

STUDIES ON THE MINERALOGY, GEOCHEMISTRY
AND ORIGIN OF THE MODERN SEDIMENTS
OF THE ASHTAMUDY LAKE, KERALA

THESIS

Submitted by

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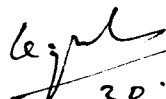
TO MY BELOVED PARENTS AND WIFE.

CERTIFICATE

This is to certify that this thesis entitled "Studies on the Mineralogy, Geochemistry and Origin of the Modern Sediments of the Ashtamudy lake, Kerala" is a bonafide record of research work done by Shri Sajan, K., M.Sc., in the Division of Marine Geology, School of Marine Sciences, Cochin University of Science and Technology. He carried out the investigations as reported in this thesis, independently under my supervision. I also certify that the subject matter of the thesis has not formed earlier the basis for the award of any Degree or Diploma of University or Institution.

Certified also that Shri Sajan, K. has passed the Ph.D. qualifying examination of the Cochin University of Science and Technology in July 1985.

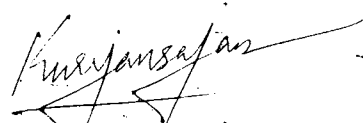
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DECLARATION

I hereby declare that the work incorporated in this thesis has been carried out entirely by me in the laboratories of the School of Marine Sciences, Cochin University of Science and Technology and that it has not been submitted earlier either wholly or in part to University or Institution for the award of any Degree or Diploma.

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PREFACE

The coastal sedimentary environment of Kerala is endowed with opulent estuarine complexes of a few major rivers (Bharathapuzha, Periyar, Kalladayar, Meenachilar, etc.), lagoons, lakes (Vembanad, Ashtamudy, Chaliyar, Beypore etc.) and backwaters (Cochin backwater). These lagoons, estuaries and backwaters are demarked from the Lakshadweep sea by the development of barrier spits and beaches. Hitherto the geochemistry and mineralogy of the sediments in these systems with particular reference to their environment of deposition have not been subjected to any detailed investigation. With the advances in environmental geology it is time that we should study the relationship between various geological aspects and the environment of deposition of sediments in these systems.

In this juncture, Dr. K. T. Damodaran's suggestion brooked my attention to take up the study entitled "Studies on the mineralogy, geochemistry and origin of the modern sediments of the Ashtamudy lake, Kerala". A textural analysis was accomplished to confer

(ii)

a nomenclature to the sediments and there upon the general sedimentary framework. The Ashtamudy lake, which is in fact an estuary lies between latitude $8^{\circ}55'N$ to $9^{\circ}N$ and longitude $76^{\circ}33'E$ to $76^{\circ}37'E$. The Ashtamudy lake completely satisfies the definition of an estuary given by Pritchard (1960). Hence it is considered under estuarine system even though it is known by misnomer 'lake', the literary translation of the word 'kayal' in the local language.

This study enfolds the environment of deposition and the lateral variation in texture, mineralogy and geochemistry of the Ashtamudy lake sediments. While the heavy mineral and clay mineral investigations enable us to decipher the nature, texture and source of sediments; organic matter and carbonate contents and the geochemical analysis of major and minor elements help establish the distribution and concentration of the same in regard to the various physico-chemical processes operating in the lake. Study of trace elements holds prime importance in this work, since their concentrations can be used to outline the extent of contaminated bottom area, as well as the source and dispersal paths of discharged pollutants. In short, this study brings out a vivid picture of the

mineralogy and geochemistry of the lake sediments in different environments, viz., the freshwater, brackish water and marine environments that are confined to the eastern, central and western parts of the lake respectively. For the better understanding and expression of the results of the analysis, the lake has been divided into 3 zones namely: eastern part, central part and western part.

The whole work is presented in 6 Chapters.

Chapter 1 covers the introduction which narrates the location, climate of the area of study and geomorphology of the Kallada river. The available information on the geology of Kerala and specially of Quilon district is also reviewed. A cursory review of literature on all the studies of Kerala lakes which includes Ashtamudy lake and Kallada river basin, as well as on lakes in east and west coast of India is included in this Chapter. A brief review of studies on some important lakes in the world is also given. The scope of the present work and a field programme are given towards the end of this Chapter.

Chapter 2 presents the sand-silt-clay ratio, the organic matter and carbonate contents of the sediments.

Chapter 3 describes the mineralogy of the heavy and light minerals and the clays.

The geochemistry of the major elements in the lake sediments is given in Chapter 4.

Chapter 5 gives the geochemistry of the trace elements in the lake sediments. The chapter also contains discussions on the aspects of pollution in the lake sediments.

Chapter 6 gives a summary of the whole study and the conclusions drawn from the results thereof. Discussion on the origin of the lake sediments is also incorporated in this chapter. The chapter also highlights the significance of the present work carried out.

The pertinent literature furnished under references are given towards the end of the thesis.

A part of the present study has been published as below:

1. Studies on the distribution of organic matter content in sediments of the Ashtamudy lake, Kerala. Bulletin of the Department of Marine Sciences, University of Cochin, XII, 2, 1981, p. 155.

2. Carbonate content of sediments in the Ashtamudy lake, West coast of India. Indian Journal of Marine Sciences, 12, 1983, p. 228.

Concisely, this could be claimed as the first substantial and integrated study of the mineralogy, geochemistry and origin of the Ashtamudy lake-sediments.

CHAPTER - 1

INTRODUCTION

1.1. LOCATION

Kerala, which is a littoral state situated on the southwestern part of Indian peninsula, extends from Manjeswar in the north to Parasala in the south and is bounded by Western Ghats on the east and the Lakshadweep Sea on the west (lat. $8^{\circ}18'N$ to $12^{\circ}48'N$, long. $74^{\circ}52'E$ to $77^{\circ}22'E$). It covers an area of 38,863 sq. kms. The width of the state no where exceeds 120 km and it narrows towards south to about 12 km, the average width being only 70 km (Location map of Kerala is given in Fig. 1.1).

1.2. PHYSIOGRAPHY

Kerala region can be divided into four longitudinal physiographic zones namely highlands (7600 m), midlands (300-600 m), lowlands (30-300 m) and the coastal strip with lagoons and sand dunes. Based on the slope, it can be further grouped into 6 units which are as follows:

- a) Steep to very steep hill ranges, the slope ranging from 70 to 100%,
- b) Moderately to steeply sloping ridges, the slope being 55 to 60%,

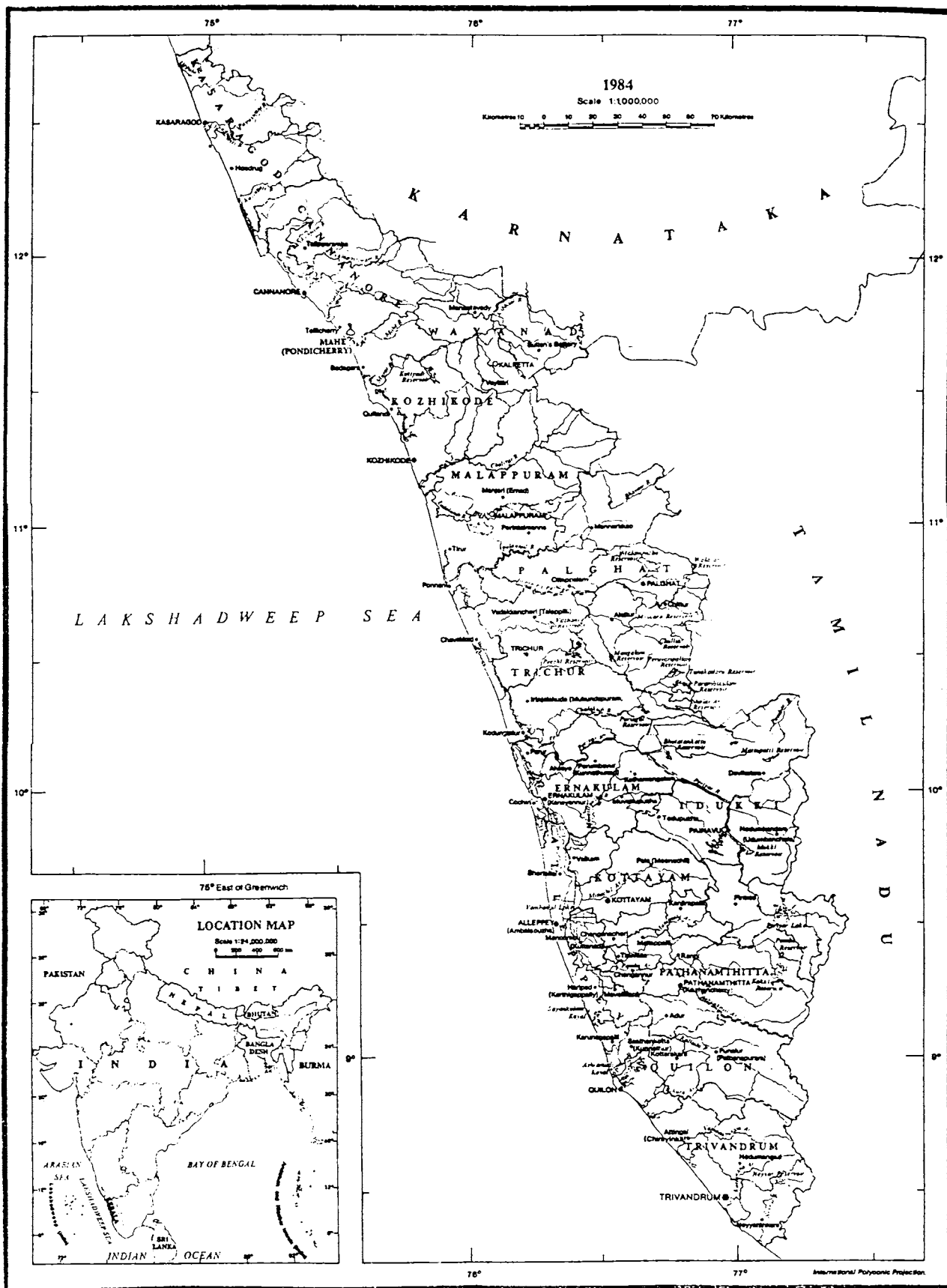


Fig. 1.1. Location map of Kerala

- c) Gently to moderately sloping spur, with a slope range of 10 to 20%,
- d) Gently to moderately sloping interhilly basins,
- e) Nearly level to very gently sloping coastal plains, which fall between the coast line and 10 m contours. Features like plains, lagoons, coastal dunes and mud flats are characteristics of this unit, and lastly
- f) Gently sloping to flat bottom units, having a slope of about 3 to 5%.

1.3. GEOLOGY

Geologically, Kerala region shows four major rock formations, namely, Quaternary sediments, laterite developed on Precambrian crystallines and Tertiary sedimentary rocks and crystalline Precambrian rocks. The crystalline rocks comprise chiefly of charnockites, khondalites, granitic gneisses, dharwar schists and granites, traversed by pegmatites and basic dykes. The charnockites form the most widespread group in the state. The khondalite group comprising garnet-sillimanite gneiss with or without graphite, garnet-biotite gneiss, garnet-quartz feldspathic gneiss or granulite and

quartzite are the predominant rock types in southern Kerala.

Occurrence of sedimentary rocks belonging to Tertiary age is found as discontinuous outcrops along coastal Kerala and extends in a north-south direction. These are mostly concealed under the laterite and soil cappings except in some cliff faces on the margins of the sea and barred lakes (Kayals). Paulose and Narayanaswamy (1968) have given the general geologic sequence of the Cenozoic sediments as Recent to sub-recent, Warkalli beds, Quilon beds and Archaean crystalline rocks. Raghava Rao (1975) considers that the Quilon beds are underlain by a thick sequence of sedimentary rocks which he named as 'Vaikom beds'. Ghosh (1982) observed that the Warkalli beds in southern Kerala has undergone lateritisation.

The Quaternary sediments are represented by laterite, alluvium, very thick shelly beds, black clays, peaty clays, sandy clays etc. deposited in marine and fluvial environments.

1.4. CLIMATE

The state falls in the region of tropical climate. The coastal locations of the state and a high

variation in relief from the coast to the western ghats, influence the climate characteristics to a large extent.

1.4.1. Temperature

It is observed that the period between March and May is the hottest, when the temperature reaches a maximum of more than 32°C. From June onwards it gradually comes down due to heavy monsoon, again an increasing trend is noticed in October and November followed by lowering of temperature to around 27°C in the month of December and January. The seasonal and diurnal variations of temperature are not uniform throughout the state. The stations located near the coast are influenced by land and sea breezes and have a seasonal and diurnal variations of temperature which are almost of the same range (5 to 7°C). The zone with the highest temperature falls in the mid-land region. Along the coast, the temperature is moderate, whereas in the east, it is low. This type of temperature variation is due to the presence of sea in the west and high relief in the east. This has endowed the state with a unique agroclimate favourable for cultivation of a wide variety of crops.

1.4.2. Rainfall

The State of Kerala receives high rainfall amounting to annual precipitation of about 300 cms. Analysing the rainfall trend, the following 3 seasons are identified (1) South-West monsoon period (June to September), (2) North-East monsoon period (October to December), and (3) Non-monsoon months (January to May).

The geographical variation of annual rainfall is from less than 100 cms to more than 500 cms. The yearly rainfall pattern records change from north to south. The stations in the northern part mark a single peak corresponding to the month of July. The southern part extending from Ponnani to Trivandrum with the sole exception of Devikulam shows two peaks in the months of June, July and October corresponding to the two monsoon seasons.

In general, rainfall increases from the coast to the foot hills and then decreases towards the hill-tops. The rainfall distribution in the state is controlled by the orography.

Nearly 60% of the annual rainfall is during south-west monsoon season. The pattern of rainfall

distribution during this season is akin to the annual rainfall pattern. The northern Kerala coast receives more rainfall compared to Cochin and Quilon coast. Southern and eastern parts of the state receive very low rainfall.

The distribution pattern of rain in North-East monsoon season is quite different from that of other seasons. The northern part receives less amount of rain compared to the south in this season.

1.5. DRAINAGE

The drainage system of the state is in conformity with the physiographic divisions. The drainage network of Kerala consists of 44 short and swift flowing rivers. Out of these, 41 flow westward and 3 eastward. The estimated total run-off of all the rivers is about 70,300 m³ (published report of Centre for Water Resources Development and Management, 1983).

The general drainage pattern of Kerala is dendritic. At places it is radial and sub parallel. Most of the rivers are structurally controlled and follow conspicuous lineaments, the general direction being NW-SE and NE-SW. Study of gradients of some selected

rivers indicates that the coastal plain extends far more eastward in the central part than in the northern and southern parts of Kerala.

1.6. LOCATION AND GEOLOGICAL SETTING OF THE STUDY AREA

Kerala, a narrow segment in the south-western part of peninsular India, extends over a distance of 570 km along the west coast with a width varying from 15-20 km. The continental shelf bordering the Kerala coast varies in width and depth and appears to be widest off west of Quilon. The coastal plain of Kerala has a few scattered hillocks with rock cliffs. In this area there are about 34 Kayals (lagoons or estuaries), big and small, all along the coast, right from Payyanur in the north to as far as Trivandrum in the south (Soman, 1980). The rivers draining the southern part of the western ghats empty into these inland lakes or lagoons with a few exceptions. Most of these lagoons or estuaries have either permanent or temporary connections with the sea and are known by 'azhi' or 'pozhi' respectively. The lagoons and estuaries are directly subjected to tidal action of the sea, with a maximum tidal range of about 4 ft. Among all the lakes, Vembanad lake, located south of Cochin is the largest, followed by Ashtamudy lake, the one which is immediately behind the barrier beach of Kayamkulam-Neendakara, in Quilon district. Quilon

district, which extends from latitude $8^{\circ}45'N$ to $9^{\circ}28'N$ and longitude $76^{\circ}28'E$ to $77^{\circ}17'E$ is linked by road, rail and water. It covers an area of 4623 sq. km. having a sea coast of 48 km ("Know your Districts", GSI Report, 1976).

Jacob and Rao (1964-65) carried out systematic mapping of parts of Quilon district. The principal rock types as mapped by them include garnet-biotite gneisses, pyroxene granulites, calc-granulites, acid charnockites, hybrid gneissic charnockites and associated migmatites. A fairly consistent band of cordierite-gneiss at the contact of charnockite gneiss and garnetiferous gneiss is considered to represent a zone of metamorphosed magnesia rich sediments. The intermediate varieties of charnockites in Quilon district are generally associated with migmatites and are often banded (Jacob, 1976). The evidence of reworking in charnockites is common in many areas (Roy and Mathai, 1979). Khondalite group of rocks are essentially garnet-sillimanite schist or gneisses. These rocks are associated with narrow bands of pyroxene-granulite and charnockites, found predominantly in south Kerala (Narayanaswamy, 1967). The ratio of quartzo feldspathic layers and schistose layers within the Khondalite suite vary from place to place. In certain parts of the area, lenticular bands of cordierite gneiss occur in association with Khondalite

group of rocks (Jacob, 1976). The metamorphic mineral assemblage of the rocks suggests that the region must have been subjected to an early phase of granulite facies of metamorphism with accompanied deformation. A second phase of deformation and metamorphism caused refolding and a high degree of reworking which led to retrogression of the rocks to a facies, intermediate between granulite and amphibolite. This event is associated with the formation of banded gneisses and migmatites. The secondary compositional layering of gneisses and migmatites have been polyphasedly deformed (Roy, 1980). In short, the major rock formations of Quilon district can be grouped into (1) the Precambrian, (2) the Tertiaries, and (3) Recent to sub recent sediments.

The Precambrian comprises gneisses with intermittent bands of charnockites. The gneisses can be further divided into (1) medium to coarse-grained, garnetiferous quartzo feldspathic rocks with gneissic and granoblastic texture which consists of perthite, quartz and garnets (porphyroblast), (2) medium to coarse-grained quartzofeldspathic gneisses with microperthite, plagioclase and biotite, and (3) medium to coarse-grained garnetiferous biotite-gneisses with microperthite, plagioclase, orthoclase, quartz and garnet as major

minerals. The charnockites have variable mineral compositions and they are medium-grained with quartz, plagioclase and orthopyroxene as the major minerals. Apatite and zircon are the common accessory minerals. In all these mineral assemblages and in some of the gneisses, the zircon have rounded shapes. Many workers have suggested that garnetiferous quartzofeldspathic gneiss is the bed rock besides charnockites and khondalites, which are the principal rock types in and around Quilon district.

The Tertiary sedimentary sequence overlies unconformably the Precambrians. This comprises of Quilon and Warkalli formations. The rocks of the Warkalli formation are lateritised at the top. Recent to Sub recent formations consist of beach sands, soils and alluvium.

