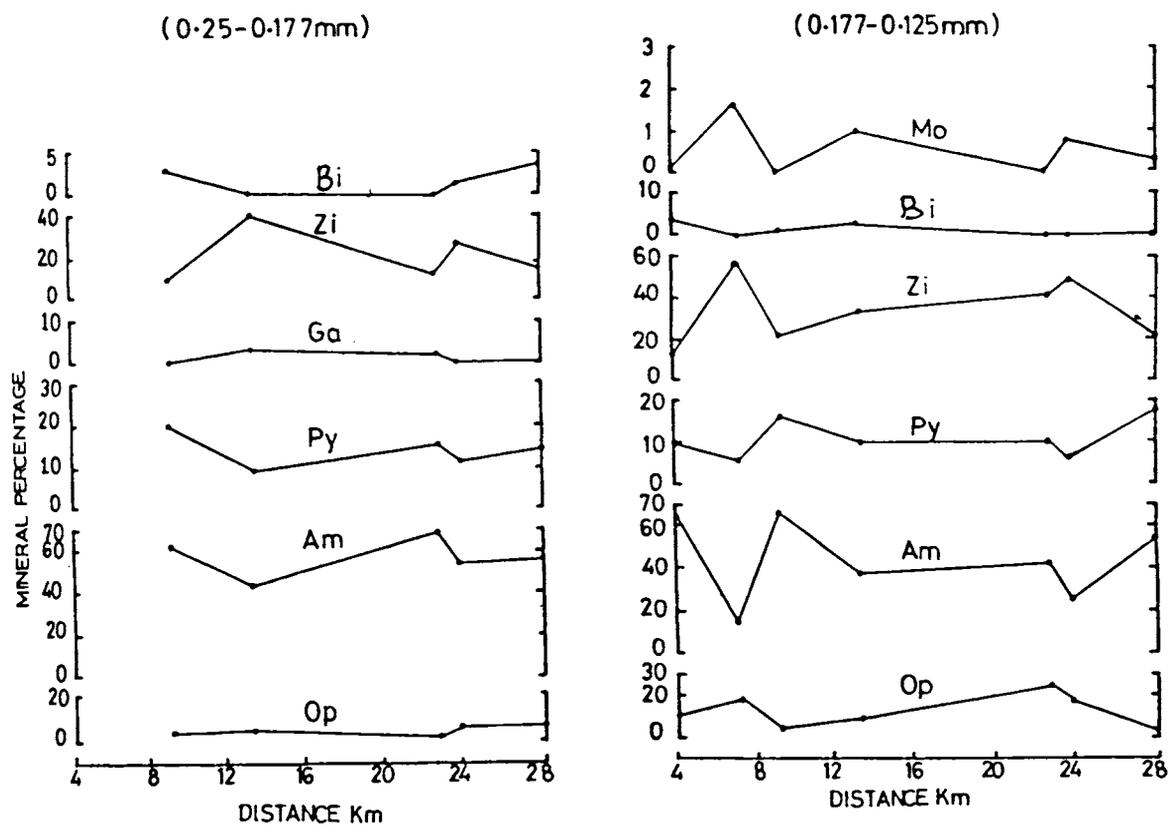


Fig.23a Variation of heavy minerals in two size fractions (0.25-0.177 mm and 0.177-0.125 mm) of estuarine sands with distance (symbols are same as that of Table 6)

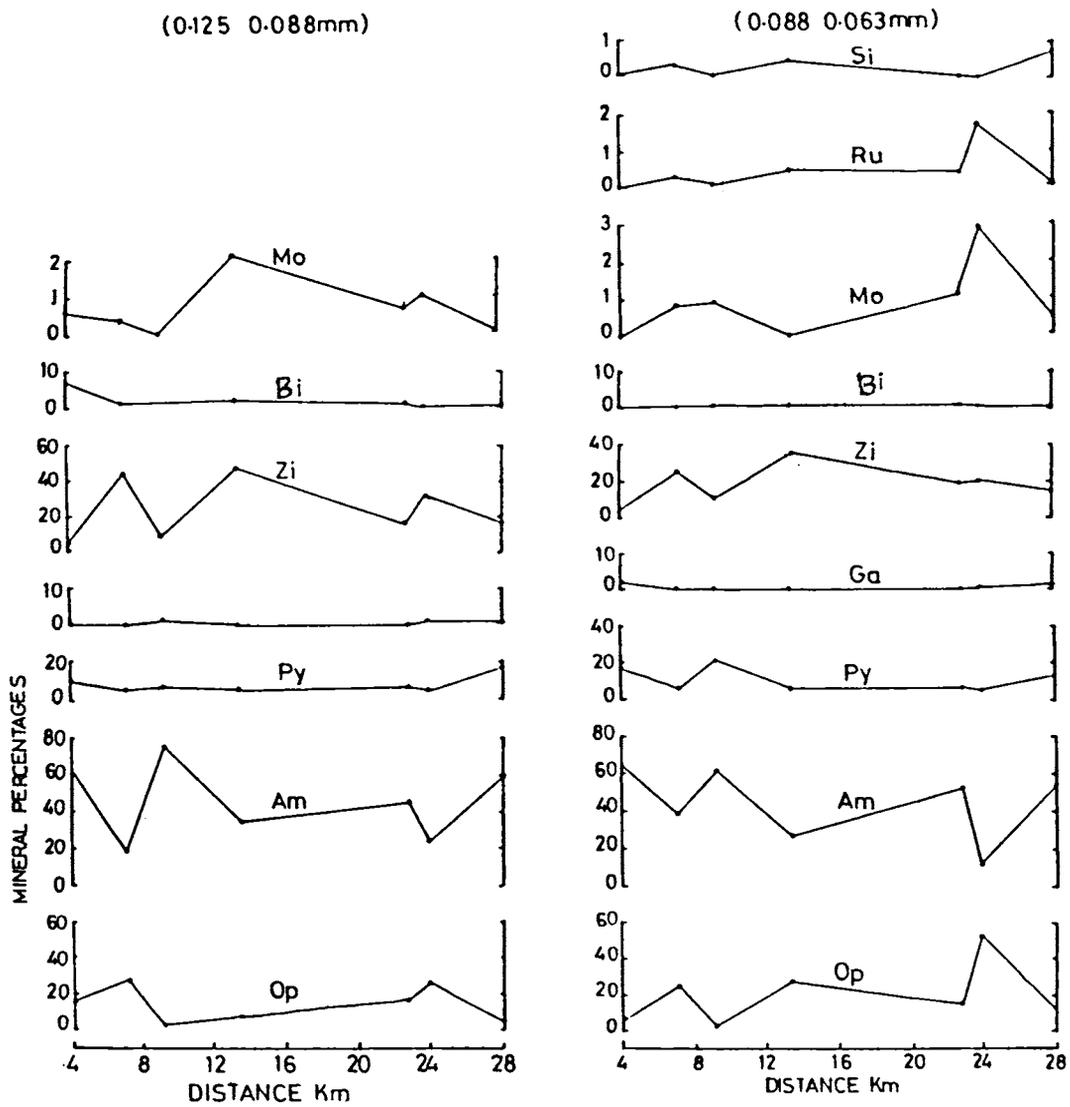


Fig.23b Variation of heavy minerals in two size fractions with distance (0.125-0.088 mm and 0.088-0.063 mm) of estuarine sands (symbols are same as that of Table 6)

of them appear to be opaque but are translucent at the edges. In the river, the content of amphiboles slightly increases downstream while it slightly decreases in the estuary towards the mouth. Kumbalam east channel shows an enhanced level of this mineral than other regions of the estuary. A distinct fall in the content of amphiboles is observed in samples 52, 64 and 67 where zircon dominates in the total heavy residue. A substantial decrease in the concentration of amphiboles from coarse to fine size grades (Figs. 24a, b; 25) is also observed.

(c) **Pyroxenes:** Hypersthene is the principal pyroxene mineral identified in the Muvattupuzha riverine and the Central Vembanad estuarine sands (Plates 10a, b; 11a, b). It occurs as irregular grains and exhibits marked pleochroism. Apart from hypersthene, augite and diopside are also recorded in traces. Average concentration of pyroxenes does not exhibit much variation in different size grades (Fig. 24a,b and 25). The respective ranges of pyroxenes in medium, fine and very fine sands of the river environment are from 6.16 to 24.36%, 5.47 to 25.33% and 4.07 to 31.28%. In estuarine environment the content of pyroxenes in fine and very fine sand fractions ranges from 1.94 to 24.32% and 1.62 to 22.33% respectively.

(d) **Garnet:** The average contents of garnet in medium, fine and very fine sands of the river environment are 6.54%, 3.62% and 2.16% respectively. In estuary, the content of garnet is substantially lower with an average of 0.70% and 0.37% in fine and very fine sand fractions. Garnet is subrounded, pinkish to colourless and often with conchoidal fracture. Pink garnet dominates in the river (Plate 12a) whereas colourless ones dominate in the estuary (Plate 12b). In general, garnet content progressively decreases downstream in all the size grades (Figs. 22a-c). It is also found that the content of garnet shows a steady decrease from coarser grade to finer (Figs. 24a,b). Further, the mineral is abundant in the +45 and +60 meshes (i.e. medium sand) than other lower size grades (Table 6). Among the tributaries, Thodupuzha

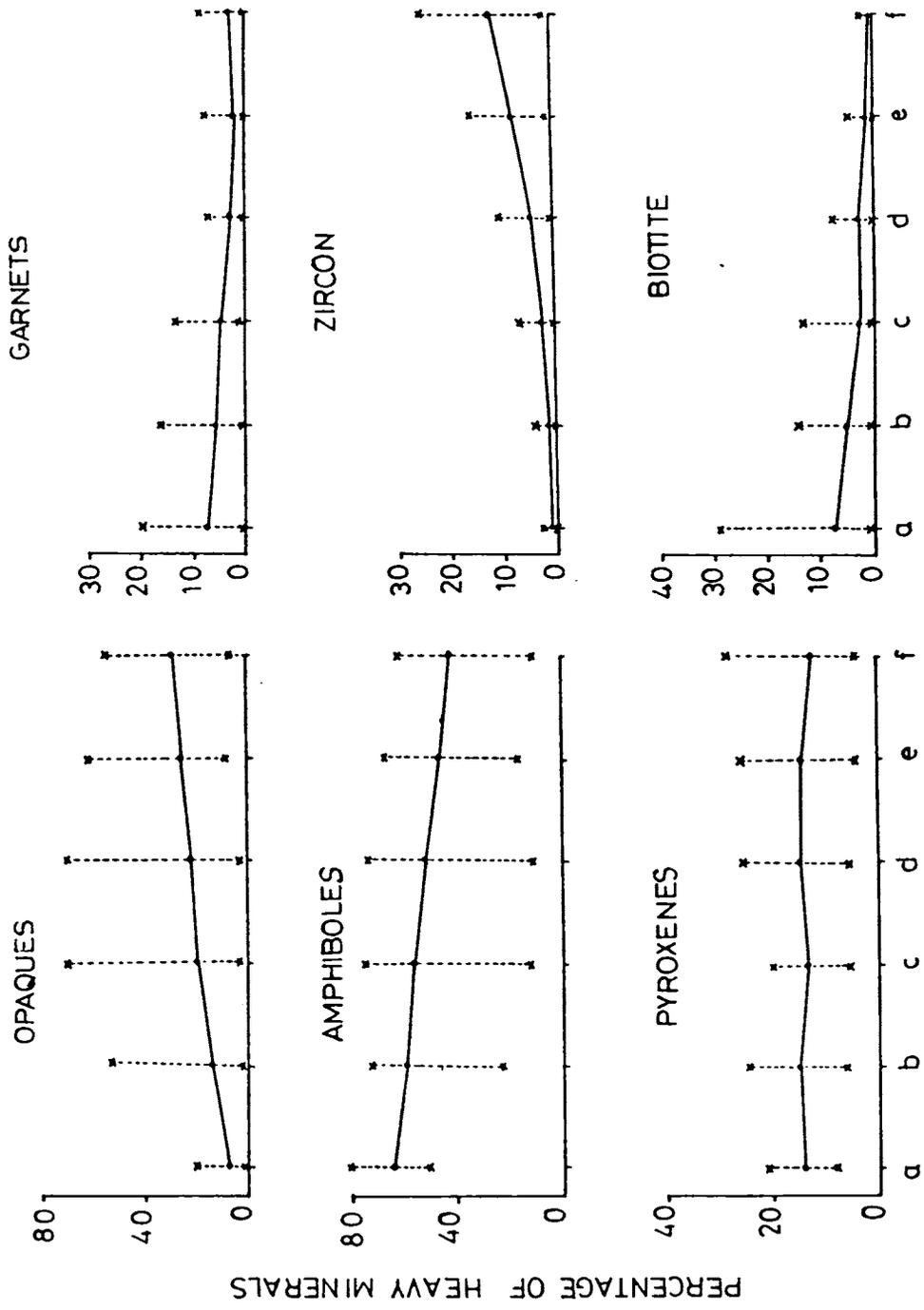


Fig.24a Granulometric variation of heavy minerals in the sand fractions of Muvattupuzha river; a 0.50-0.35 mm, b 0.35-0.25 mm, c 0.25-0.177 mm, d 0.177-0.125 mm, e 0.125-0.088 mm and f 0.088-0.063 mm;  $\uparrow$  = range  $\downarrow$  = range

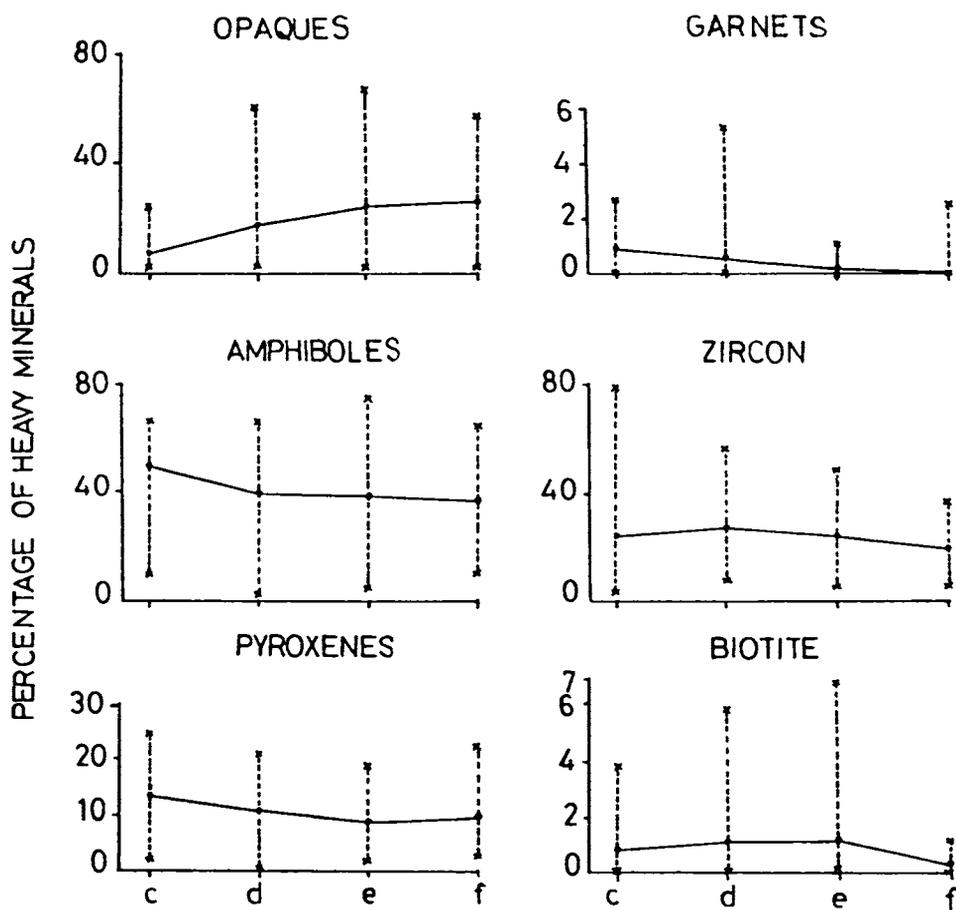


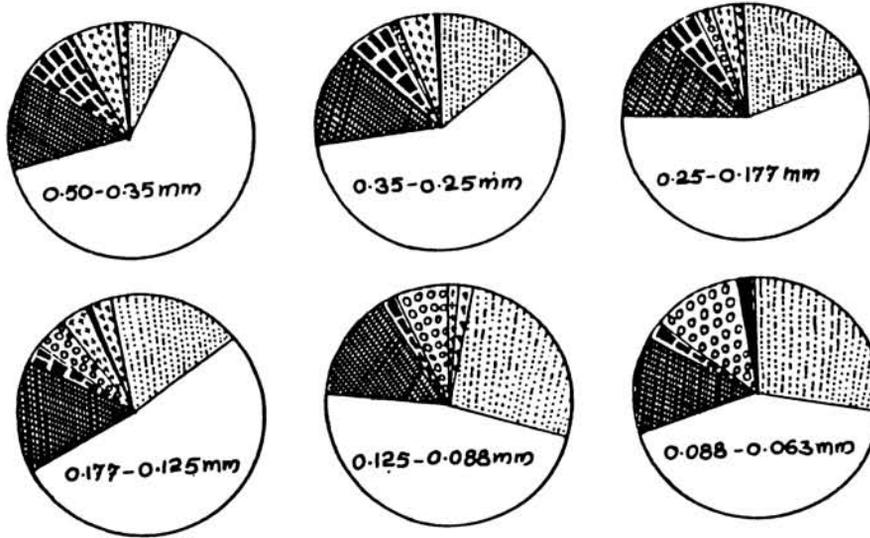
Fig.24b Granulometric variation of heavy minerals in the sand fractions of Central Vembanad estuary; c 0.25-0.177 mm, d 0.177-0.125 mm, e 0.125-0.088 mm and f 0.088-0.063 mm;  $\ast$  = range

registers higher concentration of garnet than the Kaliyar.

(e) **Zircon:** Although zircon is one of the important components of the heavy mineral residue of this study, it is found missing in some of the coarser fractions. In estuary, zircon is widely distributed and in some stations (Samples 52, 64 and 67), it predominates over the other minerals (Table 6). Average concentration of zircon in medium, fine and very fine sand fractions of the river environment are 0.85%, 3.39% and 9.85% respectively. In the estuary the average contents of zircon in the fine and very fine sand fractions are several fold higher than that in the river (fine sand 26.74%; very fine sand 23.07%). The variations of zircon along the profile of river and estuary are shown in Figs. 22(a-c) and 23 (a,b). Mainly two varieties of zircon are noticed in the study area. The riverine zircons are elongate (length 200-250  $\mu\text{m}$ ; breadth 60  $\mu\text{m}$ ) and prismatic with pyramidal terminations (Plates 4a,b; 13a) some of them are found to be broken and with inclusions (Plates 6a, 14a, b). Under plane polarised light, riverine zircon shows cloudy appearance. Contrary to the river, majority of the estuarine zircons are subrounded to rounded (length 300  $\mu\text{m}$  and breadth 170  $\mu\text{m}$ ) and exhibit marked zoning (Plates 5a, b; 13b; 15a). Scanning electron microscopic study of the estuarine zircon shows wide variety of surface textures indicative of abrasion and chemical alteration (Plates 5a, b) to which the grains are subjected. The average zircon content in the various size grades shows a progressive enrichment from coarse to fine size grades particularly in the river environment, though this type of variation is not so pronounced in the estuary.

(f) **Biotite:** Biotite occurs commonly as flaky and appears brownish under plane polarised light. They also show strong pleochroism. The variation of biotite in riverine and estuarine sands are depicted in Figs. 22(a-c) and 23 (a,b).

### MUVATTUPUZHA RIVER



### VEMBANAD ESTUARY

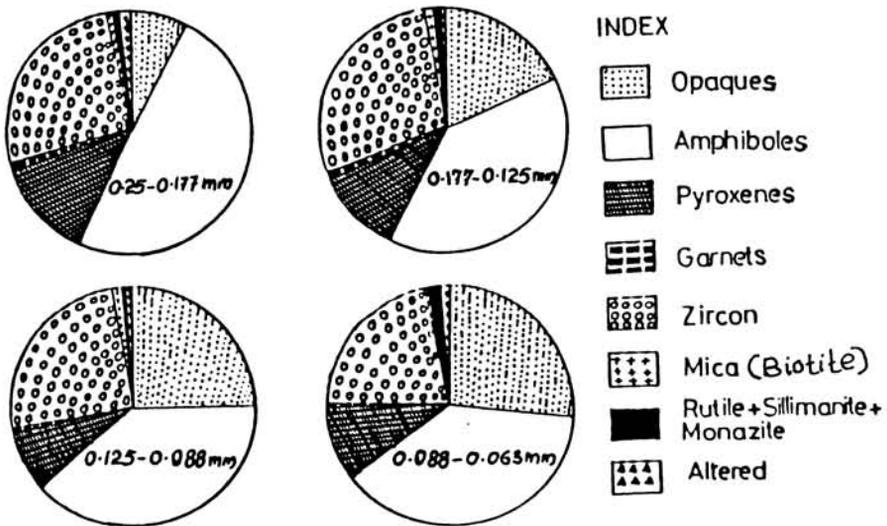


Fig. 25 Average concentration of heavy minerals in various size fractions of riverine and estuarine sands.

(g) **Monazite, Rutile and Sillimanite:** These minerals are present only in smaller amounts (less than 2% of the total heavies). Monazite grains are rounded to subrounded with honey yellow colour under plane polarised light (Plate 15b). They also show high relief and distinct borders. The mineral rutile is rounded to subrounded in shape and also shows blood-red colour under plane polarised light. Rutile exhibits high refractive index and straight extinction. Sillimanite is slender, prismatic (Plate 6b, 16a,b) and colourless under plane polarised light. They show high relief, straight extinction, moderate birefringence and biaxial positive optical characteristics.

(h) **Altered minerals:** In this category, minerals which could not be confirmed because of their highly altered appearances are included. Majority of the altered minerals appear to be hypersthene, hornblende and biotite based on their shapes and colours.

**Causes of mineralogical diversities observed in the study area:** The heavy mineral assemblage of the Muvattupuzha riverine and the Central Vembanad estuarine sands consists predominantly of opaques, amphiboles, pyroxenes, garnet, biotite and zircon. Monazite, rutile and sillimanite are present only in minor quantities and are mainly present in finer size grades of estuarine sands. Among the major minerals of the river environment, opaques, garnet and zircon are found to be decreasing downstream while amphiboles and pyroxenes increase. Biotite contents in the coarse grades (0.50 mm - 0.125 mm) show a decreasing trend downstream while the contents in the fine grades (0.125 mm - 0.063 mm) do not show any variation.

The overall mineralogical diversities observed along the profile of the Muvattupuzha river sands could be explained mainly by progressive sorting based on densities of the minerals. During deposition, the denser minerals such as opaques (Sp. Gr. of ilmenite = 4.7), garnet (4.3) and zircon (Sp. Gr. 4.6) settle quickly at the point

of current impingements owing to its greater settling velocities; while the less denser amphiboles (Sp. Gr. of hornblende = 3.21) and pyroxenes (Sp. Gr. of hypersthene = 3.43) are transported still further downstream. Moreover, the high competency of the river water does not allow the free settling of amphiboles and pyroxenes in the upstream, and as a result, these minerals will be flushed farther downstream and deposited. Therefore, opaques, garnet and zircon remain upstream owing to its higher specific gravities. Monazite, though confined only to the finer fractions, also follows opaques in its concentration behaviour downstream. This again supplement the role of progressive sorting based on density in the segregation of minerals in the Muvattupuzha river system. Earlier reports have pointed out that denser minerals once deposited will not be entrained as easily as the lighter heavy minerals like hornblende and hypersthene (Seralathan, 1979; Lewis, 1984 and Kundras, 1987).

From Figs. 22(a-c) and 23(a,b) it is evident that the locations showing positive anomalies of denser heavy minerals in each size fractions coincide with negative anomalies of lighter heavy minerals. Moreover, the maximal values of amphiboles and pyroxenes are found to be shifted slightly downstream with respect to that of the opaque and other denser minerals. All these clearly indicate the role of progressive sorting based on density in differentiating the heavy minerals downstream. High content of denser heavy minerals at stations 8, 9, 23 and 33 is attributed to the local hydraulic conditions owing to the presence of bridges slightly upstream of these stations. While working on the lower Rio-Grande river of south western Texas, Shideler and Flores (1980) also observed a similar type of enrichment of denser heavy minerals immediately below bridges and spillways. The anomalous increase of denser heavy minerals at station 1 is due to the natural turbulence resulted from the presence of rock exposures in the stream channel and also they are not diluted by lighter quartz/feldspar grains of sand size grade.

Many investigators (Pollack, 1961; Briggs et al., 1962; Shideler, 1975 and Flores and Shideler, 1978) opined that progressive sorting based on shape of heavy minerals also plays a significant role in the differentiation of heavy minerals. During the progressive decrease in the competency of the river, most of the medium to fine sand particles are being transported in suspension (graded suspension as per CM pattern; Fig. 14) and they do not settle at the same place. Assuming that all factors including the size of the grains are constant, the settling rates of different heavy minerals would depend not only on their densities but also on their shapes. When particles of the same volumes and densities having different shapes are allowed to settle through a column of liquid, the particles with greatest sphericity will have the highest settling velocity (Pettijohn, 1957 and Blatt et al., 1972). This may also attribute some role in the observed diversity of heavy mineral assemblage in the Muvattupuzha river. Since opaques are more spherical than amphiboles and pyroxenes, the former would have settled considerably first (i.e. in the tributary channels) than the latter, consequently the amphiboles and pyroxenes suite would be depositing farther downstream.

In the estuarine environment, the contents of heavy minerals are highly variable due to the wide differences in sediment types. But the antipathetic relationship between denser and lighter heavy minerals is recognisable in this environment too (Fig. 23a, b and Table 7). The diversity in the content of heavy mineral species in the estuarine environment is influenced by factors like river inputs, estuarine hydrography, sediment types, tidal activities and dredging operations. Another reason for the observed variability of heavy mineral assemblage in the estuarine environment is the lack of progressive and effective sorting processes after deposition. Heavy minerals once deposited in the muddy estuarine substratum will not be subjected to further sorting processes as the grains are entrapped within the muddy sediments. Further, floc formation in the estuary also adversely affects the sorting

TABLE 7 - Matrix analysis of heavy minerals in various size fractions of MUVATTUPUZHA RIVER SANDS, Central Vembanad estuarine sands.

a) MUVATTUPUZHA RIVER											
	Op	Am	(0.50 - 0.35 mm)			Op	Am	Py	(0.35 - 0.25 mm)		
			Py	Ga	Zi				Ga	Zi	Bi
Op	1					1					
Am	-0.37	1				-0.87	1				
Py	-0.34	-0.21	1			-0.62	0.47	1			
Ga	-0.27	-0.30	0.18	1		-0.04	-0.22	-0.40	1		
Zi	-0.27	0.18	-0.18	-0.63	1	-0.26	0.24	0.88	-0.41	1	
Bi	0.04	0.56	-0.21	-0.30	0.48	0.21	-0.50	-0.41	0.21	0.54	1
	(0.25 - 0.18 mm)					(0.18 - 0.125 mm)					
	Op	Am	Py	Ga	Zi	Op	Am	Py	Ga	Zi	Bi
Op	1					1					
Am	-0.93	1				-0.96	1				
Py	-0.79	0.63	1			-0.76	0.69	1			
Ga	0.01	-0.39	-0.13	1		0.12	-0.30	0.06	1		
Zi	0.13	-0.22	-0.15	-0.06	1	0.20	-0.24	-0.47	-0.47	1	
Bi	-0.12	-0.16	0.14	0.66	-0.14	0.36	-0.46	-0.48	0.46	0.18	1
Mo						0.19	-0.31	-0.35	0.18	0.12	-0.18
	(0.125 - 0.088 mm)					(0.088 - 0.063 mm)					
	Op	Am	Py	Ga	Zi	Op	Am	Py	Ga	Zi	Bi
Op	1					1					
Am	-0.87	1				-0.92	1				
Py	-0.76	0.40	1			-0.80	0.60	1			
Ga	-0.31	-0.32	0.49	1		-0.20	0.12	0.24	1		
Zi	0.73	-0.84	-0.52	0.26	1	0.79	-0.89	-0.66	-0.35	1	
Bi	-0.51	0.21	0.21	0.07	-0.46	-0.62	0.65	0.67	-0.25	0.77	1
Mo	-0.04	-0.19	0.21	0.53	0.21	-0.17	0.16	0.17	-0.44	-0.09	0.41
Si						0.17	0.23	-0.63	0.02	-0.22	-0.24

b) VEMBANAD ESTUARY

	(0.25 - 0.18 mm)				(0.18 - 0.125 mm)								
	Op	Am	Py	Zi	Bi	Mo	Op	Am	Py	Ga	Zi	Bi	Mo
Op	1						1						
Am	-0.39	1					-0.83	1					
Py	0.07	0.52	1				-0.82	0.88	1				
Ga	0.22	-0.34	0.57	1			-0.48	-0.49	0.71	1			
Zi	0.10	-0.91	-0.78	0.05	1		0.49	-0.88	-0.76	-0.56	1		
Bi	0.47	-0.25	0.68	-	-0.53	1	-0.26	0.27	-0.09	-	-0.11	1	
							-0.42	0.10	0.06	-	0.29	0.74	1

	(0.125 - 0.088 mm)				(0.088 - 0.063 mm)											
	Op	Am	Py	Zi	Bi	Mo	Si	Op	Am	Py	Ga	Zi	Bi	Mo	Si	Ru
Op	1							1								
Am	-0.87	1						-0.96	1							
Py	-0.64	0.63	1					-0.84	0.79	1						
Ga	-0.42	0.75	0.13	1				-0.75	0.82	0.75	1					
Zi	0.22	-0.65	-0.50	-0.99	1			0.58	-0.70	-0.75	-0.94	1				
Bi	-0.25	0.42	0.17	-	-0.38	1		-0.06	0.12	-0.09	-	0.07	1			
Mo	-0.25	0.01	0.24	-	0.28	-0.12	1	-0.11	-0.81	-0.68	-0.68	0.27	0.30	1		
Si	0.25	0.72	-0.45	-	0.95	0.30	-0.63	1	-0.34	0.26	-0.78	-	0.62	0.50	0.44	1
Ru								-0.11	0.04	0.62	-	-0.66	0.15	0.95	0.99	1

Op = Opaque      Am = Amphibole      Py = Pyroxene      Ga = Garnet      Zi = Zircon  
 Bi = Biotite      Mo = Monazite      Si = Sillimanite      Ru = Rutile

TABLE 7 - (Contd.)

River/Estuary	r - values	Level of significance
a) MUVATTUPUZHA RIVER	0.35 to 0.42	0.1 to 0.05
	0.42 to 0.49	0.05 to 0.02
	0.49 to 0.54	0.02 to 0.01
	> 0.54	< 0.01
b) CENTRAL VEMBANAD ESTUARY	0.44 to 0.51	0.1 to 0.05
	0.51 to 0.59	0.05 to 0.02
	0.59 to 0.64	0.02 to 0.01
	> 0.64	< 0.01

process.

#### **Correlation matrix of heavy minerals:**

Riverine environment: Correlation matrix of the individual heavy minerals among various fractions in different samples with respect to mean size and total heavies is worked out to delineate the relationship existing among them. Table 8 shows significant positive and negative loadings especially between major heavy mineral components. The total heavy fraction (HMs) yields a significant positive loading on opaques, zircon and monazite. Whereas amphiboles and pyroxenes depict negative relation with total heavies. The increase in the content of the denser heavy minerals with the increase of total heavies in sediments illustrates a high energy regime required for the selective sorting of these minerals. The depletion of amphiboles and pyroxenes with increase of total heavies manifests that these lighter heavy minerals are transported along with the lighter mineral fraction of the sediments (mainly quartz and feldspar) which implies that the river flow is incompetent to transport denser heavy minerals. This is further evidenced from the very high negative correlation of opaques with amphiboles ( $r = -0.94$ ) and pyroxenes ( $r = -0.74$ ) and positive affinity with zircon ( $r = 0.41$ ) and monazite ( $r = 0.37$ ). The strong association of amphiboles with pyroxenes ( $r = 0.63$ ) and its negative relation with zircon ( $r = -0.46$ ) and monazite ( $r = -0.46$ ) re-affirms the above view. Garnet exhibits a negative relation with mean size implying its poor availability in the finer fractions.

The clustering pattern of minerals (Fig. 26) show closely knitted group of minerals such as opaques, zircon and monazite along with total heavies, which indicates a high energy denser group. Apart from this, amphiboles and pyroxenes show strong bonding as they represent lighter and low energy heavy regime. There is no appreciable clustering of other minerals observed in the dendrogram as either they are available

Table 8— Interrelationship between heavy minerals and mean size in the sand fraction of (a) Muvattupuzha river and (b) Central Vembanad estuary

(a) MUVATTUPUZHA RIVER												
	HMs	Op	Am	Py	Ga	Zi	Bi	Ru	Mo	Si	Al/Ot	Mz
HMs	1.00											
Op	0.71	1.00										
Am	-0.70	-0.94	1.00									
Py	-0.45	-0.74	0.63	1.00								
Ga	-0.36	-0.20	0.90	0.06	1.00							
Zi	0.63	0.41	-0.46	-0.43	-0.44	1.00						
Mi	-0.28	-0.16	-0.02	0.07	0.32	-0.36	1.00					
Ru	-0.18	-0.22	0.24	0.03	0.24	-0.07	-0.05	1.00				
Mo	0.51	0.37	-0.46	-0.13	-0.29	0.40	-0.13	-0.21	1.00			
Si	0.001	0.03	-0.01	-0.14	-0.14	0.08	-0.06	-0.07	0.29	1.00		
Al/Ot	0.003	-0.14	0.06	0.30	-0.03	-0.08	-0.11	-0.10	-0.03	-0.07	1.00	
Mz	-0.31	-0.15	0.20	-0.01	-0.32	0.01	0.04	-0.01	-0.37	0.03	0.08	1.00
(b) CENTRAL VEMBANAD ESTUARY												
	HMs	Op	Am	Py	Ga	Zi	Bi	Ru	Mo	Si	Al/Ot	Mz
HMs	1.00											
Op	0.60	1.00										
Am	-0.41	-0.81	1.00									
Py	-0.37	-0.66	0.72	1.00								
Ga	-0.15	-0.18	0.15	0.17	1.00							
Zi	-0.07	0.13	-0.65	-0.60	-0.09	1.00						
Mi	-0.17	-0.30	0.27	0.11	-0.29	-0.10	1.00					
Ru	0.08	0.02	-0.001	0.003	-0.17	-0.07	0.50	1.00				
Mo	0.49	0.30	-0.28	-0.12	-0.31	0.05	-0.02	0.04	1.00			
Si	0.33	0.17	-0.11	-0.15	-0.06	-0.02	-0.15	-0.10	0.07	1.00		
Al/Ot	-0.13	-0.24	0.11	0.10	0.05	0.14	-0.12	-0.19	0.15	-0.11	1.00	
Mz	-0.09	-0.11	0.13	-0.11	-0.11	-0.004	0.13	0.14	-0.21	0.25	-0.15	1.00

TABLE 8 - (Contd.)