Unlike any other lake, Ashtamudy has got 8 branches and hence got the name Ashtamudy (Ashtam means 8). For the present study, only the main strip of the lake falling between latitude $8^{\circ}55'N$ to $9^{\circ}N$ and longitude $76^{\circ}30'E$ to $76^{\circ}37'E$ alone has been considered (Fig. 1.2). It has got a length of 16 km, an average width of 3.2 km and covers an area of 51.2 sq. km. The depth of the lake is highly variable, usually ranging between 1-5.5 m

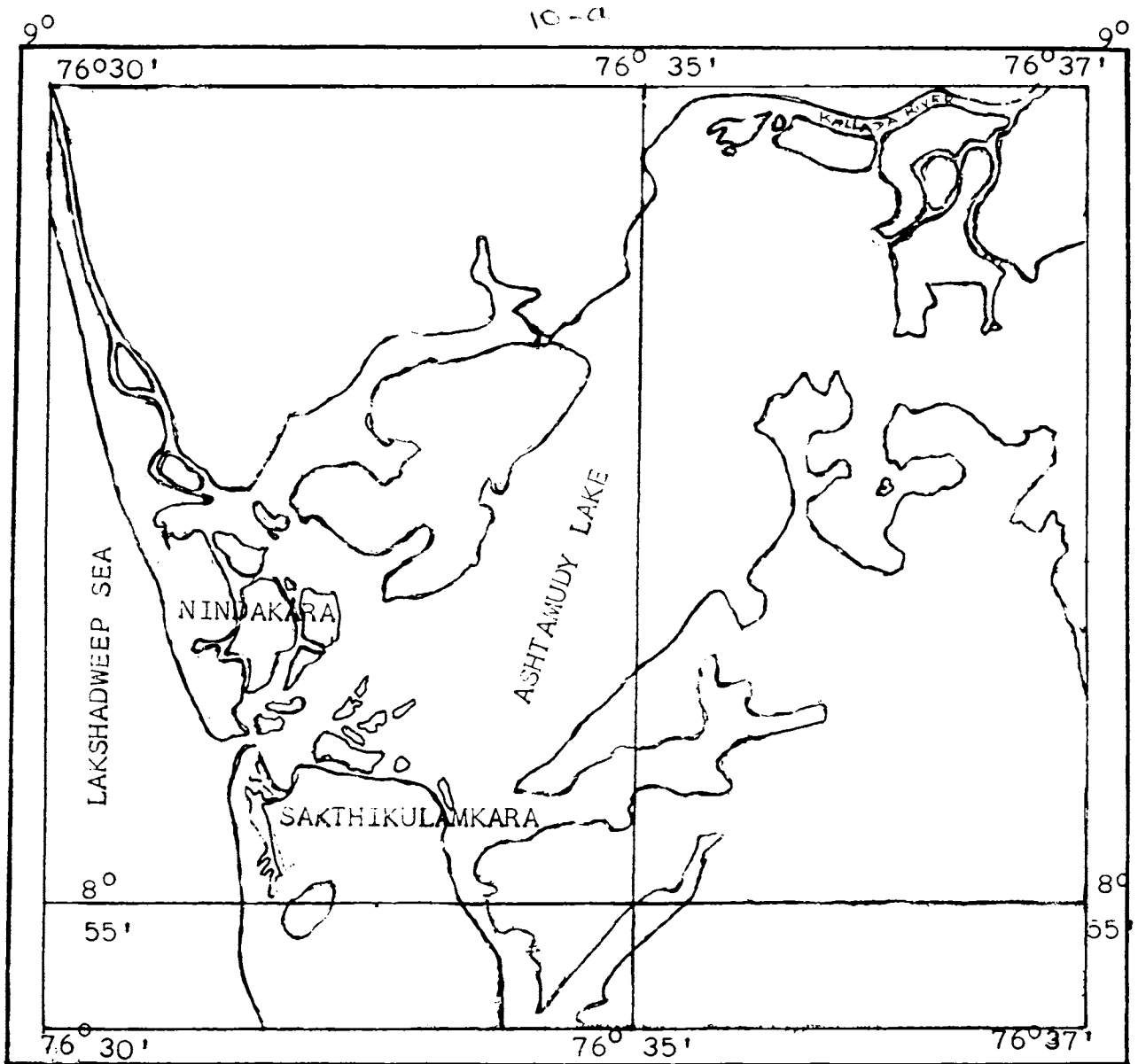


Fig. 1.2. Location map of Ashtamudy Lake

the deeper portions being confined to the eastern part. The lake is connected permanently to the Lakshadweep sea by 'Neendakara Azhi'. It is older than the Kayamkulam lake, which originated in the late Holocene as a part of a lagoon-barrier complex (Thrivikramaji, 1979). Though Kallada and Ithikara rivers flow entirely in this district, only the Kallada river empties into the lake. The Kallada river has got a length of 121 km and a catchment area of 1699 sq. km. The annual run-off is estimated at $2140.8 \times 10^6 \text{ m}^3$. The tributaries start independently in high land at a height of 1200 m and at about 300 m they join together to form the Kallada river. The Kallada river reaches the coast at an altitude of 0-10 m and there upon it empties into the lake.

The highland is formed of steep to very steep hill ranges and where all the tributaries joins to form the Kallada river, it is of gently to moderately sloping ridges. At Punaloor, the area becomes gently to moderately sloping spurs. Near the lowland, the coastal area becomes nearly level to very gently sloping coastal plain. The highland mainly consists of lower Precambrian rocks of khondalites and charnockites and extends upto the lower

regions of the midland. The lowland consists mainly of tertiary formations, namely the Quilon and Warkalli beds and the coast is of recent alluvium (Fig. 1.3).

At present a very reliable runoff figure of the river is difficult to obtain, as a dam for irrigation is under construction near Punaloor across the river course. But Prabhakar Rao (1968) who worked on some aspects of the lake, gives a figure of $2140.8 \times 10^6 \text{ m}^3$. In regard to the water potential in the river basin, it has an annual yield of $2270 \times 10^6 \text{ m}^3$ from the basin alone and the annual utilisable yield is $1368 \times 10^6 \text{ m}^3$ (Report of CWRDM, 1983). The river basin location can be given in the highland, midland and lowland as in between latitudes $8^{\circ}45'$ to 9° , $8^{\circ}54'$ to $9^{\circ}6'$ and $8^{\circ}51'$ to $9^{\circ}8'$ respectively and is in between longitudes $6^{\circ}30'$ to $77^{\circ}11'$.

The Kallada river drainage basin belongs to intense chemical weathering zone of Strakhov (Ollier, 1979). At the Kallada Irrigation Project Canal (Manampuzha - $8^{\circ}59'N$, $76^{\circ}38'E$) weathered and or partially lateritised zone of garnetiferous quartzo-feldspathic gneisses are exposed, which are underlain by unaltered biotite-gneisses and charnockites. The major minerals are feldspar, quartz and

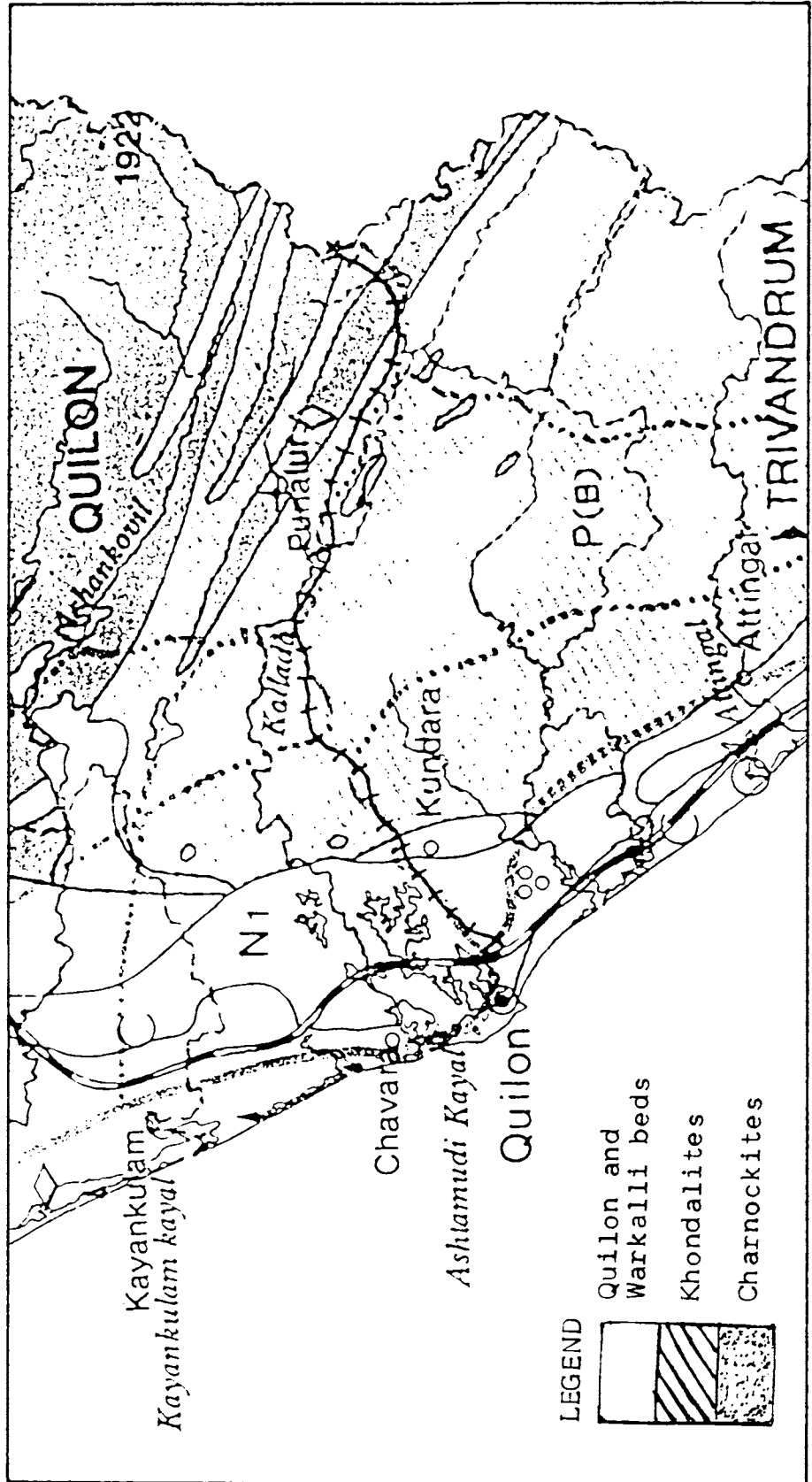


Fig. 1.3. Geology of the Kallada river basin

garnet. Sillimanite and biotite occur as minor constituents. Ilmenite, haematite and magnetite are the opaque minerals found as accessories and so also zircon and apatite. Sillimanite grains do not show any alteration. No unaltered feldspar is found in the laterites. This clearly shows that sillimanite is the most stable of all silicate minerals followed by quartz, biotite, garnet and K-feldspar.

The drainage pattern of the river basin is dendritic (Fig. 1.4). The mean annual rain-fall is 227.2 cms. The average temperature varies from 32°C to 33°C in the coastal region and 35°C to 36°C in the interior areas.

1.7. REVIEW OF LITERATURE

Hitherto, the area under investigation has not been subjected to any exhaustive study from the mineralogical or geochemical perspectives. However, a preliminary study of the mineralogy of the lake sediments was carried out by Prabhakar Rao (1968). In addition, studies on organic matter (Sajān and Damodaran, 1981) and that on carbonate content (Damodaran and Sajan, 1983) were also undertaken. Detailed studies on the lake sediments of Vembanad lake have been carried out by Murty and Veerayya (1972), and in

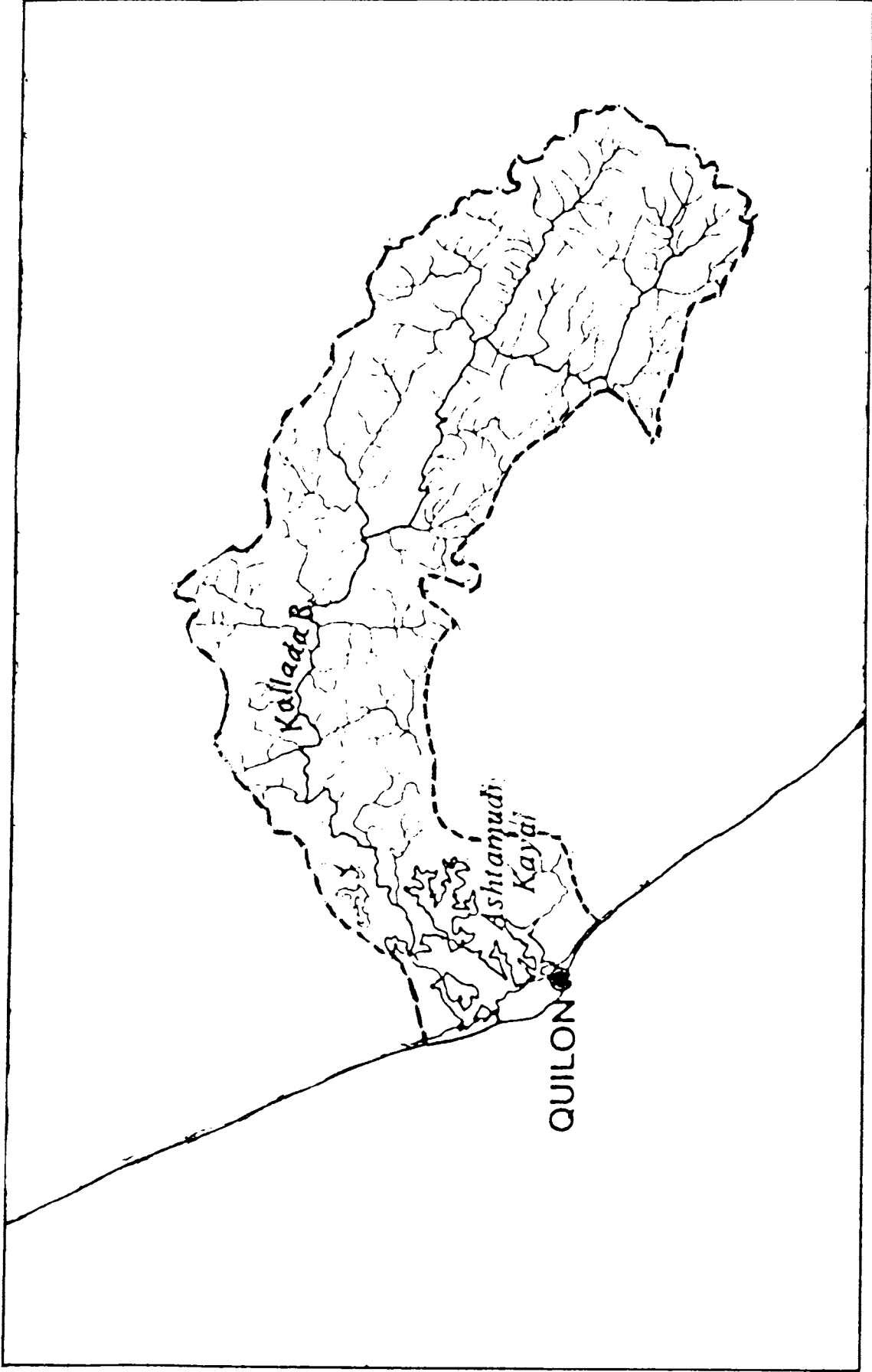


Fig. 1.4. Drainage pattern of Kallada river

Cochin backwaters by Venugopal et al. (1982) and Joseph (1987). Now studies are going on in Beypore estuary in the northern part of Kerala and Mandovi and Zuari estuary in the west coast of India. Sukhna lake in Chandigarh was scrutinised for the heavy mineral assemblage (Choudhri and Gill, 1983). Detailed investigations have been done on estuarine sediments for the following lakes on the east coast of India, viz: Pulicat lake (Durgaprasada Rao, 1971), Chilka lake (Venkataratna, 1965), Kolleru lake (Rama Murty, 1972) and Iskapalli lagoon (Subba Rao, 1985). Likewise studies on modern deltaic sediments of the Godavari river (Naidu, 1968), Krishna river (Seetaramaswamy, 1970), Mahanadi river (Satyanarayana, 1973), and Cauvery river (Seralathan, 1979) were also carried out. Sediment movement, heavy mineral associations and the C.N.P. content in the sediments of the Hooghly estuary had been studied by Shanmughom (1964) and Ghosh and Choudhary (1987).

Numerous published work on various aspects of the estuarine sediments can be cited from world literature. Among them, the most comprehensive study is on Chesapeake bay (Helz, 1976; Firck et al., 1977; Sinex and Helz, 1980/81). Other lakes for which studies

were made are lake Windemere (Gorham, 1960), lake Minnesōta (Swain, 1961), Salton sea (Arnal, 1961), lake Michigan (Moore, 1963), lake Sabine (Kane, 1963), lake Qarum (Wakeel, 1964), estuaries of the Atlantic coastal plain (Meade, 1969), lake Manzalah (Wakeel and Wahby, 1970), lake Mendota (Bortleson and Lee, 1972), James River estuary (Nichol, 1972), Solway Firth (Perkin et al., 1973), Palmlico estuary (Edzwald et al., 1974), lake Victoria (Mothersill, 1976), Miramichi estuary (Willey and Fitzgerald, 1980), lake Zurich (Sigg, 1981), Raritan river estuary (Motta, 1983), Ninegret lagoon (Rosenberg, 1983), Saint John Harbour sediments (Ray and Macknight, 1984), and Tamar estuary (Watson et al., 1985).

1.8. SCOPE OF THE STUDY

Limnology is the scientific study of the various aspects of lakes. In the present investigation the Ashtamudy lake sediments were studied setting the following objectives:

- 1) To obtain an account of the origin of fine sediments by studying the clay minerals, (2) to assimilate the mineralogy of the lake sediments and their provenance, (3) to elucidate the geochemical distribution of major and trace elements in the bulk sediment as well as in the clay fractions of the lake and (4) to evaluate the extent of pollution in the lake sediments. The present

study pertains to the modern surficial sediments of the Ashtamudy lake with emphasis on the areal distributions of various constituents.

1.9. FIELD PROGRAMME

Modern surficial sediments of the lake were sampled at 103 locations, covering an area of 51.2 sq. km. on board R.V. Sagitta, having a draft of 1 m. The samples were collected during 1982 and 1983. Locations of the bottom sediments were selected to give an even coverage. The sediment samples were collected using van-Veen grab at an interval of 500 m and then logged for their colour, texture, shell content, and depth of collection. After logging, the sediment samples were labelled and stored in polythene bottles. These samples were collected from the upstream of the river Kallada, eastern part of the lake (estuarine head), and the central and the western parts of the lake (estuarine mouth) for the investigations.