River/Estuary	r - values		Level of significance
a) MUVATTUPUZHA RIVER	0.21	to 0.25	0.1 to 0.05
	0.25	to 0.30	0.05 to 0.02
	0.30	to 0.33	0.02 to 0.01
	>0.33		< 0.01
b) CENTRAL VEMBANAD ESTUARY	0.23	to 0.27	0.1 to 0.05
	0.27	to 0.32	0.05 to 0.02
	0.32	to 0.35	0.02 to 0.01
	>0.35		< 0.01

in traces or due to differential transportation pattern owing to its peculiar crystal habit.

**Estuarine Environment:** Most of the minerals exhibit a similarity in correlation as described above except for zircon. In estuarine environment, zircon is found to be totally unrelated to total heavies and opaques. Higher amount of zircon obtained for the estuarine sand samples than riverine sands is presumably very significant as zircon is an indicator of cyclicity. The sudden increase in the content of zircon at many stations (Sample Nos. 52, 64, 67) in the estuarine environment is an indication of an additional supply of zircon from the localized sources. Here it is significant to note that the surface features of zircon from scanning electron microscopic studies (Plate 5a) have shown intense mechanical and chemical activities which are characteristic of high energy subaqueous collisions and subsequent diagenetic changes as a part of polycyclic sedimentation pattern. The distinctive dissimilarities in the nature of zircon grains between riverine and estuarine sediments with the latter showing characteristic beach derivation also reiterates an additional source of zircon in the estuarine environment presumably from the innumerable relict beach ridges lying parallel to the coast and often forms the boundary of the Vembanad estuary (Fig. 15). Amphiboles and pyroxenes yield high negative correlation with zircon. Apart from this, many of the other minerals in the estuarine sediments show much deviation in their association from that of river environment. The primary difference among the two environments is that the estuarine sediments contain considerable amount of mud. The cohesive nature of the mud rich sediments restricts the hydrodynamically controlled sorting processes. The clustering pattern depicts some similarity, though zircon is not grouped with any of the principal minerals. The two prominent groups identified from the clustering pattern are (1) opaques, monazite, and total heavies and (2) amphibole and pyroxene. This is in consonance with that of river environment.

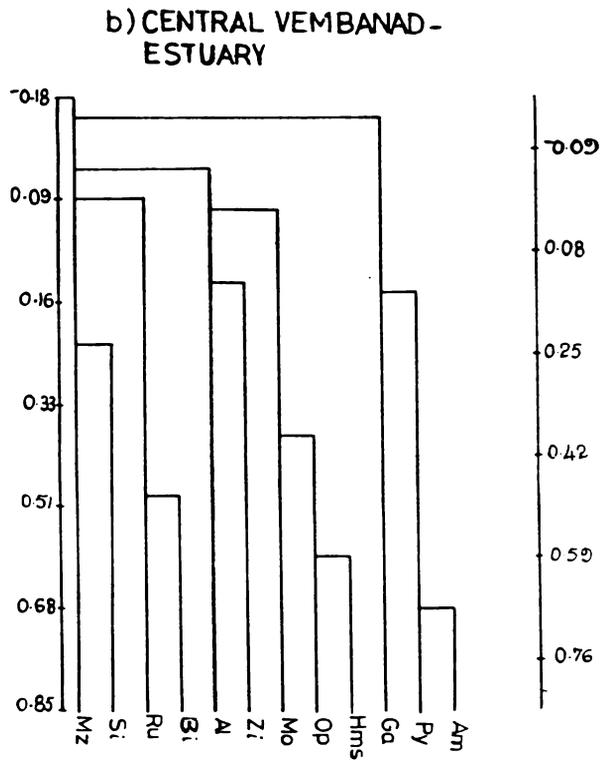
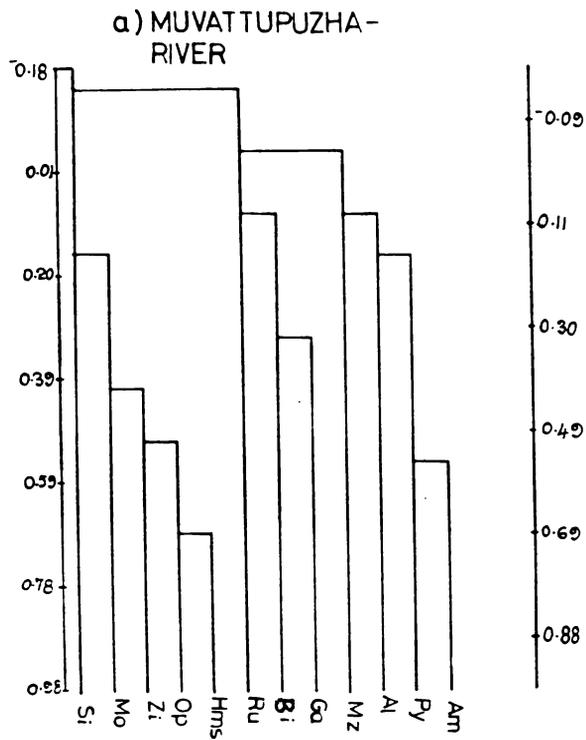


Fig. 26 Dendrogram showing grouping patterns of various heavy minerals (symbols are same as that of Table 6) and mean size (Mz)

**Provenance:** Studies on heavy mineral assemblage can be used for demarcating the probable sources from which they have been derived. The heavy mineral assemblage of the Muvattupuzha river sand is characterised by the predominance of ilmenite (major opaques) hornblende (major amphiboles), hypersthene (major pyroxenes), garnet, zircon and biotite. Monazite, sillimanite and rutile are present only in traces (Table 6). From Chapter 1, it is clear that the drainage basin of the Muvattupuzha river is mainly occupied by biotite-hornblende gneisses, unclassified gneisses and charnockites. At many places these rock types are found to have been intruded by acidic (granite and pegmatite) and basic (gabbro and dolerite) igneous rocks. Closer to the mouth, the river drains through laterites and lateritized Miocene sedimentary rocks.

This study reveals that a considerable amount of sediments in the Muvattupuzha river has been derived from denudation of metamorphic rocks. Van Andel and Poole (1960) have pointed out that bluish green hornblende (the predominant hornblende type in the present study area) is characteristic of metamorphic rocks. The hornblende and biotite gneisses as well as other unclassified gneisses can contribute blue green hornblende. Colourless and pink garnet might be derived from charnockites. From a detailed petrographic study, Mallik (1981) has stated that the charnockites of the western ghats especially in the catchment area of Pamba, Muvattupuzha and Periyar rivers are characterised by colourless and pink garnets. The occurrence of substantial amount of hypersthene also supports the role of charnockites in contributing sediments to the Muvattupuzha river system. Basely and Buddington (1958) opined that the opaque minerals can also be used for the recognition of source rocks. According to them, ilmenite-magnetite association is indicative of metamorphic provenance. Apart from this, a considerable amount of opaques can also be derived from the laterites and Miocene sedimentary rocks that constitute the lower reaches of the river. Biotite can be derived from all of the above mentioned

crystalline rocks. Monazite and rutile in the study area are indicative of igneous provenances especially of granites and pegmatites. Presence of sillimanite also points to a metamorphic source. The cloudy prismatic zircon might be derived from charnockitic sources as reported earlier by Narayanaswami and Soman (1990).

Though the Central Vembanad estuarine sands also constitute the same suites of minerals as observed in the Muvattupuzha river sands, the former can be easily distinguished from the latter from the variation in the morphological and optical characteristics of grains. Further, the content of monazite, sillimanite and rutile are higher in the estuarine sediments than the river. Perfect rounding of the estuarine heavy sands (Plate 17) than the river (Plate 18) as well as surface textures especially of zircon (Plate 5b) clearly indicate a polycyclic nature and high energy environments to which the sediments are subjected. Majority of the estuarine zircons are coarser, and spherical than the normal prismatic cloudy zircons observed upstream. The sphericity noticed in the estuarine zircons together with its surface texture clearly indicate either the intensity of the transport which it had undergone or the residence time in the surf zone where the to and fro motion of the mineral is unavoidable. These zircons are derived from palaeo-beach ridges and mixed up with river borne zircons. The occurrence of similar type of zircons from the beach sands of Kerala has also been reported earlier by Mallik (1986).

#### 4.3.1B LIGHT MINERALS

The riverine and estuarine sands of the study area exhibit a very high content (> 90%) of light minerals. Quartz is the dominant component in the light mineral crop which is followed by feldspars (plagioclase and orthoclase).

TABLE - 9 The quartz/feldspar ratio in river and estuarine environments.

Sample No.	Quartz/Feldspar		
	0.50-0.35mm	0.25-0.177mm	0.125-0.088mm
<b>River</b>			
1	3.15	18.08	14.56
2	4.66	8.09	9.50
4	3.12	15.22	8.58
9	4.28	5.68	7.14
14	8.32	5.11	8.62
15A	4.12	5.28	6.14
17	9.21	17.02	49.00
20	4.67	7.74	19.21
23	8.55	18.19	16.28
25	25.86	39.98	32.33
30	16.28	23.09	48.61
33	18.70	21.27	56.42
36	14.19	11.78	12.15
41	32.58	50.54	42.97
44	38.55	26.19	32.76
Average	13.08	18.22	24.28
<b>Estuary</b>			
47	47.21	52.19	43.25
52	45.65	38.41	50.32
54	31.05	36.58	42.46
74	37.45	39.25	58.10
78	56.14	39.25	58.10
86	44.99	45.73	49.98
Average	43.75	41.95	49.38

Table 9 furnishes the quartz/feldspar ratios in three selected size fractions (viz: +45, +80 and +170 meshes) of the riverine and estuarine sands. In river environment, the quartz/feldspar ratio ranges from 3.5 to 38.55, 5.11 to 50.54, and 6.14 to 56.42 respectively in +45, +80 and +170 mesh size fractions, while the respective ranges in the estuarine environment are 31.05 - 56.14, 39.25 - 52.12 and 42.46 - 58.16. In river, the ratio exhibits a general increase downstream. Earlier, Pettijohn (1957), Pollack (1961) and Seralathan (1979) also observed a similar variation of quartz/feldspar ratio downstream. Since there is not much variation in the densities of these minerals (quartz 2.65 gm/cc and feldspar 2.70 gm/cc), the downstream increase in quartz content in each size fraction is presumably due to selective abrasion as well as selective chemical decomposition of feldspars as suggested earlier by Unnikrishnan (1987). It is well known that feldspars are less stable than quartz. The quartz/feldspar ratio is markedly high in estuarine environment than the river. The ratio slightly decreases in the river influenced zones of the estuary due to the supply of feldspar rich sands by the Muvattupuzha river. Granulometric analysis of quartz/feldspar ratio shows a marked increase towards the finer size grades. It clearly indicates the easiness in the susceptibility of feldspar to chemical weathering processes especially in the finer fractions.

#### 4.3.2 MINERALOGY OF SILT

The results of the semiquantitative study of silt using X-ray diffractometer (Table 10) indicate that the silt fraction of the sediments of the Muvattupuzha river and the Central Vembanad estuary is primarily composed of quartz, feldspar and clay minerals such as kaolinite, illite and gibbsite. Small amount of montmorillonite (av. 4.71%) is also recorded in some estuarine samples which are very close to the mouth. In the river, the quartz/feldspar ratio is slightly lower (av. 1.50) than in the estuary (av. 2.54). It clearly indicates that the feldspar in the

TABLE 10.— Mineralogy of silt and clay fractions of Muvattupuzha river and Vembanad estuarine sediments (minerals in %).

Sample No.	Quartz	Feldspar	Kaolinite	Illite	Gibbsite	Montmorillonite
<b>SILT FRACTION</b>						
<b>River</b>						
17	40.98	28.02	15.73	8.55	6.72	-
20	42.45	27.46	19.68	7.08	3.32	-
<b>Estuary</b>						
48	36.99	17.98	21.86	18.70	4.46	-
54	28.59	26.81	20.37	10.09	11.13	-
67	52.05	15.83	16.12	8.20	3.10	4.71
76	57.76	13.57	17.25	6.64	2.66	2.12
80	48.95	19.87	18.36	10.52	2.29	-
85	50.85	14.18	19.68	6.56	3.05	5.68
<b>CLAY FRACTION</b>						
<b>River</b>						
17			77.37	13.47	9.16	-
20			65.00	29.24	5.76	-
<b>Estuary</b>						
48			65.36	22.41	7.02	5.21
54			70.93	22.05	7.02	-
67			52.10	20.61	5.84	19.20
76			35.18	25.51	3.18	36.13
80			38.13	35.56	1.84	24.47
85			31.65	14.50	1.33	52.52

latter environment is subjected to intensive chemical alteration than in the former. The average contents of kaolinite, illite and gibbsite in the silt fraction of the river are 17.71%, 7.82% and 5.02%, while in the estuary the above minerals shows 18.94%, 13.28% and 4.45% respectively.

#### 4.3.3 MINERALOGY OF CLAY

Plate 19(a,b) depicts the clay mineral assemblage of the river and the estuary. The estuarine clays are highly 'aggregated' while the river clays are platy and well crystallised. Table 10 also shows the percentage of various clay minerals recorded in the study area. In the river, kaolinite (av. 71.18%), illite (av. 21.35%) and gibbsite (av. 7.46%) are the three clay minerals present. Montmorillonite is totally absent in the river environment, however, it becomes one of the major constituents of the estuarine clay in addition to the above three. The average concentrations of montmorillonite, kaolinite, illite and gibbsite in the estuary are 27.51%, 48.89%, 27.26% and 4.37% respectively. The clay fractions of the riverine as well as the southern (fresh water influenced) estuarine region are characterised by high content of kaolinite. However, kaolinite decreases progressively towards the high saline zones of the estuary. Contrary to this, the montmorillonite content shows an opposite trend. Gibbsite, which is found only in nominal amount follows kaolinite in its distribution pattern. Illite does not exhibit any specific trend in the estuary. The observed high proportions of kaolinite in river sediment reflects greater intensity of laterite denudation processes operating in the drainage basin of the Muvattupuzha river. Biscaye (1964) and Fairbridge (1967) have observed that kaolinite is one of the stable products of lateritization. In Kerala, the occurrences of high amount of kaoline along with laterite were reported by Soman and Machado (1986). Ghosh (1986) reported the presence of small amount of gibbsite and montmorillonite along with kaolinite deposits. Comparatively high proportions of kaolinite and illite near the river mouth stations in the Central Vembanad estuary

might be due to the physical sorting of clay minerals depending on size. Whitehouse et al. (1960) explained that some of the changes, which the river-borne clay minerals undergo, based on differential settling velocities of clay minerals in water of increasing salinity are in the following order: illite, chlorite, kaolinite and montmorillonite. Illite and kaolinite flocculate at lower salinities than montmorillonite and get deposited near the river mouth stations whereas montmorillonite will be deposited further down the estuary. This kind of physical sorting of clay minerals is supported by investigators like Laughman and Craig (1962), Gibbs (1977a) and Seralathan (1979).

The decrease in the content of kaolinite and increase in the content of montmorillonite towards the high saline zones of the Vembanad estuary could be explained in the light of the above attributes. Further, Grim et al. (1949); Griffin and Ingram (1955) and Grim (1968) have stated that kaolinite is unstable in alkaline waters and therefore it would alter either to illite or chlorite in estuarine and marine environments. However, in the present study illite does not show marked variation in its proportion and further, chlorite is not at all recorded in this study. This again supports the role of physical sorting and size segregation processes in the observed clay mineralogical diversities of the study area. Hence, it is evident that the above clay minerals are source controlled and the lateral variations in the riverine and the estuarine regions are due to physical sorting.



Plate 3a Ilmenite grains of the Muvattupuzha river

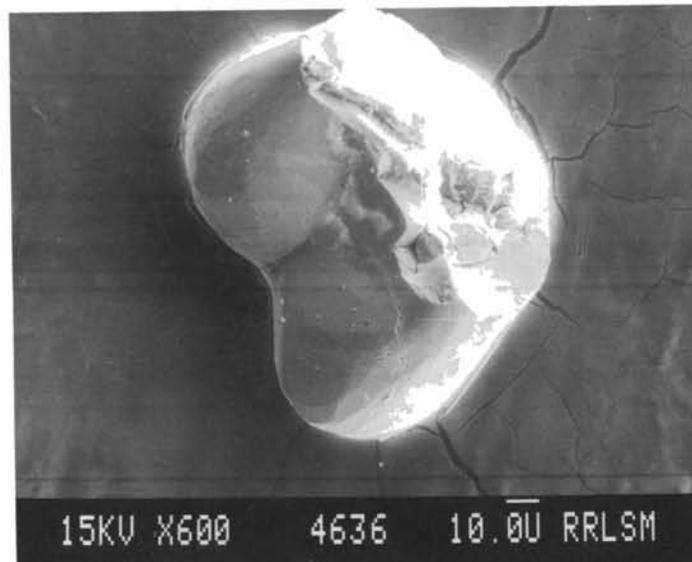


Plate 3b Ilmenite grain of the Central Vembanad estuary



Plate 4a Elongated zircon grain (+120 mesh) with pyramidal terminations. On the left, it is partially overlapped by a book of biotite

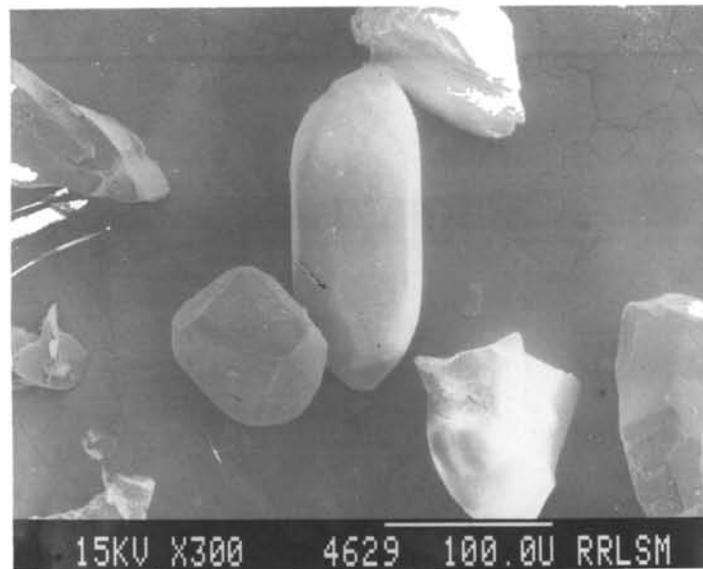


Plate 4b Pyramidally terminated zircon (+230 mesh) with smooth surface. Note the bright ilmenite grain below it



Plate 5a Subrounded estuarine zircon (+120 mesh) showing intense mechanical and chemical surface textures

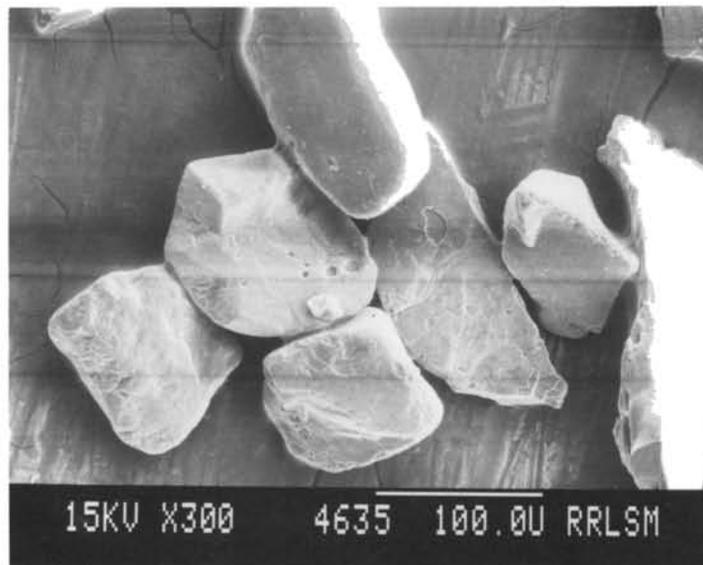


Plate 5b Subrounded - well rounded estuarine heavy (+230 mesh) grains. Note the zircon