Laboratory investigation comprises (a) the preparation of the sample, (b) sieving, both dry and wet, (c) heavy and light mineral separation and their study, (d) clay separation and their mineralogical study by X-ray diffraction (XRD), differential thermal analysis (DTA)

and scanning electron microscope (SEM), and (e) geochemical analysis for the major and trace elements.

CHAPTER - 2SAND, SILT, CLAY, ORGANIC MATTER AND CARBONATE CONTENTS
OF THE SEDIMENTS

2.1. GENERAL SEDIMENTARY FRAME WORK

2.1.1. Introduction

Grain size is one of the basic attributes of sediments and hence its determination is necessary to interpret the depositional environments. According to Krumbein and Sloss (1951), the analysis of a sediment to obtain the size range of particles is called mechanical analysis and its numerical or graphical representation gives the size distribution of the sediments. The present study is confined to mechanical analysis only. Among all methods, sieving is the most popular method for mechanical analysis especially for sand sized material.

Numerous methods are available for the granulometric studies and these have been reviewed by Herden (1960) and Irani and Callis (1963). Most of the methods use volume frequency, but some methods use number frequency. Hence, it warrants to select a few methods primarily on the basis of their soundness and convenience. Sieving is found to be the best method for the mechanical analysis

particularly for sand sized sediments (Folk, 1966; Isphording, 1970,1972; Jaquet and Vernet, 1976; Swan et al., 1978), whereas pipette analysis for the finer sediments (Folk, 1966; Carver, 1971).

2.1.2. Methods of study

About 30 gms of the air-dried sample was treated with 30% H_2O_2 and 2N HCl to remove the organic matter and carbonate, as the sediment consists of sand, silt and clay. Any left out shell material after treatment with HCl was removed since it is added by the organisms and is not a transported sediment (Mc-Kinney and Friedman, 1970). Afterwards the sample was washed with distilled water and dried perfectly. 10 gms of the dried sediment sample was transferred to 1000 ml beaker, to which 7.5 gms of sodium hexametaphosphate was added. To that, minimum quantity of distilled water was added and kept overnight with intermittent stirring in order to disaggregate the flocculated clay particles and to dissolve any minor amount of salt which might tend to cement the grains (Shepard and Moore, 1955; Barnes, 1959). Subsequently, the aliquot was washed into a 1000 ml sedimentation cylinder after sieving through 63 μ sieve. The coarser material greater than 63 μ was dried and sieved into different size grades at one phi interval.

Pipette analysis for the fine sediments was carried out following the method of Folk (1966) and Carver (1971). Whitehouse et al. (1960) stated that the results of pipette analysis for clays can vary depending upon not only their mineralogy and the physico-chemical environment but also the kind of peptizer used. Hence in the present study a uniformity in the separation of clays has been maintained throughout the analysis.

2.1.3. Results and discussion

Sand-silt-clay ratios as determined is given in Table 2.1. These ratios are plotted in a triangular co-ordinate paper adopting textural nomenclature of Shepard (1954) and Folk (1968) to present a general sedimentary frame work of the Ashtamudy lake [Figs. 2.1.(A) and 2.1. (B)]. The areal distribution of the sediment is given in Fig. 2.2. Dry sieving of the sediment above 63 μ size yielded medium to very fine sand.

Sand is the most dominating sediment in the western part of the lake. The proportion of sand decreases towards the eastern part where silt and clay dominate. But sand increases again in the upstream

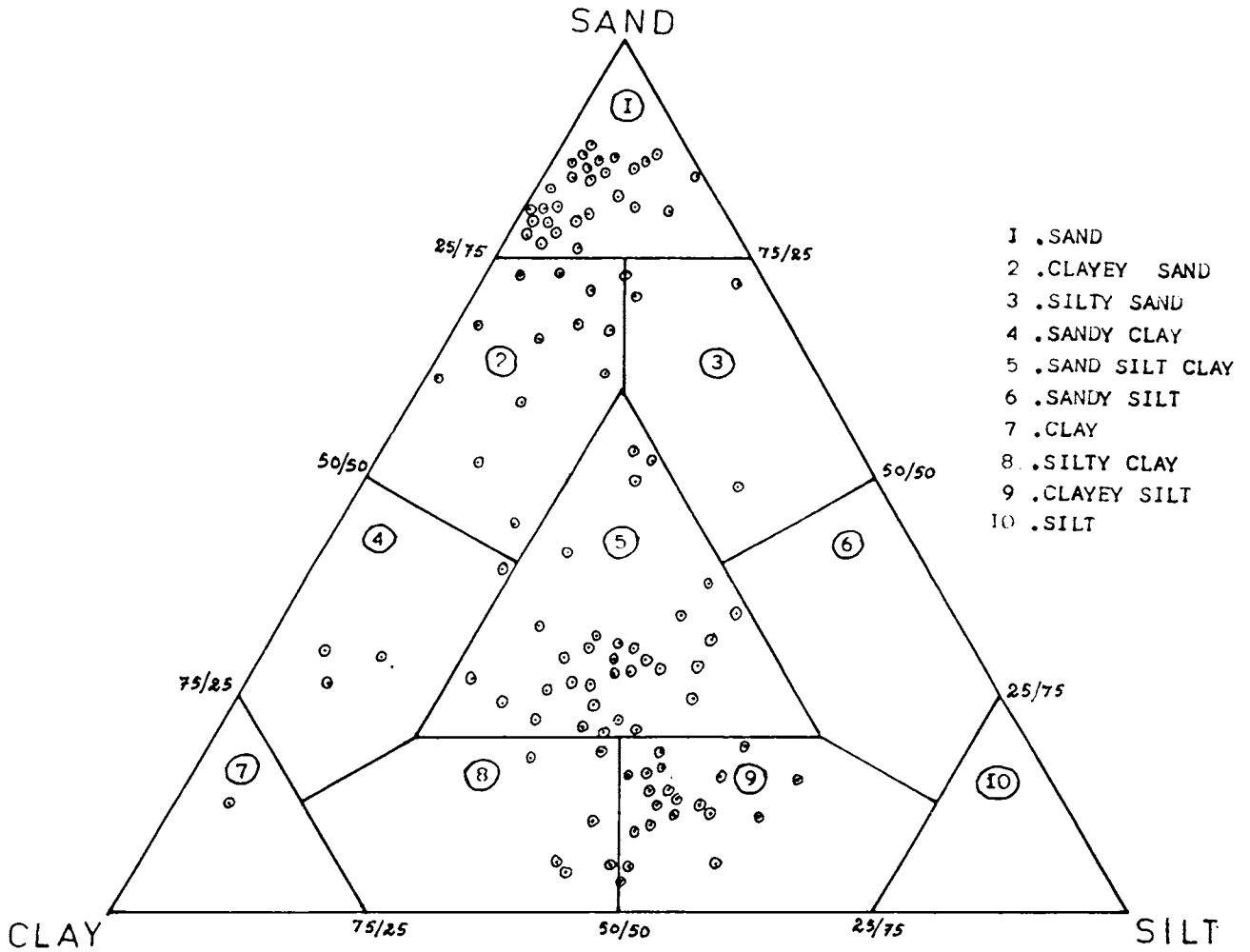


Fig. 2.1.(A) Shepard's textural nomenclature of the Ashtamudy Lake sediments, based on sand-silt-clay ratios

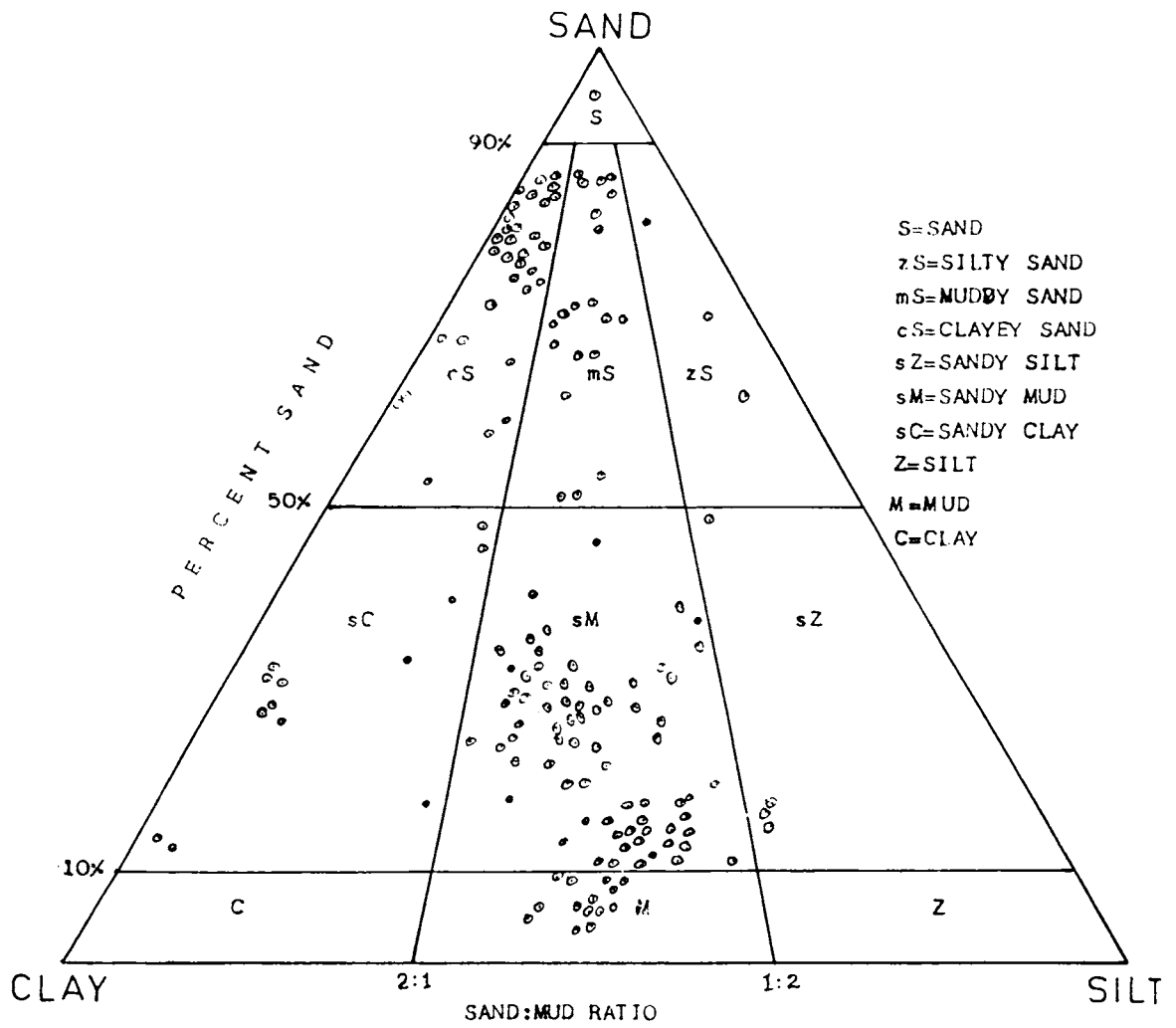


Fig. 2.1.(B) Folk's textural nomenclature of the Ashtamudy lake sediments, based on sand-silt-clay ratios

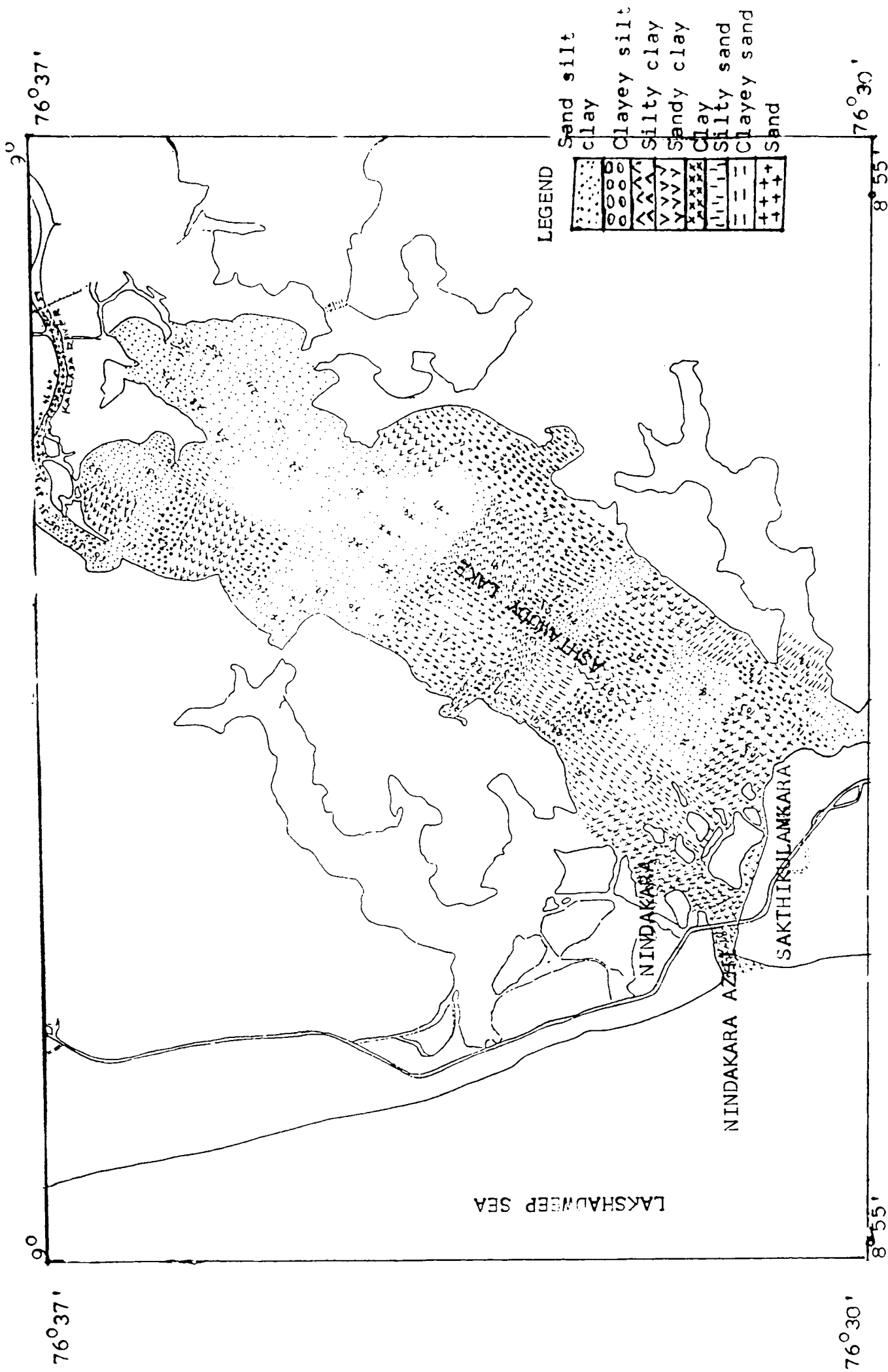


Fig. 2.2. Areal distribution of sediments based on Shepard's textural nomenclature and sample locations

Table 2.1. Nomenclature of the sediments based on the sand silt clay ratios

Sample No.	Sand (%)	Silt (%)	Clay (%)	Nomenclature by Shepard	Nomenclature by Folk	Depth of collection in (m)
1	2	3	4	5	6	7
1	86.47	8.58	4.95	Sand	Muddy sand	2.50
2	88.01	2.54	9.45	Sand	Clayey sand	2.00
3	84.07	4.04	11.90	Sand	Clayey sand	1.00
4	77.99	3.91	18.10	Sand	Clayey sand	3.00
5	72.10	4.90	23.00	Clayey sand	Clayey sand	1.25
6	73.79	6.66	19.55	Clayey sand	Clayey sand	2.00
7	46.91	26.84	26.25	Sand silt clay	Sandy mud	2.50
8	37.62	39.63	22.75	Sand silt clay	Sandy mud	2.25
9	70.71	15.44	13.55	Silty sand	Muddy sand	3.00
10	85.68	2.02	12.30	Sand	Clayey sand	1.25
11	86.46	3.34	10.20	Sand	Clayey sand	1.50
12	29.60	35.05	35.30	Sand silt clay	Sandy mud	1.75
13	16.48	42.40	41.15	Clayey silt	Sandy mud	2.75
14	13.35	46.80	39.85	Clayey silt	Sandy mud	2.50
15	18.77	43.73	37.50	Clayey silt	Sandy mud	2.75
16	13.67	48.21	38.20	Clayey silt	Sandy mud	2.75
17	80.00	6.53	13.47	Sand	Sand	2.50
18	79.48	4.97	15.55	Sand	Clayey sand	3.50
19	18.64	38.56	42.80	Silty clay	Sandy mud	2.50
20	27.60	36.80	35.60	Sand silt clay	Sandy mud	2.50
21	30.15	34.20	35.65	Sand silt clay	Sandy mud	1.50
22	31.19	43.00	25.85	Sand silt clay	Sandy mud	3.50
23	51.75	27.15	21.10	Sand silt clay	Muddy sand	2.25
24	33.72	38.93	27.35	Sand silt clay	Sandy mud	3.25
25	28.61	39.60	32.80	Sand silt clay	Sandy mud	2.00
26	28.93	37.52	33.55	Sand silt clay	Sandy mud	1.25
27	21.80	40.51	37.70	Sand silt clay	Sandy mud	1.50
28	28.85	28.05	43.10	Sand silt clay	Sandy mud	2.25
29	26.92	32.83	40.25	Sand silt clay	Sandy mud	2.50
30	45.08	17.26	37.66	Clayey sand	Sandy mud	2.25
31	21.53	35.32	43.15	Sand silt clay	Sandy mud	2.25
32	25.44	30.01	44.45	Sand silt clay	Sandy mud	1.50
33	17.53	33.12	49.35	Silty clay	Sandy mud	3.50

Table 2.1. Contd.