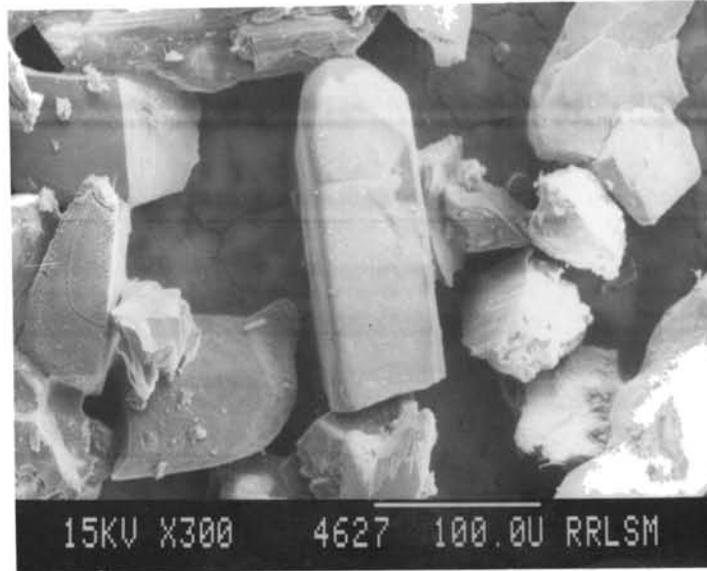


Plate 6a Broken zircon (+230 mesh) in the Muvattupuzha riverine sediments



Plate 6b Estuarine sillimanite (+120 mesh). Note the well rounded terminals

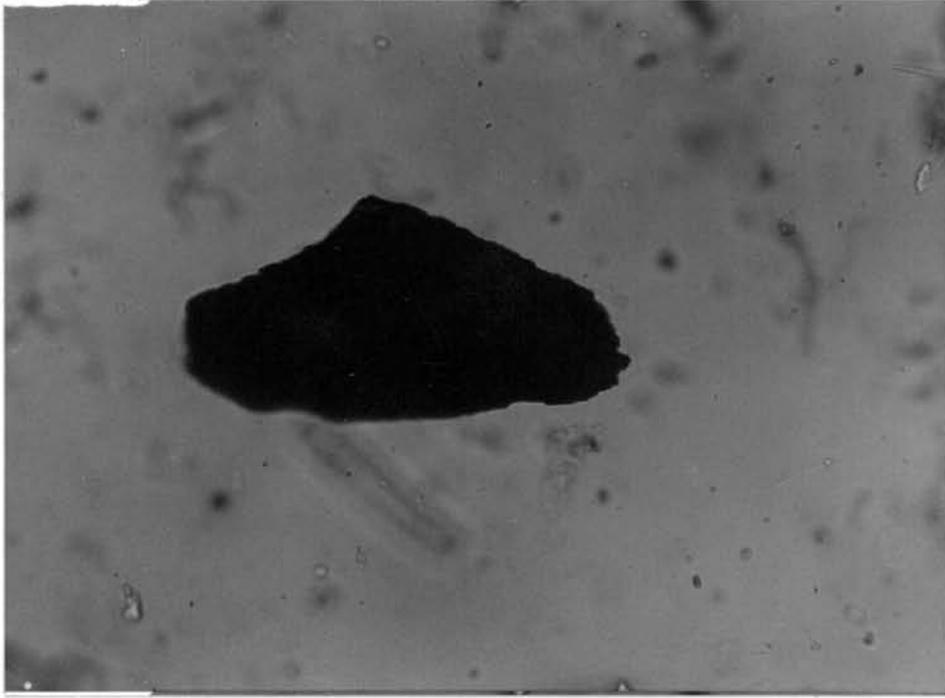


Plate 7a Subrounded ilmenite grain of Muvattupuzha river

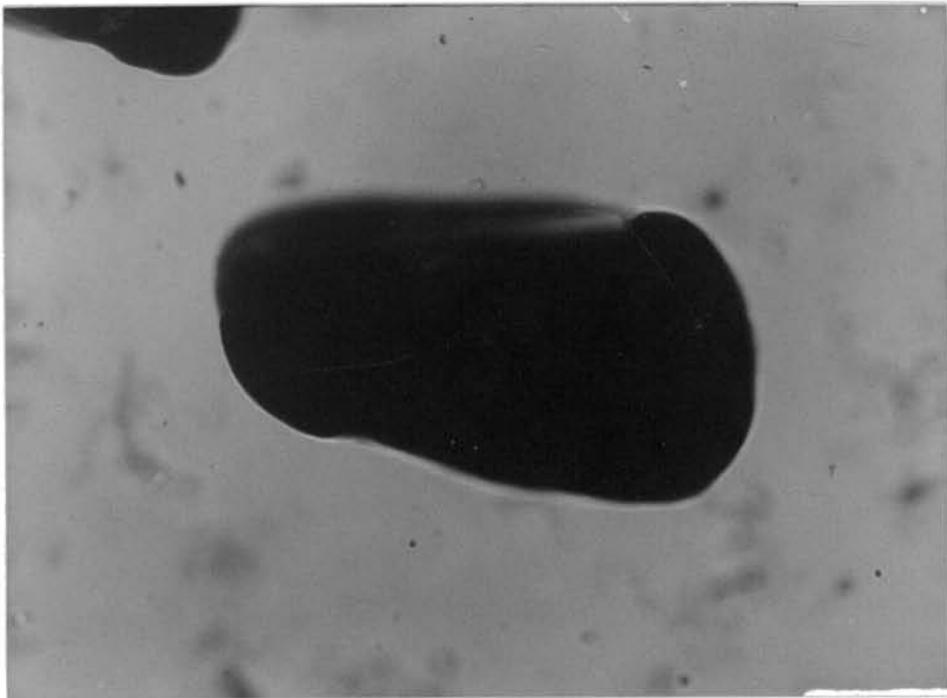


Plate 7b Well rounded ilmenite grain of Central Vembanad estuary

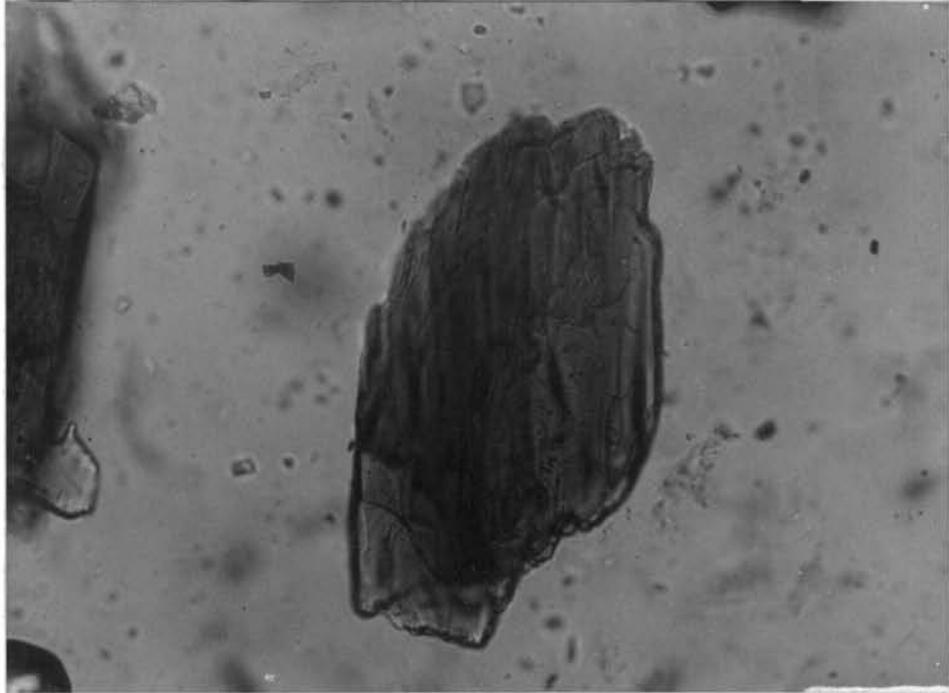


Plate 8a Hornblende (riverine) under plane polarised light

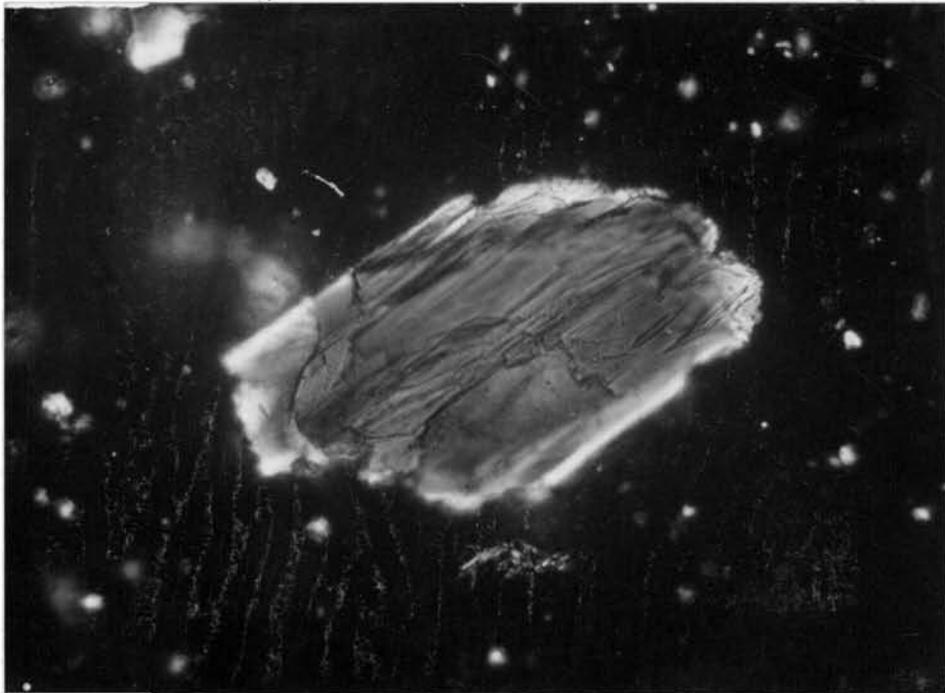


Plate 8b Hornblende (riverine) under crossed nicol

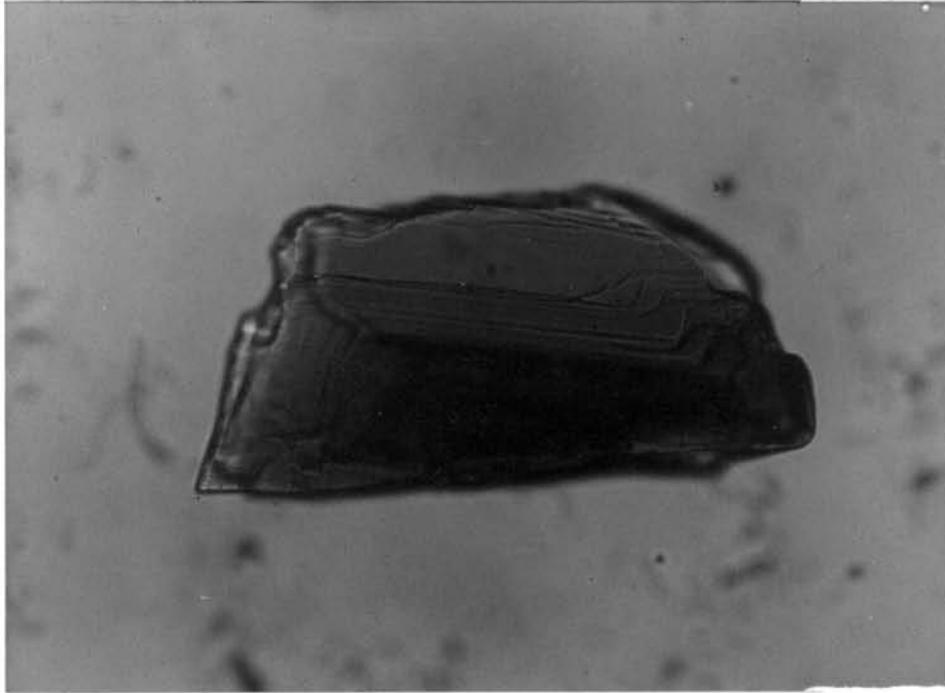


Plate 9a Hornblende (estuarine) under plane polarised light

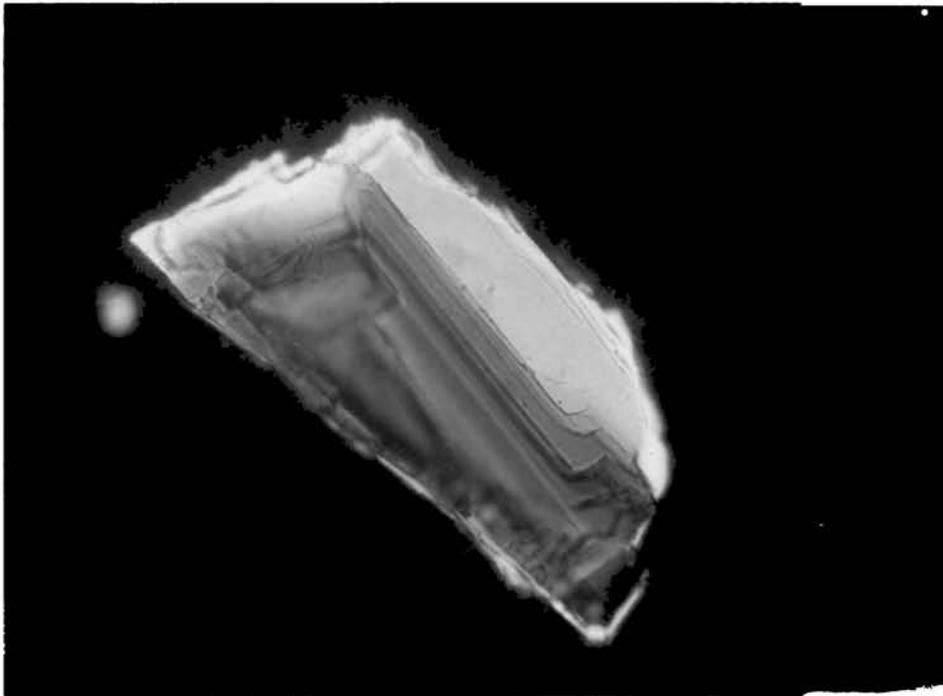


Plate 9b Hornblende (estuarine) under crossed nicol

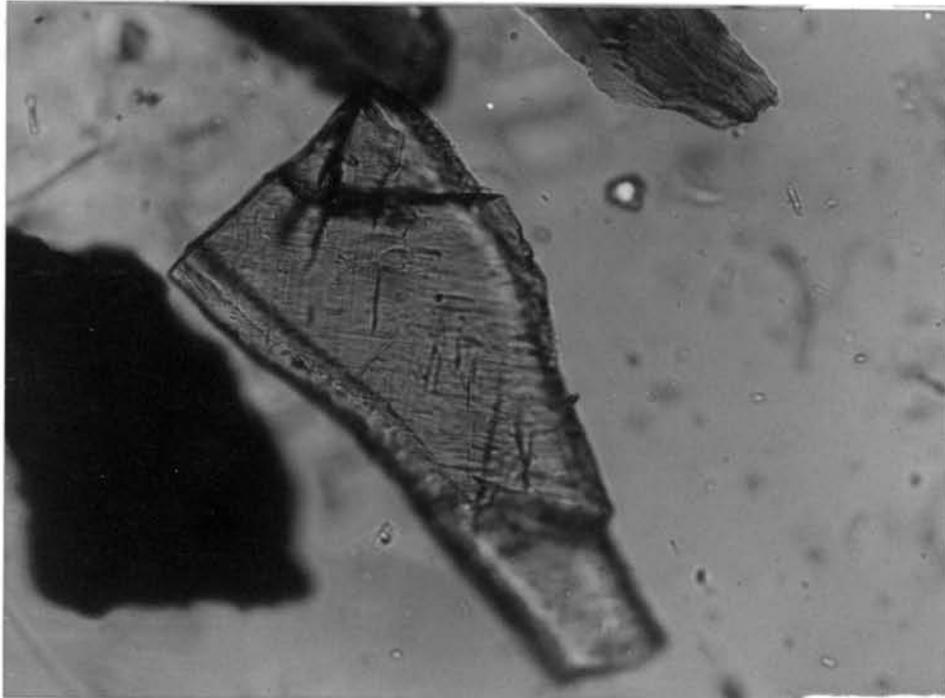


Plate 10a Hypersthene (riverine) under plane polarised light

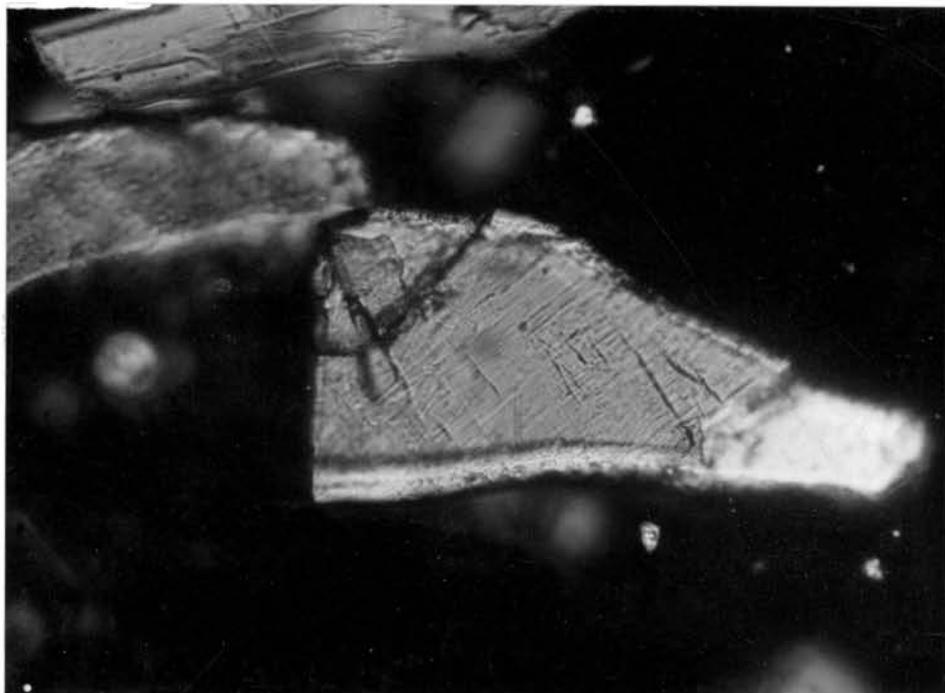


Plate 10b Hypersthene (riverine) under crossed nicol

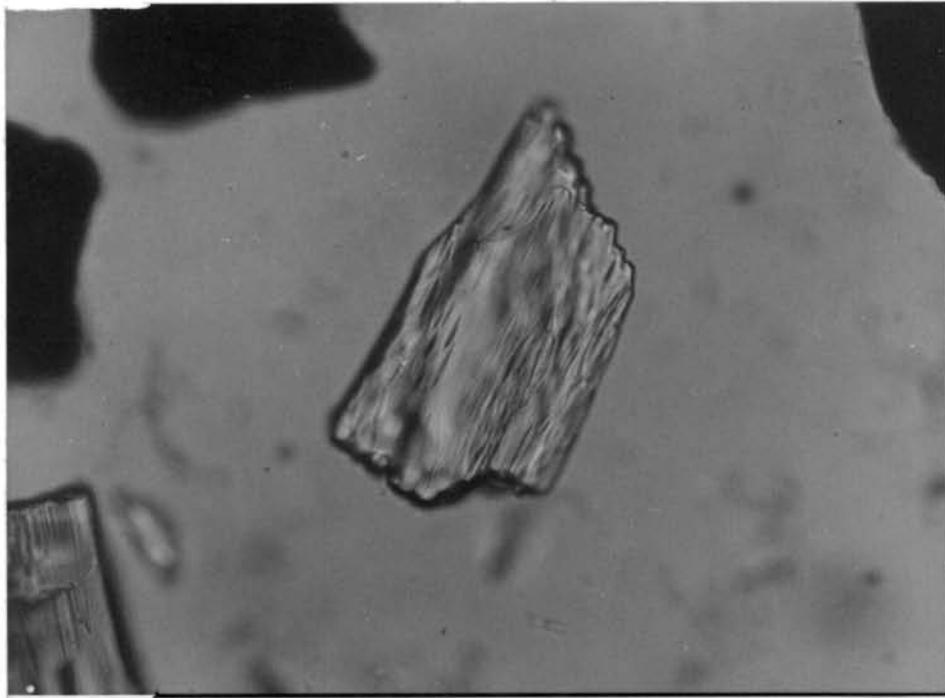


Plate 11a Hypersthene (estuarine) under plane polarised light

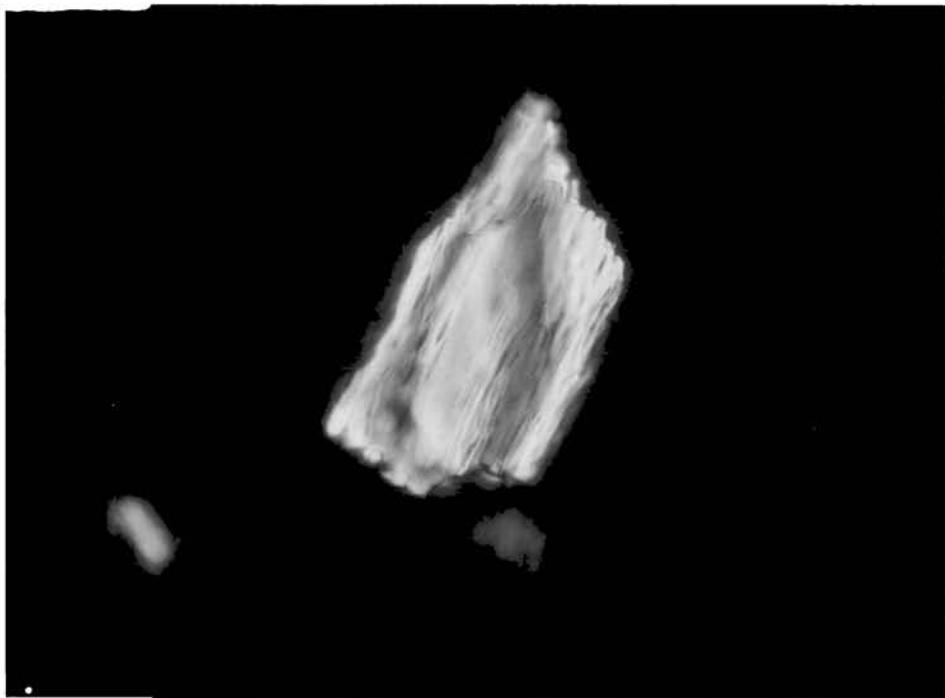


Plate 11b Hypersthene (estuarine) under crossed nicol

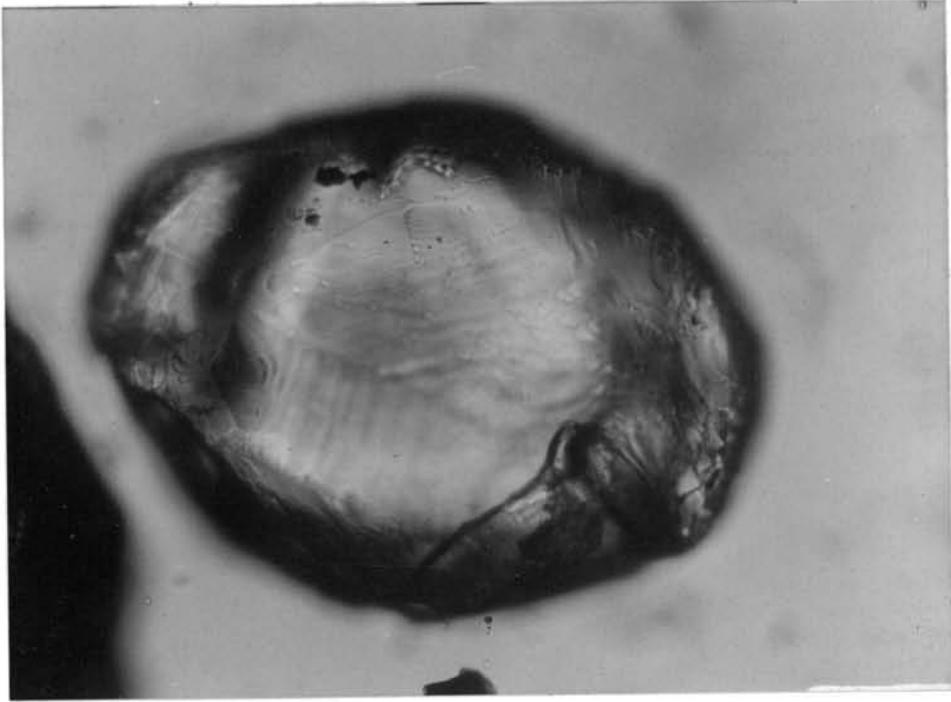


Plate 12a Garnet (riverine) under plane polarised light

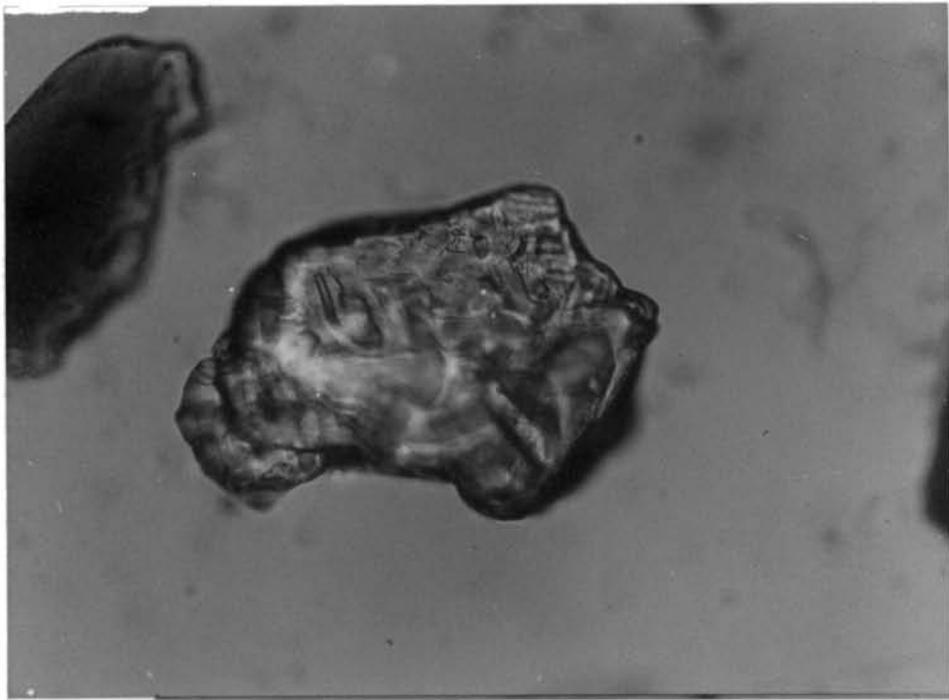


Plate 12b Garnet (estuarine) under plane polarised light

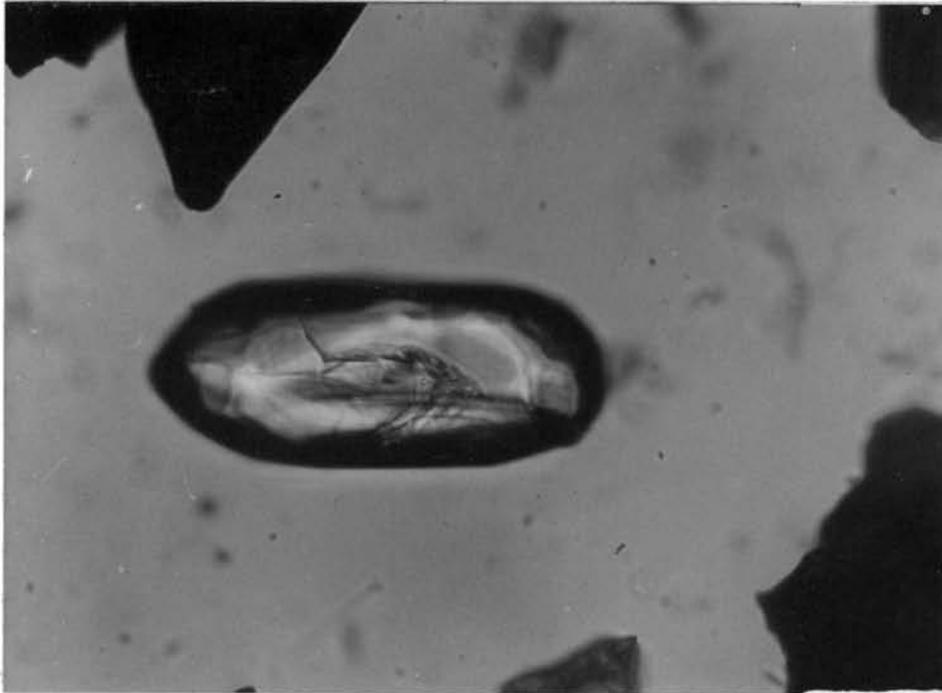


Plate 13a Cloudy zircon (riverine) under plane polarised light



Plate 13b Estuarine zircon showing inclusions. Note its subrounded nature

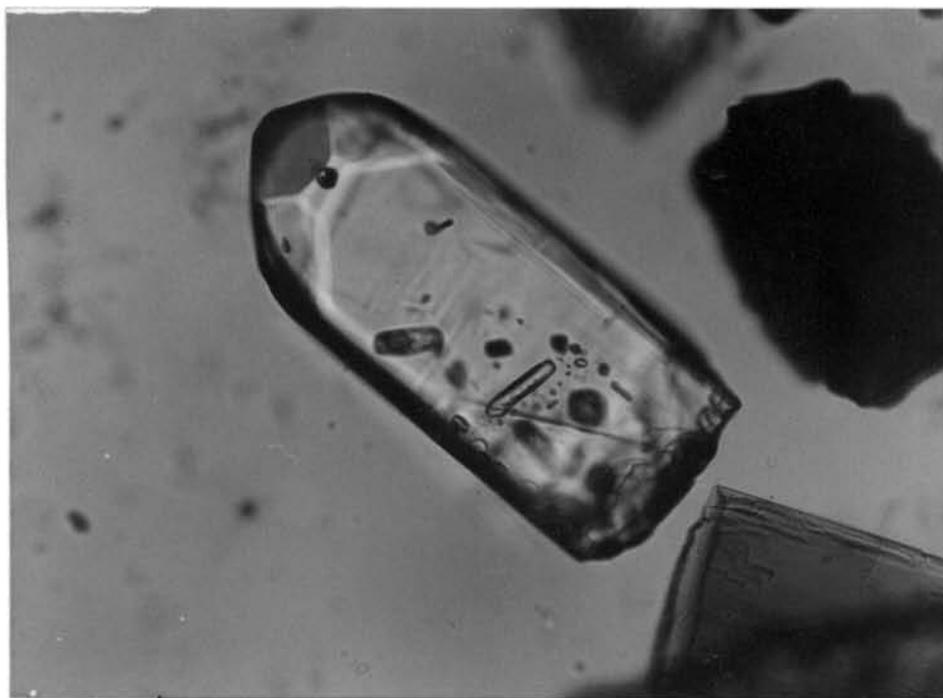


Plate 14a Broken zircon (riverine) showing first and second order pyramids. Note the inclusions (plane polarised light)

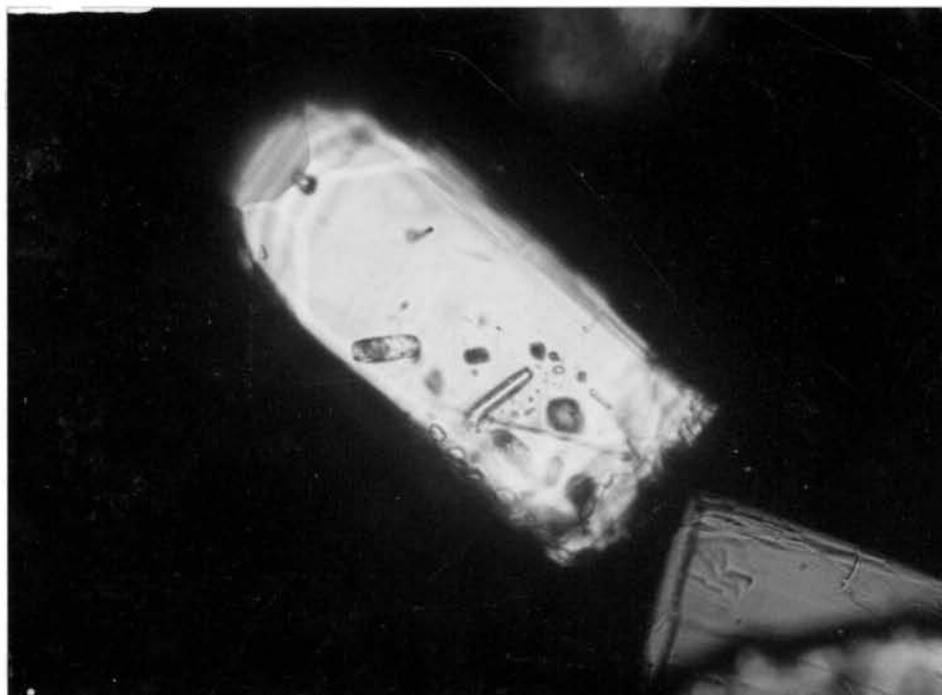


Plate 14b Broken zircon (riverine) under crossed nicol

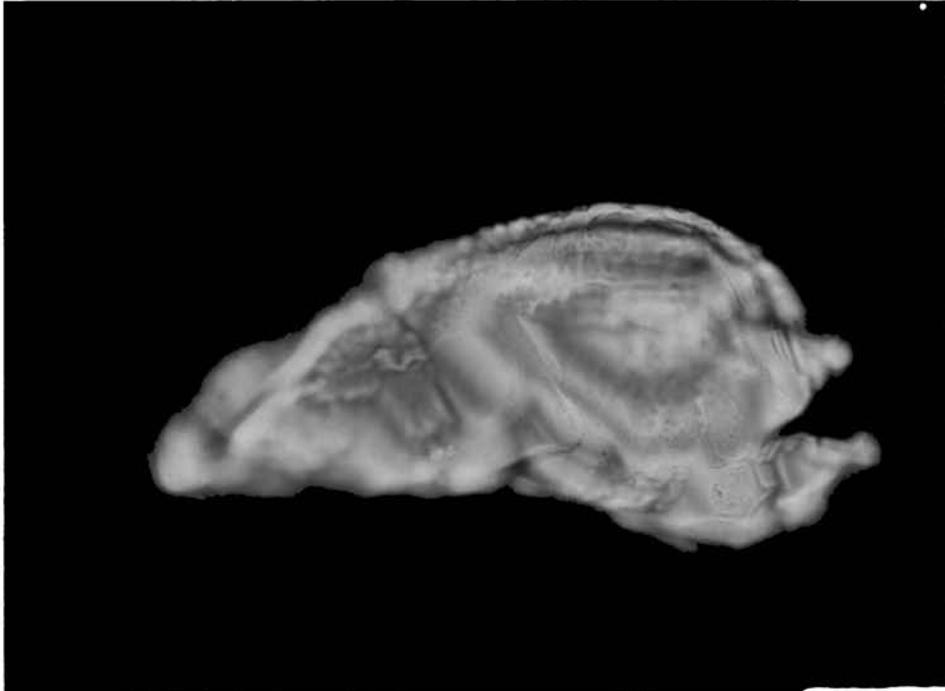


Plate 15a Estuarine zircon showing well marked zoning

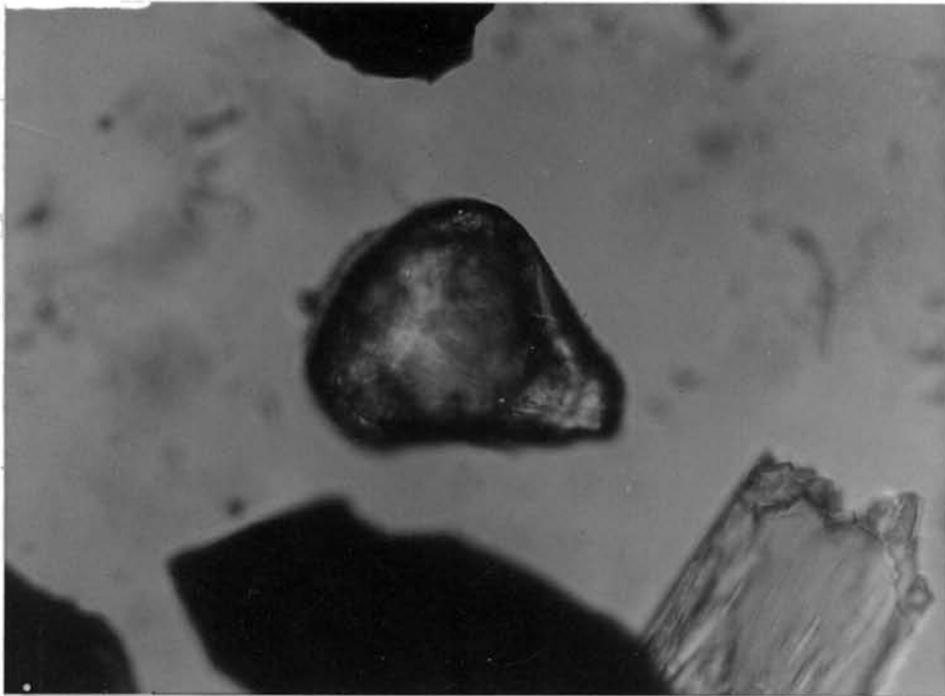


Plate 15b Monazite (riverine) under plane polarised light

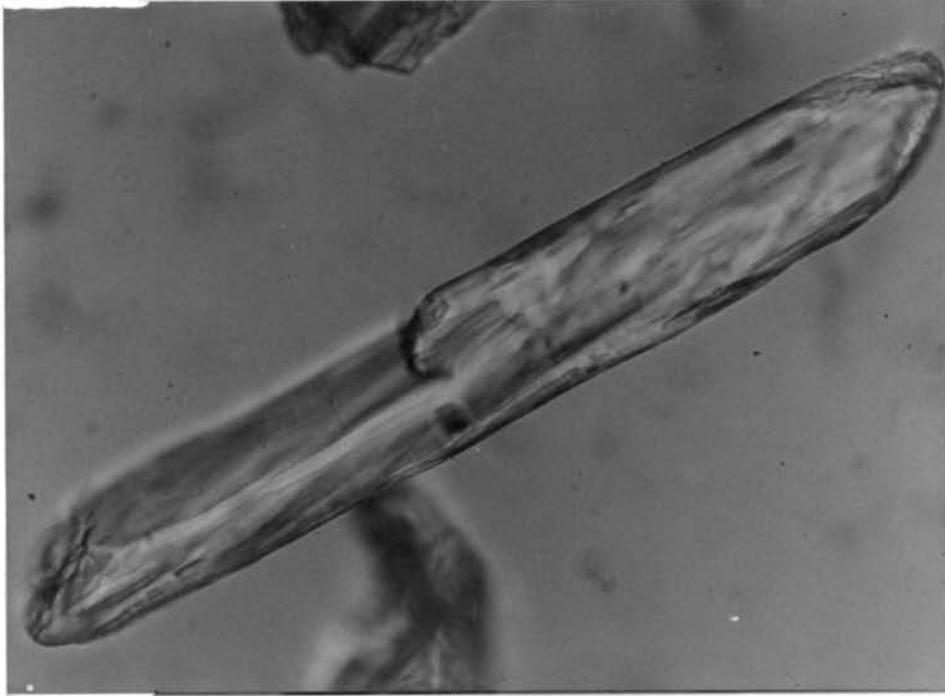


Plate 16a A sillimanite needle with rounded terminations (plane polarised light)

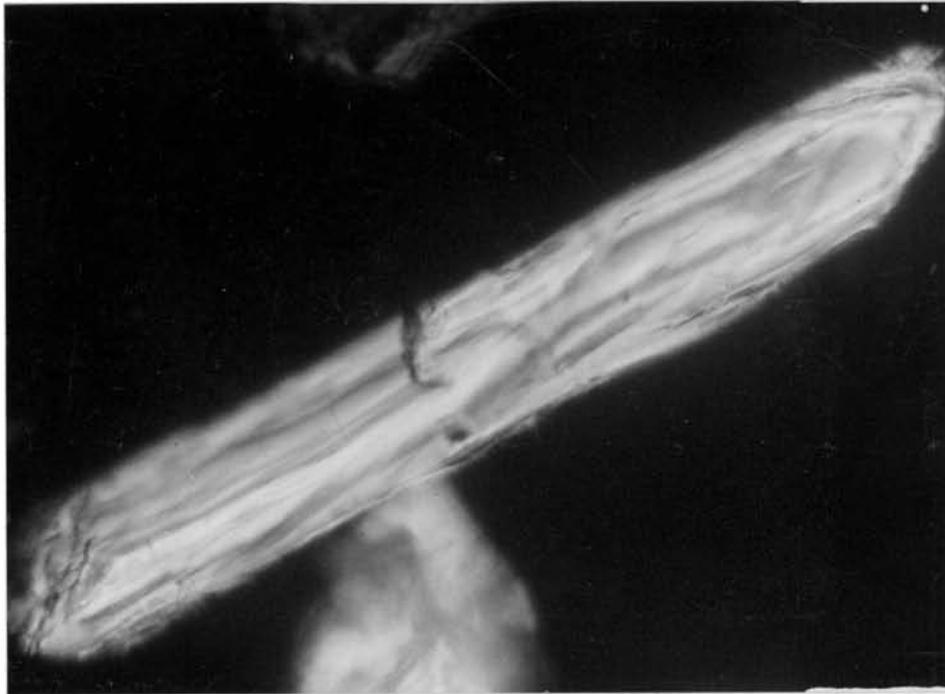


Plate 16b Sillimanite needle under crossed nicol



Plate 17a Scanning electron photomicrograph of total heavies in the +120 mesh fraction of Central Vembanad estuarine sediments

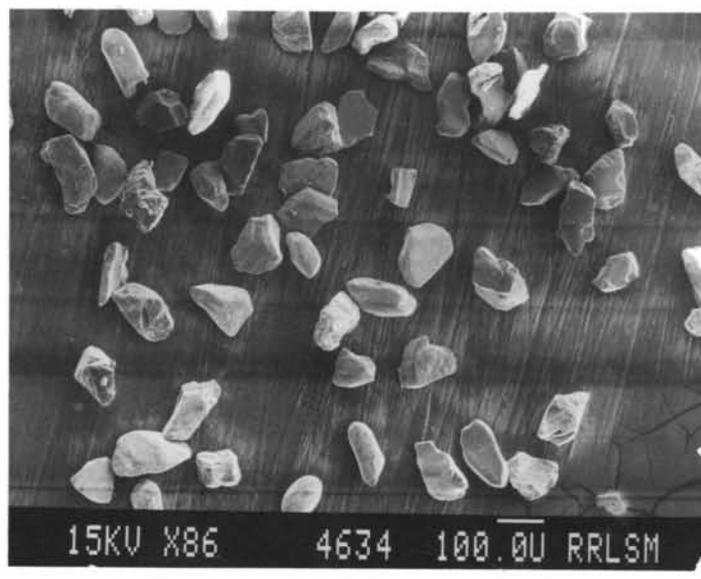


Plate 17b Scanning electron photomicrograph of total heavies in the +230 mesh fraction of Central Vembanad estuarine sediments

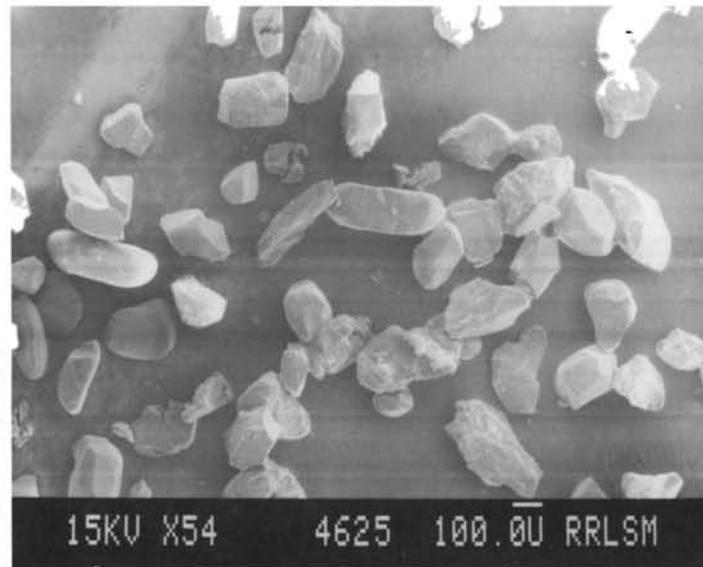


Plate 18a Scanning electron photomicrograph of total heavies in the +120 mesh fraction of Muvattupuzha riverine sediments

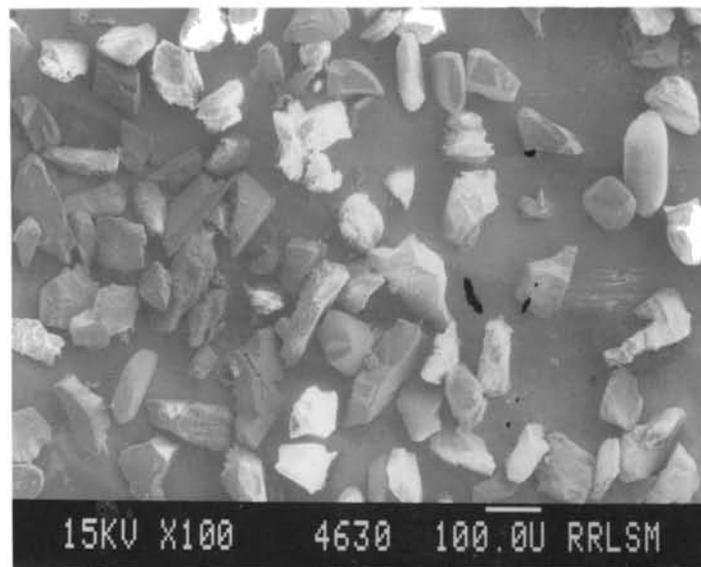


Plate 18b Scanning electron photomicrograph of total heavies in the +230 mesh fraction of Muvattupuzha riverine sediments

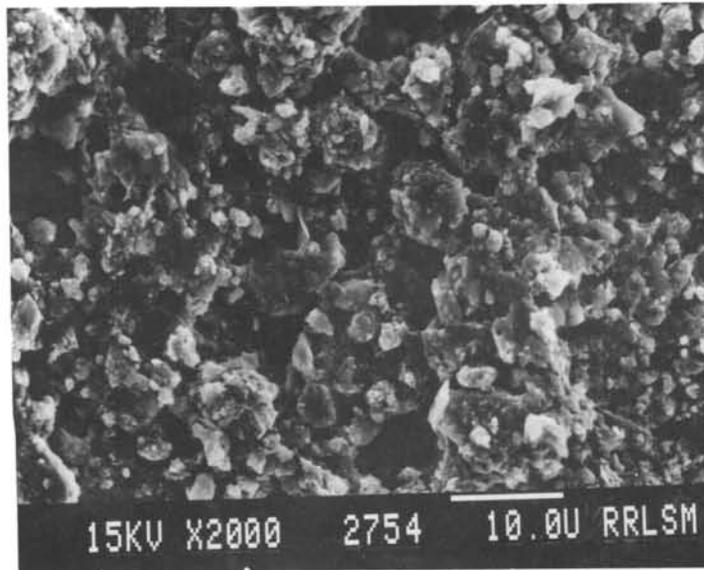


Plate 19a Scanning electron photomicrograph of estuarine clay

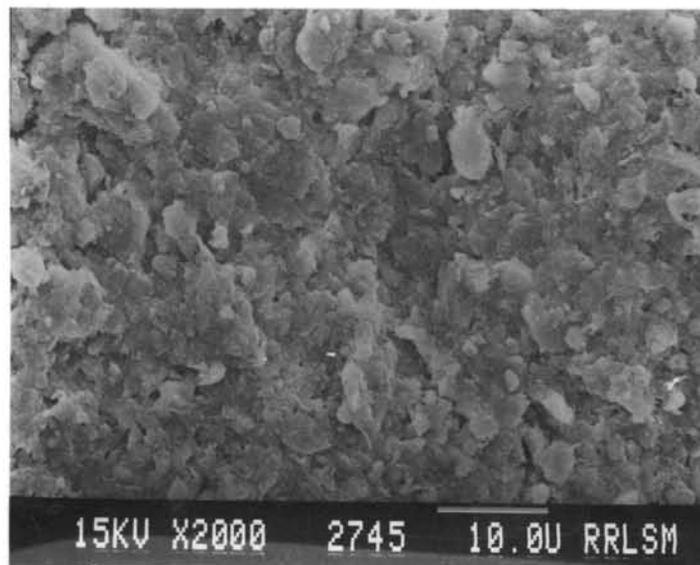


Plate 19b Scanning electron photomicrograph of riverine clay

## CHAPTER 5

## GEOCHEMISTRY

### 5.1 INTRODUCTION

In recent years, decisive break through in the study of sediment geochemistry has been recorded, which led to a better understanding of the fluvial processes. Sediments are both carriers and potential sources of natural geochemical constituents derived principally from rock weathering. However, over the 200 years following the beginning of industrialization, huge changes in the global budget of chemical signals, particularly of toxic contaminants, have occurred challenging regulatory systems which took millions of years to evolve. In the early seventies, following the catastrophic events of cadmium and mercury poisoning, sediment associated toxic elements, its carrier phases and the natural regulating mechanisms have received wide public attention.

In any aqueous environment, the transport phases of elements are generally controlled by the size spectrum of clastic sediments (De Groot et al., 1982 and Forstner, 1990). A large part of fluvial transport of matter occurs in the form of suspended sediments. During decreased rate of flow, these geochemical carriers sink to the bottom as bed sediments. In a classic study of the transport phase of heavy metals, Gibbs (1977b) formulated calculations with metal levels in relation to grain size spectrum and revealed that the heaviest enrichment of metals occur in the finer grades ranging from 0.2  $\mu\text{m}$  - 20  $\mu\text{m}$  diameters.

This chapter deals with the aspects of organic carbon, P, Na, K, Ca and heavy metals (Fe, Mn, Pb, Cu, Co, Ni, Cr, Cd and Zn) in sand, silt and clay fractions and bulk sediments as well as suspended sediments of the Muvattupuzha river and the Central Vembanad estuary. An attempt has also been made to relate the geochemical abundance of

these metals in rocks and soils of the drainage basin. A few analyses have been carried out in the sand fraction to know the content of radioactive elements such as U and Th.

## 5.2 REVIEW OF LITERATURE

Geochemical studies of the river especially bed and suspended sediments have been extended in the last three decades due to the growing awareness of environmental pollution and its impact on the ecosystem. Geochemical processes have been studied in great detail in river basins by several investigators (Gibbs, 1967; Seetharamaswamy, 1970; Satyanarayana, 1973; Seralathan, 1979; Stallard and Edmond, 1983 and Subramanian et al., 1985a). The overall balance between dissolved and sedimented load carried to the oceans has been computed on the basis of world's major river input studies by Holeman (1968), Meybeck (1976), Martin and Meybeck (1979) and Milliman and Meade (1983). Gibbs (1970) discussed the mechanisms that control the world river water chemistry.

In recent years, there have been a great spurt of renewed activity to identify the sources and sinks of heavy metals in rivers, estuaries and nearshore environments. The fate of heavy metals in these environments is of extreme importance due to their impact on ecosystem (Vale, 1986; Mance, 1987; Klomp, 1990; Windom, 1990). Recent interest in anthropogenic contamination of the hydrosphere by heavy metals has magnified the urgency of elucidating the cyclicity of toxic metals in rivers and estuaries. Chemical analysis of river waters and sediments is being carried out for the exploration as well as environmental monitoring and management. Extensive work has been done in the world's major rivers by several investigators (Reeder et al., 1972, in Mackenzie river; Trefrey and Presley, 1976, in Mississippi river; Duinker and Nolting, 1976, in Rhine river; Gibbs, 1977b, in Amazon and Yukon rivers; Meybeck, 1978, in Zaire river; Yeats and Bewer, 1982, in

St. Lawrence river; Sarin and Krishnaswami, 1984, in Ganges - Brahmaputra rivers and Qu and Yan, 1990, in Chang Jiang and Don Jiang rivers). Trefrey and Presley (1976) estimated the total flux of particulate and dissolved heavy metals from Mississippi river to the Gulf of Mexico. They have computed that over the past 25-30 years, the Pb and Cd fluxes in the Mississippi river sediments have increased about 60% and 100% respectively. The relationship between solid concentration and river water chemistry has been studied on the western Australian rivers by Imerson and Verstraten (1981). Several researchers opined that the metal pollution assessment can effectively be carried out from sediment analysis (Forstner and Wittmann, 1983 and Allen, 1990).

From economical point of view, it must be realized that, sediments are also a medium in which certain substances can be concentrated from solution and thereby represent profitable sources of raw materials (Turekian and Scott, 1967). The size dependent analytical study by Gibbs (1977b) showed that particle size has a strong bearing on metal enrichment in sediments. Later, this view was supported by investigations made by Williams et al. (1978), Forstner (1982), Forstner and Wittmann (1983) and Lee (1985).

Milliman and Meade (1983) estimated that nearly 30% of the transport of sediments by world rivers takes place within Indian subcontinent. Mass transfer studies of geochemical constituents in Indian rivers have been activated by researchers like Subramanian (1980), Sarin and Krishnaswami (1984), Sitasawad (1984), Seralathan and Seetharamaswamy (1987) and Chakrapni and Subramanian (1990). The geochemical transfer of metals through Cauvery river has been carried out intensively by Seralathan 1979, Subramanian et al. (1985b) and Seralathan (1987). Seetharamaswamy (1970), Rao et al. (1988) and Ramesh et al. (1989, 1990) made a thorough study on the mineralogical and geochemical association of metals in the Krishna river sediments.

Much geochemical work has not been carried out in the rivers and estuaries of Kerala particularly in relation to the granulometry of the sediments. Murty and Veerayya (1972a, b and 1981) made a preliminary survey on organic carbon, phosphorus and trace element contents in the bulk sediments of the Vembanad lake. They established the existence of a close relationship between organic carbon and phosphorus in this sedimentary environment. The trace metal concentration and its association in various chemical phases in the sediments of Periyar river and Varapuzha estuary have been investigated by Paul and Pillai (1983a, b). The water quality studies of Muvattupuzha river by Balchand (1983) and Nair et al. (1990) revealed that considerable changes have taken place in the water quality of this river after the commencement of Hindustan Paper Corporation Limited located at the lower reaches of the river near Velloor. Mallik and Suchindan (1984) have analysed a few major and minor elements in the bulk sediments of the Vembanad estuary. Later, Ouseph (1987) and Purandara (1990) have also studied the geochemical characteristics of a few sediment samples of Vembanad estuary. The speciation studies on the trace metals were carried out by Shibu et al. (1990) and Nair et al. (1991). In the present study, a systematic attempt has been made to unravel the geochemical characteristics of sand, silt and clay fractions in relation to the bulk sediments of the Muvattupuzha river and the Central Vembanad estuary.

### 5.3 RESULTS AND DISCUSSION

#### 5.3.1 ORGANIC CARBON

Organic carbon constitutes an integral part of riverine and estuarine sediments. The increased attention in recent years to the geochemistry of organic carbon in sediments of various aquatic environments is due to its significant role in the biological, chemical and geological processes operating in these environments (Sholkovitz,

1976; Mantoura et al., 1978; Dawson and Duursma, 1981; Laanne, 1982; Degens and Ittekkot, 1983; Romankevich, 1984 and Laanne and Ruardij, 1988). The organic carbon in riverine and estuarine sediments may be derived from either autochthonous or allochthonous processes. The relative proportions of its supply is a function of the characteristics of the catchment area in relation to the productivity of the aquatic system (Parson and Seki, 1970; and Hakanson and Jansson, 1983). Organic carbon plays a significant role in the genesis of hydrocarbon. Sedimentation followed by diagenetic decomposition of organic carbon can alter the Eh-pH conditions of the aquatic environments. Further, it provides the main energy source for the heterotrophic organisms and also acts as sink as well as source for various metals under different geochemical set up.

The organic carbon content in the bulk sediment and various size fractions (sand, silt and clay) is given in Table 11 and its variation along the profile of the river and estuary is depicted in Fig. 27. The average organic carbon content in the bulk sediment and the size fractions is as follows; River : bulk 0.99%, sand 0.14%, silt 3.8% and clay 3.79%; Estuary : bulk 2.36%, sand 0.14%, silt 3.99% and clay 4.16%. Earlier, Murty and Veerayya (1972a) have recorded an average of 1.5% organic carbon in the bulk sediments of the Vembanad estuary. Sajjan and Damodaran (1981) have reported an average of 2.4% for the bulk sediments of Ashtamudi lake. A comparison of the organic carbon content in the bulk sediments of the Central Vembanad estuary with that of the world nearshore sediments indicates 1.5 fold increase in the former than the latter.

In the river the organic carbon content in the bulk sediment is much lower than that in the estuary. This observed low values of organic carbon is due to the abundance of coarser clastics in the bulk sediment. In the estuary, the organic carbon content in the bulk sediment is markedly high and increases toward the mouth. This

TABLE 11 - Concentration of various geochemical parameters in bulk sediment and sand, silt and clay fractions of Muvattupuzha river and Central Vembanad estuary (Organic carbon, Fe, Na, K and Ca in % and others in ppm)

Sample No.	Organic carbon	Fe	Na	K	Ca	P	Mn	Pb	Cu	Co	Ni	Cr	Cd	Zn
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
<b>A. BULK SEDIMENT</b>														
<b>River</b>														
1	0.55	12.30	0.80	2.00	1.25	5	2060	32	17	21	78	193	4	148
4	0.35	2.10	0.76	2.00	0.89	6	360	11	9	14	26	30	3	32
8	0.37	1.94	1.40	1.40	1.18	5	480	11	6	BDL	13	64	1	22
9	0.36	12.57	1.20	1.02	1.03	17	1580	32	11	36	52	243	7	107
12	0.55	6.19	1.20	1.40	0.81	13	970	21	9	11	65	158	3	82
15	0.72	3.25	0.86	1.38	1.16	11	360	11	11	14	26	59	4	42
17	1.03	2.54	0.60	1.42	0.36	14	730	11	11	14	26	44	2	48
20	0.62	3.21	1.40	2.00	0.89	10	480	11	48	BDL	39	188	3	47
23	1.48	3.29	1.24	1.60	0.81	21	480	21	30	BDL	39	79	3	49
31	0.80	10.71	1.04	1.24	0.72	11	950	11	6	BDL	26	50	4	38
34	0.85	5.98	1.06	1.24	0.98	20	730	11	40	7	105	62	4	78
42	2.12	4.25	1.60	2.22	1.12	19	360	11	21	25	52	84	3	63
44	2.75	5.87	1.84	1.28	1.16	49	360	21	33	28	69	134	4	101
Average	1.18	5.71	1.08	1.55	0.87	16	762	17	19	12	51	107	4	65
<b>Estuary</b>														
45	0.52	0.99	1.16	0.60	0.63	20	120	BDL	11	BDL	39	89	2	28
47	3.27	7.57	1.96	1.72	1.29	55	480	21	58	46	156	148	5	135
49	1.87	6.31	2.32	1.68	1.52	43	970	21	34	43	143	123	5	104
50	3.69	7.66	1.12	1.44	1.43	41	850	21	37	39	143	233	8	108
52	0.62	2.18	1.56	0.92	0.63	25	240	11	34	14	91	59	3	47
54	0.85	5.98	1.06	1.24	0.98	20	730	11	40	7	105	62	4	78
55	0.73	1.19	2.03	0.52	0.89	17	120	BDL	15	7	52	54	3	33
57	0.90	2.22	0.48	0.72	0.18	26	240	BDL	21	25	78	84	3	49
58	2.78	5.88	1.88	1.30	1.18	49	360	21	32	28	131	131	4	103
59	0.24	1.31	1.12	0.64	0.54	19	240	BDL	13	4	52	50	3	34
60	0.21	1.51	0.52	0.40	0.54	37	120	BDL	17	BDL	52	64	2	34
63	0.81	0.42	0.92	0.64	0.18	18	120	BDL	9	BDL	39	40	3	16
66	4.31	7.22	0.81	1.36	1.29	48	480	32	41	39	181	193	4	128
67	0.57	1.39	0.72	0.56	0.72	32	240	BDL	13	7	52	153	2	36
68	3.69	7.82	0.92	1.32	1.12	43	240	21	45	28	156	168	5	128
69	0.26	8.25	0.84	1.20	1.21	86	730	21	47	32	156	183	6	145
70	5.17	6.06	1.36	1.28	0.94	50	480	21	47	32	169	178	6	158
71	4.74	5.16	1.68	1.00	0.98	63	240	21	34	25	130	144	6	116
77	0.81	1.39	2.00	1.16	1.29	40	240	11	15	11	65	54	3	34
78	0.76	2.38	2.32	1.68	1.43	27	240	11	15	14	70	109	3	50
79	0.89	1.43	1.60	1.16	1.25	32	240	11	15	11	65	54	3	37
80	3.27	5.36	1.96	1.48	0.98	27	240	11	34	21	104	139	5	104
83	3.97	7.02	2.48	1.32	1.56	86	360	21	43	25	169	223	6	172
84	3.75	7.40	1.20	1.16	1.38	102	360	32	52	36	181	208	8	199
85	1.42	3.09	2.88	1.72	1.69	56	360	11	21	14	91	109	4	151
88	4.4	6.98	1.12	1.36	1.43	78	480	21	63	21	156	188	6	109
Average	2.26	4.39	1.51	1.16	1.05	44	366	14	31	20	109	125	4	90

Sample No.	Organic carbon	Heavy metal	Fe	Na	K	Ca	P	Mn	Pb	Cu	Co	Ni	Cr	Cd	Zn
<b>B. SAND FRACTION</b>															
<b>River</b>															
1	0.05	10.21	8.50	0.85	1.82	1.26	5	1980	32	18	22	69	186	4	116
4	0.075	3.85	2.10	0.75	1.83	0.86	6	480	BDL	9	14	28	32	3	43
8	0.20	2.65	1.94	0.42	1.40	0.26	5	370	32	6	BDL	15	64	1	25
9	0.20	11.16	8.45	1.12	1.12	1.02	8	1580	21	13	32	45	238	5	112
12	0.0	7.82	6.19	1.20	1.40	0.82	12	970	BDL	10	11	65	158	3	99
15	0.20	3.25	2.16	0.75	1.38	1.16	9	360	11	8	12	24	55	3	41
17	0.10	4.15	2.56	0.60	1.42	0.36	12	730	BDL	8	12	22	32	2	38
20	0.0	2.25	3.28	1.20	2.00	0.86	9	480	21	34	BDL	39	88	3	48
23	0.20	5.12	4.32	1.12	1.12	0.72	12	360	BDL	27	BDL	26	68	3	36
31	0.20	7.18	5.77	1.04	1.12	0.70	8	620	11	8	BDL	27	92	3	42
42	0.25	4.32	3.25	1.40	1.82	1.12	16	360	BDL	12	10	32	82	3	56
Average	0.14	5.63	4.41	0.94	1.49	0.88	9	754	13	14	10	36	100	3	60
<b>Estuary</b>															
49	0.14	4.79	1.32	1.36	1.05	0.82	4	160	21	8	18	30	60	1	37
52	0.10	5.20	1.24	0.43	0.22	2.05	2	180	11	7	7	33	65	1	55
54	0.20	4.80	2.32	1.41	1.00	1.12	6	260	21	9	13	22	61	1	34
61	0.082	3.21	0.86	1.25	1.05	0.92	3	150	16	2	20	22	45	1	47
63	0.15	3.95	1.32	0.51	0.63	0.75	8	140	BDL	5	BDL	19	61	BDL	12
64	0.052	2.08	0.47	0.13	0.44	1.00	2	50	11	2	2	5	20	BDL	26
67	0.32	1.06	0.43	0.22	0.18	0.82	10	50	BDL	5	6	6	23	1	12
71	0.15	4.15	1.28	0.43	0.36	0.95	4	180	11	9	6	19	42	1	37
76	0.082	2.78	0.89	0.72	0.55	0.86	3	130	21	8	9	11	38	BDL	22
78	0.095	3.94	1.25	0.52	0.76	0.95	4	180	11	5	7	25	60	1	34
83	0.12	2.12	0.82	0.73	0.37	1.12	4	120	11	10	21	22	23	1	20
85	0.095	3.80	1.09	1.06	0.60	1.78	3	140	31	5	13	19	48	1	41
86	0.20	2.80	0.85	0.64	0.45	1.52	7	120	11	3	7	10	32	1	18
Average	0.14	3.40	1.09	0.72	0.59	1.13	5	143	14	6	10	19	44	1	30

Sample No.	Organic carbon	Fe	Na	K	Ca	P	Mn	Pb	Cu	Co	Ni	Cr	Cd	Zn
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
<b>C. SILT FRACTION</b>														
<b>River</b>														
1	3.09	8.41	0.60	2.40	0.72	56	1510	42	69	25	130	134	5	165
4	4.27	9.13	0.70	1.80	0.80	67	1340	64	78	50	130	158	5	159
8	4.32	8.06	0.48	1.40	0.31	54	1450	32	99	53	156	139	5	143
9	4.08	9.17	0.62	1.20	0.49	47	1090	32	73	50	130	193	5	144
12	2.78	9.92	0.50	1.18	0.36	44	1090	42	108	50	181	228	5	128
15	2.97	10.79	0.80	1.70	0.63	53	1820	42	90	43	130	178	5	167
17	4.30	8.06	0.36	1.16	0.45	55	1510	32	88	43	130	144	5	140
20	3.49	7.78	0.40	1.38	0.31	51	1210	32	97	32	130	169	5	148
23	2.68	8.53	0.38	1.40	0.31	67	610	74	134	32	143	158	5	167
31	4.54	8.85	0.40	1.24	0.27	56	610	32	91	20	169	129	6	160
34	4.26	9.41	1.04	0.92	1.12	58	840	32	65	50	220	158	12	148
42	4.35	8.85	0.40	1.20	0.45	66	610	64	65	39	117	134	5	123
44	4.25	9.92	0.80	1.20	0.89	57	740	21	43	32	118	193	4	162
Average	3.80	8.99	0.57	1.39	0.54	56	1110	42	84	41	145	163	6	150
<b>Estuary</b>														
45	4.62	7.89	0.80	1.56	1.25	29	1330	32	45	50	181	149	11	135
46	4.51	7.97	0.96	1.36	0.72	30	1090	21	47	46	167	208	5	141
47	3.70	8.49	0.88	2.08	0.58	34	910	21	34	44	143	149	7	128
48	3.73	7.66	0.88	1.60	1.10	43	850	21	35	36	130	143	6	122
49	3.62	7.58	1.16	1.92	0.36	27	970	21	45	39	194	158	6	126
50	3.11	4.21	1.56	1.56	1.52	23	530	21	49	32	156	149	3	132
51	3.12	2.58	0.84	1.72	1.07	18	630	21	39	32	104	178	4	140
52	3.65	2.98	2.21	1.16	0.29	31	1010	21	50	36	143	137	4	133
53	4.17	9.56	1.16	1.44	1.20	51	1330	21	54	43	143	144	5	138
54	4.26	9.41	1.04	0.92	1.12	58	850	32	65	53	220	158	12	148
55	3.89	8.21	1.40	1.36	0.94	66	730	32	49	32	156	198	6	160
56	4.16	7.78	1.52	1.04	1.12	83	730	21	62	36	169	178	6	150
57	3.95	9.36	1.56	1.60	1.07	62	610	32	56	36	194	173	9	143
58	4.25	9.92	0.80	1.20	0.89	57	740	21	43	32	116	193	4	160
59	4.65	8.33	0.52	1.28	0.52	42	850	21	37	39	156	168	4	143
60	3.92	6.89	0.76	1.16	1.03	42	480	32	49	36	143	178	8	152
61	3.89	8.45	1.68	2.20	0.67	55	610	32	45	39	207	178	10	148
62	3.70	7.18	0.76	1.20	1.12	55	480	32	45	25	130	173	5	143
63	4.33	8.17	0.48	0.80	2.24	72	360	32	54	25	152	173	5	172
64	4.38	8.41	0.52	1.20	0.63	46	360	21	56	32	143	168	5	142
65	4.20	7.50	0.72	0.80	0.89	52	480	21	49	28	156	168	4	143
66	3.00	7.22	1.20	1.68	0.40	63	480	21	50	21	143	149	3	138

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
67	3.92	6.55	1.56	1.60	0.72	49	480	21	43	18	143	212	4	151	
68	4.31	7.89	0.92	1.12	0.67	70	240	32	49	28	155	168	10	122	
69	3.98	7.34	1.04	1.56	1.07	55	240	32	37	21	144	183	6	147	
70	3.88	7.78	0.80	1.20	0.76	71	360	32	41	21	143	168	5	164	
71	3.26	8.29	0.72	1.56	0.45	58	120	21	35	21	130	158	7	162	
72	3.50	7.02	2.06	2.24	1.07	53	120	21	35	18	117	163	4	167	
74	4.24	7.62	0.96	1.28	1.25	61	480	32	49	25	156	183	7	161	
75	3.82	5.08	0.82	1.36	0.85	69	360	21	39	14	117	193	5	162	
76	3.41	9.76	0.72	1.28	1.12	58	220	42	42	28	181	228	8	167	
77	3.53	7.38	2.00	1.60	1.25	42	360	32	45	25	143	152	6	144	
78	3.33	5.83	1.52	1.68	1.12	66	360	21	37	18	104	168	5	130	
79	4.54	7.38	1.20	1.72	1.12	68	120	21	39	16	104	153	7	138	
80	4.75	7.89	0.72	0.96	0.93	92	240	32	47	25	143	168	8	151	
82	4.27	8.41	0.52	0.80	0.36	69	480	32	37	25	169	178	8	185	
83	3.48	5.69	1.08	1.44	0.80	48	120	21	35	18	104	168	6	230	
84	4.72	7.98	1.40	2.00	0.80	72	360	21	52	18	143	168	4	229	
85	4.67	4.01	1.20	1.60	1.20	56	360	21	37	18	104	178	4	171	
86	3.91	8.17	0.96	1.20	1.03	60	360	21	35	21	143	173	6	139	
87	3.88	7.62	0.40	1.52	0.98	63	360	21	35	21	169	183	6	164	
88	4.38	7.86	0.72	1.72	1.25	53	240	32	37	32	168	158	10	121	
Average	3.97	7.32	1.06	1.44	0.96	54	533	25	44	29	148	171	6	151	

D. CLAY FRACTION

River	1	4	8	9	12	15
1	4.00	9.92	0.24	1.20	0.58	67
4	4.05	10.23	0.26	1.26	0.36	76
8	3.70	9.21	0.30	1.00	0.40	58
9	4.10	10.63	0.18	0.64	0.36	55
12	3.38	10.12	0.12	0.64	0.13	55
15	3.73	10.83	0.38	0.86	0.49	75
17	3.72	8.89	0.16	0.88	0.31	60
20	3.50	8.25	0.36	0.88	0.40	52
23	3.56	8.93	0.38	0.86	0.22	69
31	4.01	8.97	0.36	1.02	0.27	84
34	3.74	8.90	0.70	0.64	0.85	86
42	3.92	9.84	0.38	0.68	0.27	65
44	3.87	8.22	0.32	1.12	0.41	61
Average	.379	9.46	0.32	0.89	0.39	66

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Estuary															
45		3.40	10.32	0.88	0.92	0.89	46	1450	32	71	53	207	153	9	177
46		3.80	10.44	0.56	0.88	0.54	38	1450	32	63	61	194	188	8	167
47		4.04	8.62	0.36	1.20	0.54	47	610	32	60	43	169	134	7	167
48		4.55	10.39	0.42	1.12	0.45	70	970	32	60	50	181	149	7	172
49		3.00	10.19	0.80	1.04	0.40	38	1210	42	73	50	181	168	5	175
50		3.45	7.50	0.40	1.20	0.67	52	730	32	65	39	194	203	4	167
51		4.50	6.11	0.96	1.52	1.14	45	850	32	60	39	143	178	4	167
52		3.75	6.97	0.56	1.16	0.54	51	1210	21	65	53	181	183	4	165
53		3.48	8.53	1.12	1.08	0.80	57	1210	32	60	39	181	144	5	168
54		3.73	8.89	0.80	0.64	0.85	86	730	32	67	43	207	158	10	153
55		4.15	8.61	1.20	1.16	0.54	88	360	42	60	36	168	178	8	189
56		3.94	9.25	0.80	0.84	0.89	82	730	32	67	39	207	104	6	171
57		4.31	8.77	0.22	1.04	0.94	84	480	32	62	36	181	188	6	163
58		3.85	8.13	0.32	0.12	0.40	61	360	32	50	25	143	163	4	160
59		4.22	9.96	0.36	0.72	0.50	67	730	32	45	46	169	178	7	175
60		3.75	7.98	0.24	1.20	0.49	44	610	32	50	21	156	129	6	166
61		3.99	8.77	1.00	0.96	0.89	62	480	42	50	36	246	183	10	167
62		4.52	7.74	0.40	0.92	0.81	67	360	32	49	25	181	193	6	164
63		2.80	6.47	0.96	1.52	0.76	42	480	21	43	21	181	149	3	138
64		2.80	7.82	0.36	0.36	0.45	79	360	32	60	25	181	178	5	168
65		4.37	8.06	0.32	1.00	0.45	44	240	32	44	28	130	193	3	170
66		4.30	7.82	0.80	1.20	0.35	69	360	21	52	18	181	193	3	172
67		5.10	8.53	0.20	1.36	0.58	104	240	32	50	25	220	193	7	179
68		4.35	8.77	0.32	0.64	0.98	93	360	42	52	32	207	173	10	161
69		4.63	8.06	0.76	1.72	0.58	68	120	32	43	25	156	198	6	164
70		4.38	7.66	0.48	1.12	0.40	82	360	21	43	25	142	183	5	178
71		5.50	7.22	0.76	1.28	0.63	76	120	21	41	25	169	208	5	183
72		3.60	7.50	1.16	1.72	0.58	61	120	32	41	21	130	213	6	183
74		4.72	8.21	0.80	0.96	0.63	71	240	42	44	28	207	203	8	196
75		4.41	7.10	0.32	1.12	0.44	89	240	32	43	18	130	193	4	174
76		3.70	7.97	1.08	1.12	0.63	64	120	32	47	25	143	180	4	191
77		3.68	8.65	1.00	0.88	0.85	79	360	42	56	46	220	173	6	177
78		5.30	6.82	0.32	0.96	0.98	109	240	32	45	21	155	178	6	164
79		4.41	7.93	1.00	1.12	0.45	88	120	21	45	18	142	163	5	175
80		4.80	8.49	0.20	0.92	0.49	85	120	32	52	32	169	193	9	174
82		5.62	8.09	0.80	1.20	0.72	90	360	32	39	28	194	203	9	182
83		5.10	8.02	0.48	1.12	0.31	95	120	32	43	18	169	193	6	184
84		4.44	7.62	0.72	1.68	0.40	84	360	32	44	21	181	188	4	186
85		3.68	8.25	0.80	0.96	0.76	74	240	32	45	18	156	218	4	217
86		4.33	7.86	0.72	1.16	0.71	74	240	32	41	21	156	193	5	165
87		4.45	7.26	0.80	0.92	1.25	76	240	32	49	18	156	193	5	192
88		4.12	8.29	0.80	0.92	0.89	90	120	42	69	55	194	173	11	146
Average		4.17	8.23	0.65	1.07	0.66	71	480	32	53	32	175	179	6	173

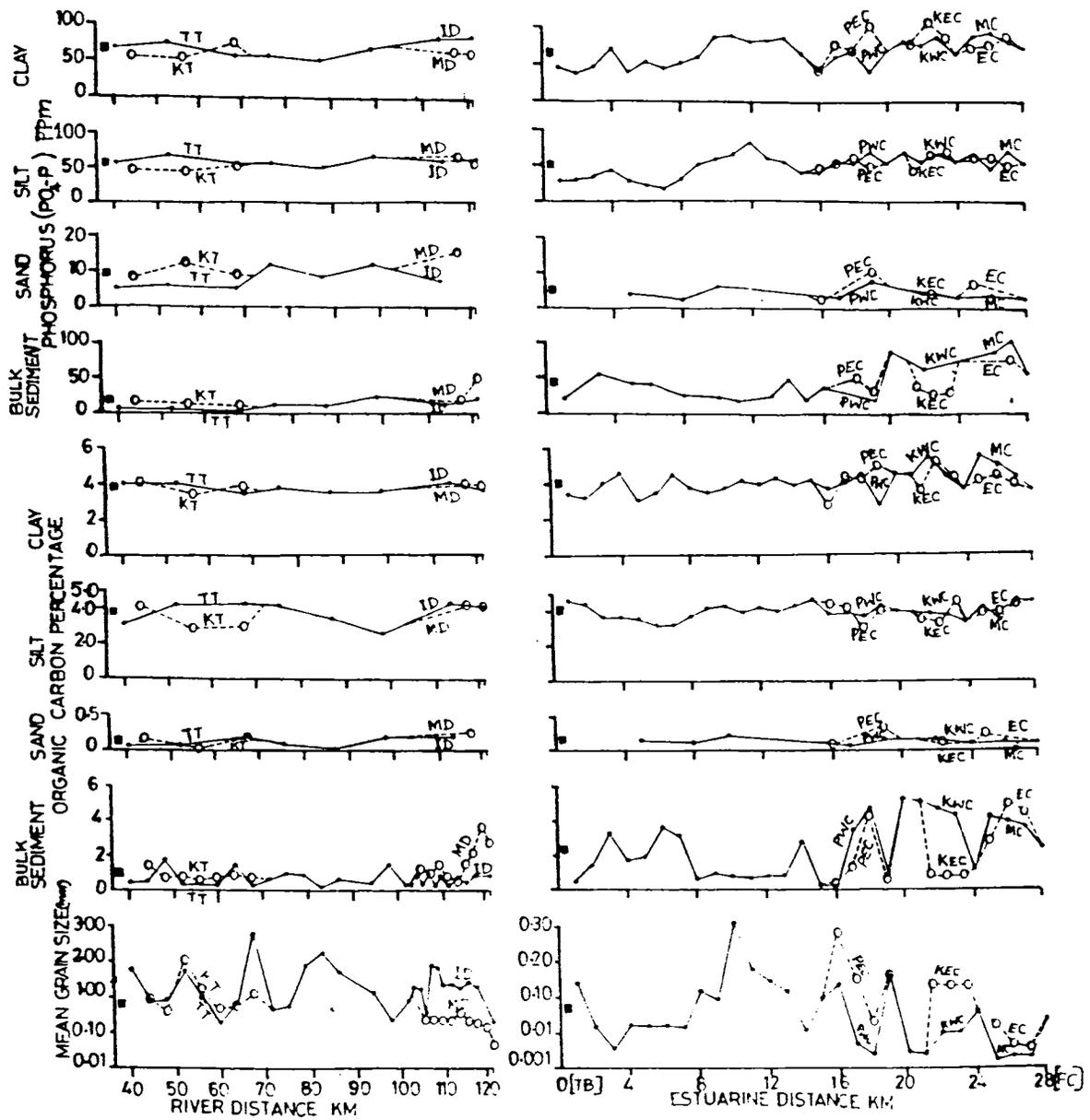


Fig. 27 Spatial variation of organic carbon (%), phosphorus (ppm) and mean grain size (mm) in the sediments of Muvattupuzha river and Central Vembanad estuary

## ABBREVIATIONS USED IN THE SPATIAL VARIATION DIAGRAMS

KT	Kaliyar tributary
TT	Thodupuzha tributary
MD	Murinjapuzha distributary
ID	Ittupuzha distributary
PEC	Perumbalam east channel
PWC	Perumbalam west channel
KEC	Kumbalam east channel
KWC	Kumbalam west channel
EC	Ernakulam channel
MC	Mattanchery channel
TB	Thannirmukham bund
FC	Fort Cochin

increase has been resulted from the floc formation followed by faster settling of organic rich suspended particulates as well as the increased productivity near estuarine mouth (Nair et al., 1975). In addition to this, a substantial amount of organic carbon rich sewage sludges are disposed (through municipal drainages) near the estuarine mouth.