1	2	3	4	5	6	7
34	39.85	18.80	41.35	Sandy clay	Sandy mud	2.75
35	53.63	24.28	22.10	Sand silt clay	Muddy sand	2.75
36	66.19	8.81	25.00	Clayey sand	Clayey sand	3.00
37	51.91	9.40	38.70	Clayey sand	Clayey sand	3.00
38	85.57	3.93	10.50	Sand	Muddy sand	3.00
39	83.90	2.80	13.30	Sand	Clayey sand	2.50
40	84.38	3.82	11.80	Sand	Clayey sand	2.75
41	77.59	3.86	18.55	Sand	Clayey sand	3.00
42	68.65	12.50	18.85	Clay sand	Muddy sand	2.50
43	78.32	1.68	20.05	Sand	Clayey sand	2.00
44	80.53	2.53	16.95	Sand	Clayey sand	2.50
45	79.95	1.50	19.45	Sand	Clayey sand	2.00
46	70.86	11.64	17.50	Clayey sand	Muddy sand	1.75
47	84.65	4.96	10.40	Sand	Clayey sand	1.75
48	66.55	15.71	17.75	Clayey sand	Muddy sand	3.50
49	58.11	11.39	30.50	Clayey sand	Clayey sand	2.50
50	78.97	2.53	18.50	Sand	Clayey sand	2.00
51	80.94	0.80	18.25	Sand	Clayey sand	1.25
52	84.11	15.84	0.05	Sand	Silty sand	1.50
53	79.85	13.90	6.25	Sand	Silty sand	2.50
54	72.33	13.77	13.90	Clayey sand	Muddy sand	2.75
55	61.67	17.83	20.50	Clayey sand	Muddy sand	2.25
56	80.63	10.67	8.70	Sand	Muddy sand	2.25
57	71.48	25.07	3.45	Silty sand	Silty sand	2.50
58	87.15	8.91	3.95	Sand	Muddy sand	1.75
59	81.12	9.43	9.45	Sand	Muddy sand	2.75
60	40.31	24.06	35.63	Sand silt clay	Sandy mud	2.50
61	21.69	39.17	39.15	Sand silt clay	Sandy mud	1.50
62	4.91	48.14	46.70	Clayey silt	Mud	1.50
63	5.75	41.60	52.65	Silty clay	Mud	1.50
64	9.93	42.17	47.90	Silty clay	Mud	3.50
65	9.80	46.65	43.55	Clayey silt	Mud	5.50
66	25.50	33.90	40.60	Sand silt clay	Sandy mud	4.50
67	24.04	26.56	49.40	Sand silt clay	Sandy mud	2.75
68	22.04	30.26	47.70	Sand silt clay	Sandy mud	2.75
69	33.13	15.87	51.00	Sandy clay	Sandy mud	2.75
70	28.83	30.17	41.00	Sand silt clay	Sandy mud	2.75

Table 2.1. Contd.

1	2	3	4	5	6	7
71	32.16	26.25	41.60	Sand silt clay	Sandy mud	2.50
72	12.04	47.46	40.50	Clayey silt	Sandy mud	2.25
73	10.55	47.20	42.25	Clayey silt	Sandy mud	2.25
74	18.15	44.71	37.15	Clayey silt	Sandy mud	1.75
75	20.75	40.60	38.68	Sand silt clay	Sandy mud	2.25
76	29.27	29.43	41.30	Sand silt clay	Sandy mud	3.00
77	24.82	43.83	35.73	Sand silt clay	Sandy mud	2.50
78	30.63	31.88	37.50	Sand silt clay	Sandy mud	2.50
79	27.80	37.06	35.15	Sand silt clay	Sandy mud	2.25
80	25.62	8.48	65.90	Sandy clay	Sandy mud	2.25
81	29.78	11.12	59.10	Sandy clay	Sandy mud	2.50
82	29.45	6.25	64.30	Sandy clay	Sandy mud	2.75
83	13.01	46.90	40.10	Clayey silt	Sandy mud	2.50
84	16.80	45.00	38.20	Sand silt clay	Sandy mud	2.75
85	9.23	50.87	39.90	Clayey silt	Sandy mud	2.50
86	13.21	50.79	36.00	Clayey silt	Sandy mud	2.25
87	5.23	11.80	82.97	Clay	Sandy mud	2.25
88	6.04	55.96	38.00	Clayey silt	Mud	2.50
89	3.76	47.59	48.65	Silty clay	Mud	2.25
91	67.62	1.33	31.05	Clayey sand	Mud	2.50
92	61.48	1.02	37.75	Clayey sand	Mud	2.50
93	4.93	41.47	53.60	Silty clay	Mud	2.60
94	10.88	58.45	30.65	Clayey silt	Sandy mud	2.00
95	15.58	51.52	32.90	Clayey silt	Sandy mud	2.00
96	6.46	46.54	47.00	Silt clay	Mud	2.00
97	11.45	52.63	35.90	Clayey silt	Sandy mud	2.50
98	49.38	36.77	13.85	Silty sand	Sandy silt	2.25
99	15.49	59.52	25.00	Clayey silt	Sandy silt	2.25
100	34.88	43.42	21.70	Sand silt clay	Sandy mud	2.75
101	19.13	52.23	28.60	Clayey silt	Sandy mud	2.50
102	75.30	7.20	17.50	Sand	Clayey sand	1.25
103	82.11	1.14	16.75	Sand	Clayey sand	2.50

direction. The variation in the sand-silt-clay ratios within the lake, which gives the distribution pattern of the lake sediments, reveals that the western part of the lake is a high energy zone where as the central and eastern parts are low energy zones. Such an energy demarkation, as reflected from the sediment distribution, is expected in the light of the fact that the western part, which is open to the sea, should naturally experience the maximum tidal effect.

2.2. ORGANIC MATTER CONTENT

2.2.1. Introduction

Study of the organic matter content in marine and estuarine sediments is important due to the following reasons:

- i) It is regarded as the source material for the hydrocarbons.
- ii) It plays a vital role in the transportation and concentration of major and trace elements.
- iii) It helps ascertain the depositional environment.
- iv) It reveals the paleogeographical condition of the ancient sediments.

- v) It delineates the influence and changes brought about by the organic matter in the physico-chemical conditions of the sediment.

A lot of work has been done on various aspects of organic matter. Studies on organic matter content in the sediments were done for Chilka lake (Venkataratnam, 1965), Krishna delta and Nizampatam bay (Seetaramaswamy, 1968), Ashtamudy lake (Prabhakar Rao, 1968), Sajan and Damodaran (1981), Eastern part of Arabian Sea (Murty et al., 1969), Pulicat lake (Durgaprasada Rao, 1971), off Bombay-Saurashtra coast (Setty and Rao, 1972), Vembanad lake (Murty and Veerayya, 1972), Kolleru lake (Rama Murty, 1972), Cauvery river (Serālathan and Seetaramaswamy, 1979) and Iskapalli lagoon (Subba Rao, 1985).

2.2.2. Methods of study

No direct method has been so far evolved to determine the organic matter content in sediments and so it is conventionally estimated from one of the major constituents C, H and N.

In the present study the method of determining the organic carbon by wet oxidation method and multiplying the value by 1.724 (Wakeel and Riley, 1957) was

followed. 0.5 gm of the salt-free powdered sample was oxidised by a known quantity of chromic acid and the excess unused acid is determined by back titration, using ferrous ammonium sulphate. Percentage of organic matter is calculated by the formula,
Organic Matter (%) = $10 \times (1 - \frac{T}{S}) \times 1.724$, where T is the titre value for the blank and S for the sample solution.

For the statistical analysis, samples of stations within a distance of 1 km are grouped together. Thus, from the river mouth to barmouth there are 14 sets of samples, since the barmouth is 14 km away from the river. Table 2.4 gives the mean percentages and standard deviations in the organic matter content of the 14 groups of stations. Fig. 2.3 gives the variation of the organic matter content with increasing distance from the river.

The average organic matter content of a particular zone is determined by the texture of the sediments. Hence, the graphic profile of the mean values through sets of stations is also reflection of the general variation in texture which in turn is governed by the kinetic energy of the currents. The standard deviation of the values in a particular zone (indicated in the figure as vertical bars) also can help in demarkating a zone as of low or high energy.

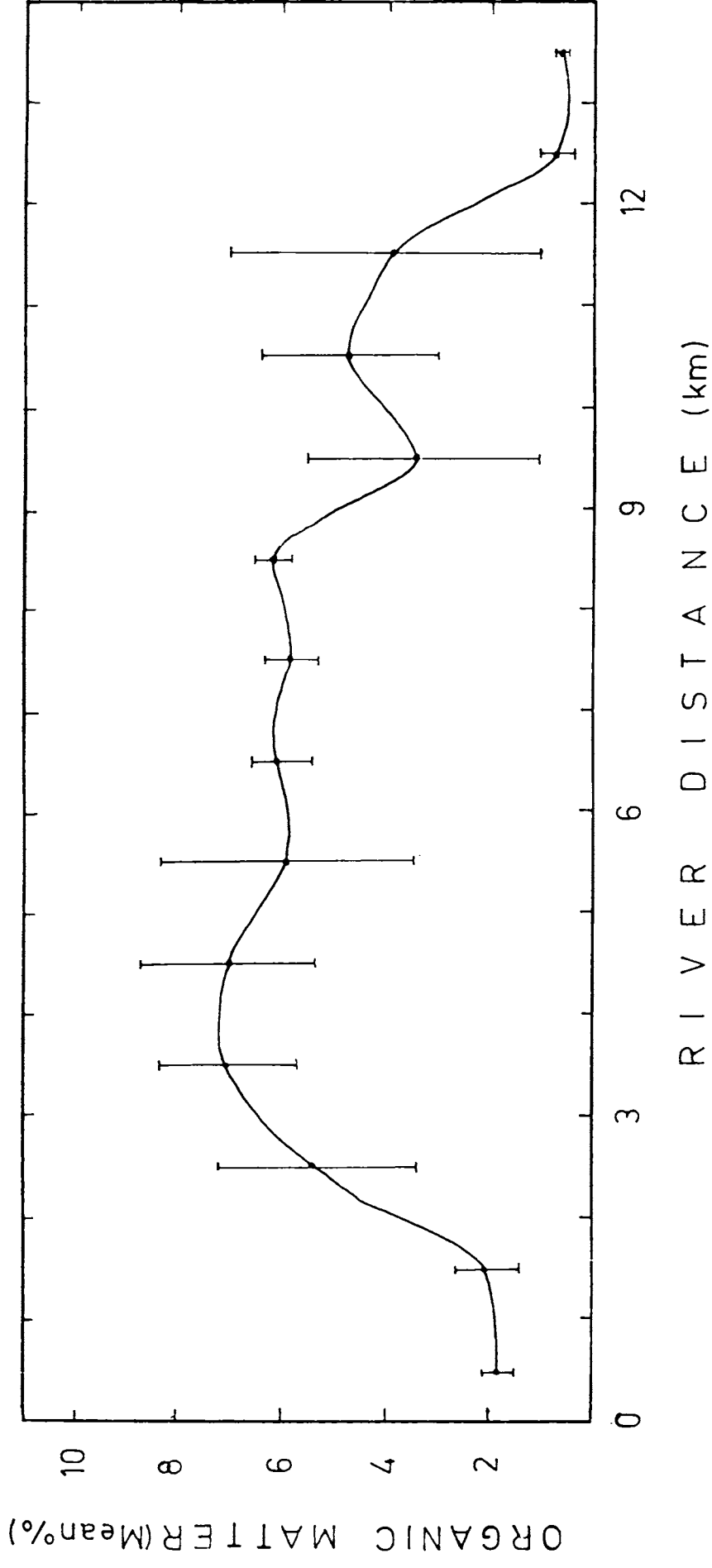


Fig. 2.3. Mean organic matter distribution against river distance (vertical bars indicate r.m.s. deviation)

2.2.3. Results and Discussion

The organic matter in the bulk samples and clays collected from various environments of Ashtamudy lake is presented in Table 2.2 A and B. The average content of organic matter in lake sediment is 4.67% and that in the bulk and clay samples are 5.12% and 4.21% respectively. The analysis shows a wide variation in the distribution of organic matter from 0.25% to 9.52%. The average percentage of organic matter in Ashtamudy lake sediments is much higher than the reported values for the sediments of the Indian lakes, and lower than that reported for some other lake sediments (Table 2.4). Here it will be worthwhile to mention that Postma (1969), Nilson and Lee (1982) and Phleger (1982) also observed that adjacent to the sea, estuarine sediments are usually rich in organic matter.

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

Table 2.2.A. Percentages of sand, silt and clay in the sediments, their organic matter and carbonate contents in weight percentages (Bulk fractions

Sample No.	Sand (%)	Silt (%)	Clay (%)	Total organic matter (%)	Total carbonate (%)
1	2	3	4	5	6
Eastern part					
23	51.75	27.15	21.10	6.08	-
24	33.72	38.93	27.35	6.86	-
25	28.61	39.60	32.80	7.54	-
26	29.93	37.52	33.55	7.10	-
27	21.79	40.51	37.70	7.46	-
30	45.08	17.26	37.66	6.60	-
32	25.54	30.01	44.45	9.00	-
36	66.19	3.81	25.00	4.54	-
40	34.36	3.83	11.80	2.05	-
44	80.53	2.53	16.95	1.45	-
48	66.55	15.71	17.75	2.65	-
52	84.11	15.84	0.05	1.71	-
54	72.30	13.77	13.90	2.31	-
58	87.15	8.91	3.95	1.62	-
59	31.12	9.43	9.45	1.62	-
60	40.31	24.06	35.63	6.60	-
62	4.91	48.14	46.70	7.80	-
64	9.93	42.17	47.90	9.52	-

Table 2.2.A. Contd.

1	2	3	4	5	6
<u>Central part</u>					
10	85.68	2.02	12.30	0.25	-
11	86.46	3.34	10.20	1.45	13
12	29.66	35.05	35.30	6.13	-
13	16.48	42.40	41.15	6.43	2
14	13.35	46.80	39.85	6.17	-
15	18.77	43.73	37.50	6.43	-
20	27.60	36.80	35.60	3.34	-
21	30.15	34.20	35.65	1.11	-
22	31.19	42.97	25.85	5.31	-
65	9.80	46.65	43.55	7.46	-
67	24.04	26.56	49.40	6.94	-
68	22.04	30.26	47.70	8.49	-
70	28.33	30.17	41.00	6.34	-
72	12.04	47.46	40.50	6.43	-
74	18.15	44.71	37.15	4.97	-
75	20.75	40.60	38.68	6.08	-
77	24.82	43.87	35.73	6.69	-
78	30.63	31.88	37.50	5.59	3
79	27.80	37.06	35.15	5.40	-
81	29.78	11.12	59.10	6.17	-
83	13.01	46.90	40.10	6.17	-
84	16.80	45.00	38.20	5.83	-
86	13.21	50.79	36.00	6.86	-
87	5.23	11.80	82.97	6.77	-

Table 2.2.A: Contd.

1	2	3	4	5	6
88	6.04	55.96	38.00	7.46	-
91	67.62	1.33	31.05	2.57	-
93	4.93	41.47	53.60	6.69	-
94	10.88	58.47	30.65	6.86	-
95	15.58	51.52	32.90	5.91	-
<u>Western part</u>					
1	86.47	8.58	4.95	0.42	17
2	88.01	2.54	9.45	0.60	6
3	84.07	4.07	11.90	1.20	8
4	77.99	3.91	18.10	5.31	4
5	72.10	4.90	23.00	3.68	6
6	73.79	6.66	19.55	2.65	10
7	46.91	26.84	26.25	4.71	2
8	37.62	39.63	22.75	4.63	7
9	70.71	15.44	13.55	2.05	2
17	80.00	6.53	13.47	0.51	4
97	11.45	52.66	35.90	6.17	-
98	49.38	36.77	13.85	5.40	-
99	15.40	59.52	25.00	7.63	-
100	34.88	43.42	21.70	6.60	-
101	19.13	52.23	28.60	6.51	-
102	75.30	7.20	17.50	2.31	5
103	82.11	1.14	16.75	0.94	8

Table 2.2.B. Clay fractions: Percentages of clay in the sediments, their organic matter and carbonate contents in weight percentages

Sample No.	Clay (%)	Total organic matter (wt. %)	Total carbonate (wt. %)
<u>Eastern part</u>			
28	43.10	6.86	-
29	40.25	7.97	-
31	43.15	5.06	-
34	41.35	4.46	-
37	38.70	4.63	-
61	39.15	5.83	-
63	52.65	7.97	-
<u>Central part</u>			
16	38.20	6.00	-
19	42.80	5.23	-
66	40.60	7.37	-
69	51.00	7.71	-
71	41.60	5.31	-
73	42.25	5.48	3.00
76	41.30	5.49	-
80	65.90	6.00	-
82	64.30	5.91	-
85	39.90	5.23	-
89	48.65	5.66	-
92	37.75	3.34	3.00
96	47.00	5.48	-
<u>Western part</u>			
18	15.55	0.81	3.00

Table 2.3. Observed values of organic matter content
in sediments of various lakes

1. Maracaipo Lake	Redfield	1958	9%
2. Lothwaite Lake	Gorham	1960	8.4 - 11.5%
3. Windemere Lake	Gorham	1960	8.1 - 14.7%
4. Qarum Lake	Wakeel	1964(a)	1.64%
5. Chilka Lake	Venkataratnam	1965	1.38%
6. Manzalah Lake	Wakeel and Wahby	1970	2.56%
7. Pulicat Lake	Durgaprasada Rao	1971	0.985%
8. Vembanad Lake	Murty and Veerayya	1972	2.55%
9. Kolleru Lake	Rama Murty	1972	2.41%
10. Iskapalli Lagoon	Subba Rao	1985	1.52%

The sediments at Kallada river mouth is characterised by high organic matter content (4.659%) which decreases in the upstream direction. This could be the reflection of the variation in the texture of the sediment. The texture that prevails at the river mouth is clayey silt, sand silt clay and clayey sand whereas in the upstream it is mainly sand. The study yielded a low organic matter in bulk samples for sands and high values for clays since they have a good adsorbing capacity. Link (1967) found an average increase of 0.2% of organic carbon for each phi unit increase in mean size.

The rate of supply of organic material by river Kallada is considerably high, as its drainage basin is thronged with thick plantations. The eastern part of the lake, where river Kallada empties, is comparatively calm and hence there is very low turbulence resulting in high rates of sedimentation. This region is rather deeper than the rest of the lake and have relatively low temperature. The organic materials thus transported are deposited faster than the inorganic material. Among all other factors, the availability of oxygen is the most important one that determines the rate of decomposition of the organic matter in a depositional sedimentary environment. Very little decomposition of organic matter

takes place in a reducing environment especially in calm regions. Fine sediments like silt and clay are deposited in relatively deeper, quiet and less aerated regions which are ideal for the deposition of organic matter. Besides, these regions are marked for coconut leaf and husk rating which also play an important role in contributing organic matter. The fine sediments of this area are predominantly greyish black muds, which sometimes emit the odour of H_2S indicating high organic matter content and reducing environment. Likewise, another important factor which ascertains the accumulation of organic matter is temperature (Wakeel and Wahby, 1970). High temperature decomposes organic matter preventing accumulation. The rate of accumulation is also directly related to bulk accumulation. (Heith et al., 1977) and preservation will be the result of high sedimentation (Richards, 1970). Thus all these parameters facilitate high organic matter content at the eastern part of the lake. It is a matter of common observation that fine sediments contain high organic matter. This could be probably due to close resemblance in the settling velocity of the organic constituents with that of fine sediments. This can be the main cause for the variation of organic matter with texture. But Carter and Mittern (1978) found that this could be due to co-sedimentation

or a hike in the surface adsorption of organic matter, since fine sediments have a greater surface area. Suess (1973) suggested that the increase in organic carbon and nitrogen is linearly related to the surface area of the finer sediments.