The antipathetic relationship of organic carbon with grain size (i.e. positive relation with phi mean size) is evident in Figs. 27 and 28. The respective correlation coefficients of organic carbon and grain size (mm) in riverine and estuarine sediments are -0.43 and -0.80. As seen from Fig. 28, particles having less than 0.05 mm diameter show a comparatively higher organic carbon than coarser grades (i.e.  $> 0.05$  mm). The high content of organic carbon in fine fraction has also been previously reported by several investigators (Emery and Rittenberg, 1952; Eisma et al., 1966; Murty and Veerayya, 1972a; Kidwai and Nair, 1972; Patel et al., 1975; Paropakari, 1979; Sankaranarayanan and Panampunayil, 1979 and Seralathan and Seetharamaswamy, 1982) and might be resulted from increased surface area of the fine particles (Van Andel and Postma, 1954; Stewart, 1958; Kemp, 1971 and Elwakeel and Mahmoud, 1978). The size fractionation study of organic carbon of the present investigation also reveals that the highest organic carbon content occurs in silt and clay fractions which is about 27-30 times higher than that of the corresponding sand fraction.

### 5.3.2 PHOSPHORUS (P)

P is one of the chief nutrients which is functionally involved in the metabolic processes of living organisms (Parson, 1975). In the quantitative study of nutrients, P (as  $\text{PO}_4$  -P) estimation received much attention because of its strong bearing on the productivity and geochemical characterisation of metals (Ishikawa and Nishimura, 1989). However, the increased P loading in recent years from cultivated lands, domestic and industrial sewages has been crucial for eutrophication

processes in aquatic environments (Rhyther and Dunstan, 1971; Golterman, 1973 and Wetzel, 1975). The chief forms of P in a sedimentary environment are the following: a) allogenic apatite minerals transported by terrestrial agents, b) organic associates and c) precipitates from inorganic complexes.

Phytoplanktons normally satisfy their P requirements by direct assimilation of orthophosphates (the most stable and predominant form of soluble P). It may be recycled back to the water column during the oxidative destruction of organic tissues after their death (Chester, 1990). Most of the regeneration process takes place through bacterial decomposition which leads to the formation of orthophosphates although chemical decomposition may also occur. The behaviour of P during estuarine mixing has been studied by several researchers (Stefansson and Richards, 1963; Pomeroy et al., 1965 and Stirling and Wormald, 1977). Their studies reveal that the buffering process operating during estuarine mixing maintains the dissolved P levels in estuarine waters. In order to form a true buffer system, the estuarine sediments must be capable of both removing and releasing P from or to the water. Dissolved P will also be effectively removed from solution by adsorption onto solid surfaces (Carrit and Goodgal, 1954; Burns and Salomon, 1969 and Chen et al., 1973). In addition, temperature (Chen et al., 1973), Eh-pH conditions (Burns and Salomon, 1969) and salinity of water (Carrit and Goodgal, 1954), mineralogy of the sediments (Burns and Salomon, 1969) and organic coating over clastic sediments play a major role in controlling the sorption-desorption behaviour of phosphorus.

The concentrations of P in the Muvattupuzha river and the Central Vembanad estuarine bulk sediments and various size fractions are given in Table 11 and their variations along the river and estuarine course are represented in Fig. 27. The relationship between organic carbon and grain size is represented in Fig. 28. The average concentrations of P (in the form of  $\text{PO}_4^-$ -P) in the bulk sediment, sand,

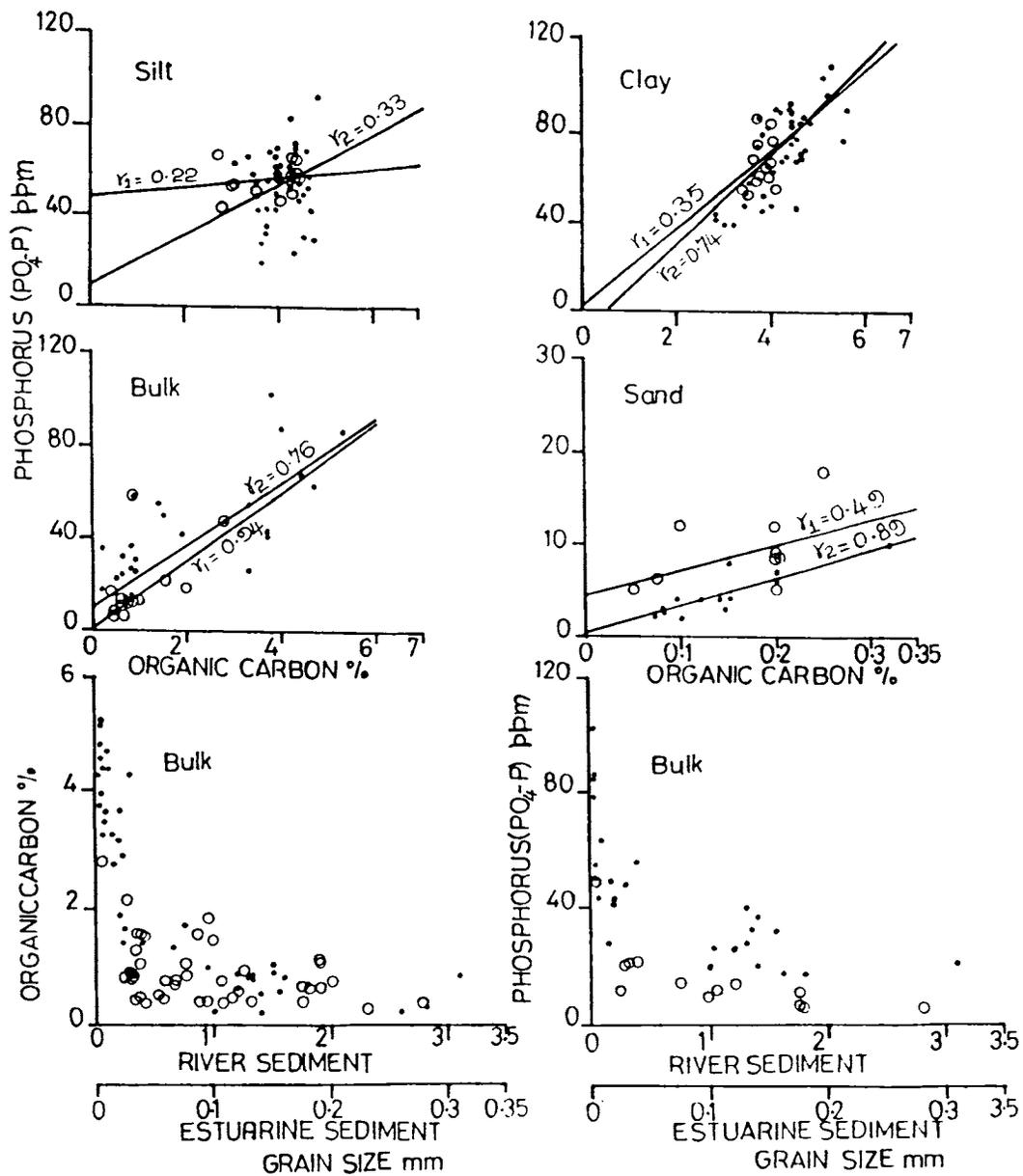


Fig. 28 The interrelationship of organic carbon vs phosphorus in the bulk sediment, sand, silt and clay fractions; and grain size vs organic carbon and phosphorus in riverine (○) and estuarine (●) environments ( $r_1$  = correlation coefficient in river and  $r_2$  = correlation coefficient in estuary)

silt and clay fractions of the river are 15 ppm, 9 ppm, 56 ppm and 66 ppm respectively and 44 ppm, 5 ppm, 54 ppm and 71 ppm in the estuary.

The bulk sediment of the estuary shows about 3 fold increase in P concentration than river sediment. High content of P is observed in the finer fractions as well as certain bulk samples in which the content of fine is more. The concentrations of P in silt and clay fractions are higher by 6-7 times in river and 11-15 times in estuary than the corresponding sand fraction. The observed high values of P in fine fractions ( $< 63 \mu\text{m}$ ) are related to the increased surface area, a fact established well by Carrit and Goodgal (1954).

From Fig. 27, it is evident that the content of P increases downstream and also from Thannirmukham bund to Fort Cochin. The comparatively lower P values in bulk sediment and size fractions of the estuary near the mouths of the Ittupuzha and the Murinjapuzha distributaries than other parts of the estuary are due to the abundance of quartz rich detrital clastics in the sediment population. The increase in P concentrations observed in the high saline zones of the estuary is resulted from the cumulative effects of several phenomena. In addition to the textural bearing, a substantial amount of P is removed from the overlying and interstitial waters by chemical precipitation under higher salinity levels and subsequently added to the sediments. In an earlier investigation Padmalal and Seralathan (1991) stated that the removal of P from overlying and interstitial waters as insoluble ferric phosphate complexes is taking place at faster rates between salinities 8 and  $28 \times 10^{-3}$ . Another significant portion of P is contributed to this area by sewage sludges. Intrusion of nutrient rich sea water resulted from upwelling (Purushan and Rao, 1974) as well as primary productivity (Nair et al., 1975) near estuarine mouth may also responsible for the observed increase in P contents near the high saline zones. The positive correlation of P with organic carbon in the bulk sediment (0.76;

n = 26), silt (0.33; n = 43) and clay (0.74; n = 43) fractions clearly indicates the role of biogenic pathway for P sedimentation in the Central Vembanad estuary, a feature described earlier by Murty and Veerayya (1972b).

### 5.3.3 SODIUM, POTASSIUM AND CALCIUM (Na, K and Ca)

The concentrations of Na, K and Ca in the bulk sediment, sand, silt and clay fractions are summarised in Table 11. Their variations with the riverine and the estuarine distance are presented in Fig. 29.

The bulk sediment (1.08%) and sand fraction (0.94%) of the river show almost similar average concentrations of Na and are also higher than that in silt (0.57%) and clay (0.32%) fractions.

In the estuary, bulk sediment (1.51%) and various size (Sand 0.72%; silt 1.06% and clay 0.66%) fractions show marked variation in the average content of Na. The bulk sediment of this environment accounts for more than 2 fold increase in Na concentration than sand fraction. The Na content of the estuarine clay is very much higher than that of riverine clay.

The metal K averages 1.55% in the bulk sediment of the river and 1.16% in the estuary. The sand fraction of the river shows 2-3 fold increase in the content of K than the estuarine counter part. K content in the river environment depicts a gradual decrease towards finer grades (sand 1.49%, silt 1.39% and clay 0.90%). The estuarine sand (0.59%) shows considerably low percentage of K than riverine sand, bulk sediment (1.16%), silt (1.44%) and clay (1.11%) fractions.

The Ca content in the bulk sediment of the two environments vary considerably and ranges from 0.18 - 1.25% (av. 0.87%) in river and

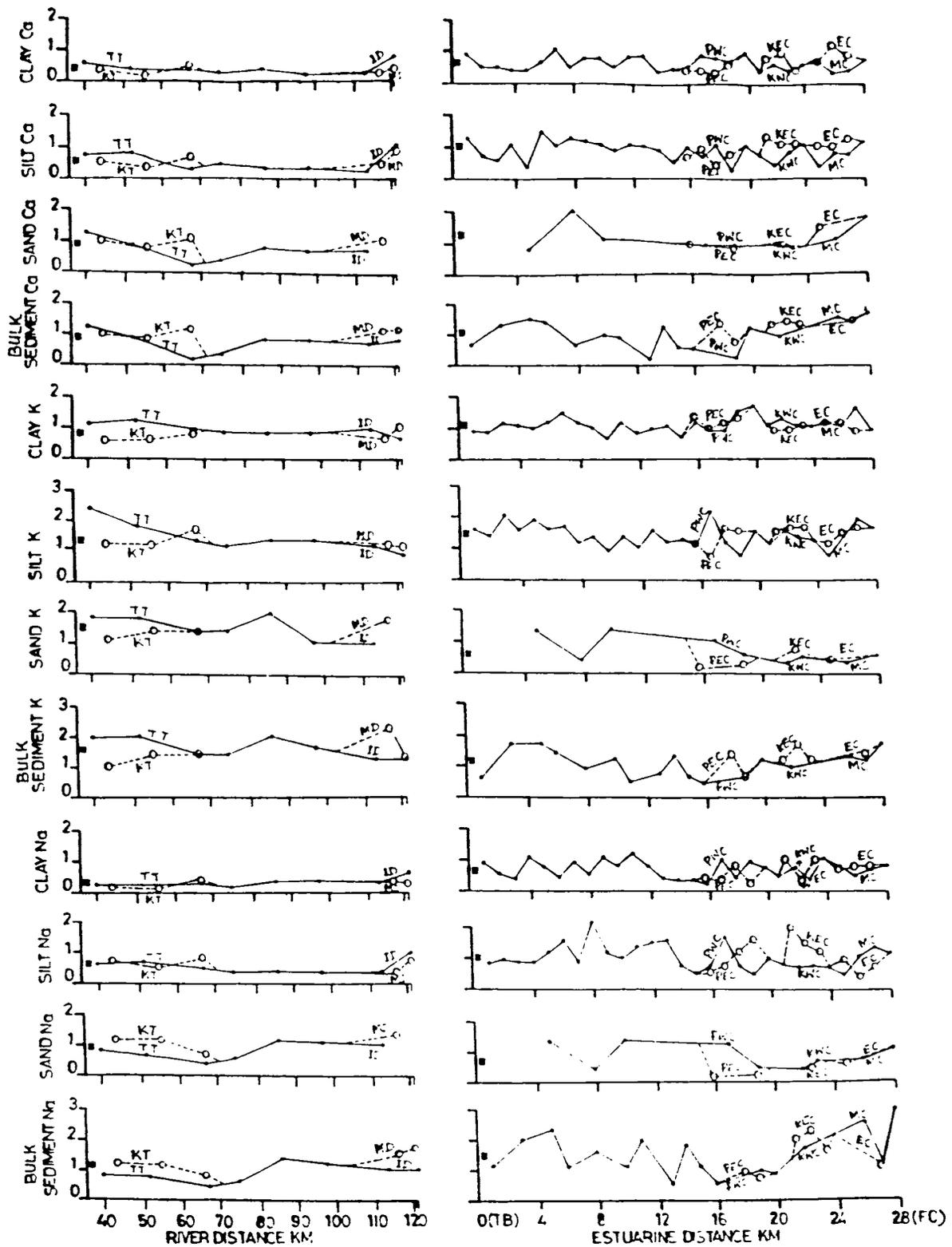


Fig. 29 Spatial variation of Na, K and Ca (metals in %) in the sediments of Muvattupuzha river and Central Vembanad estuary

0.18 - 1.6% (av. 1.05%) in estuary. The sand, silt and clay fractions of the river sediment account 0.88%, 0.54% and 0.39% of Ca respectively, whereas in the estuary, the observed average levels of this metal are 1.13%, 0.97% and 0.65% in the above fractions.

Although the concentrations of Na, K and Ca show a gradual decrease downstream in the three size grades (sand, silt and clay) in the river, the concentration factor as well as the decreasing trend are almost identical in the case of Na and Ca than K (Fig. 30). This clearly indicates that the source rock is the controlling factor for these elements. Such a trend is not observed in the estuarine environment indicating a difference in the depositional characteristics of these elements. In general, the sediments of the Kaliyar tributary show a slightly higher content of Na than the Thodupuzha tributary, while K content exhibits an opposite trend. This could be attributed to the difference in the sub-basin rock types. From petrochemical studies, it is evident that the drainage basin of the Thodupuzha tributary is characterised by K-rich igneous and metamorphic rocks (Table 16). The geochemical analysis of various rock types collected from Thodupuzha drainage basin accounts for 3.02% of K and 2.72% of Na (average of 8 samples) while the major rock types of the Kaliyar drainage basin account for 1.48% of K and 2.83% of Na (average of 6 samples).

The variation of Na, K and Ca downstream in the bulk sediment and sand fraction is almost identical with subtle differences between them (Fig. 29). It indicates that the part played by silt and clay in regulating the geochemistry of the bed sediment of the river is comparatively less. In other words geochemistry of the bulk sediment of the river environment is governed by the geochemistry of sand. Such a sand dependent geochemical variation is not so pronounced in the estuarine region. Here, the geochemical variation is primarily attributed to the availability of silt and clay in the bulk sediment.

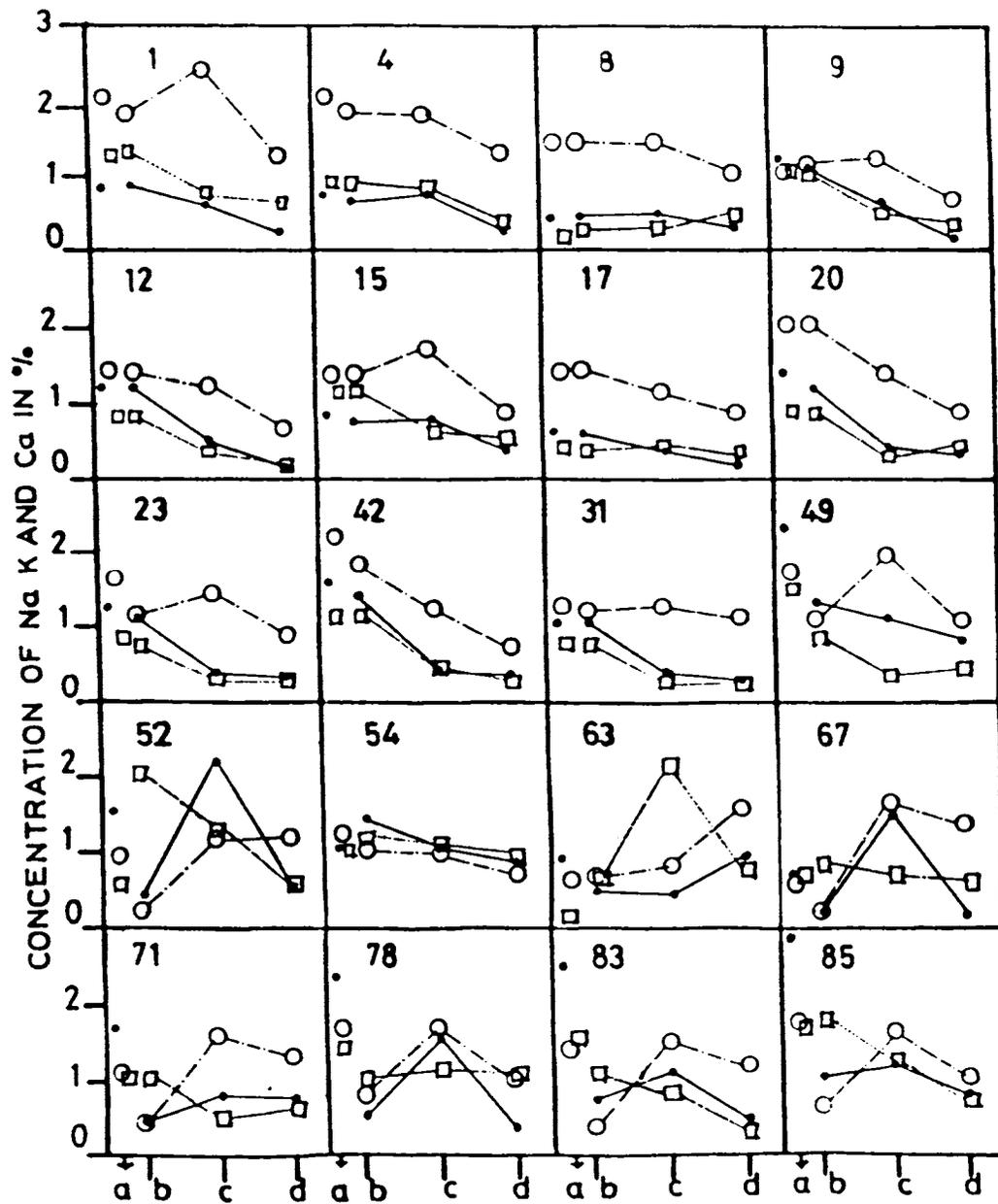


Fig. 30 Granulometric variation of Na (•), K (◊) and Ca (◻) in the sediments of Muvattupuzha river and Central Vembanad estuary (a bulk, b sand, c silt and d clay)

From Fig. 29, it is evident that the Na content of the bulk sediment increases markedly towards the estuarine mouth. It is presumably due to the high availability of Na in the interstitial waters of the estuarine sediments (Sholl, 1965). The chemical analysis of the bulk sediments has been performed without removing salts as the soluble salts enriched in interstitial waters are considered to be an integral part of the bulk sediment. Further, the process of desalting can also remove a significant part of exchangeable elements (Welby, 1958).

A comparative study of Na, K and Ca in silt and clay fractions of river with that of estuary reveals that the content of these metals is markedly higher in the estuary than river (Fig. 29). This could be due to the replacement of exchangeable ions like Fe, Mn, Co and Cu in clay mineral by Na, K and Ca during estuarine mixing (Potts, 1959; Weaver, 1967; Russel, 1970 and Sayles and Mangelsdorf, 1977).

#### 5.3.4 IRON (Fe) AND MANGANESE (Mn)

The concentrations of Fe and Mn in the bulk sediment as well as in sand, silt and clay fractions are furnished in Table 11. Fig. 31 shows the variation of these elements along the course of the riverine and the estuarine environments. The concentration of Fe in the bulk sediment ranges from 1.94-12.57% (av. 5.71%) in the river and 0.42 - 8.25% (av. 4.39%) in the estuary. The average concentration of Fe in sand, silt and clay fractions of the river sediment are 4.41%, 8.99% and 9.46% respectively. In the estuary, the concentration of Fe in sand (1.09%) is very much lower than that of silt (7.32%) and clay (8.23%). The observed average value of Fe in the bulk sediment of the estuary is comparable to earlier reports. Murty and Veerayya (1981) estimated an average of 3.74% of Fe (range 0.22-9.61%) in the bulk sediments of Vembanad estuary (South of Fort Cochin). Later, Mallik and Suchindan (1984) also reported an almost similar Fe values (range 1-9.06%; av. 4.41%) for the bulk sediments of this region. A comparative evaluation

of Fe (and other elements) in the sediments of the Muvattupuzha river and the Central Vembanad estuary with that of the major rivers and estuaries in India and abroad is given in Table 13.

Like Fe, the metal Mn also exhibits wide ranges of values in the bulk sediment of the riverine (range: 360 - 2060 ppm; av: 762 ppm) and the estuarine (range : 120 - 970 ppm; av: 366 ppm) environments. In the river, Mn averages 754 ppm, 1110 ppm and 1079 ppm in sand, silt and clay size fractions respectively. However, the concentrations of this metal in sand (143 ppm), silt (533 ppm) and clay (480 ppm) fractions of the estuary are very much lower than in the river. Mn concentration reported for the bulk sediments of the Vembanad estuary by Mallik and Suchindan (1984; av. Mn 400 ppm) is slightly higher than the values of this investigation.

In the river channel, the Fe and Mn contents of the bulk sediment and sand fraction exhibit an almost similar downstream variation (Fig. 31) indicating a common controlling factor (probably heavy minerals). For example, the bulk sediment and sand fraction of sample No.s 1, 9, 12 and 31 show anomalous high values of Fe and Mn (Table 11). These variations are directly related to the heavy mineral content in these samples. The sand fraction of these stations contains 10.21%, 11.6%, 7.82% and 7.18% heavy minerals respectively. The strong positive correlation of heavy mineral content in sand fraction with Fe ( $r = 0.96$ ;  $n = 11$ ) and Mn ( $r = 0.88$ ;  $n = 11$ ) also supports the above view.

Fig. 31 shows that the Fe and Mn contents in the bulk sediment and sand fraction of the Kaliyar tributary are higher than that of the Thodupuzha tributary. But the finer fractions (silt and clay) of the former record only lower content of Mn than the latter. The observed enrichment of Fe and Mn in the bulk sediment and sand fraction of the Kaliyar tributary is a function of the heavy mineral content in

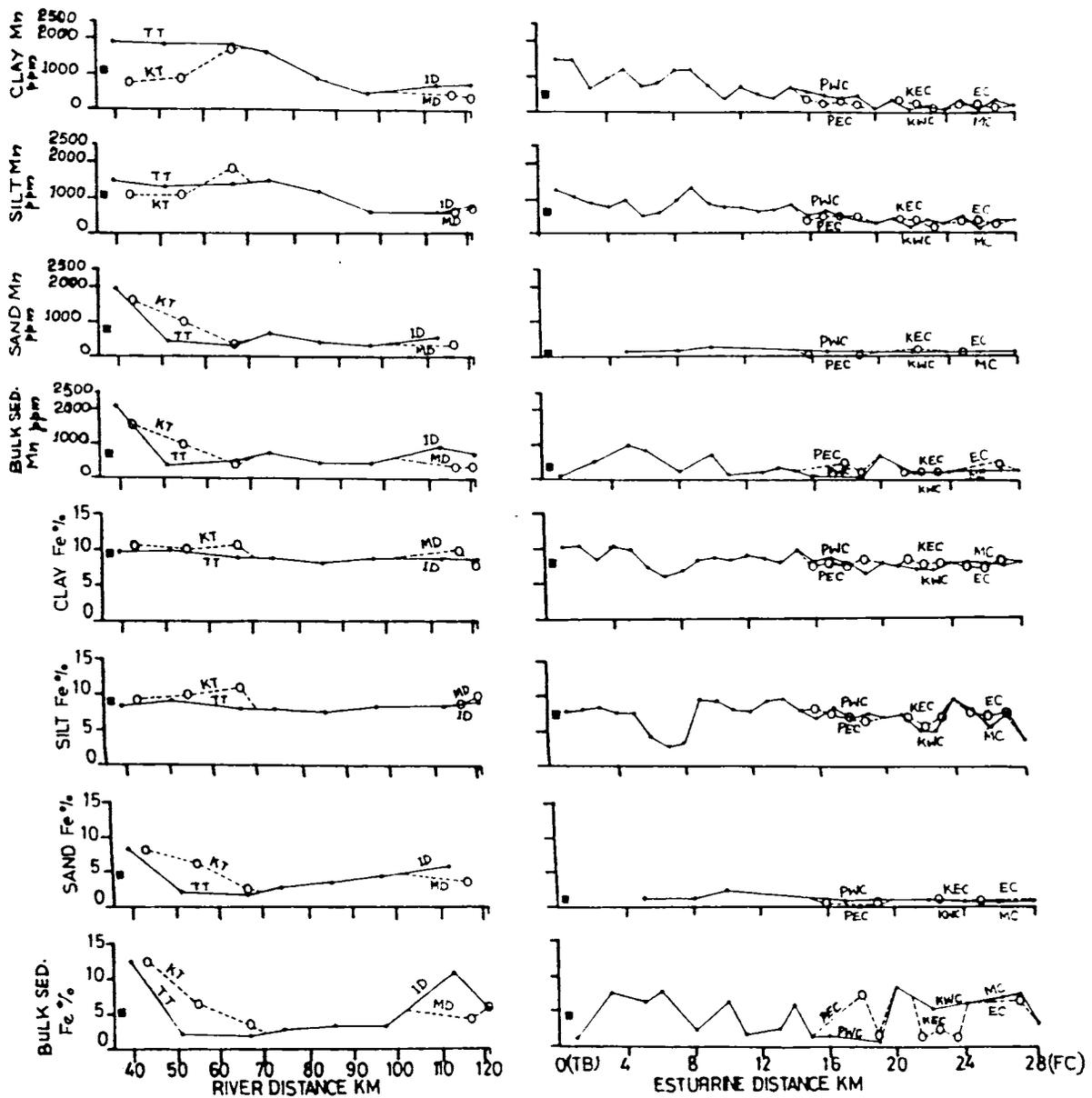


Fig. 31 Spatial variation of Fe (%) and Mn (ppm) in the sediments of Muvattupuzha river and Central Vembanad estuary

these samples. Further, petrochemical studies of the source rocks of the two drainage basins (Table 15) reveal that the Kaliyar drainage basin is characterised by Fe rich rocks (Fe 4.7%) than the Thodupuzha drainage basin (Fe 3.75%).

The size fractionation study shows that the metals Fe and Mn are highly enriched in fine fractions than sand (Fig. 32). The silt and clay fractions of the river exhibit 2-3 fold increase of Fe and Mn than sand fraction, while the estuarine counter part shows 4-8 fold increase. This increase in the association of metals, especially of Fe and Mn with fine grained sediments is axiomatic (Trefrey and Presley, 1976; Mudroch, 1984; Seralathan, 1987 and Nair et al. 1990). Kemp and Thomas (1976) opined that the increase in the association of metals with fine grained sediment is due to the greater surface area of the particulates which in turn activates the adsorptive ability. Further, precipitation of Fe and Mn hydrolysates over finely dispersed particulates in aquatic sediments can also enhance the level of these metals (Lee, 1985).

In the estuarine environment, Fe values in the bulk sediment yield highly significant covariation with organic carbon ( $r = 0.89$ ). Several researchers repeatedly advocated the dependance of Fe and other metals with organic carbon and also the precipitation of organometallic complexes during estuarine mixing (Holiday and Liss, 1976; Boyle et al., 1977 and Sholkovitz, 1981). However, the poor correlation of Fe with organic carbon (Table 12; Fig. 33) in the clay fraction indicates that Fe in this fraction is mainly associated with clay minerals or hydrolysate coating rather than organic carbon. Deer et al. (1962) and Grim (1968) stated that a substantial amount of Fe may be fixed by clay minerals. Therefore, in the bulk sediment too only a part of Fe might be of organic origin.

In the Muvattupuzha river the Mn contents in the silt and clay fractions show a steady decrease after 90 Km (Fig. 31). Between 40 and

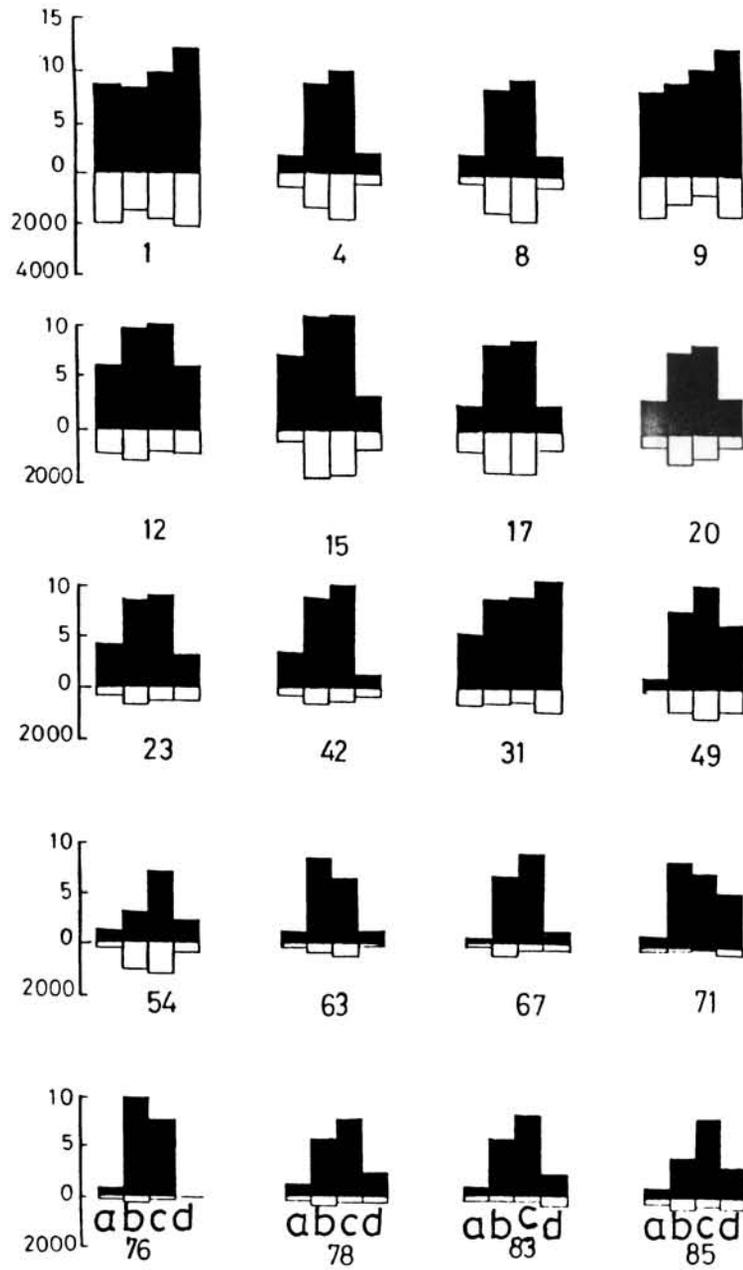


Fig. 32 Distribution of Fe (■) and Mn (□) in sand (a), silt (b) and clay (c) fractions and bulk sediments (d) of Muvattupuzha river and Central Vembanad estuary (Fe in % and Mn in ppm)

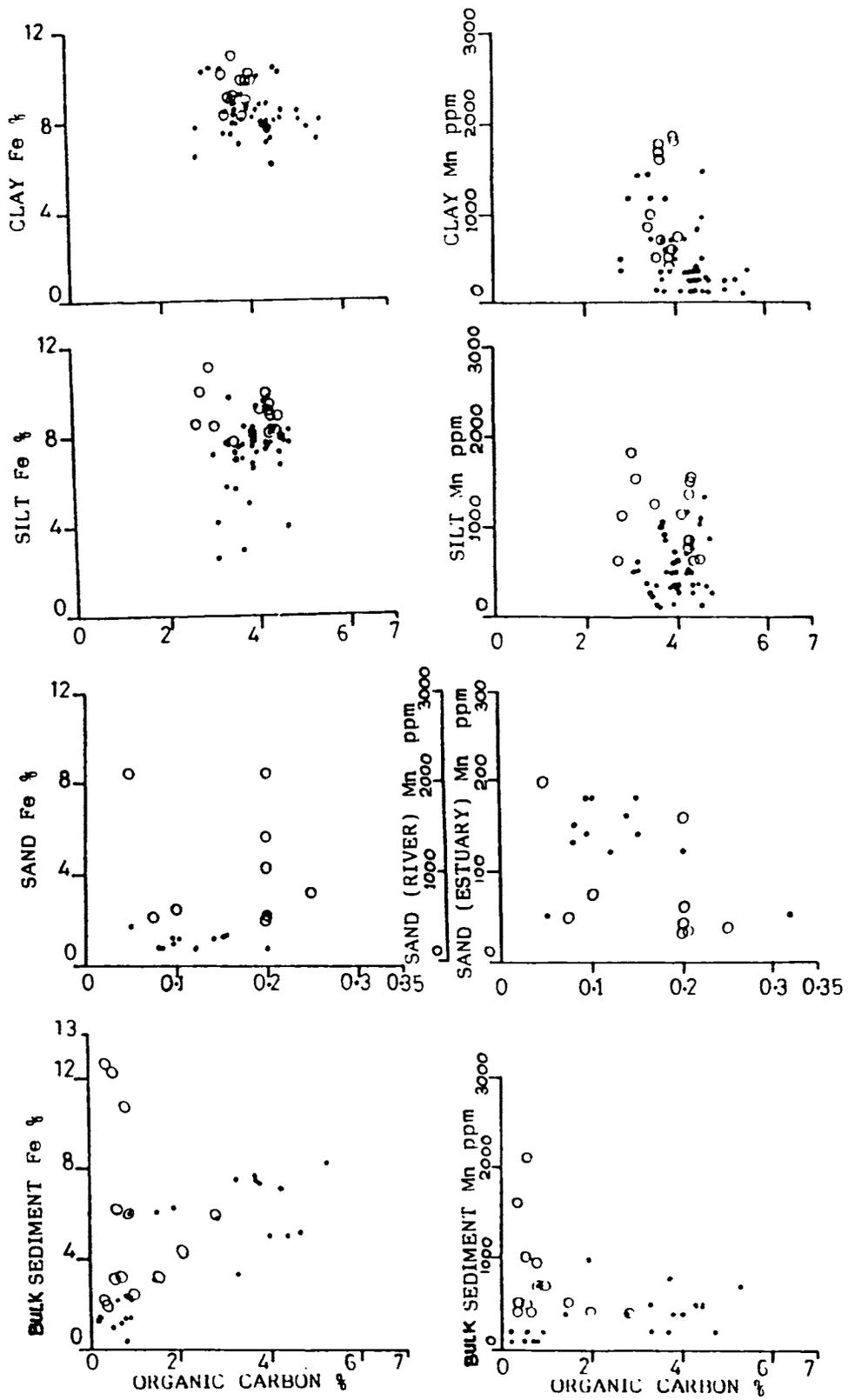


Fig. 33 The interrelationship of organic carbon vs Fe and Mn in bulk sediment, sand, silt and clay fraction of Muvattupuzha river (○) and Central Vembanad estuary (●)

90 Km, the content of Mn shows an average of 1380 ppm in the silt and 1420 ppm in the clay but further downstream (i.e. 90-121 Km), Mn registers a substantial low average value in the above two fractions (silt 680 ppm; clay 530 ppm). A marked decrease of Mn content in the silt and clay fractions is also recorded in the estuarine sediment from Thannirmukham bund to Fort Cochin. The above depletion of Mn in the estuary and also in the lower reaches of the river can be interpreted based on the desorption characteristics of Mn from sediments to the interstitial waters or to the overlying waters during estuarine mixing as suggested by Trefrey and Presley (1976) and Borole et al. (1977). A similar observation in the behaviour of Mn was also made by Murty and Veerayya (1981) in this part of the study area. The scatter plot of organic carbon and Mn (Fig. 33) in silt and clay fractions does not yield any specific trend suggesting that Mn in organic matter is negligible.

#### 5.3.5 TRACE METALS (Pb, Cu, Co, Ni, Cr, Cd and Zn)

The concentrations of various trace metals in the Muvattupuzha riverine and the Central Vembanad estuarine sediments are given in Table 11 and their variations with distance are presented in Figs. 34, 35 and 36. Fig. 37 presents the average concentrations and ranges of trace metals together with Fe and Mn. The concentrations of metals in sand, silt and clay fractions are compared with the corresponding metal enrichment in the bulk sediment for some selected samples of the river and the estuary (Fig. 38). The interelemental correlations in bulk sediment and sand, silt and clay fractions are depicted in Table 12. The covariations of trace metals with organic carbon (Figs. 39 and 40a, b) and heavy mineral content in sand (Fig. 41) are also studied and discussed below.

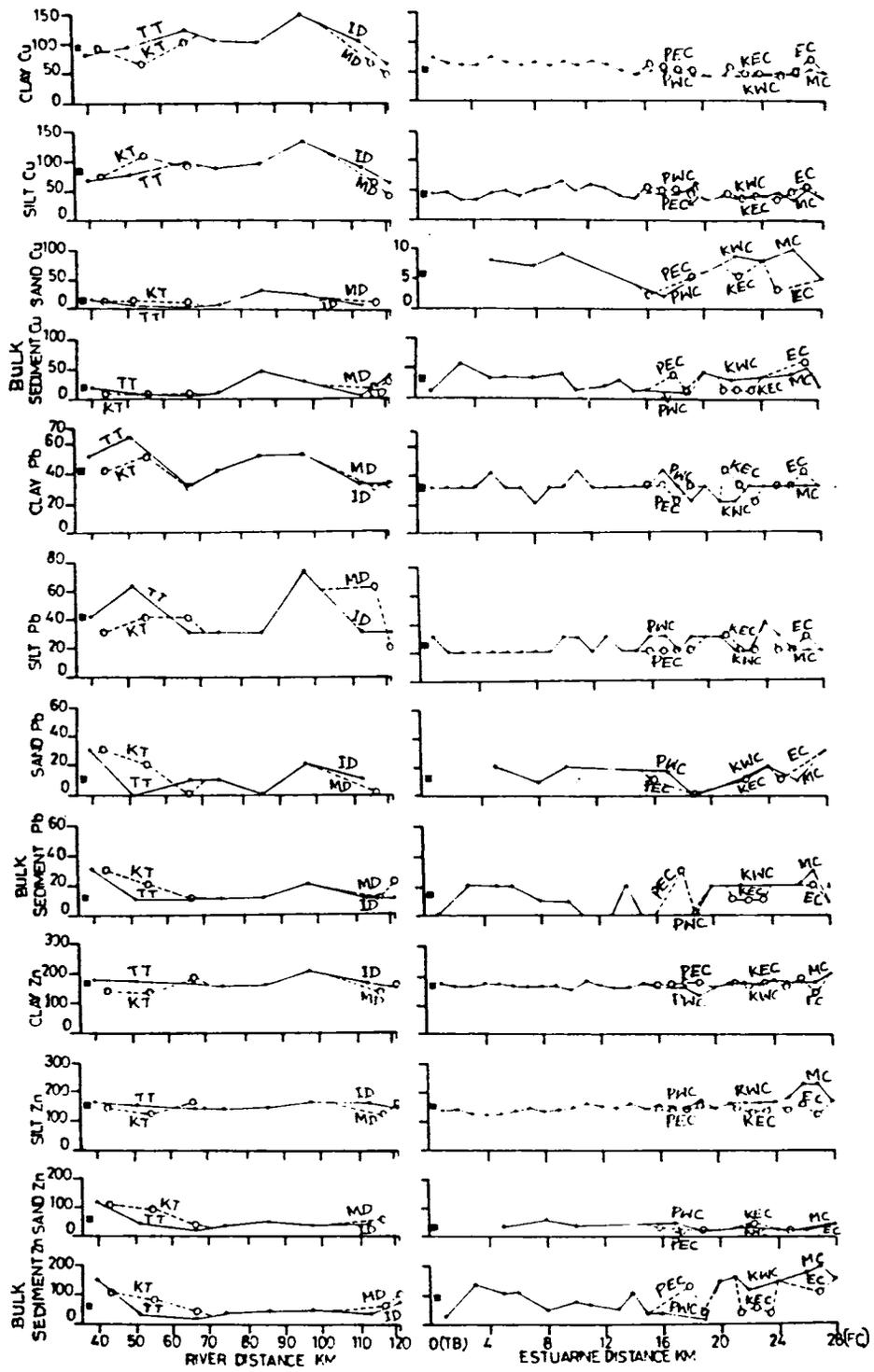


Fig. 34 Spatial variation of Zn, Pb and Cu (metals in ppm) in the sediments of Muvattupuzha river and Central Vembanad estuary

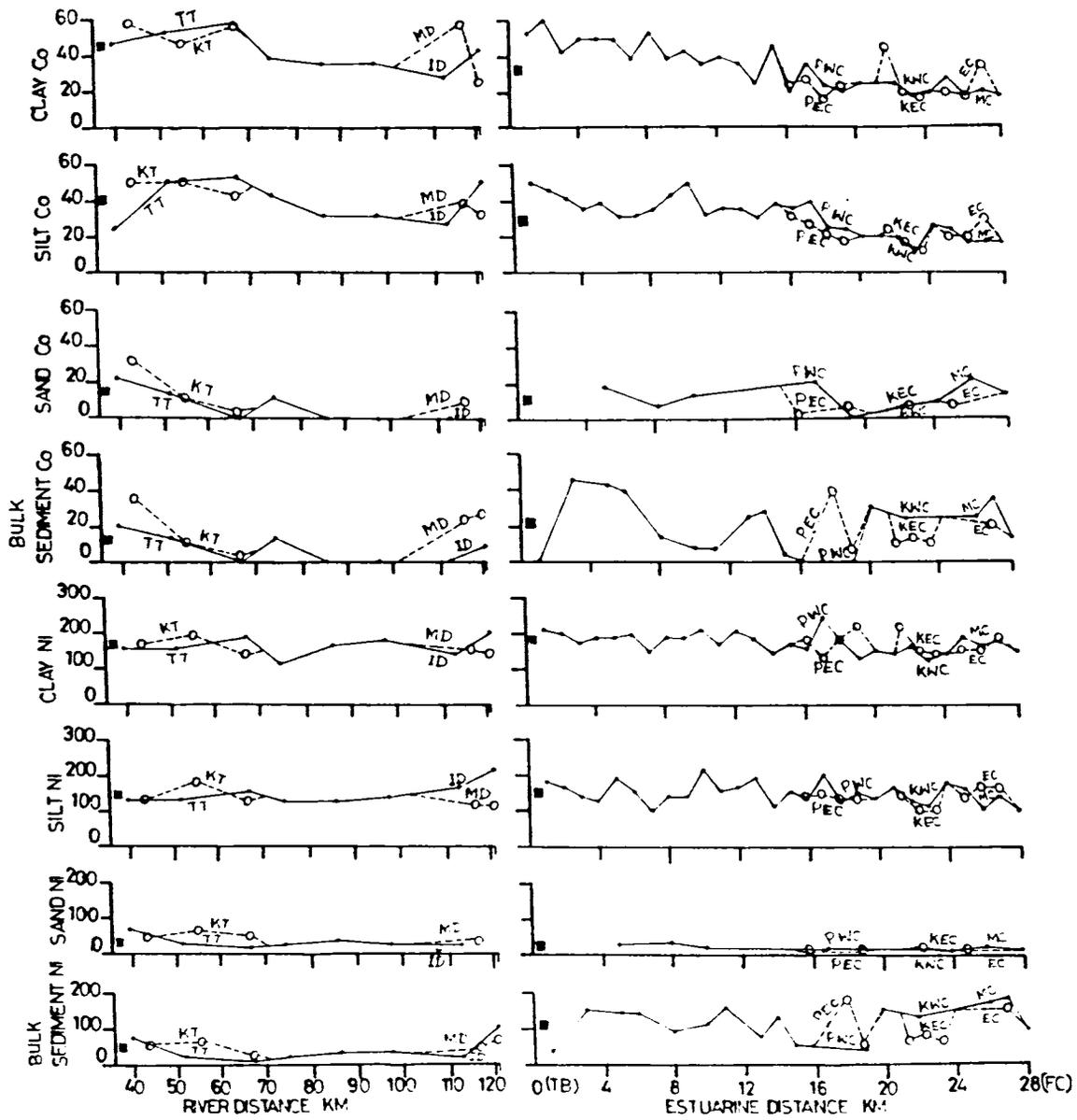


Fig. 35 Spatial variation of Ni and Co (metals in ppm) in the sediments of Muvattupuzha river and Central Vembanad estuary

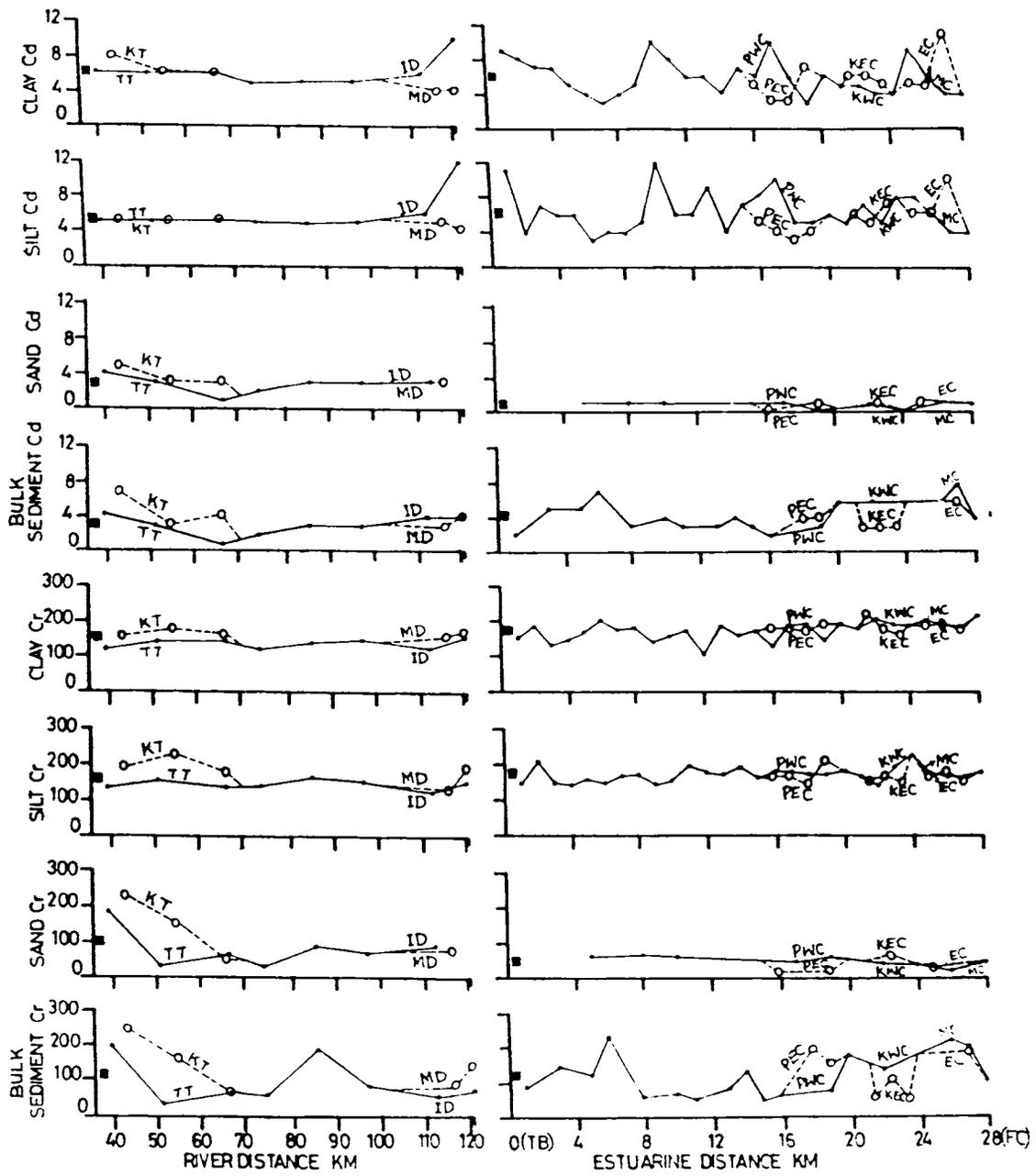


Fig. 36 Spatial variation of Cr and Cd (metals in ppm) in the sediments of Muvattupuzha river and Central Vembanad estuary

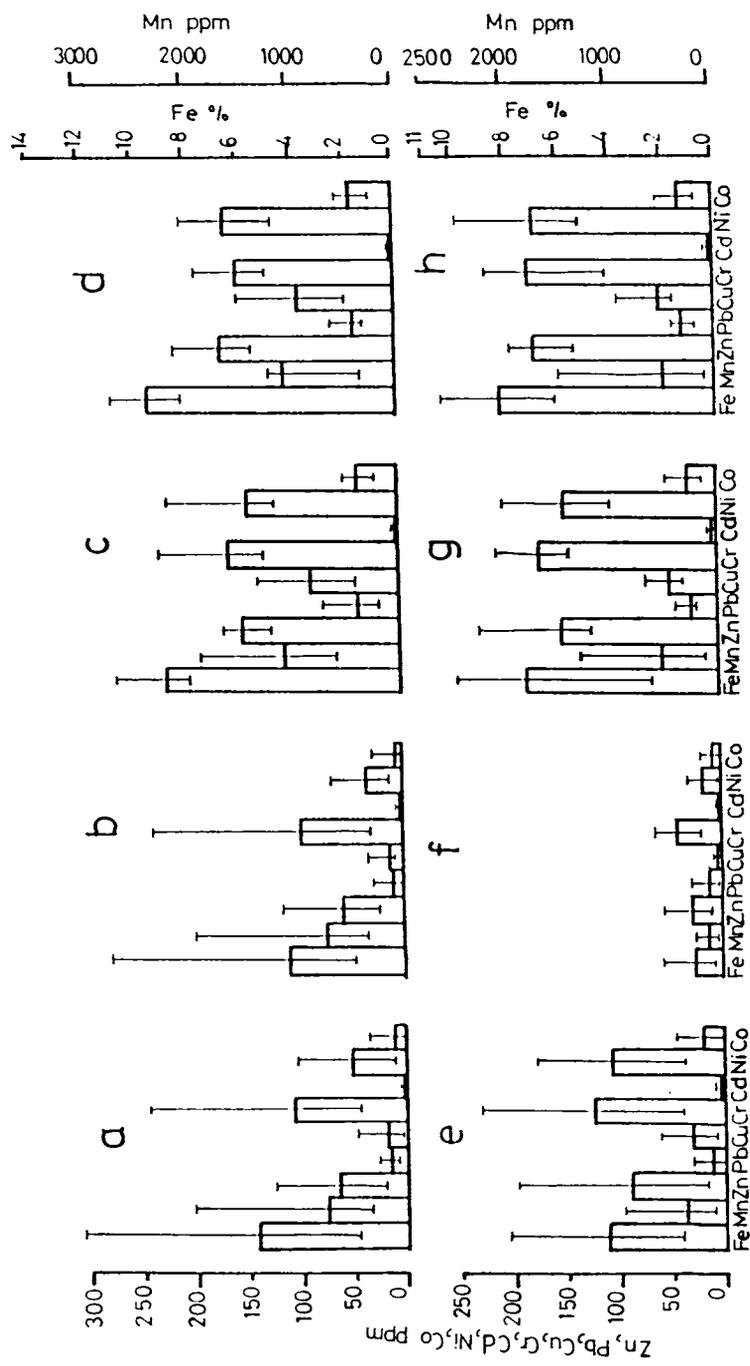


Fig. 37 Average heavy metal concentrations in river (a bulk sediment, b sand, c silt and d clay) and estuary (e bulk sediment, f sand, g silt and h clay); I - Range

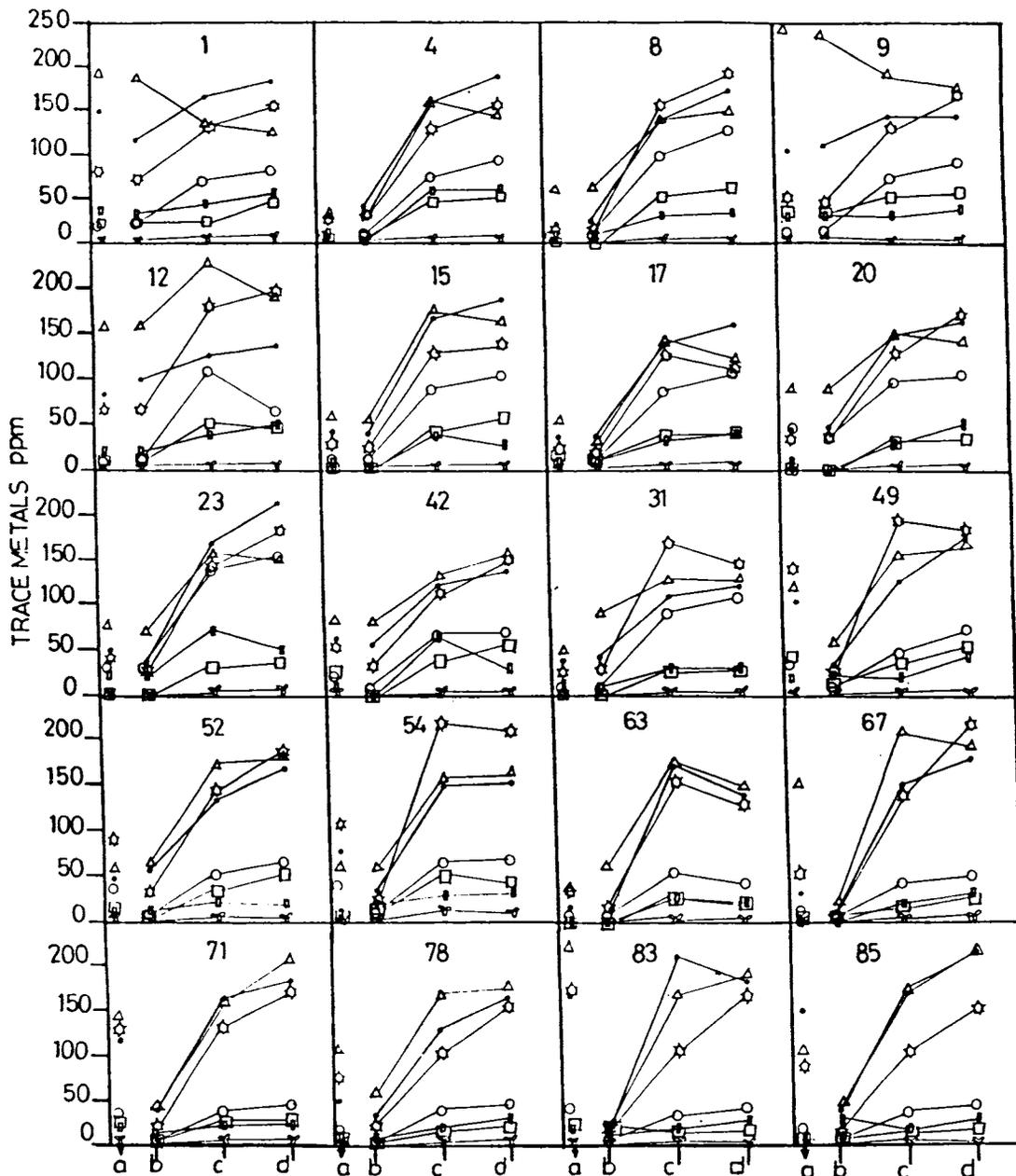


Fig. 38 Granulometric variation of Cr ( $\Delta$ ), Ni ( $\star$ ), Zn ( $\circ$ ), Cd ( $\nabla$ ), Co ( $\square$ ), Pb ( $\blacksquare$ ) and Cu ( $\diamond$ ) in reverine and estuarine environments (a bulk sediment, b sand, c silt and d clay)

TABLE 12 - Interrelationship among various geochemical parameters in the bulk sediment and sand, silt and clay fractions of Muvattupuzha river and Central Vembanad estuary

	Fe	Mn	Na	K	Ca	P	Cd	Co	Ni	Pb	Zn	Cr	Cu	C-Orig.
<b>A. BULK SEDIMENT</b>														
Fe	1.00													
Mn	0.86	1.00												
Na	0.12	-0.15	1.00											
K	-0.28	0.19	1.00											
Ca	-0.28	0.22	0.60	1.00										
P	0.03	-0.19	0.87	-0.07	1.00									
Cd	0.75	0.51	0.36	-0.33	0.65	1.00								
Co	0.61	0.33	0.52	-0.10	0.32	0.63	1.00							
Ni	0.29	0.15	0.83	0.08	0.60	0.34	0.50	1.00						
Pb	0.72	0.78	-0.01	-0.25	0.38	0.61	0.50	0.50	1.00					
Zn	0.72	0.72	0.42	0.05	0.67	-0.60	0.75	0.59	0.73	1.00				
Cr	0.61	0.64	0.34	-0.07	0.44	0.61	0.61	0.59	0.73	0.73	1.00			
Cu	-0.20	-0.23	0.56	0.42	0.28	-0.01	0.46	0.46	0.35	-0.13	0.10	1.00		
C-Orig	-0.09	-0.29	-	-	-	0.94	0.06	0.37	0.79	-0.18	0.29	-0.02	0.36	1.00
	(0.89)	(0.53)	-	-	-	(0.76)	(0.78)	(0.84)	(0.84)	(0.62)	(0.76)	(0.80)	(0.81)	(1.00)
<b>B. SAND FRACTION</b>														
Fe	1.00													
Mn	0.88	1.00												
Na	0.41	0.06	1.00											
K	-0.24	-0.05	0.06	1.00										
Ca	0.61	0.56	0.50	0.08	1.00									
P	-0.16	-0.04	0.62	-0.85	0.01	1.00								
Cd	0.77	0.67	0.53	-0.06	0.92	-0.03	1.00							
Co	0.80	0.81	0.15	-0.27	0.58	-0.46	-	1.00						
Ni	0.78	0.78	0.77	0.56	-0.11	-	-	1.00						
Pb	0.86	0.84	0.42	0.24	0.53	-0.06	0.61	0.44	1.00					
Zn	0.24	0.19	0.49	0.38	0.29	-0.36	-	0.50	0.76	1.00				
Cr	0.45	0.63	0.37	0.05	0.71	-0.10	0.76	0.81	0.76	0.88	1.00			
Cu	0.89	0.81	0.38	-0.29	0.51	-0.70	-	0.21	0.77	0.87	1.00			
HMS	0.12	0.01	0.41	-0.17	0.69	-0.12	0.76	0.78	0.77	0.87	0.92	1.00		
	(0.46)	(0.42)	(0.24)	(-0.05)	(-0.03)	(0.11)	(-)	(0.05)	(0.43)	(0.10)	(0.05)	(0.22)	1.00	
	(0.92)	(0.84)	(0.46)	(0.38)	(0.32)	(0.32)	(-)	(0.15)	(0.81)	(0.24)	(0.66)	(0.92)	(0.34)	1.00



TABLE 12 - (Contd.)

River/Estuary	r - values		Level of significance	
a) MUVATTUPUZHA RIVER				
Bulk sediment, Silt and Clay fraction	0.44	to 0.51	0.1	to 0.05
	0.51	to 0.59	0.05	to 0.02
	0.59	to 0.64	0.02	to 0.01
	>0.64		<0.01	
Sand fraction	0.48	to 0.55	0.1	to 0.05
	0.55	to 0.63	0.05	to 0.02
	0.63	to 0.68	0.02	to 0.01
	>0.68		<0.01	
b) CENTRAL VEMBANAD ESTUARY				
Bulk sediment	0.32	to 0.38	0.1	to 0.05
	0.38	to 0.44	0.05	to 0.02
	0.44	to 0.49	0.02	to 0.01
	>0.49		<0.01	
Sand fraction	0.44	to 0.51	0.1	to 0.05
	0.51	to 0.59	0.05	to 0.02
	0.59	to 0.64	0.02	to 0.01
	>0.64		<0.01	
Silt and Clay fraction	0.25	to 0.30	0.1	to 0.05
	0.30	to 0.36	0.05	to 0.02
	0.36	to 0.39	0.02	to 0.01
	>0.39		<0.01	

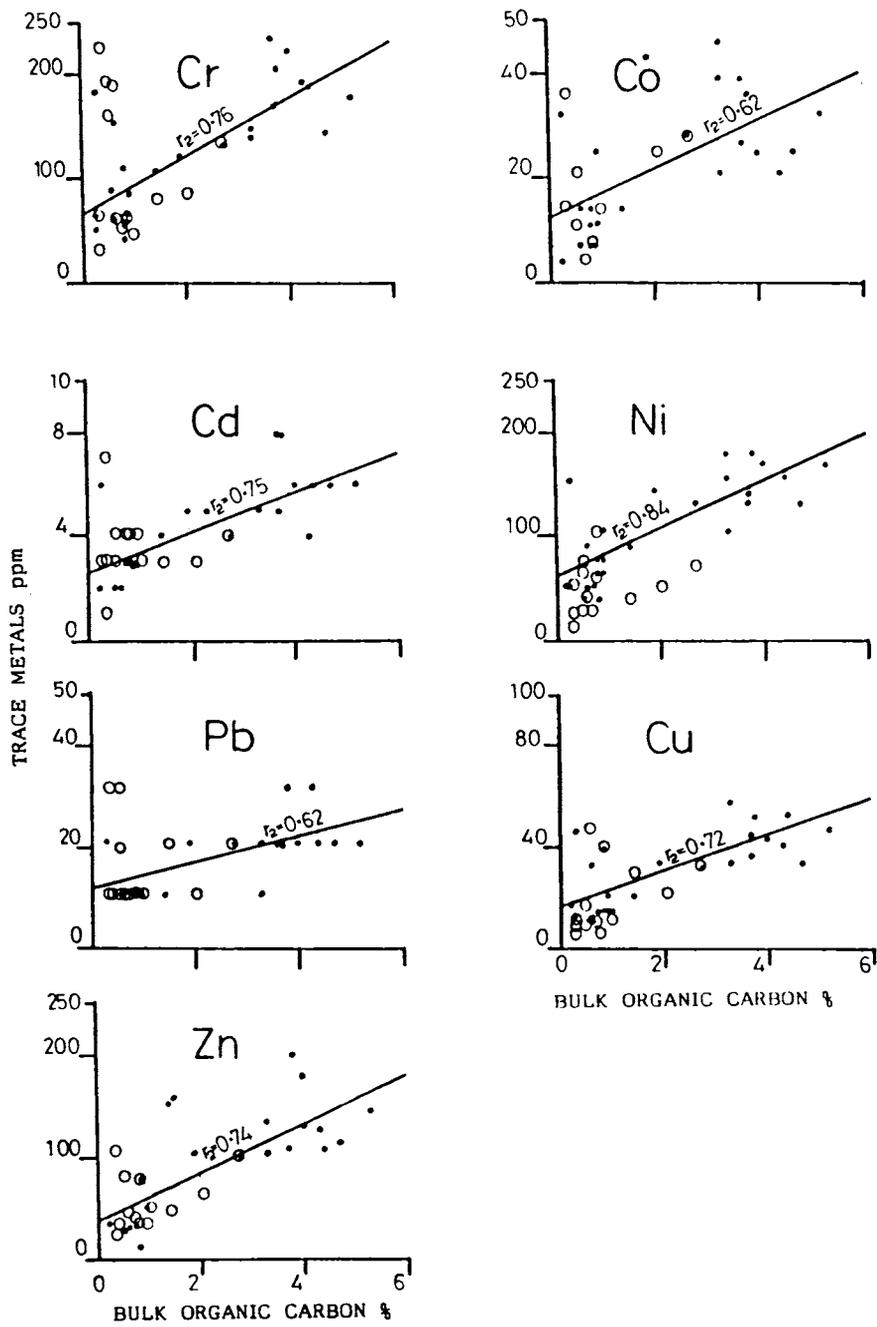


Fig. 39 The interrelationship between organic carbon and tracemetals in the bulk sediments of Muvattupuzha river (○) and Central Vembanad(●)  
 $r_2$  = correlation coefficient of estuarine sediment

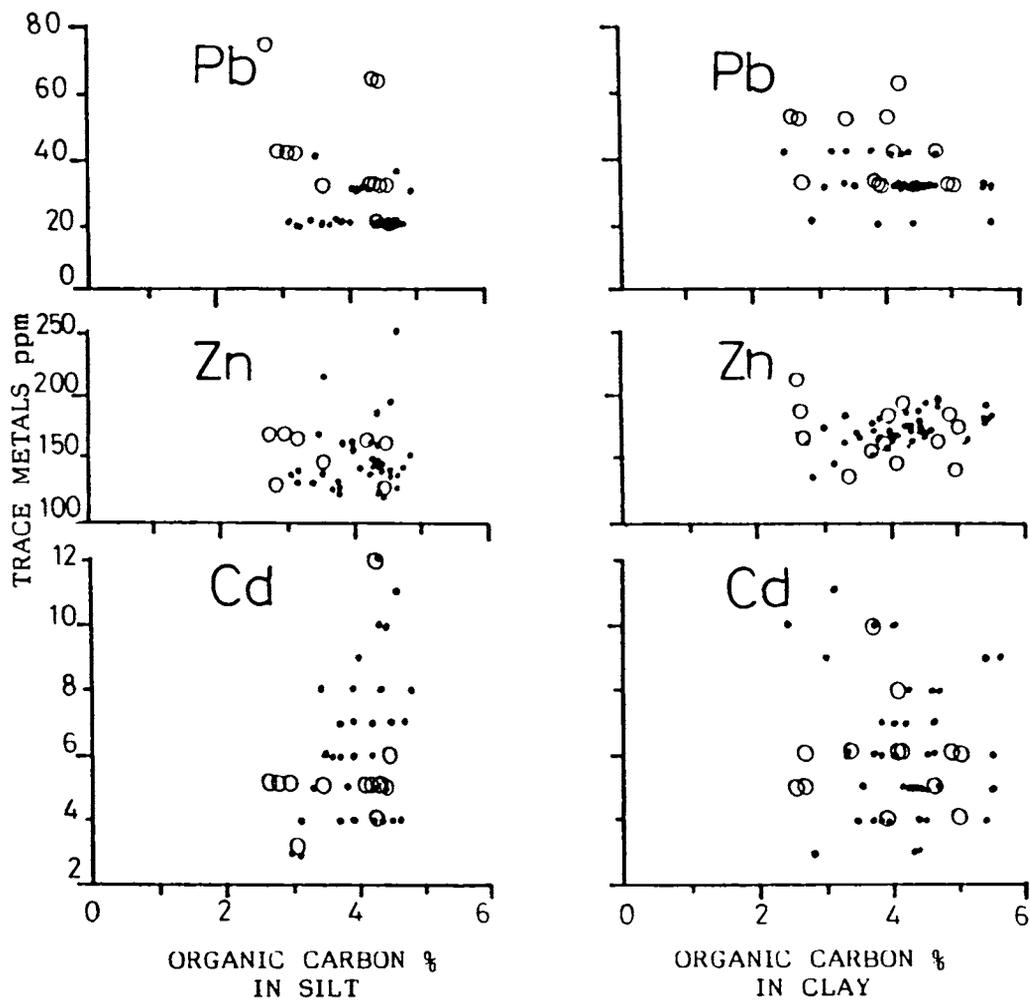


Fig.40a Interrelationship between organic carbon and trace metals (Cd, Zn and Pb) in the silt and clay fractions of Muvattupuzha river (○) and Central Vembanad estuary (•)