Again in the Central part, a high value for the organic matter (5.59%) is noticed. This reflects the texture where clay and silt exceeds 50%. This region is comparatively shallower and has a relatively higher temperature. Eventhough the rate of influx of sediment is low, the central part, especially close to the western part of the lake is turbulent. The high organic matter content is due to the texture and organic productivity in spite of the shallow depth, higher oxygen content, turbulence and temperature. The organic matter is derived mainly from the phytoplanktons which is associated with high organic productivity in the overlying water column. The central part is marked for high organic productivity. Similar observations have been reported by Arnal (1961), Wakeel and Wahby (1970) and Sankaranarayanan and Panampunnayil (1979). Hence the high organic matter in the central part owes its source to the high organic productivity prevailing in that region besides the river run off. Fig. 2.3 shows consistency in the organic matter content at the central

Table 2.4. Mean Organic Matter Content and the Standard Deviations

Distance in kms	No. of samples	Mean (\bar{x})	Standard deviation (σ)
0 - 1	4	1.82	0.29
1 - 2	2	2.05	0.60
2 - 3	7	5.36	1.76
3 - 4	7	7.04	1.30
4 - 5	5	6.98	1.55
5 - 6	8	5.87	2.42
6 - 7	8	6.05	0.55
7 - 8	10	5.84	0.46
8 - 9	7	6.29	0.36
9 - 10	6	3.28	2.22
10 - 11	12	4.74	1.67
11 - 12	6	3.91	3.03
12 - 13	2	0.62	0.20
13 - 14	1	0.51	0

part (i.e., less standard deviation compared to other parts of the lake). There would have been considerably larger variation in the central part, if any of the factors other than texture and organic productivity had played a prominent role.

The sediments of the western part of the lake recorded the lowest percentage of organic matter (0.708%). This is mainly due to the sandy nature. The higher levels of turbulence, oxygen content, temperature, very low sedimentation and the sandy texture lower the organic matter content in the western part of the lake. Kuenen (1965) observed that most of the organic matter will be washed away along with the finer sediments by the tidal currents in highly agitated water. These strong currents also prevent the organic constituents from settling down at the bottom.

Variations in the mean organic matter content are considerably large in the eastern and western zones of the lake, whereas the central part shows consistency in variation (Fig. 2.3). This difference can be attributed to the textural variation of the sediment. The 0-2 km region of the study area is the upstream part of the River Kallada, where the sediment is mainly sand the texture of which does not vary much, hence the small

standard deviation. The eastern part of the lake which is from 2-5.5 km shows large standard deviation where the sediment texture is mainly clayey silt, sand silt clay and clayey sand. Therefore changes in the organic matter content of this region occurs as and when the proportion of sand/silt/clay varies. The same is the case with the western part of the lake, the region between 9-12 km. The central part of the lake (6-8.5 km) shows consistently low standard deviations. This is the reflection of a more or less uniform texture in which silt and clay exceeds 50%. Thus as mentioned in section 2.2.2, the mean organic matter content values together with standard deviations can be used in demarkating the various energy zones of a lake. Thus Fig. 2.3 reveals that the eastern and central part of the Ashtamudy lake are low energy zones whereas the western part is a high energy zone.

2.3. CARBONATE CONTENT

2.3.1. Introduction

Carbonate constituents are products of the environment whereas noncarbonate fractions are generally terrigenous and hence may be considered as a dilutant of the carbonate fraction (Milliman et al., 1972).

Bathurst (1971) and Milliman (1974) reviewed the use of carbonate component in understanding the depositional sedimentary processes. In 1972, Setty and Rao concluded that variation in the carbonate content indicates the differences in the environmental conditions of deposition like temperature, salinity, organic productivity etc. The present study is an attempt to elucidate the source, the distribution of the carbonates, and the sedimentary processes.

2.3.2. Methods of study

The total carbonate in the bulk and clay samples were carried out by rapid volumetric method of Hutchinson and Meclennan (Piper, 1947). This involves treatment of the sample with a known amount of HCl and estimation of unused HCl by back titration with NaOH. The percentage is calculated by the formula $\text{CaCO}_3(\%) = 10(T-S)$ where T and S are titre values for the blank and sample solutions respectively.

2.3.3. Results and Discussion

The total carbonate including calcium as well as magnesium carbonates in the bulk and the clay samples in the sediments of the Ashtamudy lake is given in Tables 2.2.A and B respectively. It shows wide variation

in distribution ranging from 17% to 0%. The average value for the carbonate content of the Ashtamudy lake sediment is 1.247%. The study has revealed that the carbonates are mainly confined to the western part of the lake and surrounding places. The sediments of the upstream and eastern part have yielded only very low values. Carbonate and non-carbonate fractions in Ashtamudy lake sediments have different origin and ages of deposition. CaCO_3 is derived mainly from transportation of the calcareous material by rivers, organic and inorganic precipitation from the overlying waters and the shell fragments and tests of organisms. Binocular microscopic observation revealed the presence of shell fragments of molluscs and tests of planktonic organisms, whereas petrological microscopic study did not show any carbonate mineral such as calcite or dolomite. This contradicts the observation on the north-eastern Michigan lake where the main proportion of carbonate occurs as calcite and dolomite grains (Moore, 1961). Hence the main source for the carbonate in Ashtamudy lake sediments probably is from the shell fragments and tests of the organisms.

The absence of any CO_3 values for eastern part and upstream sediments of the Kallada river are due to

(1) the non supply of calcareous material by the river Kallada, (2) the fine texture of the sediment, (3) greater depth and (4) high sedimentation rates of fine sediments. These factors are detrimental to the existence of the shell bearing organisms. As mentioned earlier, the prevalence of reducing environment at the eastern part also contribute to the decrease in CO_3 content.

The sediments of central part gave a low CO_3 value (av. 0.54%). However, the CO_3 values increase progressively towards the western part of the lake. Western part of the sediments yielded the highest CO_3 values (av. 3.83%). Any sudden changes in the sedimentary environment resulting after the influx of terrigenous material presumably will lead to oxidising conditions favourable for high CO_3 values (Setty and Rao, 1972).

Photosynthesis and respiration bring about CaCO_3 precipitation from the overlying water by effecting the CO_2 flux. Cloud (1965) stated that certainly any biological process which affects the amount of CO_2 in solution, disturbs the CO_3 equalibria. Binocular microscopic examination of the lake sediments revealed

the presence of molluscan shells and tests of foraminifera in and nearby western part, which indicates maximum amount of biogenic activity. Therefore it can be taken for granted that a part of the CaCO_3 occurring in the lake sediments is due to precipitation resulting from photosynthetic CO_2 intake by plants and respiration by organisms. A similar observation has also been made by Nair and Pylee (1968) and Dora (1979).

In the sediments of the western part, the carbonates are of biogenic origin consisting mostly of shells, shell fragments and tests of planktonic organisms. The concentration of these biogenic calcareous material assigned them a good value when compared to the eastern and central parts of the lake. The tidal current is responsible for this constitution. It could be concluded that comparatively lower values of the carbonate contents in the clays and sands of the Ashtamudy lake may be due to the absence of any carbonate contribution to the sediments by any agencies other than biogenic activity.

CHAPTER - 3

MINERALOGICAL COMPOSITIONS OF THE SEDIMENTS

3.1. INTRODUCTION

Although the mineralogical composition of the clastic sediments is a function of provenance, it is also governed by transportation and environment of deposition. The study on the mineralogical composition of sediment reveals some of the important aspects regarding the source-rock from which they have been released. Certain heavy minerals are even characteristic of some source-rocks. Again, a knowledge of the mineral composition of sediments, the mineral stability with respect to both climate and mechanical wear, and an understanding of the relationship between the mineral frequencies and the extent of transportation of a sediment, will be of immense use in tackling the problem of provenance and correlation. Often sediments that belong to the same provenance should have identical associations of minerals. However, in some cases, the samples that belong to one association can vary considerably in mineralogical composition. Rapid changes in composition, especially for the fluvial sediments can occur due to addition of new minerals by tributaries, erosion of

bottom materials by varied hydrodynamic conditions during transportation and deposition, selective weathering of certain unstable minerals, sorting according to size and density, and mechanical wear from the original sediments.

3.2. METHODS OF STUDY

The methods which were adopted for the mineralogical study of the sediments are given below.

3.2.1. Heavy and Light minerals

For heavy mineral analysis the samples were washed thoroughly with water to remove very fine sediments. The sand fraction, free of silt and clay was treated with dilute HCl acid to remove the shell content and ferruginous coating on the mineral grains. Addition of a small quantity of stannous chloride facilitated the easy removal of iron coating. After washing with distilled water and drying, the samples were sieved into two size-fractions namely: 1.0 mm to 0.25 mm, and 0.25 mm to 0.063 mm following the method of Krumbein and Pettijohn (1938). While referring to the mineralogical studies of sediments, they stated that since it is well known that mineral frequencies in different grade sizes of the same sediments are not alike, it is necessary for scientific work to study the mineral composition of each grade size by itself; or

in the case of comparative study of many samples, to study the same grade size in all the investigated samples'. Similarly, while evaluating some of the factors that determine the variation in the frequency in the different grade sizes Rubey (1933) suggested that the heavy minerals from at least two size fractions of each sample should be studied.

For the present study, two size-grades viz. 1.0-0.25 mm and 0.25-0.063 mm were examined for the heavy mineral assemblage. About 2-5 gm of the representative portion of the sieved fraction of the samples were obtained with a spliths and the heavy minerals were separated from the lighter fractions following the traditional bromoform method (Carver, 1971). As the bromoform could not completely separate the micas from the lighter fractions, since specific gravities of the micas range from 2.8-3.1, they were also included under heavies while on counting. After separation, the heavy fractions were weighed and representative amounts of the heavy residues (300-400 grains) of each of the above two size grades were mounted on glass slides using Canada balsam. The heavy minerals from the representative samples were examined under Leitz petrological microscope for the types and percentage of minerals present. The grain counting were made using a mechanical stage.

Staining is the ideal method for identifying the soda lime and potash feldspars in the light fractions. In the present study, the staining method as described by Gabriel and Cox (1929) is followed and the reliability of the method is established following the method of Hayes and Klugman (1959). The staining method, in brief, consists of etching the sand grains mounted on glass slides with hydrofluoric acid by exposing the slides to the fumes of hydrofluoric acid and subsequent treatment with concentrated solution of cobaltinitrite for two minutes. Then the rinsed and dried slide is treated with 0.5% eosine 'B' which subsequently stains the soda lime feldspars with pink and potash feldspars with orange-yellow colours respectively. Quartz remains unaffected. About 1000 grains were stained from which the number percentages of quartz and feldspar were estimated.

3.2.2. Clay minerals

Twenty one representative sediment samples from the 3 different zones of the lake, as mentioned earlier, have been studied for their clay mineralogy. Organic matter in the selected samples were removed by treating with hydrogen peroxide and then dispersing in deionised distilled water with a few drops of ammonia.

Aliquots of less than 2 micron size were decanted from the stable suspension. Oriented smear slides, as suggested by Gibbs (1965), were made from the separated aliquot (less than 2 microns), which was then analysed under Phillips X-ray diffractometer using Nickel filter and CuK_α radiation. The slides controlled under high and low humidity after treatment with ethylene glycol. Likewise, less than 2 micron clays were separated, dried at 50 to 55°C, powdered and were subjected to differential thermal and chemical analyses. Differential thermal analysis was carried out with a home-made D.T.A. facility incorporating a Haltmann and Braun temperature programmer and a Rikadenki Kogyo 3 pen recorder (model R 13). The thermocouple used is platinum and the cups platinum. The samples were heated upto 1100°C and the heating range was 10° per minute. The chart speed was 30 cm per hour. The sensitivity for Δf and T are 1 mv and 50 mv full scale respectively.

Kaolinite was identified by their endothermic peaks at 100°C and 576°C and an exothermic peak at 975°C which are due to the removal of adsorbed and combined water and structural rearrangement respectively, Montmorillonite by that of endothermic peaks at 132°C and 683°C and exothermic peak at 967°C which are due to

dehydroxylation and decomposition. Their characteristic peak is that of Na montmorillonite (Grim, 1953). Illite was identified by their endothermic peaks at 133°C, 560°C, 870°C and endothermic peak at 926°C.

Photomicrographs for the various clay minerals were taken using Stereoscan-180 Scanning Electron Microscope under selected area diffraction (s.a.d.) to supplement the results of the above mentioned instrumental analyses (Plates V-VII). The magnification was 1500 times. Gold coating was done on the specimens using sputter coater (S. 150 B); Edward.

Identification and quantification of clay minerals were made as given by Biscaye (1964,1965) and Carroll (1970). The peaks after glycolation and the weighing factors used were: 17 Å⁰ peak area for smectite, 4 times the 10 Å⁰ for illite and 2 times the 7 Å⁰ peak area for kaolinite. A semi-quantitative technique (Biscaye, 1965) was followed and the weighted peak percentages of different clays were calculated from the peak areas.

3.3. HEAVY MINERALS

As a correlation tool, heavy mineral study is of great interest in sedimentary petrographic investigations, particularly for the subsurface correlation in certain sedimentary basins (van Andel, 1959). In clastic sediments the mineralogy of each grain is rather independent of the surrounding grains because source-areas are mineralogically complex and weathering conditions may vary dramatically in geographically adjacent areas (Blatt, 1967). Therefore mineralogical study of detrital constituents of the sediments is of profound importance in bringing out the depositional history of a sedimentary basin.

In the present investigation, an attempt has been made to find out the source rocks for the lake sediments based on the relative abundance of heavy minerals, petrological character of the source area, and regional distribution of heavy minerals. To facilitate a better understanding and an easy explanation of the results of mineralogical analysis, the Ashtamudy lake, which is in fact an estuary, is divided into the following 3 zones: (i) the eastern part - where the river Kallada empties into the lake, (ii) central part of the lake and, (iii) the western part - where it joins with open sea.

3.3.1. Description of heavy minerals

The important characteristic features of the heavy minerals that were identified are given below (Plates I-IV). Since no magnetic separation was carried out, magnetite and ilmenite are grouped together under opaques.

Opaques

Opaques are in considerable proportion and dominate the heavy mineral assemblage. Ilmenite grains altering to leucoxene were seen occasionally. The grains are mostly subrounded to rounded.

Sillimanite

The grains are colourless, irregular to prismatic in shape, shows good relief and straight extinction. Inclusions or alterations are not common.

Garnet

They are generally subangular to subrounded. Two varieties observed were the colourless and pink garnets. The colourless type is generally clear, whereas the pink variety shows a cloudy appearance. They are identified by their high relief and isotropic behaviour. Inclusions of iron oxides are seen. Mainly occurs as fresh and unaltered grains.

Zircon

Prismatic with pyramidal terminations. Some rounded grains were also noticed. Almost all grains are colourless. The refractive index is fairly high. Zoning is the characteristic feature of these grains.

Monazite

Mostly rounded grains. Characteristic property is their yellow colour. Shows high relief with distinct borders.

Kyanite

Grains are colourless and occurs usually as elongated grains with rectangular outlines. Cross-cleavage present is conspicuous, giving rise to step like appearance. Shows high-order interference colours and inclined extinction.

Amphibole

Two varieties are noted namely green and bluish green varieties. Grains are irregular in shape, some are elongated and some are corroded. Pleochroism is strong from dark green to light green. Shows high order interference colours. The bluish green grains may be of

actinolite, which is present in minor proportions. The green and greenish brown variety of Hornblende is the predominant amphibole.

Pyroxene

They have irregular shapes with one set of cleavage and are brownish green in colour. Hypersthene is the most dominant mineral. Exhibits pleochroism from brownish green to green. Shows straight extinction. Augite, when present is in very small proportion which is identified by strong birefringence and inclined extinction.

Tourmaline

Prismatic and irregular varieties were identified. Colour is usually dark brown. Pleochroism is strong from dark brown to light brown to pale yellow.

Rutile

Most of the grains are rounded to subrounded and shows thick reddish brown colour. High refractive index with thick borders and hence the colour is seen at the central part of the grain. Exhibits straight extinction.

Apatite

Colourless, rounded, elongate prismatic grains, straight extinction, length fast and weak birefringence.

Biotite

Occurs mostly as flakes. Brown in colour. Shows pleochroism from brown to brownish yellow and high order interference colours. Inclusions are common.

3.3.2. Results

The total weight percentages of heavy minerals and the number percentages of heavy minerals in the two grades namely 1.0-0.25 mm and 0.25-0.063 mm are presented in Tables 3.1 and 3.2 respectively.

Within the lake, the heavy mineral residue shows a different trend in concentration. Highest per cent of heavies are found in medium to very fine grained sand, whereas low values for the coarse sand. The existence of such a relationship between heavy mineral percentages and grain-size has been pointed out by many workers. Pollack (1961), Seibold (1963), Naidu (1966), Venkataratnam and Tilak (1968), Seetaramaswamy (1970) and Sastry et al. (1987) have also found a relatively

Table 3.1. Percentages of heavy minerals by weight
in the sediments of Ashtamudy lake

Sample No.	Size	Size
	1 - 0.25 mm	0.25 - 0.063 mm
1	14.471	49.072
2	10.041	84.131
10	5.015	42.914
13	7.268	69.980
14	4.621	10.746
15	7.583	76.923
16	18.910	88.073
17	28.579	95.640
18	10.776	92.311
19	17.583	74.222
21	2.398	10.722
35	4.252	11.019
38	4.990	24.726
40	3.043	18.279
42	3.516	14.983
44	3.674	12.626
47	5.706	12.053
50	1.831	16.817
53	1.785	13.887
56	2.966	13.438
59	2.020	9.850
91	-	1.340
103	0.577	10.126

Table 3.2. Number percentages of the heavy minerals in the two size grades of Ashtamudy lake sediments

Sample No.	Size ^a	(Op)%	(Ga)%	(Si)%	(Zr)%	(Mo)%	(Ky)%	(Am)%	(Py)%	(Tr)%	(Ru)%	(Ap)%	(Bi)%
1	A	38.83	2.91	42.72	7.79	4.85	1.94	-	-	-	0.97	-	-
	B	83.61	0.24	6.51	0.96	7.23	-	-	-	-	0.96	-	0.48
2	A	53.51	0.88	31.58	5.26	4.39	2.63	-	-	0.88	0.88	-	-
	B	85.17	0.32	7.57	0.32	5.68	-	0.32	-	-	0.63	-	-
10	A	62.29	-	22.91	6.15	5.03	2.51	-	-	-	1.12	-	-
	B	69.36	0.43	16.60	4.26	6.38	0.21	0.43	-	0.21	1.49	-	0.64
13	A	49.37	1.67	41.84	3.77	0.84	0.42	0.84	-	0.42	0.84	-	-
	B	82.23	1.05	8.36	0.70	5.23	-	0.70	-	0.70	1.05	-	-
14	A	35.71	0.77	45.41	11.43	2.30	0.51	-	-	-	0.26	-	3.57
	B	29.96	1.32	18.94	26.43	7.93	-	9.25	1.44	2.96	-	-	1.76
15	A	30.83	0.75	42.11	16.54	8.27	-	-	-	1.50	-	-	-
	B	74.32	-	12.84	0.68	9.46	-	0.68	-	-	2.03	-	-
16	A	71.28	0.53	22.87	2.13	2.13	-	-	-	-	1.06	-	-
	B	74.46	1.09	13.04	0.54	9.24	-	0.54	-	-	1.09	-	-
17	A	66.37	2.24	18.83	4.48	5.38	1.35	-	-	-	0.45	0.90	-
	B	85.34	0.72	6.01	-	7.45	-	0.24	-	-	0.24	-	-
18	A	64.36	1.49	14.36	9.90	6.93	0.99	-	-	-	0.99	0.99	-
	B	73.29	1.63	14.93	0.33	7.49	-	0.66	-	-	0.98	-	0.65
19	A	75.00	0.75	10.82	7.84	4.10	-	-	-	0.37	-	1.12	-
	B	81.00	0.67	7.33	2.00	7.00	-	0.33	-	0.33	1.33	-	-
21	A	60.00	-	26.67	1.67	1.67	1.67	1.67	-	1.67	-	-	5.00
	B	37.75	1.61	42.17	6.02	8.84	0.80	-	0.80	0.40	0.40	-	1.20
35	A	16.19	30.46	8.59	3.81	2.86	1.90	3.81	6.52	3.00	-	-	22.86
	B	24.88	18.43	23.96	3.69	8.29	-	7.83	4.23	3.61	-	-	5.07
38	A	18.92	44.59	6.76	10.81	2.70	1.35	1.35	6.10	2.01	-	-	5.41
	B	31.94	26.13	16.77	4.84	7.74	0.32	4.84	4.12	1.04	-	-	2.26
40	A	15.00	39.29	6.43	3.57	1.43	2.14	7.14	4.53	1.18	-	-	19.29
	B	30.74	23.99	16.22	5.07	3.04	-	12.50	3.26	1.81	0.68	-	2.70
42	A	11.56	34.01	14.29	10.20	-	3.40	8.84	-	1.36	-	-	16.33
	B	27.34	28.84	20.60	3.00	3.00	0.37	8.61	4.32	1.30	-	-	2.62
44	A	21.05	27.63	15.53	2.63	-	0.66	3.29	-	-	-	-	34.21
	B	33.78	21.96	21.62	5.41	5.07	-	6.42	3.22	0.16	-	-	2.36
47	A	19.16	23.35	13.17	7.78	0.60	0.60	5.99	0.60	-	-	-	28.74
	B	22.82	19.82	25.23	7.81	4.80	0.60	3.41	5.06	3.05	-	-	2.40
50	A	23.61	31.94	8.39	-	-	1.3	9.72	1.39	-	-	-	23.61
	B	38.08	14.74	19.66	4.42	7.37	0.7	7.37	3.34	1.82	-	-	2.46
53	A	16.03	11.45	19.08	5.34	-	1.53	6.87	1.53	-	-	-	38.17
	B	19.21	13.91	31.46	10.93	7.28	1.99	7.62	4.66	0.64	-	-	1.99
56	A	29.03	10.48	21.77	4.84	-	-	0.81	-	-	3.23	-	29.84
	B	31.34	7.83	29.72	14.93	4.38	1.38	4.61	3.47	0.91	-	-	1.38
59	A	15.38	2.56	35.04	2.56	-	1.71	1.71	-	1.71	1.71	-	36.75
	B	25.30	3.58	17.42	28.16	6.21	0.43	9.06	5.49	0.72	-	-	3.58
91	A	-	-	-	-	-	-	-	-	-	-	-	-
	B	2.01	0.86	30.57	21.44	6.59	-	22.70	8.29	4.07	0.29	-	3.16
103	A	10.16	1.56	39.06	3.13	-	3.13	0.78	-	-	2.34	0.78	36.72
	B	53.05	0.23	17.38	17.61	0.48	-	0.68	0.23	-	1.35	-	-

* Size A represents 1.00 to 0.250 mm and Size B represents 0.250 to 0.063 mm

Op - Opaque, Ga - Garnet, Si - Sillimanite, Zr - Zircon, Mo - Monazite, Ky - Kyanite, Am - Amphibole, Py - Pyroxene, Tr - Tourmaline, Ru - Rutile, Ap - Apatite, Bi - Biotite

higher amount of heavy minerals in lower size grades and the relationship has been explained on the basis of size density. Heavy minerals are noticeably abundant in the eastern and western parts of the lake. But in the central part, since the texture is mud the heavy minerals were not studied.

It is found that the predominant heavy minerals in the eastern part are garnet, opaque, sillimanite, and zircon. The less abundant are monazite, pyroxene, amphibole, kyanite, tourmaline, biotite and apatite. At the western part, it is characterised by the predominance of opaques, sillimanite, zircon and monazite. The other heavy minerals are garnet, kyanite, rutile, amphibole, tourmaline, pyroxene, and biotite. A few mounted polished sections of the opaques under transmitted light indicated the dominance of ilmenite and magnetite among the opaques. Among garnets, almandine (pink) occurs more in the eastern part and upstream of the river, whereas grossularite occurs in the other part of the lake. Pyroxenes are virtually absent in the western part in all the two fractions, while it is present in minor amounts in the eastern part. Hypersthene is the most frequently occurring pyroxene. Amphiboles

occur only as a minor heavy mineral and that too in the lower fractions in the western and eastern parts. Hornblende is the most abundant mineral among amphiboles even though some minor amount of actinolite was detected. Rutile is confined only to the western part where a more or less uniform distribution was observed in both the size grades. Biotite is seen mostly in the eastern part and mainly in the coarse fractions (1.0-0.25 mm).

The down stream variations of the heavy minerals in the two size grades are shown in Figs. 3.1 and 3.2. Fig. 3.1 shows the variation in the weight percentage of total heavies, while Fig. 3.2 indicates that in the number percentages of the heavy minerals. The down stream variation of opaques, garnets, sillimanite, zircon, monazite, amphibole and pyroxene for the two size grades are illustrated in Fig. 3.3 and 3.4. The scattergrams for opaque versus garnet, sillimanite, zircon, monazite, amphibole and pyroxene (Figs. 3.5 and 3.6) and garnet versus sillimanite, zircon, monazite, amphibole and pyroxene (Fig. 3.7) are given to elucidate their relationships. Higher concentration of heavies are seen in 0.25 to 0.063 mm size grade. The scattergram of opaque versus garnet shows a slight positive correlation in the coarse fraction, both for sediments of the western and eastern parts, whereas in the finer grade a negative

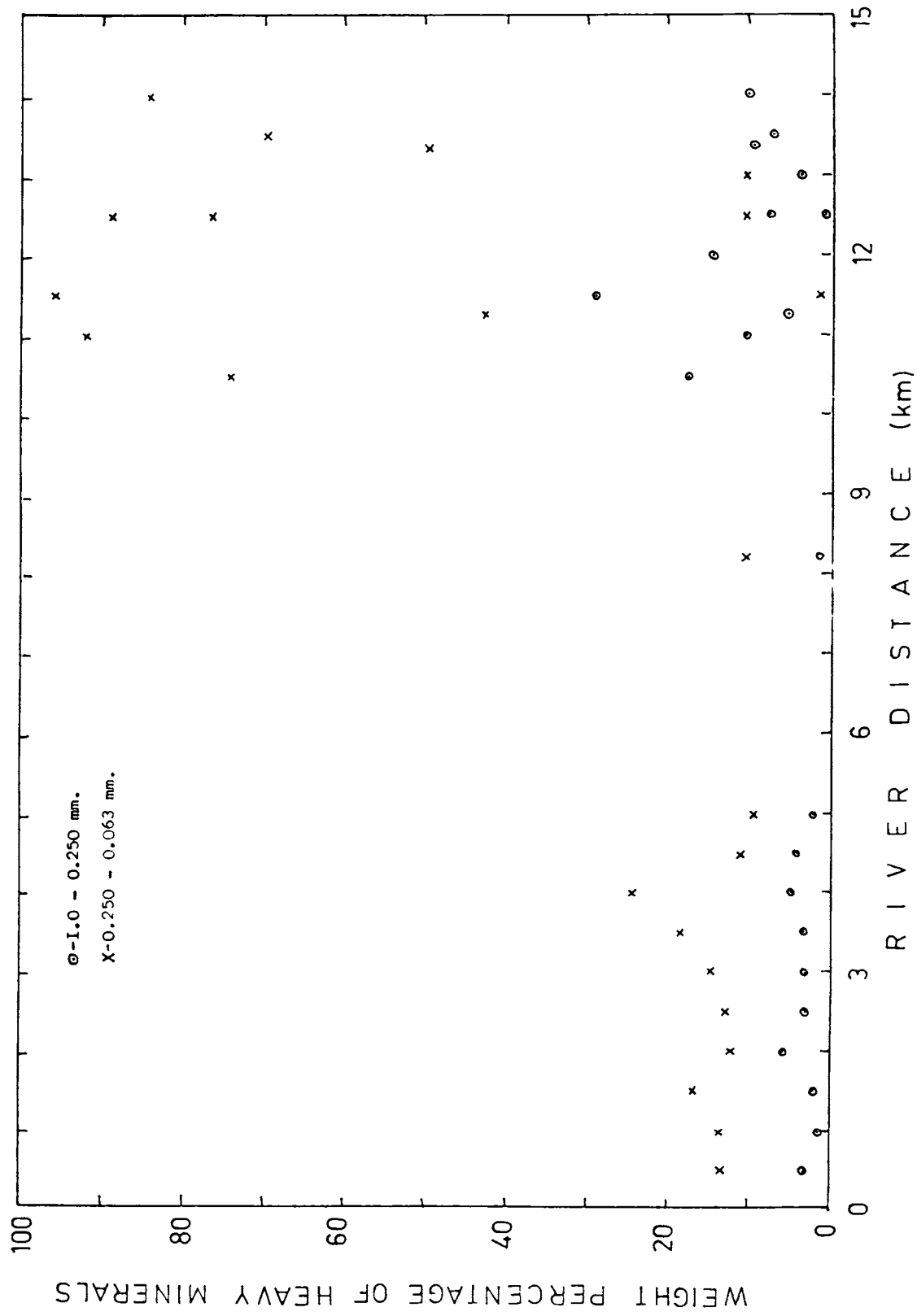


Fig. 3.1. Downstream variation of total heavies

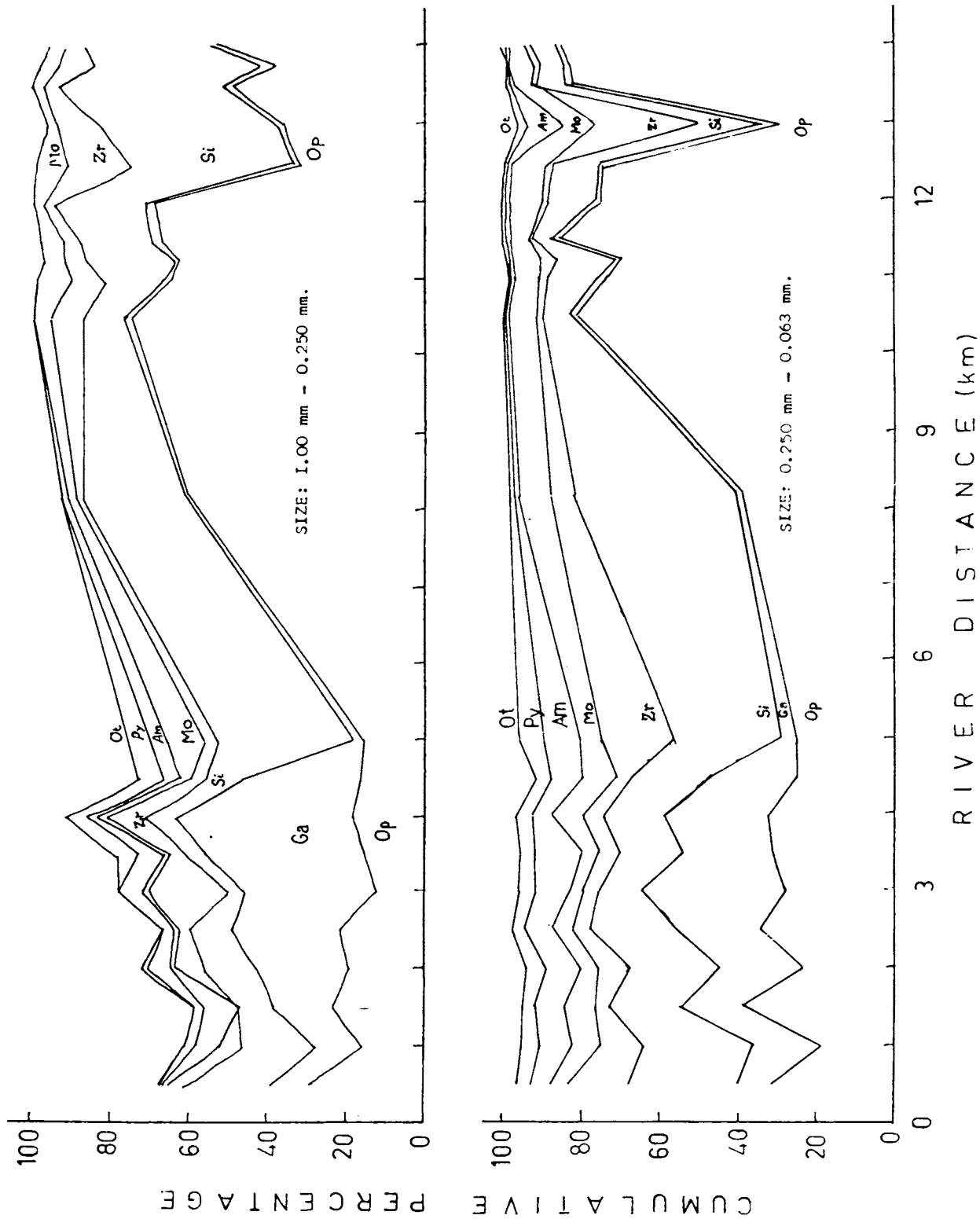


Fig. 3.2. Downstream variation of cumulative percentage of heavy minerals
 Op: Opaque, Ga: Garnet, Si: Sillimanite, Zr: Zircon, Mo: Monazite,
 Am: Amphibole, Py: Pyroxene and Ot: Others.

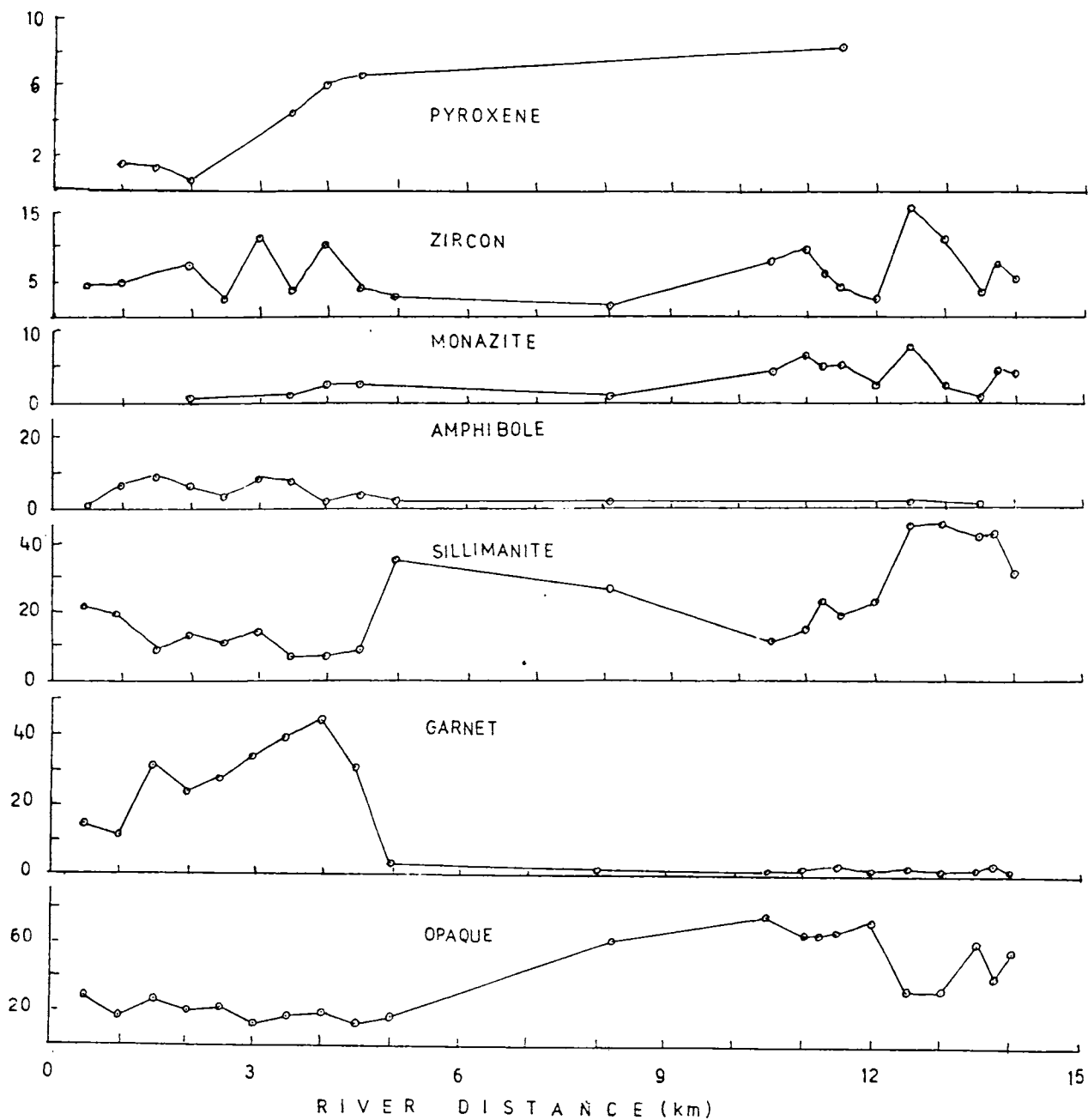


Fig. 3.3. Downstream variation of heavy minerals
(size: 1.000-0.250 mm)