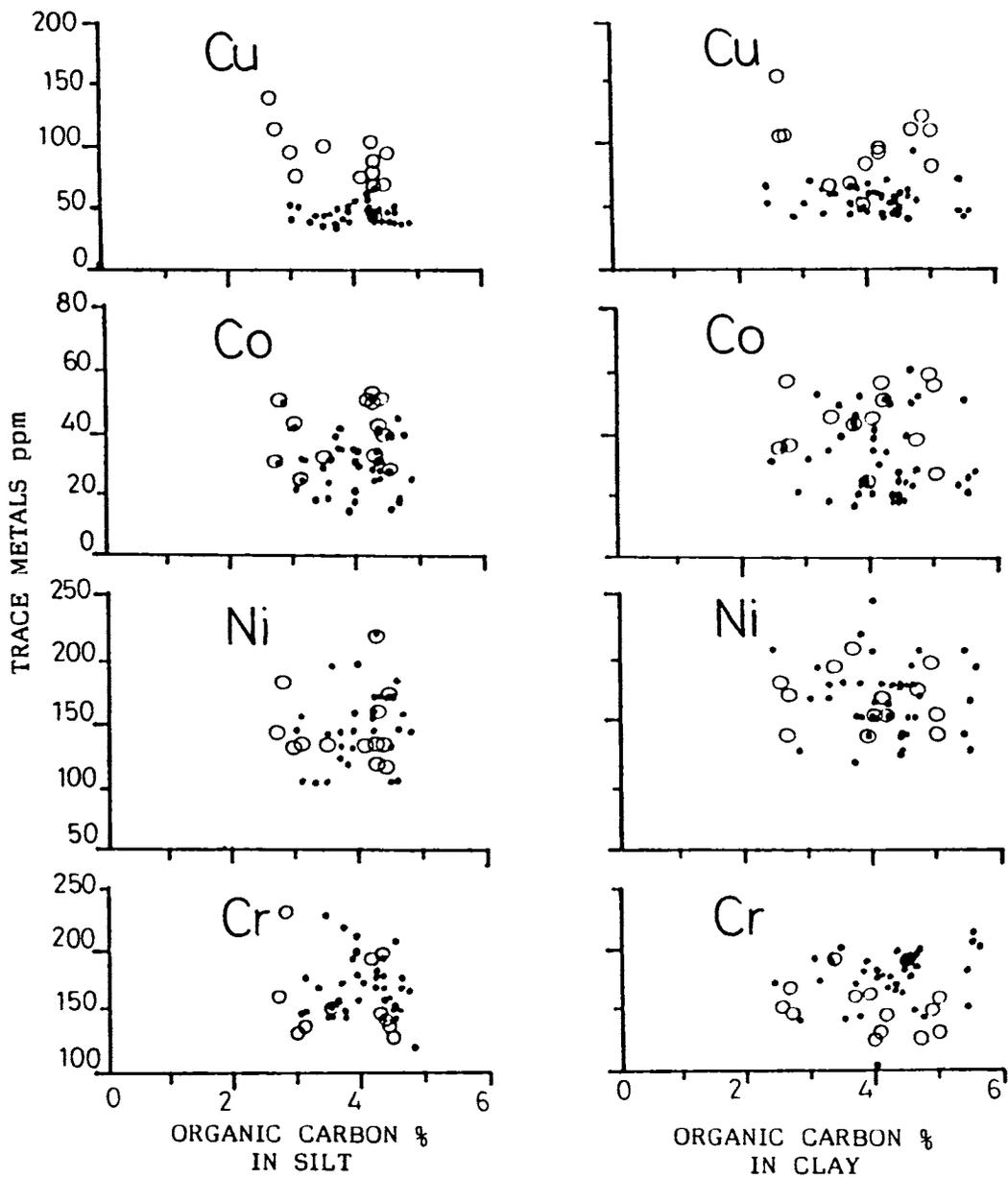


Fig.40b Interrelationship between organic carbon and trace metals (Cr, Ni, Co and Cu) in the silt and clay fractions of Muvattupuzha river (○) and Central Vembanad (•)

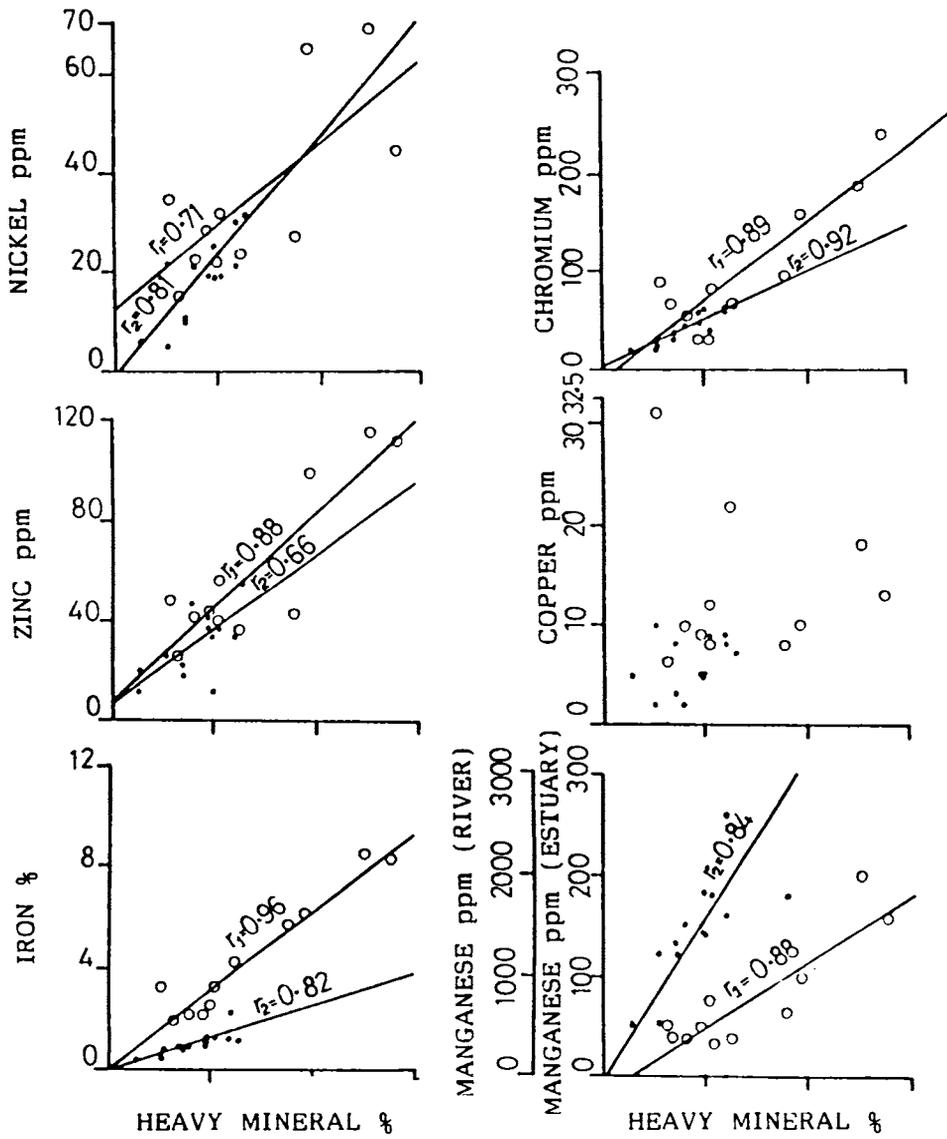


Fig. 41 Interrelationship between the contents of heavy metal and total heavy minerals in Muvattupuzha riverine (○) and Central Vembanad estuarine (●) sands, ( $r_1$  = correlation coefficient in river;  $r_2$  = correlation coefficient in estuary)

a) **Lead (Pb):** The ability of many organisms to accumulate Pb poses a potential threat to mankind through ingestion of contaminated products. The toxic effects of Pb on humans have been well documented, as Pb is being used by man for thousands of years (Branica and Konrad, 1980). It enters in aquatic environment through precipitation, dust fall out, erosion and leaching of soil as well as municipal and industrial waste disposals. The average concentration of this metal in the earth crust is 16 ppm (Davis, 1990). Nriagu (1978) calculated the mean Pb content of gabbro as 2 ppm, granites as 23 ppm and shales and clays as 20 ppm.

This metal depicts considerable variation in both riverine and estuarine environments. In bulk sediment, the metal ranges from 11-32 ppm (av. 17 ppm) in the river and 0-32 ppm (av. 14 ppm) in the estuary. Granulometric partitioning analysis illustrates Pb enrichment in silt (river 42 ppm and estuary 25 ppm) and clay (river 42 ppm and estuary 32 ppm) fractions than sand fraction (river 13 ppm and estuary 14 ppm). The anomalous high values of Pb especially in the silt and clay fractions from samples collected near Hindustan Paper Corporation Limited (St. No. 23 - Table 11) are in agreement with the earlier report of Nair et al. (1990) indicating an industrial input of Pb to this area.

Matrix analysis (Table 12) reveals strong relationship of Pb with other metals like Fe, Mn, Co, Zn and Cr. In the estuary, Pb also shows marked covariation with organic carbon ( $r_2 = 0.62$ ;  $n = 23$ ). This indicates the association of atleast a part of Pb with organic carbon. The Pb-organic carbon relationship has been well documented earlier by Cocker and Mathews (1983) and Glegg et al. (1988).

Considerable quantity of Pb enters into aquatic environments through weathering of rocks. Analysis of Pb in the bulk sediment and different size fractions reveals the association of Pb with the silt and

clay fractions of the two environments with a slightly elevated levels in the river. From Table 11, it is evident that the major source of Pb in this drainage system is from weathering of rocks i.e. lithogenous source. In accordance with this view, Paul and Pillai (1983b) has stated that about 80% of Pb in the Vembanad estuarine system is bound with lithogenous fraction. A significant amount of Pb occurs in the structure of minerals which constitutes the igneous and metamorphic rock. Pb released from the weathering of rocks can easily replace K and Ca diadocally from the structural positions of clay minerals which are either present in particulate form or as coating. Another significant portion of soluble Pb can be scavenged by Fe and Mn hydrolysates (Krauskopf, 1967). Wedepohl (1978) opined that this metal can be effectively carried by kaolinite than montmorillonite. The increased levels of kaolinite and Pb in the clay fraction of the river strongly suggest the association of this metal with kaolinite.

b) **Copper (Cu):** Cu is one of the essential elements for plants and animals, however, at elevated concentrations the metal turns to be highly toxic (Flemming and Trevors, 1989). Average abundance of this metal in the lithosphere is considered to be 70 ppm while the values for the earth's crust ranges from 24-55 ppm (Baker, 1990). The abundance of Cu in basaltic rocks is greater than that of the granitic rocks while it is very low in carbonate rocks (Krauskopf, 1972). Gabbro, dolerite and basalt have the highest Cu content while granodiorite and granite the lowest. Mudstones and other argillaceous rocks show a range of 10-27 ppm of Cu (Shorrocks and Alloway, 1987).

The bulk sediment and sand fraction of the Muvattupuzha river record an average of 19 ppm and 14 ppm of Cu respectively. Silt (84 ppm) and clay (94 ppm) fractions account 6-7 fold increase of Cu than sand in the river. The estuarine bulk sediment, sand, silt and clay account 31 ppm, 6 ppm, 44 ppm and 53 ppm of Cu respectively. Similar to the present investigation, earlier Murty and Veerayya (1981) and

Mallik and Suchindan (1984) have reported an average of 36.5 and 25.7 ppm of Cu respectively for the bulk sediment of the Vembanad estuary. Like Pb and Zn, the content of Cu in silt and clay is markedly high near the Hindustan Paper Corporation Limited influenced zones (St.No. 23 - Table 11) of the Muvattupuzha river (Fig. 34). The observed variation is in accordance with the earlier report of Nair et al. (1990) and the increase was attributed to the effluents from the paper factory. The content of Cu in the estuary shows a steady decreasing trend and this phenomenon is recorded even in the two distributaries of the Muvattupuzha river (Fig. 34). It is well known that Eh-pH changes and salinity variations in the overlying water strongly influence the geochemical behaviour of Cu in aquatic sediments (Aston and Chester, 1976). Dissolution of Cu from sediments to overlying water in presence of chloride bearing solutions of the estuarine and marine environments is also well documented by several previous investigators (White, 1968; Rose, 1976 and Sholkovitz and Copeland, 1981). In addition to the chemical mechanisms, biological uptake of this metal can also cause substantial loss of Cu budget in aquatic sediments (Kremling et al., 1983). Selective affinity of fine particulates, especially clay minerals for certain heavy metals also has tremendous influence on the dissolution of Cu (Mitchell, 1964 and Soong, 1974). During estuarine mixing, metals like Pb and Ni repel Cu and Zn from the clay minerals. This results in the returning of a part of the already adsorbed Cu from the clay minerals to overlying waters (Forstner and Wittmann, 1983). Further, this competitive affinity among the metals tends to increase towards the high saline zone of the estuary.

c) **Cobalt (Co):** Co is one of the important metals which is closely linked to our industrial civilization and also the maintenance of life within it. This metal is most abundant in relatively unstable ferromagnesian minerals such as pyroxenes, amphiboles and biotite (Smith, 1990) and hence Co content in sediments and sedimentary rocks reflects the composition of the source rocks from which they have been

derived.

In the river, the concentration of Co in sand fraction is almost same as that of the bulk sediment and both of them exhibit a similar pattern of variability downstream. The average concentrations of Co in the bulk sediment, sand, silt and clay of the river are 12 ppm, 10 ppm, 41 ppm and 45 ppm respectively. In estuary, the respective concentrations of the above sediments are 20 ppm, 10 ppm, 29 ppm and 32 ppm. Earlier, Murty and Veerayya (1981), while carrying out investigation on Co in various sediment types of Vembanad estuary and the adjoining river systems, estimated 41 ppm and 45 ppm of Co respectively for the riverine and the estuarine sands; 65 ppm and 49 ppm respectively for clayey silt and clay of the estuary. In bulk sediment and sand fraction, Co content is highly variable with texture and mineralogy. In finer fractions (silt and clay) Co content shows a general decrease downstream between 85 and 110 Km and thereafter, the content increases.

The silt and clay fractions of the river exhibit substantially higher Co enrichment than the estuarine counterpart. In the river, Co shows 4-5 fold enrichment in the silt and clay fractions than sand fraction whereas in the estuary the silt-clay fractions just show 2-3 fold increase than sand. Several investigators have repeatedly shown that river borne-particulates with multiple layers of Fe and Mn oxides and hydroxides and organic complexes scavenge trace metals with better efficiency than the estuarine counterparts (Goldberg, 1954; Krauskopf, 1967; Jenne, 1968; Murray, 1975 and Ramesh et al., 1990). The positive correlation of Co with Fe and Mn as well as organic carbon in the bulk sediments is suggestive of its association.

From Fig. 35, it is evident that the content of Co in silt and clay decreases from Thannirmukham bund to Fort Cochin. The pattern of variability of Co follows as that of Mn and marginally with Fe. This 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 (Graham et al., 1976; Evans et al., 1977; Borole et al., 1977; Seralathan, 1979 and Murty and Veerayya, 1981). Kharker et al. (1968) stated that, trace elements like Co and Cu, which have been adsorbed onto clay minerals and clay coated particulates of river-borne sediments are desorbed when the latter comes into contact with high saline waters. This phenomena could be interpreted in terms of the displacement of Co by Mg and Na as suggested by O'Conner and Kester (1975).

d) **Chromium (Cr):** Cr is seventh most abundant element on earth, but 21st in abundance in the crustal rocks with an average concentration of 100 ppm (McGrath and Smith, 1990). Granitic rocks hold comparatively low amount of Cr (av. 20 ppm) than basaltic rocks (220 ppm). Sandstones and shales account 35 ppm and 120 ppm of Cr respectively (McGrath and Smith, 1990).

The concentrations of Cr in the bulk sediment of the Muvattupuzha river and the Central Vembanad estuary vary considerably (Fig. 36). In the former the metal varies from 44 ppm to 243 ppm (av. 107 ppm) while in the latter from 40 ppm to 233 ppm (av. 125 ppm). The average concentrations of this metal in the three size fractions of the two environments are as follows: River:- sand 100 ppm, silt 163 ppm, clay 152 ppm; Estuary:- sand 44 ppm, silt 171 ppm, clay 179 ppm. The observed levels of Cr in the bulk sediment of the estuary are higher than the earlier reports of Mallik and Suchindan (1984; Cr 44.8 ppm). But the values of this study are slightly lower than that reported by Mohan (1990) for Vellar estuary (221.7 ppm) and Seralathan (1979) for Coleroon estuary (271 ppm).

From Fig. 36, it is evident that the content of Cr in the Kaliyar tributary is slightly higher than that of the Thodupuzha. This may be resulted from the variations in the rocks and soils of the drainage basins. From Table 15, it is evident that the rocks (29 ppm) and soils (223 ppm) of the Kaliyar drainage show slightly higher concentration of Cr than the Thodupuzha drainage (rock 23 ppm, soil 125 ppm). In general, the Cr content in the sand fraction of the river exhibits an identical downstream variation with that of the bulk sediment (Fig. 36). Further, the Cr level in the sand fraction of the two environments holds strong positive correlation with heavy mineral percentages (river  $r_1 = 0.89$ ,  $n = 11$ ; estuary  $r_2 = 0.92$ ,  $n = 13$ ). This clearly indicates the heavy mineralogical bearing on Cr in the sand fraction. Mitchell (1964) opined that Cr is bound in the opaque heavy minerals such as ilmenite and magnetite. From heavy mineralogical studies it is proved that ilmenite forms the chief opaque mineral in the heavy crop. So any variation in the Cr content in the sand fraction and sand rich bulk sediment could be explained by the abundance of ilmenite in these samples. The silt and clay fractions of the river show an almost steady distribution of Cr.

In the estuary, the content of Cr in the bulk sediment is highly variable with sediment texture. But in general, its content shows an increasing trend after 8 Km from Thannirmukham bund. This may be due to the faster settling of Cr rich suspended particulates in the high saline zones of the estuary. Moreover, the finer particles scavenge Cr from solution with better efficiency due to its higher surface area than coarser particles (Williams et al., 1978).

The content of Cr in the bulk sediment of the estuary shows strong positive correlation with all other metals as well as organic carbon. In clay fraction Cr shows strong positive correlation with Zn and negative relation with Cd (Table 12). Cr also exhibits marginal negative relation with Fe, Mn and Co. It clearly indicates that the

scavenging of Cr by Fe and Mn complexes is rather insignificant and a considerable amount of Cr might be fixed in clay minerals or in organic ligands as observed elsewhere (Sajan, 1988 and Mohan, 1990).

e) **Cadmium (Cd):** Cd pollution in aquatic sediments has been rapidly increasing in recent decades as a result of the increasing consumption of this metal by industries. Unlike Pb, Cu and Hg, which have been utilised for centuries, Cd has been widely used only in this century. More than half of the Cd ever used in industries was produced in the last 20 years (Hutton, 1987). Cd reaches the aquatic environments mainly from the mining and smelting of Cd and Zn, atmospheric pollution from metallurgical industries, the disposal of wastes containing Cd, (such as incineration of plastic containers and batteries) and burning of fossil fuels (Hutton, 1982). Average concentration of Cd in the earth's crust is estimated to be 0.1 ppm (Bowen, 1979). The metal Cd is closely associated with Zn in its geochemistry: both elements have similar ionic structure and electronegativities and both of them are strongly chalcophile although Cd has a higher affinity for S than Zn. Page et al. (1987) computed that igneous rocks of the earth crust have a Cd content ranging from 0.1 - 0.3 ppm. Metamorphic and sedimentary rocks contain 0.1 - 1 ppm and 0.3 - 11 ppm of Cd respectively. The rocks of the Muvattupuzha river drainage basin exhibit comparatively high content of Cd (5.52 ppm) than soils (1.25 ppm).

In the bulk sediment of the river, Cd concentrations vary between 1 ppm and 7 ppm (av. 4 ppm). The average concentrations of the metal in sand, silt and clay fractions of the river are 3 ppm, 6 ppm and 6 ppm respectively. In the finer fractions (silt and clay) of the river, the Cd levels are almost uniform throughout the river course except at station 34. Estuarine Cd contents in the bulk, sand, silt and clay averages 4 ppm, 1 ppm, 6 ppm and 6 ppm respectively. The average bulk Cd value of this study is almost similar to that of Mallik

and Suchindan (1984; Cd = 5 ppm). A comparison of Cd content of present study with the major rivers and estuaries of other localities is given in Table 13.

An analysis of the relative abundance of Cd in the river and estuarine environments reveals that a considerable amount of Cd is associated with finer sizes. It is due to the increased surface area of the finer particles and the presence of trace metal scavenging clays, Fe-Mn complexes and colloidal humic materials. Cd shows strong positive correlation with metals like Fe, Mn, Ca, Co, Pb, Zn, Cr and Cu as well as organic carbon in bulk sediment. Minor, but distinct isolated peaks in stations located at 10, 15 and 27 Km from Thannirmukham bund might be resulted from the localised pollution (from the Cochin Refinery).

f) **Nickel (Ni):** The average Ni content in the earth's crust is 75 ppm and is twice as abundant as Cu (McGrath and Smith, 1990). This metal usually substitutes to Fe and Mg in rock forming minerals. The occurrence of this siderophile element varies between different rock types. Granitic igneous rocks show an average of 8 ppm and basaltic rocks 140 ppm. Sandstones and clays exhibit an average of 2 ppm and 68 ppm of Ni respectively. Nriagu (1980b) computed that the world's major rivers transport about  $1.1 \times 10^{10}$  gm of dissolved and  $135 \times 10^{10}$  gm of particulate Ni annually.

The Ni content in the bulk sediment of the Muvattupuzha river shows wide range of variation from 13 to 105 ppm (av. 51 ppm). The silt (145 ppm) and clay (163 ppm) fractions of the river samples exhibit 4-5 fold increase in Ni content than sand (36 ppm) fraction. In estuary Ni level in the bulk sediment ranges between 39 and 181 ppm (av. 109 ppm). The respective average concentrations of Ni in the estuarine sand, silt and clay fractions are 19 ppm, 148 ppm and 175 ppm. The observed ranges of Ni contents of the estuarine bulk sediment are slightly higher than the earlier report (14 - 85 ppm) of Mallik and

TABLE 13 - Comparative evaluation of heavy metal concentrations in Muvattupuzha riverine and the Central Vembanad estuarine sediments with that of some other major rivers and estuaries of India

River/Estuary	Sample	Author/Year	Fe	Mn	Pb	Cu	Co	Ni	Cr	Cd	Zn
Muvattupuzha river	Bulk	Present study	5.71	762	17	19	12	51	107	4	65
	Sand	"	4.41	754	13	14	10	36	100	3	60
	Silt	"	8.99	1110	42	84	41	145	163	6	150
	Clay	"	9.46	1079	42	94	45	163	152	6	167
Central Vembanad estuary	Bulk	"	4.39	366	14	31	20	109	125	4	90
	Sand	"	1.09	143	14	6	10	19	44	1	30
	Silt	"	7.32	533	25	44	29	148	171	6	151
	Clay	"	8.32	480	32	53	32	175	179	6	173
Ganges river	Bulk	Subramanian et al. (1985a)	2.16	400	--	21	--	20	52	-	46
	Bulk	Ramesh (1985)	2.50	906	--	35	32	32	82	-	26
	Sand	"	10.37	2104	35	196	219	132	246	-	192
	Silt	"	10.03	2065	30	186	213	126	24	-	178
Cauvery river	Clay	"	4.52	656	23	83	91	55	120	-	93
	Bulk	Subramanian et al. (1985b)	1.64	299	13	6	16	24	102	-	19
	Clay	Seralathan (1979)	7.89	2630	84	122	24	119	240	-	120
	Clay	"	6.58	3130	62	95	14	121	271	-	119
Vellar river	Bulk	Mohan (1990)	1.84	3631	--	7	19	110	252	5	117
	Clay	"	6.82	6454	--	64	102	256	272	4	239
Vellar estuary	Bulk	"	3.94	5245	--	49	48	190	222	7	196
	Clay	"	6.55	5245	--	41	71	205	263	3	196
Nearshore sediments	-	Wedepohl (1978)	--	--	--	48	--	55	100	-	95
Deep sea clays	-	Turekian (1972)	--	--	--	250	--	225	90	0.4	195
Shale	--	"	--	850	--	45	19	68	90	0.3	95

Suchindan (1984). In the sand fraction of the river as well as estuary, the Ni content covaries with heavy mineral content (river:  $r_1 = 0.71$ ;  $n = 11$ ; estuary:  $r_2 = 0.91$ ,  $n = 13$ ). In the bulk sediment of the river Ni shows positive correlation with Na, Ca, Pb, Co and Zn which indicates that apart from heavy minerals, a considerable amount of this metal might also have transported to the estuary through clay mineral or altered plagioclase bound form (Krauskopf, 1967). In estuary, Ni content of the bulk sediment exhibits strong positive correlation with all metals (except Na) as well as with organic carbon. On the other hand silt and clay fractions show only marginal correlation with Fe, Mn, Cd, Co, Pb and Cu. The Ni that are released from weathering of rocks may be fixed up in Fe and Mn complexes as well as metal scavenging clays and organic matter (Rankama and Sahama, 1950) and carried to the estuarine environment. Aquatic organisms are well known for their ability to take up trace metals from solution and particulates (Bowen, 1966; Riley and Chester, 1971 and Sholkovitz and Price, 1980) and finally being incorporated to the sediments after their death. Vembanad estuary with very high primary productivity (Qasim, 1970 and Nair et al., 1968), is favourable ground for biological segregation of trace metals in sediments. In addition to the above, direct adsorption of Ni, organic carbon and Fe-Mn hydrolysates can also fix substantial amount of Ni in sediments (Shimp et al., 1970, 1971).

g) **Zinc (Zn):** Zn is an essential trace metal for animals and plants; but in higher quantities, the metal is potentially hazardous to living organisms. The total Zn content in soils and sediments is largely dependent on the composition of the parent rock (Sillanpaa, 1972 and Kabata Pendias and Pendias, 1984). In magmatic rocks, Zn seems to be quite uniformly distributed and it generally vary from 40 ppm in acid igneous rocks (granite) to 100 ppm in basic rocks (basalt). In sedimentary rocks, the highest content of Zn (80-120 ppm) is found in shales and clayey sediments (Krauskopf, 1972). Seralathan (1979) has recorded an average of 119.2 ppm of Zn in the clay fraction of Cauvery

river sediment and 118.6 ppm in the Coleroon estuary. However, in some highly polluted sedimentary environments abnormally high values of Zn have been reported (Schneider, 1974). Ouseph (1987) has recorded 780 ppm of Zn in the Periyar river sediments especially near the river mouth stations.

In the present study, the average concentrations of Zn in the bulk sediment of the Muvattupuzha river (65 ppm) and the Central Vembanad estuary (90 ppm) show substantial variation. The sand, silt and clay fractions account an average of 60 ppm, 150 ppm and 167 ppm in river and 30 ppm, 151 ppm and 173 ppm in the estuary respectively. The observed value of Zn in the bulk sediment of the estuary is in accordance with the earlier report (av. 85.4 ppm) of Mallik and Suchindan (1984).

The Zn content of the bulk sediment as well as sand fraction does not show any marked variation downstream except a slightly high value in the upstream samples (stations 1, 9 and 12). This high concentration in the upstream samples is mainly due to the enrichment of heavy minerals. Similarly, silt and clay fractions of the river do not show any marked variation of Zn downstream and also along the estuary except a slight increase in the high saline region. High content of this metal especially in the clay fraction near the high saline zone can be attributed to the high availability of montmorillonite. Experiments of Demumbrum and Jackson (1956) show that montmorillonite have high exchange capacity for Zn in different pH conditions, however, greater metal scavenging is observed in alkaline conditions. The enhanced level of Zn near the estuarine mouth could also be due to Zn rich contaminant outfall from the Zn smelter as well as pesticide industries situated at the northern part of the study area.

The silt and clay fractions of the two environments show marked enrichment of Zn when compared to the corresponding sand fraction. On an average, silt account 2-3 fold and clay 5-6 fold increase of Zn, than sand fraction. The abundance of Zn in fine grained sediments is due to the increased surface area of the fine particulates which favour metal adsorptivity (Williams et al., 1978). Further, Fe-Mn complexes, clay minerals and organic matter coating over these particulates also scãvenge a significant amount of Zn.

The scatter plot of Zn and organic carbon of the estuarine bulk sediment (Fig. 39) exhibits a positive covariation ( $r_2 = 0.74$ ). The Zn content in the clay fraction also shows marginal positive correlation with organic carbon (Fig. 40a,b). It clearly indicates that a part of Zn in these sediments is associated with organic carbon. From laboratory experiments Farrah and Pickering (1977) and Wada and Abed-Elfattah (1978) stated that the Zn adsorption in organic carbon is quite strong and is primarily by means of two different mechanisms. One is in acidic condition related to cation exchange cites and the other in alkaline condition that is considered to be chemisorption which highly affects organic ligands. The association of Zn with inorganic and sulphide phases of the sediments of the Vembanad estuary near the Periyar mouth has been investigated earlier by Paul and Pillai (1981).

In bulk sediment, Zn exhibits good correlation with Fe, Mn, Cu, Cd, Ni, Pb and Cr (Table 12). It distinctly points to a common source for all these metals (Loue, 1986). At station 23, Zn content in the clay fraction of the Muvattupuzha river shows an anomalous high value. This is due to the Zn contaminated effluents from the Hindustan Paper Corporation Limited - a feature also reported by Nair et al. (1990).

### 5.3.6 CLUSTER ANALYSIS

Cluster analysis was carried out for the bulk sediment of the riverine and the estuarine environments (Fig. 42) to find out the grouping of various geochemical parameters. Dendrograms derived (Davis, 1973) for the two environments show marked differences in the clustering pattern of various geochemical parameters. In river sediments, three intercorrelated groups of elements are identified: The first group consists of organic carbon ( $C_{org}$ ), P, Na, Cu and Ni controlled primarily by the content of mud (silt + clay) in the sediments, the second group consists of Fe, Mn, Zn, Pb, Cr, Ca, Cd and Co, controlled by the heavy mineral content of the sediment, and the lone element K, constitutes the third group presumably having a bearing on the aluminium silicate factor (feldspars and clay minerals) in the sediments, a feature also observed earlier by Ramachandran (1989).

In the estuarine sediments, the grouping pattern depicts wide difference which in turn reveal the difference in the behaviour of elements in the estuarine environment. Three groups are identified in this environment too. Group 1 is characterised by the association of organic carbon, Cr, Cd, Fe, Ni, Pb, Zn, Cu, Co and P. This group is controlled by the texture of the sediments. The granulometric control over the deposition of organic carbon as well as its metal scavenging ability are well documented earlier by several researchers (Eisma et al., 1966; Seralathan, 1979 and Sholkovitz, 1981). Group 2 consists of Na, K and Ca controlled by the clay content in sediments. Group 3 is represented by lone element Mn which is presumably attributed to the increased rate of desorption of this metal towards the estuarine mouth.

### 5.3.7. SUSPENDED SEDIMENT

The concentrations of various heavy metals in the suspended sediments of the Muvattupuzha river and the Central Vembanad estuary

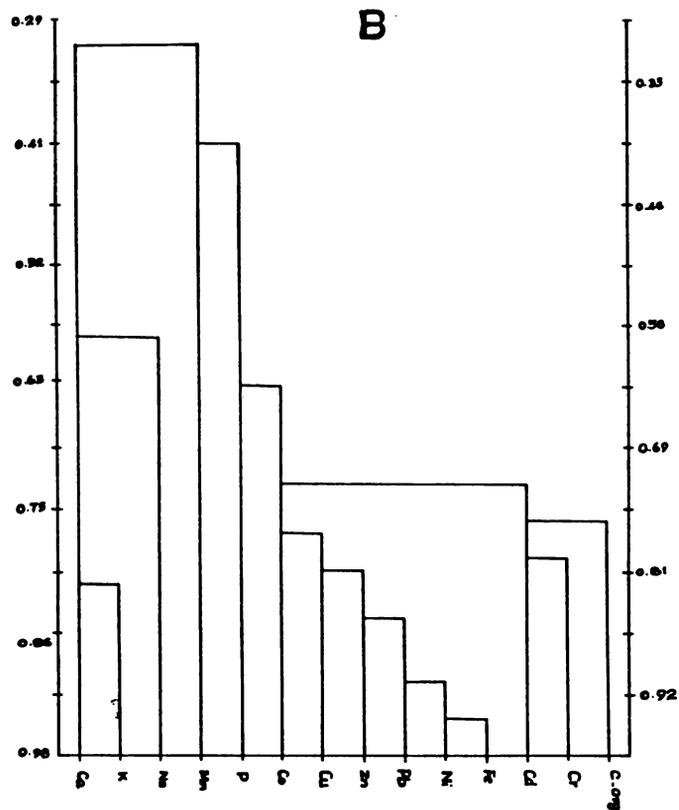
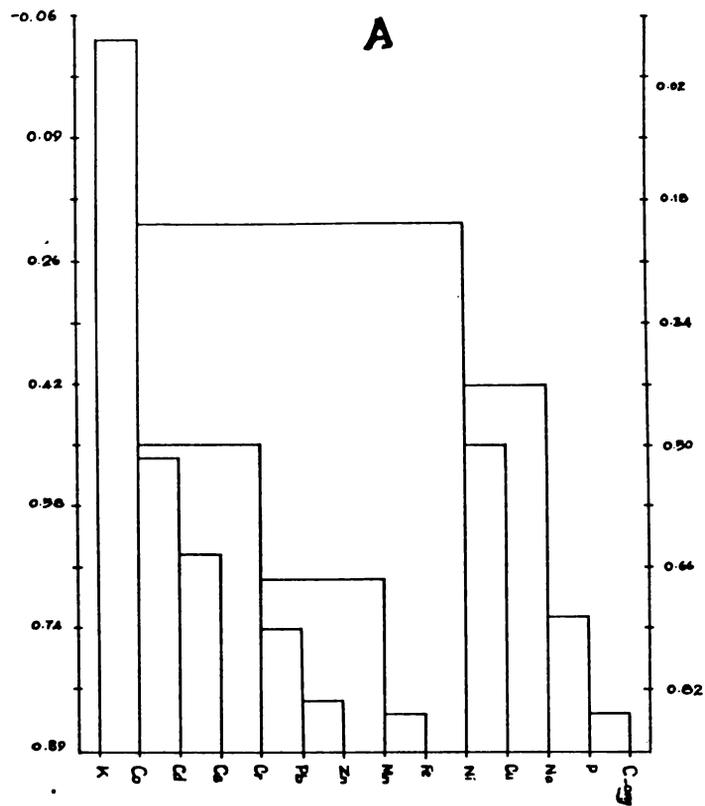


Fig. 42 Dendrogram of various geochemical parameters in the bulk sediment of Muvattupuzha river (A) and Central Vembanad estuary (B)

TABLE 14 - Concentration of various Geochemical parameters in the suspended sediments of the study area (Fe and Organic carbon in %; others in ppm)

Sample No.	Organic Carbon	Fe	Mn	Zn	Cu	Cr	Cd	Ni	Co
4	2.04	0.69	110	28	69	159	6	163	58
15	2.16	1.48	370	28	83	221	4	145	54
17	2.31	0.83	120	25	48	178	2	149	47
20	3.02	0.99	220	21	63	239	4	192	43
31	2.68	0.78	130	45	64	187	7	133	40
42	2.44	0.52	110	83	103	209	2	202	52
69	3.31	0.31	50	64	98	141	BDL	199	41
70	2.90	0.24	40	17	24	193	BDL	138	38
79	2.25	0.12	40	27	26	145	BDL	139	25
85	3.01	0.36	60	73	77	206	BDL	135	37

BDL - Below Detection Limit

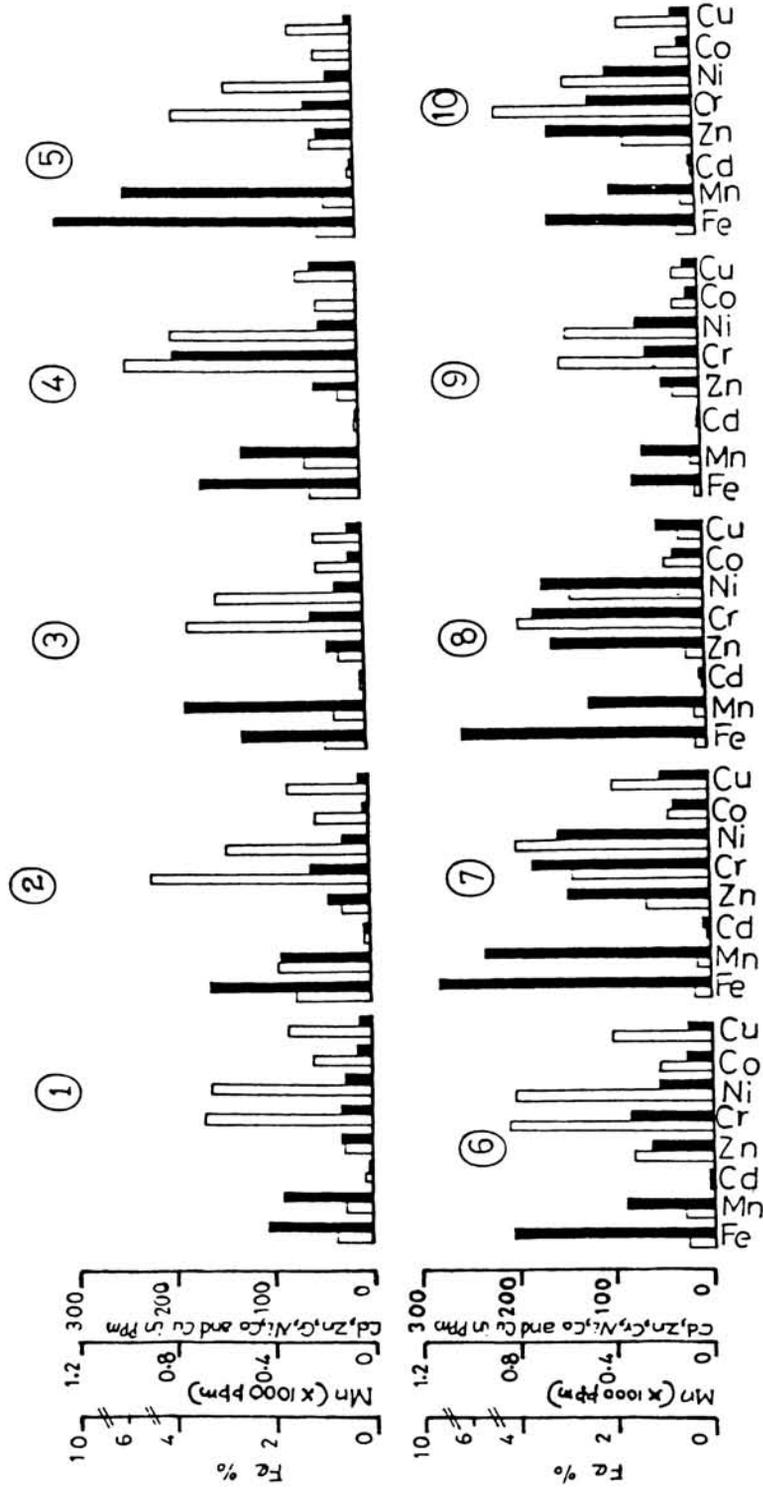


Fig. 4.3 Concentration of heavy metals in suspended (□) and bed sediments (■) of the study area

are depicted in Table 14. The content of Fe and Mn is markedly high in the river (stations 1-6) than the estuary (station 7-10). In the river environment the content of Fe ranges from 0.52% to 1.48% (av. 0.88%) whereas in the estuarine environment the range is from 0.12% to 0.36% (av. 0.26%). The respective ranges of Mn in the river and the estuary are 110-370 ppm (av. 176.6 ppm) and 40-60 ppm (av. 47.5 ppm). The metals Cu and Co also exhibit an almost similar downstream variation as that of Fe and Mn. The substantially low content of Fe, Mn, Cd and Co (particularly Fe and Mn) in suspended sediment of the estuary is due to the result of the desorption of these metals from particulate phases to water column during estuarine mixing as observed elsewhere (Evans et al., 1977; Borole et al., 1977 and Murty and Veerayya, 1981). This variation is registered in the bulk sediment, silt and clay fractions as well. However, the depletion of Fe is masked by the input of Fe from sewage sludges as well as ilmenite rich heavy minerals from the land. Cr and Ni occur in high concentrations in suspended sediments than bed sediments (Fig. 43) and appear to be non-variant in river and estuary. From a comparative evaluation of the metal enrichment between suspended and bed sediments (bulk only), it is clear that the metals Fe, Mn and Zn are transported primarily through bed sediments. Whereas the transportation of all other metals are mainly through suspended sediments.

### 5.3.8 HEAVY METALS IN ROCKS AND SOILS

The flux of metals transported by rivers reflects the intensity and type of weathering as well as the mineralogical constitution of rocks and soils. Mitchell (1964) made a detailed study on the trace element distribution of some common rock forming minerals (Table 15) and found that many of the toxic metals are substituted isomorphously within the lattices of easily to moderately susceptible minerals. In this investigation an attempt has been made to study the elemental concentration of a few rock and soil samples of the Muvattupuzha river

TABLE 15— Trace elements in common rock forming minerals  
 [Source : Mitchell (1964)]

Mineral	Trace elements	Susceptibility of Weathering	
Olivine	Ni, Co, Mn, Li, Zn, Cu, Mo	Easily weathered	
Hornblende	Ni, Co, Mn, Sc, Li, V, Zn, Cu, Ga		
Augite	Ni, Co, Mn, Sc, Li, V, Zn, Pb, Cu, Ga		
Biotite	Rb, Ba, Ni, Co, Sc, Li, Mn, V, Zn, Cu, Ga		
Apatite	Rare earths, Pb, Sr		
Anorthite	Sr, Cu, Ga, Mn		
Andesine	Sr, Cu, Ga, Mn		
Oligoclase	Cu, Ga		
Albite	Cu, Ga		Moderately weathered
Garnet	Mn, Cr, Ga		
Orthoclase	Rb, Ba, Sr, Cu, Ga		
Titanite	Rare earth, V, Sn		
Ilmenite	Co, Ni, Cr, V		
Magnetite	Zn, Co, Ni, Cr, V		
Tourmaline	Li, F, Ga		
Zircon	Hf, U	Very resistant to weathering	
Quartz	_____		

drainage basin to evaluate the metal enrichment in the riverine and estuarine sediments.

Table 16 shows the concentration of various elements in rocks and soils of the Muvattupuzha river drainage basin. The average concentrations of elements in rock (charnockite and gneiss), soil and bulk sediment as well as sand, silt and clay fractions are furnished in Table 17. The metals Na, K and Ca are highly enriched in rock than soil. It is due to the predominance of feldspar and mica minerals in the rocks. The substantially low amounts of Na, K and Ca in soil might be due to the cumulative effects of biological uptake by plants and leaching by surface and subsurface waters (Alloway, 1990). The contents of these metals are comparatively lower in riverine silt and clay fractions than estuarine counterparts. The observed enhanced levels of Na, K and Ca in the latter environment are due to the replacement of Fe, Mn, Co and Cu of the river borne sediments by Na, K and Ca of the estuarine waters during estuarine mixing (Trefrey and Presley, 1976 and Borole et al., 1977).

The contents of Fe and Mn are highly enriched in silt and clay fractions of the two environments than rock and soil samples. All other heavy metals (except Cr) are present in comparable levels in rock, soil and sediments, however, the finer fractions (silt and clay) and suspended sediments show substantially higher values. The content of Cr is considerably low in charnockite, gneiss, granite and pegmatite. But it is enriched in basic intrusives such as dolerite and gabbro. An over all evaluation of the chemical results of rock, soil, bulk sediment and size fractions reveals that the elemental dispersal of the study area is, in general, controlled by the texture and mineralogy of the sediments. However, a few localities in the vicinity of the Thodupuzha town (Station 4) and the Hindustan Paper Corporation Limited (Station 23) are influenced to some extent by waste disposals.

TABLE 16 - Concentration of metals in rocks and soils of the drainage basin of Muvattupuzha river (Fe, Na, K and Ca in % and others in ppm)

Sample No.	Rock type	Fe	Na	K	Ca	Mn	Pb	Cu	Co	Ni	Cr	Cd	Zn
R1	Charnockite	6.88	2.00	3.60	2.32	1940	32	19	32	104	10	7	127
R2	Dolerite	2.94	2.76	3.20	1.25	1820	11	203	7	156	89	12	111
R3	Biotite gneiss	4.36	2.40	2.16	2.59	480	21	30	39	156	29	10	96
R4	Charnockite	1.67	2.12	2.16	2.86	360	21	9	11	65	10	4	45
R5	Charnockite	3.88	2.08	1.96	2.15	480	74	17	11	78	15	4	88
R6	Charnockite	5.63	4.12	1.52	2.15	1210	21	54	50	104	13	4	155
R7	Pegmatite	0.47	3.48	4.76	2.68	-	32	15	11	65	10	3	16
R8	Charnockite	4.15	2.72	4.76	2.78	220	11	39	14	91	10	4	57
R9	Bio-Hb-gneiss	1.39	2.32	1.20	2.59	120	21	9	11	65	10	4	39
R10	Charnockite	4.21	3.21	1.21	1.82	520	21	9	18	91	15	7	47
R11	Charnockite	5.83	2.98	1.87	2.52	480	32	19	32	103	10	7	129
R12	Charnockite	6.67	3.60	0.94	1.83	240	32	21	36	104	50	8	102
R13	Granite	2.02	2.08	3.32	2.46	120	53	9	18	65	10	4	54
R14	Dolerite	8.02	2.76	0.32	1.04	1580	21	222	60	142	79	5	111
R15	Gabbro	9.96	2.60	0.80	1.34	1090	32	68	57	130	40	6	144
R16	Charnockite	2.94	4.12	3.04	2.32	360	32	22	21	143	15	3	51
R17	Charnockite	6.21	3.56	1.72	2.15	1920	21	19	32	91	10	4	126
R18	Pegmatite	0.06	3.00	4.36	3.35	-	11	12	11	65	10	5	19
R19	Charnockite	4.64	3.60	3.80	1.61	610	21	17	28	104	59	4	82
<u>Soil Samples</u>													
S1	Kanjar area	4.72	0.19	0.42	0.44	270	26	32	28	56	125	1	81
S2	Kaliyar area	4.07	0.48	0.21	0.22	240	40	52	32	72	223	1	68
S3	Muvattupuzha area	3.69	0.83	0.92	0.11	160	26	56	37	108	176	2	82
S4	Piravam area	1.50	1.17	1.35	0.11	290	39	56	37	79	106	1	106

TABLE 17 - Average concentrations of metals in rocks, soils, bulk sediments and size fractions of the study area (Fe, Na, K and Ca in % and others in ppm)

Serial No.	Sample	Fe	Na	K	Ca	Mn	Pb	Cu	Co	Ni	Cr	Cd	Zn
1	Cnamockite	4.79	3.10	2.42	2.23	760	28.91	20.73	25.91	98.00	20.00	5.10	91.73
2	Gneiss	2.88	2.36	1.68	2.52	300	21.00	19.50	25.00	110.50	19.50	7.00	67.50
3	Soil	3.50	0.67	0.73	0.22	240	32.75	49.00	33.50	78.00	157.50	1.25	84.25
4	Riverine bulk sediments	5.71	1.08	1.55	0.87	760	16.50	19.46	13.69	50.30	106.78	3.46	66.85
5	Estuarine bulk sediments	4.39	1.51	1.16	1.05	370	13.50	31.00	20.35	109.00	124.60	4.30	89.85
6	Riverine sand	4.41	0.94	1.49	0.88	750	12.64	14.09	9.50	35.64	99.55	3.00	59.64
7	Estuarine sand	1.09	0.72	0.59	1.13	140	13.54	6.00	9.92	18.69	44.46	0.77	30.38
8	Riverine silt	8.99	0.57	1.39	0.54	1110	41.60	84.61	40.54	144.90	161.15	5.54	150.30
9	Estuarine silt	7.32	1.06	1.44	0.96	530	25.43	44.43	29.05	148.20	170.74	6.21	151.00
10	Riverine clay	8.22	0.32	0.89	0.39	1080	42.15	94.08	44.69	163.30	151.70	5.90	167.08
11	Estuarine clay	8.23	0.65	1.07	0.66	480	32.10	52.81	32.31	175.19	178.74	6.07	172.67

### 5.3.9 RADIOACTIVE ELEMENTS (U and Th)

U and Th are members of the actinide series of elements. Both the elements occur in nature in tetravalent oxidation state and they have similar ionic radii ( $U^{+4} = 1.05\text{\AA}$ ,  $Th^{+4} = 1.10\text{\AA}$ ). Consequently, the two elements can substitute extensively for each other, which explains their geochemical coherence. The concentrations of U and Th in common rock forming silicate minerals are uniformly low, in the order of a few parts per million or less. However, these two elements occur primarily in certain accessory heavy minerals like zircon, thorite, allanite, monazite, apatite and sphene, in which they occur either as a major constituents or replacement of other elements (Heinrich, 1958 and Faure, 1986). The average concentrations of U and Th in certain common igneous, sedimentary and metamorphic rocks are given in Table 18.

Radioactive element studies, especially of U and Th, received special attention in Kerala due to its profuse occurrence in the sandy beaches of this State. In the heavy mineral rich beach sands, these radioactive elements are associated primarily with monazite and zircon. The natural radiations from the beach sands become one of the potential threats to the coastal population. Several attempts have been carried out to find out the provenance of these elements (Aswathanarayana, 1964; Prabhakara Rao, 1968 and Santhosh and Vijayakumar, 1986). From a detailed study of the various rock types of Kerala, Santhosh and Vijayakumar (1986) opined that the acid igneous rocks (eg. granites, syenites and pegmatites) in the wester ghats form the possible provenance of U and Th. Hence an attempt is made here to study the input of these elements through the Muvattupuzha drainage system.

The concentrations of U and Th in the Muvattupuzha river and the Central Vembanad estuarine sands are given in Table 19. In the river sands, the concentration of Th is very high and ranges from 15.95 ppm to 168.57 ppm (av. 67.98 ppm). Contrary to the river, the

TABLE 18 - Average concentrations of U and Th in various rock types  
(source : Roggers and Adams [1969])

Rock Type	U (ppm)	Th (ppm)
Ultramafic rocks	0.014	0.05
Gabbro	0.84	3.80
Basalt	0.43	1.60
Granitic rocks	4.80	21.50
Granitic gneiss	3.50	12.90
Granulite	1.60	7.20
Shale	3.20	11.70
Sandstone	1.40	3.90

TABLE 19 - Concentration of radioactive elements (U and Th) in the sand fraction of the study area.

Sample No.	Heavy mineral (%)	Th (ppm)	U (ppm)
8	10.21	168.57	-
12	7.82	126.06	-
17	4.15	60.74	-
23	5.12	64.76	-
26	6.18	45.52	-
33	4.32	32.62	-
36	2.45	15.65	-
41	3.25	29.95	-
49	4.79	2.62	-
60	3.21	4.28	-
64	2.08	3.09	-
74	2.78	1.85	0.04
78	3.94	2.13	0.47
85	3.40	2.68	-

estuarine sands record considerably lower levels of Th concentration (range 1.85 - 4.28 ppm; av. 2.78 ppm). The presence of U is detected only in two stations of the estuarine environment; viz. stations 74 (0.04 ppm) and 78 (0.47 ppm). From Table 19, it is evident that, the content of Th is strongly covaried with the heavy mineral content in sand fraction ( $r = 0.91$ ;  $n = 14$ ). The bearing of Th contents on the heavy minerals especially in the monazite-zircon rich heavy minerals was also observed earlier by Parthasarathy and Sankardas (1976) and Hari et al. (1991) respectively from the beach and river sands of Kerala. Mineralogical analysis (Table 6) also shows that the heavy mineral residue of the Muvattupuzha riverine and the Central Vembanad estuarine sands registers significant amounts of zircon and monazite which are well known for their radioactivity (Heinrich, 1958). The unique occurrence of U in sample 74 and 78 might be due to the high availability of monazite in these stations.

## CHAPTER 6

## SUMMARY AND CONCLUSIONS

The study deals with the mineralogical and geochemical constitution of the sediments of Muvattupuzha river and Central Vembanad estuary. Textural properties of sediments have also been worked out to substantiate the mineralogical and geochemical study.

The grain size of the sediments vary considerably in the river as well as in the estuary. Pebbles and granules dominate upstream (in the Thodupuzha and Kaliyar tributaries) whereas coarse, medium and fine sands progressively enrich downstream. The overall variation in the size distribution pattern is resulted from abrasion and progressive sorting, of which the former predominates in the pebble-granule rich upper reaches and the latter in the sand dominant mid-lower reaches of the river. The gradient of the river course also plays major role for the observed granulometric variation. The minor fluctuations observed in the size population have a direct bearing on the natural and man-made obstacles encountered in the river channel. Contrary to the river environment, the particle size distribution along the estuary is highly variable. However, in general, the content of silt and clay are found to be increasing towards the high saline zones of the estuary. It can be explained by the floc formation followed by the faster settling of suspended particles during estuarine mixing. In addition to the tidal activities, seasonal maintenance dredging operations by the Port authorities also affect considerably the particle size distribution in the estuary.

The phi mean size of the sediments is highly variable with distance and varies between  $-0.90 \phi$  and  $2.58 \phi$  in the river and  $1.76 \phi$  and  $8.70 \phi$  in the estuary. The sorting of the sediments is also highly variable along the profile of the river ( $0.55 \phi - 2.04 \phi$ ) and estuary ( $0.77 \phi - 4.17 \phi$ ). In river sands, the sorting improves as the

particle size decreases. In the estuary, the sediments are, in general, poorly to very poorly sorted. However, the stations located in the immediate vicinity of the Ittupuzha and the Murinjapuzha distributaries depict moderately sorted sediments. The river sediments show very coarse to very fine skewness and leptokurtic to platykurtic; whereas in estuary the sediments are nearly symmetrical to very fine skewed and very leptokurtic to extremely leptokurtic in nature.

Bivariate plots of phi mean versus standard deviation (sorting), phi mean versus skewness and phi mean versus kurtosis yield perfect trends. The plots of phi mean versus standard deviation exhibit a general linear pattern, which indicates poor sorting as the phi mean decreases. The plots between phi mean and skewness as well as phi mean and kurtosis perfectly agree to the earlier finding of Folk and Ward (1957) and Hakanson and Jansson (1983). The other bivariate plots do not yield any specific trend.

The sediment types of the river and estuary are highly variable with distance. Sandy gravel, gravelly sand, slightly gravelly sand, sand and muddy sand are the dominant types of sediments encountered in the river course. Among the sediment types of the river, muddy sand is confined only to the lower reaches of Murinjapuzha distributary. Sand, muddy sand, sandy mud, clayey mud and sandy silt are the major sediment types identified in the estuary.

The CM pattern of the riverine and estuarine sediments show a complete model of tractive current as shown by Passega (1964). Rolling mode of transportation is effective in the pebble rich tributary channels characterised by high gradient profile. Rolling and suspension, suspension and partly rolling and graded suspension are mainly effective in the mid and low land regions of the river. Deposits of uniform suspension are totally missing in the river environment. On the other hand, the estuarine sediments are transported by graded suspension and

uniform suspension in which the former dominates in the sand rich zones whereas the latter in the mud rich zones. The scattering in CM plot around the RS segment is indicative of the complexity in the transportational pattern and poorly sorted particle dispersion.

Surface textural studies of quartz grains exhibit well defined features. The riverine quartz collected from the Thodupuzha tributary shows sharp edges and planar surfaces. V-shaped impact pits, characteristic of subaqueous collisions, are only in the initial stages of development. It clearly indicates low amount of wear and tear under which the grain is subjected to. Contrary to the river, the estuarine quartz grains exhibit bulbous edges, characteristic of subaqueous action. These surfaces in turn register pitted surfaces, suggesting beach derivation. In addition to the above, the estuarine quartz grains and heavy minerals (zircon) show highly complicated surface features, primary derived from chemical (diagenetic) activities.

The total heavy minerals in the Muvattupuzha river sands depict higher concentration in the upstream stations. This increase is in consonance with the high energy based transportational pattern owing to the high gradient of the profile. The content of total heavies, in general, shows a decreasing trend downstream. Selective sorting based on shape/density plays a pivotal role in their entrainment and transportation. The minor fluctuations observed in the content of total heavies downstream might be resulted from the local hydraulic phenomena due to natural and man-made obstacles encountered across the river course. Granulometric fractionation studies on total heavies show its enrichment towards finer size grades. The fine and very fine sands account for higher contents of total heavies than medium sands. The granulometric behaviour of heavy minerals in the sand rich zones of the estuary is similar to that of the river, but its behaviour in the mud rich zones depicts considerable variation. It is presumably due to the inefficiency of sorting processes owing to the cohesive nature of the

muds. Further, the low energy conditions prevailing in these zones are inadequate for density/size based sorting.

The heavy mineral assemblage of the Muvattupuzha riverine and the Central Vembanad estuarine sands consist of opaques, amphiboles, pyroxenes, garnet, biotite and zircon as the major and monazite, sillimanite and rutile as the minor constituents. Some of the grains are highly altered in nature. The physical and optical properties of the mineral assemblages of these two environments show considerable variation. In the river, opaques and other high dense minerals are concentrated in the upstream (i.e. in the tributary channels). While less dense amphiboles and pyroxenes increases downstream. It is due to the difference in the competency of the river water in these two zones owing to the variation in the gradient of the profile. The high competency of the river water in the upstream does not allow the free settling of the lighter amphiboles and pyroxenes in the upstream side. Hence, these minerals will be flushed to the downstream and deposited; whereas the denser heavies will be deposited in the upstream and further shielded by the light minerals (quartz and feldspars). Moreover, the denser minerals will not be entrained as easily as that of lighter heavies. In addition to density, shape factor also has a substantial role in the observed heavy mineralogical variability downstream. In the estuary, the heavy minerals show marked variations and the variability has a direct bearing on the river inputs, estuarine hydrography, sediment types, tidal activity and dredging operations.

Matrix analysis of heavy minerals of the river sediments pinpoints the negative loading between lighter and denser heavies. The increase in the content of denser heavies with the increase of total heavies illustrates a high energy regime required for selective sorting. The depletion of amphiboles and pyroxenes with increase in the content of total heavies manifests that these lighter heavies are transported along with the light minerals (quartz and feldspars). In river

environment garnet grains exhibit a negative loading against phi mean size which implies their poor availability in the finer fractions. The similarity of the denser heavies and total heavies is also depicted in their clustering pattern. Most of the minerals in the estuarine environment exhibit the same kind of relation as identified in the river. But zircon is totally unrelated to the total heavies and opaques. This clearly indicates an additional source for this mineral. Scanning Electron Microscopic studies reveal the occurrence of a spectrum of micro relief features (mechanical and chemical/diagenetic) on the estuarine zircons. This clearly suggests subaqueous collisions and subsequent diagenetic changes as a part of polycyclic sedimentation. These zircon grains are presumed to be derived from the relict beach ridges (formed during Pleistocene) which forms the boundary of the Vembanad estuary.

The heavy mineral suite of the Muvattupuzha river sands distinctly points to a major metamorphic provenance for these sediments. The blue-green hornblende might be derived from the hornblende/biotite gneisses. Colourless garnet - hypersthene suite is indicative of charnockitic source. Monazite and rutile can be derived from acid igneous rocks (granites and pegmatites). The heavy mineral assemblages of Central Vembanad estuarine sands are also similar to that of river sands but differs considerably from their morphological and optical characteristics. The perfect rounding of estuarine heavy minerals particularly of zircon together with its surface textures distinctly points to a polycyclic nature and high energy-environments under which the grains are subjected to, prior to deposit in the Central Vembanad basin. The sporadic enrichment of zircon and the surface textural characteristics of estuarine quartz grains confirm that a considerable quantity of sediments in the Central Vembanad estuary are reworked polycyclic sediments that constitute the relict beach ridges.

Quartz and feldspars are the light minerals present in the study area. The quartz/feldspar ratio increases downstream. It is presumably due to selective abrasion and selective chemical decomposition of feldspars. In the estuary, the ratio is markedly high compared to the river. Further, the quartz/feldspar ratio shows an increase towards finer size grades. In the silt fraction, in addition to quartz and feldspars, a substantial amount of clay minerals (River : Kaolinite, illite and gibbsite; Estuary : Kaolinite, illite, gibbsite and montmorillonite) are also identified. Kaolinite, illite and gibbsite are the three clay minerals identified in the clay fraction of the river environment. However, montmorillonite becomes one of the major constituents in the estuarine clay in addition to the above. The clay fraction of the river as well as the fresh water influenced southern part of Central Vembanad estuary are characterised by kaolinite. The content of this mineral decreases towards the high saline zones of the estuary, but montmorillonite depicts an opposite trend. The observed variation of clay minerals are resulted from progressive sorting based on size rather than chemical transformations.

Organic carbon although, constitutes an integral part of riverine and estuarine sediments its content in the former is much lower than that in the latter. It is due to the abundance of coarser clastics (sand) in the river than estuary. The size fractionation study of organic carbon shows its abundant occurrence (27-30 times) in silts and clays than sand fraction. The P content in the bulk sediments of the estuary depicts about 3 fold increase in its concentration than the river. The concentration of P in silt and clay fractions are higher by 6-7 times and 11-15 times respectively in the estuary than the corresponding sand fractions. The increase in the occurrence of P in the finer fractions is due to the increased surface area of the finer particles which favours the adsorptive ability of P. The content of P increases downstream and also from Thannirmukham bund to Fort Cochin. The increase in the P values towards the high saline zones of the estuary is resulted from the

cumulative effects of chemical precipitation of phosphate complexes and greater input of P rich sewage sludges near the estuarine mouth. Flooding of upwelled waters and increased primary production near the estuarine mouth also enhance the P budget in the estuarine sediments.

The concentration of Na, K and Ca shows gradual decrease downstream. The concentration factor as well as the decreasing trend clearly suggest the role of source rocks in contributing these metals to the sediments. The behaviour of Na, K and Ca in the estuarine environment is quite different from that of the river. It is due to the difference in the depositional characteristics of these elements in the estuary. A comparative study of Na, K and Ca in silt and clay fractions of the river with that of the estuary reveals that these elements are enriched markedly at higher levels in the latter than in the former. This could be due to the replacement of exchangeable ions like Fe, Mn, Cu and Co in the clay minerals by Na, K and Ca during estuarine mixing. The marked increase in the content of these elements (particularly Na) in the estuarine bulk sediments towards the estuarine mouth reaffirms the above view.

The Fe and Mn contents of the bulk sediment of the two environments exhibit wide variations. In bulk sediment and sand fraction of the river, the content of Fe and Mn are related to the total heavy mineral contents. In the estuary, the availability of Fe and Mn in the bulk sediment is a function of the percent occurrence of muds (silt + clay). The silt and clay fractions of the river exhibits 2-3 fold increase of Fe and Mn than sand fraction, while the estuarine counter parts show 4-8 fold increase. This increased association of Fe and Mn with finer fractions might be resulted from the greater surface area which in turn activates the adsorptive ability. Further Fe-Mn hydrolysates coated over the finer particulates also enhance the level of these metals.

In Muvattupuzha river, the Mn contents in the silt and clay fractions show a steady decrease down 90 Km. The silt and clay fractions of the estuarine environment too record a depletion of Mn towards the estuarine mouth. This could be explained on the basis of the desorption characteristics of Mn from sediments to the interstitial water or to the overlying water during estuarine mixing. Further, the competitive exchange between Na, K and Ca and Mn in sediments and water favours the desorption.

The trace elements (Pb, Cu, Co, Ni, Cr, Cd and Zn) show marked variations in riverine and estuarine sediments. The trace metal contents of the estuarine environment are several fold higher than that of the river. It is due to the greater availability of finer particles (silt + clay) in the former than in the latter. In the bulk sediment of the river, the contents of heavy minerals also have a strong bearing on the trace element contents. In the silt and clay fractions, the elements are enriched at higher levels than the corresponding sand fraction. This attribute can be explained on the basis of the increased ability of the fine particulates to scavenge the tracemetals. Further, enhanced levels of organic carbon and Fe-Mn complexes also favour the enrichment of trace elements in silt and clay fractions. The anomalous high values of Pb, Zn and Cu (Particularly in silt-clay fractions) in the vicinity of Hindustan Paper Corporation Limited and Cd, near Cochin Refinery have been explained based on localized pollution due to the discharge of metal rich effluents from these industries. Like Mn, the metals Co and Cu also exhibit a marked depletion (in the silt and clay fractions) towards the estuarine mouth. This is presumably due to the desorption of these metals at higher salinity values.

Cluster analysis of geochemical parameters in the bulk sediments of the riverine and estuarine environments shows three distinctly knitted groups. In the river, the first group consists of organic carbon (C<sub>org</sub>) P, Na, Cu and Ni. It is controlled by the content

of mud (silt & clay) in the sediments. Fe, Mn, Zn, Pb, Cr, Ca, Cd and Co, which are controlled by the heavy mineral contents, form the second group. The element K alone constitutes the third knit. In the estuarine environment, the grouping pattern depicts some differences from that of the river. Organic carbon, Cr, Cd, Fe, Ni, Pb, Zn, Cu, Co and P together constitute group 1. It is controlled by the sediment texture and organic matter. The group 2, consisting of Na, K and Ca, has a strong bearing on the availability of clay minerals in the sediments. The lone knit of Mn forms the third group. The increased rate of desorption towards the high saline zones of the estuary might be responsible for its unique knitting cluster pattern.

The contents of Fe and Mn in the suspended sediments of the river are markedly higher than that of the estuary. Cu and Co exhibit a similar geochemical behaviour as that of Mn. The substantial low values of the above said elements in the estuarine environment are resulted from the desorption characteristics of these metals during estuarine mixing. A similar type of variation is also recorded in the silt and clay fractions too. But the variation of Fe in these fractions is not distinct as it is masked by the heavy input of Fe rich sewage sludges as well as heavy mineral rich sediments. An overall evaluation of the metal budgets between suspended and bed sediments reveals the enrichment of Cu, Co, Ni, Cr, Ni and Cd in the former and Fe, Mn and Zn in the latter.

The flux of metals transported by the river reflects the intensity and type of weathering processes and the chemical constitution of rocks and soils. The metals Na, K and Ca are enriched in rocks than soils. The observed low values of these elements in the latter might be resulted from the cumulative effect of biological uptake and leaching by subsurface waters. Fe and Mn are highly enriched in silt and clay fractions of the two environments than rocks and soils. Except Cr all other trace elements are at comparable levels in rocks, soils,

sediments and size fractions. The content of Cr is considerably low in charnockites, gneisses, pegmatites and granites whereas it is highly enriched in gabbros and dolerites. In general, the elemental assessment of rocks, soils, sediments and size fractions suggests that the area of the present investigation is non-polluted (except a few pocket sources near Thodupuzha town, Hindustan Paper Corporation Limited and Cochin Refinery) and hence this data set can be used as a background level for estimating and comparing the level of heavy metal pollution in other industrially influenced and anthropogenic impacted areas.

The radioactive element Th is enriched at higher levels in river sands than estuarine sands. U is recorded only in two stations of the estuarine environment. The concentration of Th shows strong positive correlation with the heavy mineral contents. The minerals zircon and monazite are the chief contributors of Th and U in this study area.

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