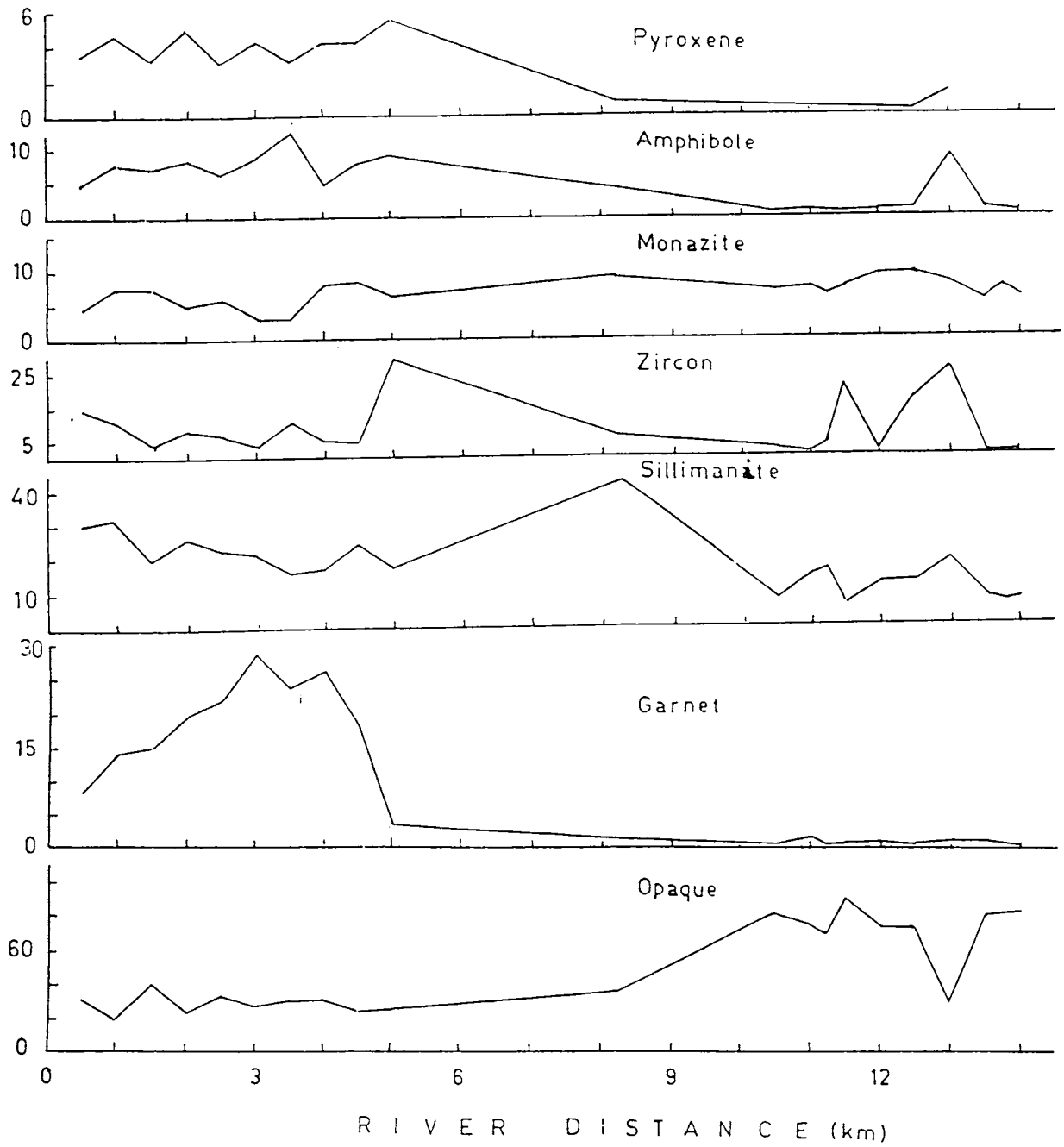
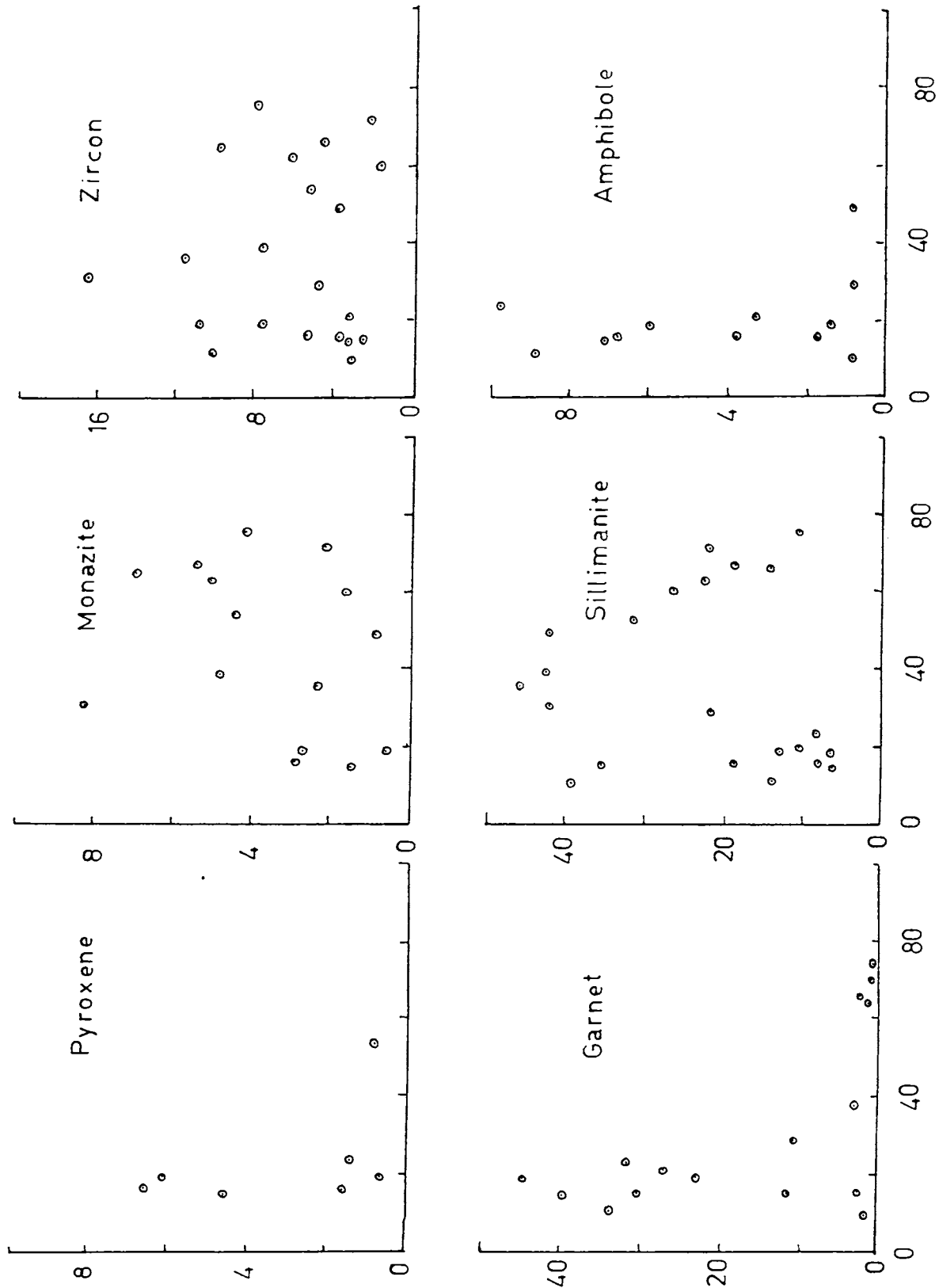
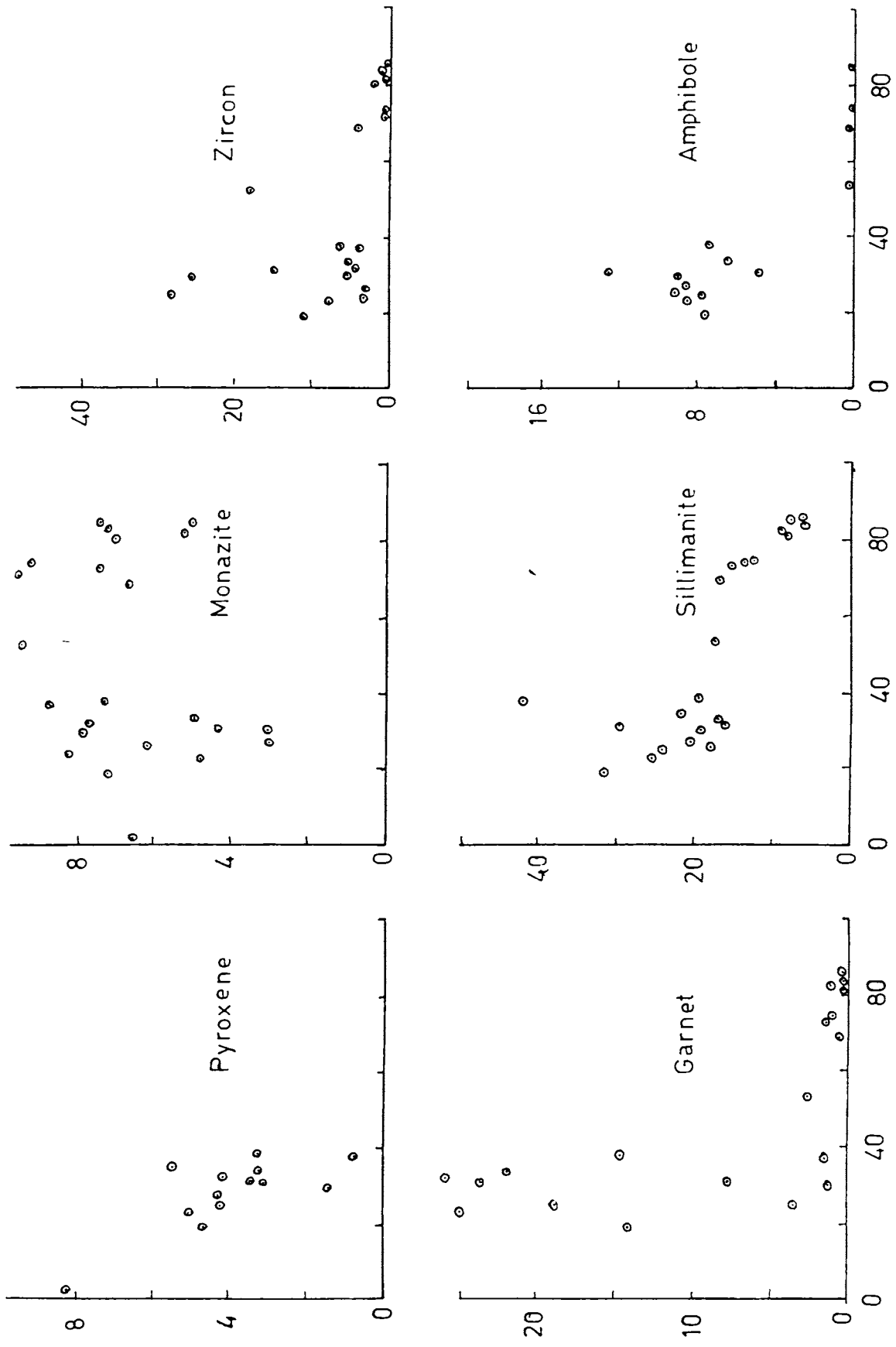


Fig. 3.4. Downstream variation of heavy minerals
(size: 0.250-0.063 mm)



OPAQUE

Fig. 3.5. Scattergram of opaque versus Garnet, Sillimanite, Zircon, Monazite, Amphibole and Pyroxene (size: 1.000-0.250 mm)



OPAQUE

Fig. 3.6. Scattergram of opaque versus Garnet, Sillimanite, Zircon, Monazite, Amphibole and Pyroxene (size: 0.250-0.063 mm)

SIZE: 1.00 - 0.250 mm

SIZE: 0.250 - 0.063 mm

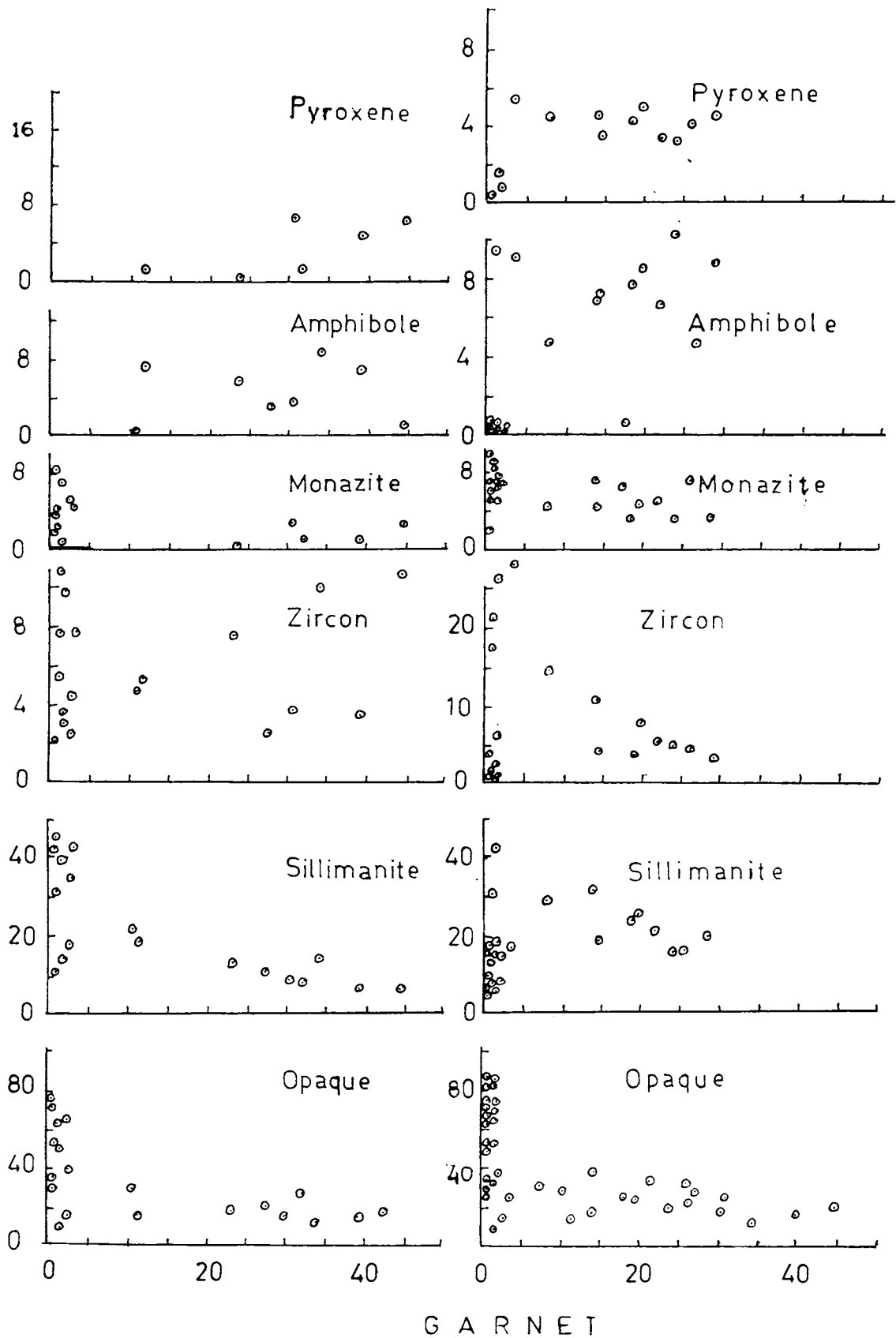


Fig. 3.7. Scattergram of Garnet versus Sillimanite, Zircon, Monazite, Amphibole and Pyroxene (size: 1.000-0.250 mm)

relation for western part sediments. No other minerals show any such relation in these size grades.

3.3.3. Discussion

3.3.3.1. Causes for the total heavy mineral variation

It is noticed that there is a general decrease in the weight percentages of total heavy minerals in the two size grades (1.0-0.25 mm and 0.25-0.063 mm) in the down stream and a higher proportion of heavies in the finer grade than in the coarser grade. It has been already mentioned that the grain size decreases in the down stream. Also, a similar trend is seen in the heavy mineral content. Pollack (1961) observed a similar variation on the South Canadian River channel sands and explained the phenomenon on the basis of relationship between size - density and hydraulic equivalence relationship, as suggested by Rittenhouse (1943). The decreasing trend of grain size and heavies are related to the competency of the current. Mc Master (1960) met with a similar decrease of heavies in the transport direction. The hydraulic equivalence concept as postulated by Rubey (1933) states that grains of different densities, if deposited together, should have the same velocities or the denser mineral should be smaller by an amount predictable on the basis of settling velocity equation.

From his theoretical observation, he could also establish that the grain size distribution of heavy minerals would be displaced towards the finer size with respect to quartz; the exact amount depending upon the density, size, shape and availability of the heavy mineral grains and the nature of the depositing medium. The term hydraulic equivalence as expressed by him denotes that minerals of different physical properties can be the result of similar dynamic responses. Rittenhouse (1943) observed that the size distribution curves for the heavy minerals were similar in form to those of the light minerals but displaced towards the finer sizes. He explained the observation on the fact that under a given set of hydraulic conditions, medium to fine grains of heavy minerals will tend to accumulate along with quartz and other lighter minerals of larger size, due to their high specific gravities. From the above discussion, it can be concluded that in Ashtamudy lake the high concentration of heavies in the finer grades is due to the settling of both medium to fine heavies along with coarser quartz whenever the competency of the river decreases, the decrease in percentage of heavies in the downstream is because of the settling further upstream due their high densities.

Subsequent studies by others proved that the causes as suggested by Rubey and Rittenhouse cannot account for all the variations in total heavy minerals. Briggs (1965) explained that the hydraulic equilibrium maintained by the heavy and light minerals are due to the availability of (i) coarser heavy minerals like that of lighter minerals or (ii) absence of coarser lighter minerals (i.e., only coarser heavy minerals are present). He emphasised the importance of source contribution. Hand (1964), White and Williams (1967) observed a non hydraulic equilibrium in modern sands and explained it as primarily caused by selective sorting based on size, density and shape of grains. They could also show that heavy minerals once settled or deposited are more difficult to sweep along hydraulically equivalent quartz. Hence heavies moving by saltation with lights would tend to be smaller than the predicted settling velocity, and these heavies are shielded from currents by larger quartz grains. Thus these heavies lag behind the larger quartz.

Hence, in the Ashtamudy lake sediments, the decrease of heavy minerals of both the grades in the down stream is due to the following reasons: (i) they are not easily entrained by low energy currents subsequent to deposition, (ii) they are protected by the coarse lighter

minerals. Above all, during transportation, the smallest lighter minerals cannot settle at the place where a heavy mineral of the same size settles by the currents, due to their density difference. The lighter minerals are transported and deposited further downstream bringing down the percentages of heavies. The two reasons for the heavy mineral concentration as given by Lowright et al. (1972) are: (1) the larger grains project higher up into the zone of fluid flow, which increases exponentially upward. In general, the heavies will be smaller in size than quartz and it may be that this size differential more than offsets the density difference between heavies and (2) the concentration of heavies with that of light, and the easy availability of quartz to currents. The heavies will not be moved with the same frequency as that of quartz.

3.3.3.2. Causes for the downstream variation in mineralogy

Pettijohn (1957) discussed elaborately the various factors that can possibly modify the heavy mineral composition of the sediment between the provenance and depositional area. Chaudhri and Grewal (1984,1985) stated that the distribution of heavy minerals is controlled by a number of factors including mode of weathering in the source area and at the site of deposition, destruction of the minerals by wear and tear,

specific gravity of minerals, grain size, selective sorting, post-depositional changes, wave motion and energy of the depositional environment. Chaudhri and Chandra (1982) stated that the variation in size of minerals is in harmony with the textural parameters and is a function of relative position of micro environment, turbulence, wave energy and rate of supply of detritus. Among the various factors which affect the total heavy mineral and downstream mineralogical variation, the most important factors are (a) selective weathering, (b) differential or selective abrasion and (c) selective sorting of minerals according to size and density. The part played by each of the aforesaid factors in regard to the variation of heavy mineral assemblages in the sediments of the Ashtamudy lake is discussed below. The downstream variations in the number percentages of the most predominant heavy minerals such as opaques, garnets, sillimanite, zircon, monazite and also of amphibole and pyroxene in the two selected grades are given in Figs. 3.3 and 3.4. For the downstream variations of the heavy minerals, size was not taken into consideration since the heavy minerals were estimated only for two size grades and not in bulk sample.

a) Selective weathering

Many workers have emphasised the importance of modification of the heavy mineral assemblages by weathering. In general, it is an accepted fact that selective removal of heavy minerals occurs as a result of subaerial weathering (Weyl and Van Andel, 1952) or due to post depositional solution (Pettijohn, 1957), as evidenced by the decrease in the unstable minerals. The results of the present heavy mineral study vividly points out the decrease of less stable minerals such as pyroxenes and amphiboles from the eastern to the western part of the lake.

A comprehensive discussion has been made by Nickel (1973) regarding the post-depositional weathering of heavy minerals. Weathering modifies the surface texture of some unstable minerals and in extreme cases, reduces the percentages of unstable minerals. The individual grains pass through successive stages of surface corrosion, destruction along weak zones, and reduction of size before complete elimination of a mineral species (Grim, 1973). The progressive weathering of a mineral in the sediment may be measured by the decrease in the total amount of unstable minerals

as well as a shift of their grain size distribution towards finer grades. This sort of shifting is seen in the case of amphiboles. The combined effect of weathering and reworking may result in a very complicated distribution of heavy minerals as discussed above. Such a phenomenon is seen in the heavy minerals of Ashtamudy lake also.

Mineral pathology is a reflection of stability of minerals (Chaudhri and Gill, 1983). Corrosion as seen in amphiboles is a manifestation of mineral pathology and it is due to comparatively unstable nature of the mineral.

b) Selective abrasion

A persistent change of the heavy mineral composition in a unidirectional flow may theoretically be attributed to particle size reduction, to changes in the average hydraulic conditions and to differences in tributary supply (Riezebos, 1979). The decreasing percentages in the direction of transport can also be explained in terms of particle size reduction. Such selective abrasion could result in progressive and systematic elimination of softer and more cleavable minerals and complementary enrichment of harder and more

durable minerals. All the minerals are not equally resistant to abrasion while on transportation. Laboratory investigation has revealed that the rate of wear for various mineral species varies considerably. However, evidence for the selective abrasion and subsequent elimination of heavy minerals in the sand size grade is inconclusive.

The sediments of the Ashtamudy lake has been mainly derived from the Kallada river - the sole river debouching into the lake. It is found that there is a decrease in the content of relatively unstable minerals, which indicate that selective abrasion mechanism has also played its role in bringing out the variation of the heavy minerals in the lake sediments.

The order of durability of the most abundant heavy minerals as given by Dana (1960) are garnets, opaques, amphiboles, sillimanites and pyroxenes. In the present study an increase of opaques and garnet is noticed towards the downstream. This again reveals that selective abrasion has taken place. Sorting of the minerals due to selective abrasion, if any, seems to have been overcompensated by sorting based on some other factors, such as specific gravity and shape of the heavy minerals. Most of the geologists do not consider

selective abrasion as the major cause for the progressive sorting. Whetten et al. (1969) stated that there is little or no mechanical breakdown by abrasion of minerals or rock fragments in low to moderate gradient stream. Change in composition are due to source and local reworking. Abrasion will be maximum in high gradient mountain streams and is negligible in low gradient streams. Chaudhri and Gill (1983) stated that lacustrine sediments generally do not suffer considerable transportation resulting in abrasion.

In the light of the above discussion, it can be concluded that the selective abrasion has only an insignificant role in causing heavy mineral variations in Ashtamudy lake.

c) Selective sorting

The possibility of differentiation by sorting of heavy mineral assemblages according to density and size during transportation and deposition has been pointed out by Seibold (1963). May (1973) observed that in shallow waters, heavy minerals will experience a unidirectional shoreward transport as compared to the light minerals mainly because of the size, density and position of heavy minerals which is in such a way that they can be moved shoreward under the crest, but not

seaward under the trough. The increase or decrease in the heavy mineral content depends on sorting based on density and size. Such selective sorting involves the lagging behind of certain constituents owing to their high specific gravity, large size or low sphericity. That is, minerals of lower density, smaller size and larger surface area may travel more rapidly and out turn the associated minerals in the direction of current. It is a well established fact that the heavy minerals settle together with lighter minerals of larger size that are hydraulically equivalent. Decrease in the amount of opaques and garnets from the confluence of the river Kallada is mostly due to the decreasing competency of the transporting medium and thereby lagging behind of opaques and garnets to lighter minerals. The result will be the continuous enrichment of minerals with lesser specific gravities in lower energy conditions.

An appraisal of the heavy mineral data reveals that, in the two size grades, garnet and zircon showed a marked increase in the direction of transport whereas opaque, sillimanite and monazite show a decrease and amphiboles and pyroxenes of finer size show an increase especially in the eastern part of the Ashtamudy lake. In the western part sillimanite, monazite, zircon and opaque show a high percentage whereas amphiboles.

pyroxenes and garnet show a low percentage. Hence, it can be inferred that selective sorting was more prominent in the western part of the lake rather than in its eastern part and is essentially due to the tidal effect.

d) Progressive sorting based on specific gravity and shape

Relatively lighter and heavier species of minerals would be separated broadly into different assemblages by sorting based on the specific gravities. Further, it is found that two grains of different densities will not be picked up with the same frequency or bounded at the same speed. The heavy mineral assemblage of the Ashtamudy lake sediments reveals a decrease of opaque and monazite and an increase of amphiboles and pyroxenes in the downstream direction. This can be explained in the light of the aforesaid factors. Due to the decrease in the river competency in the downstream, there is a decrease of opaque and monazite, which will tend to lag behind the relatively lighter minerals such as amphiboles and pyroxene. It is also possible that under high competency further upstream, the relatively lighter heavy minerals like amphiboles and pyroxenes are not allowed to settle in large amounts. This will naturally result in the concentration of relatively heavier minerals like opaque and monazite in the upstream and concentrations,

of comparatively lighter minerals in the downstream. Eastern and central parts of the lake is marked as a low energy zone as evidenced from the texture of the sediment which itself indicates that no further transportation has taken place. Relatively higher percentages of monazite, zircon, opaque, sillimanite and lesser concentrations of amphiboles and pyroxenes in the western parts can also be explained in the above line. But here, instead of river competency, tidal current effect has to be considered. The western part of the lake is a high energy zone as evidenced by the absence of fine sediments and the presence of relatively coarser sediments. The difference in the concentration of heavy minerals can be attributed to sorting by density. Hence selective sorting based on specific gravity can explain the heavy mineral variation in the eastern and western parts of the lake.

A cursory analysis of the existing literature shows, that only a few investigations namely Pollack (1961) and Briggs et al. (1962) had made some attempts to evaluate the role of shape on sorting of heavy minerals. Pollack suggested that the selective sorting on the basis of shape is not an important criterion in the heavy mineral variation along downstream.

In contrast, Briggs et al. (1962) pointed out that both density and shape of minerals are important parameters in bringing out sorting of minerals in the downstream. It is generally accepted that the settling rates of different heavy minerals would depend not only on their densities but also on their shapes. When particles having the same volume and density but of different shapes are made to settle through a column of liquid, the particles with greatest sphericity will have the highest settling velocity because of the least surface area (Krumbein, 1942; Rittenhouse, 1943). Pettijohn (1957) summarised about transportation under suspension that 'the more spherical particles tend to be deposited, whereas less spherical particles tend to be carried away'. This was strongly supported by Shideler et al. (1975) and Flores and Shideler (1978) who postulated that shape along with other factors can cause mineralogical variation.

The results of the present study and observation are in accordance with the sphericity-settling rate relationship, as envisaged by Pettijohn (1957). It is observed that there is a general decrease in the relatively more spherical heavy minerals in the downstream direction along the Kallada river. Thus, difference in the shapes of heavy minerals is also a factor which causes down-stream variations in the heavy mineral assemblages.

From the above discussions, it is very clear that selective weathering has played the prominent role in the variations of heavy mineral assemblages and next to it comes the progressive sorting of the heavy minerals based on their specific gravity.

3.3.3.3. Variations of less abundant heavy minerals

The less abundant heavy minerals are kyanite, tourmaline, rutile, apatite and biotite, which together constitutes less than 10% of the total heavies. Among these minerals, kyanite and tourmaline do not show any specific trend and are more or less uniformly distributed in the lake sediments. Apatite is present only in a few sediment samples. Rutile is confined to western part alone and biotite to the eastern parts of the lake.

Biotite content is high in coarse fraction and the decrease in its content in the downstream tells us that the eastern part of the lake is a low energy zone and beyond that no more transportation has taken place as biotite is considered as an indicator of the current direction. The reason is that usually biotite, once entrained, will take some time to settle due to its flaky nature and can be easily carried away by the swift

outflow of the river water. But biotite will get deposited whenever there is a check in the river current. Hence wherever there is a concentration or deposition of biotite, it indicates a check to the transporting current and thereby a low energy zone.

Similarly, presence of rutile at the western part can be explained as one transported into the lake by the tidal currents. The absence of rutile at the eastern parts indicate that there is no supply by the river. Mallik and Suchindran (1984) while working on some sedimentological aspects of Vembanad lake, pointed out that the sediment composition is related to physical factors of the lake namely waves, tides and currents besides to its geology and bathymetry. This is in agreement with Darby (1984) who stated that estuaries can receive sand from both the river and off-shore sources as well as from older coastal deposits outcropping along the estuary. Sastry et al. (1981), while working on the distribution of garnet sands along Visakhapatnam-Bhiminipuram beach stated that reworking of the sediments by the waves can concentrate heavy minerals or even individual mineral. May (1973) observed the transportation of heavy minerals under the crust to the shore in shallow waters. In the Ashtamudy, the central and the eastern parts of the lake have been identified as low energy zones and hence there have been identified as low energy zones and hence there is no transportation of sediments from eastern to western parts. The virtual absence of biotite and presence of rutile at

the western part is the characteristic of a high energy zone i.e., a highly agitated area. Examination of the individual heavy mineral content within and outside the assemblage reveals that the variation is related partly to source rocks and partly to the reworking by currents and waves on the basis of specific gravity, size and shape. Furthermore, the current direction in this area is variable during different seasons of the year. It is from south to north between November and January (northeast monsoon season) and north to south during June to September (southwest monsoon months) (Published Report of Kerala Engineering Research Institute, 1978). Such reversing currents may lead to the mixing of various minerals. Kidwai et al. (1981) accounted in the same way for the variations in the heavy mineral assemblages on the outer continental shelf sediments between Vengurla and Mangalore.

The relationship as seen in the scattergrams between opaque versus garnet, sillimanite, zircon, monazite, amphibole and pyroxene (Figs. 3.5 and 3.6) and also that in the case of garnet versus sillimanite, monazite, zircon, amphibole and pyroxene (Fig. 3.7) for the two size grades broadly indicate that opaques and garnet behave hydraulically as one entity, whereas monazite and zircon as another, and sillimanite, amphibole and pyroxene a

yet another entity. The opaques and garnets, as a result of their high specific gravity and sphericity, tend to get deposited together. Figures clearly reveal that with increase of garnet, opaque also increases, while the other scattergrams namely that for the opaque versus sillimanite, amphibole and pyroxene, and garnet versus sillimanite, amphibole, and pyroxene indicate a negative relationship whereas zircon and monazite do not exhibit any specific relationship. In the above figures, the hydraulic differentiation between these minerals is very well illustrated. Seibold (1963) has said that the hydraulically equivalent 'groups' of sand grains are transported and deposited together. Flores and Shideler (1978) have also found that hydraulically equivalent minerals are concentrated whereas hydraulically non equivalent heavies are winnowed out.

3.3.4. Provenance

From the study of the heavy mineral assemblages and their relative abundance, one can say about the probable source rock from which they have been liberated. Here the probable source rock for the heavy minerals in the lake sediments is inferred from the relative abundance of the heavy minerals and their assemblages. Since the present study has yielded

different concentrations of heavy minerals in the eastern and western parts of the lake, they are discussed separately.

The drainage basin of the river Kallada is mainly occupied by Khondalites, charnockites, garnetiferous quartzo-feldspathic gneisses and biotite gneisses of which khondalite and charnockite are widely spread out. Khondalite is quartz feldspar garnet-sillimanite gneiss and is rich in garnet and sillimanite. The garnets are derived from high-grade metamorphic rocks. The distribution of this mineral can be related to nature and distribution of garnet-bearing rocks in the source area. Colourless to pale pink garnet is characteristic of khondalites, pink of charnockites and deep brown to deep pink garnet is characteristic of the gneissic rocks (Mallik, 1963). Prismatic character of sillimanite suggests its derivation from khondalite. Zircons may be derived from a variety of rocks. The probable source can be inferred from morphological characters. Rounded and rounded terminated zircons and those showing overgrowths are characteristic of derivation from khondalites, charnockites and gneissic rocks respectively. Hornblende may be derived from igneous and metamorphic rocks. Bluish green to green hornblende is typical of high grade metamorphic rocks. They could have been derived from retrograde basic

charnockites. Monazite seems to have been derived from charnockites and khondalites; and hypersthene from charnockites. Hence khondalites contributed a considerable amount of garnet and sillimanite. The heavy minerals at the eastern part of the lake in the order of decreasing abundance are garnet, opaque, sillimanite, monazite, zircon, pyroxene and amphibole. Less abundant minerals are kyanite, tourmaline and biotite. Opaque, monazite, zircon, amphibole (green hornblende), pyroxene and kyanite from the charnockite and gneissic rocks. The same is true for tourmaline. Biotite is mainly from the biotite gneiss. This holds good for the provenance of heavy minerals along the eastern part of the lake.

Western part of the lake is characterised by a decrease of garnet, amphibole and pyroxene, but an abundance of opaque, sillimanite, zircon and monazite. Rutile is present in all two size grades. Rutile is generally derived from acid igneous and metamorphic rocks and is characteristic of high-grade metamorphic terranes. It is most abundant in metamorphic rocks of granulite facies (Force, 1976a; Goldsmith and Force, 1978). The source for Rutile and the other heavy minerals can be regarded as the barrier beach of Kayamkulam-Neendakara, where world's richest placer deposit occur. These

minerals are believed to have been transported from there to the western part of the lake mainly by littoral currents and then tidal currents. Many investigators established that sediments can be transported into the lake by the tidal currents (May, 1973; Darby, 1984; Mallik and Suchindran, 1984). In conclusion, the source for the heavy minerals at the western part is the barrier beach of Kayamkulam-Neendakara.

Typical heavy minerals found in the sediments are opaque, sillimanite, garnet, monazite and zircon which reveal that the terrain comprises khondalites, charnockites and gneisses. Abundance of garnet and sillimanite reflects the contribution from high rank metamorphic rocks. However, in general, the various rock types in the western ghats is the 'Home' for all the heavy mineral assemblages in the Ashtamudy lake sediments.

3.4. Light minerals

The composition of light fraction (Bromoform floats) of sandy sediments has been studied for a better understanding of the mineralogical maturity of the lake sediments. In 1957, Pettijohn has pointed out that the mineralogical maturity of a sediment may be expressed by

Table 3.3. Quartz/Feldspar ratios for the sediments
of Ashtamudy lake

Sample No.	Size	
	1 - 0.25 mm	0.25 - 0.063 mm
1	100.00	16.39
2	71.46	18.19
10	100.00	11.90
13	249.00	18.88
14	61.69	8.20
15	124.01	15.86
16	999.00	1.81
17	999.00	30.38
18	100.01	26.32
19	71.46	14.95
21	141.86	199.00
35	19.10	25.04
38	12.33	52.48
40	21.27	11.17
42	7.81	8.20
44	28.59	4.07
47	11.76	90.74
50	10.00	7.19
53	12.19	23.22
56	11.11	10.24
59	18.88	41.56
91	-	20.83
103	141.86	55.50

its quartz content or by the disappearance of feldspar content, as most of the quartz will be generally associated with feldspars. Feldspars of detrital nature in sediments seems to be an index of climate and tectonic activity. The quartz/feldspar ratios as given in Table 3.3 are plotted against river distance to determine the stability of feldspar relative to quartz during transportation (Fig. 3.8). The quartz/feldspar ratios which was determined for the two size grades (1.0-0.25 mm and 0.25-0.063 mm) show a very wide variation. From the figure it is observed that the ratios increase downstream.

3.4.1. Discussion

Causes for variation of quartz/feldspar ratio is discussed below.

Progressive changes in the sand composition would occur because of unequal resistance of these two constituents to abrasion and weathering. Selective abrasion and chemical weathering result in the progressive elimination of feldspars and subsequent enrichment of harder and durable quartz. Therefore, sands during transportation would be enriched in quartz and impoverished in feldspars. The increasing trend of

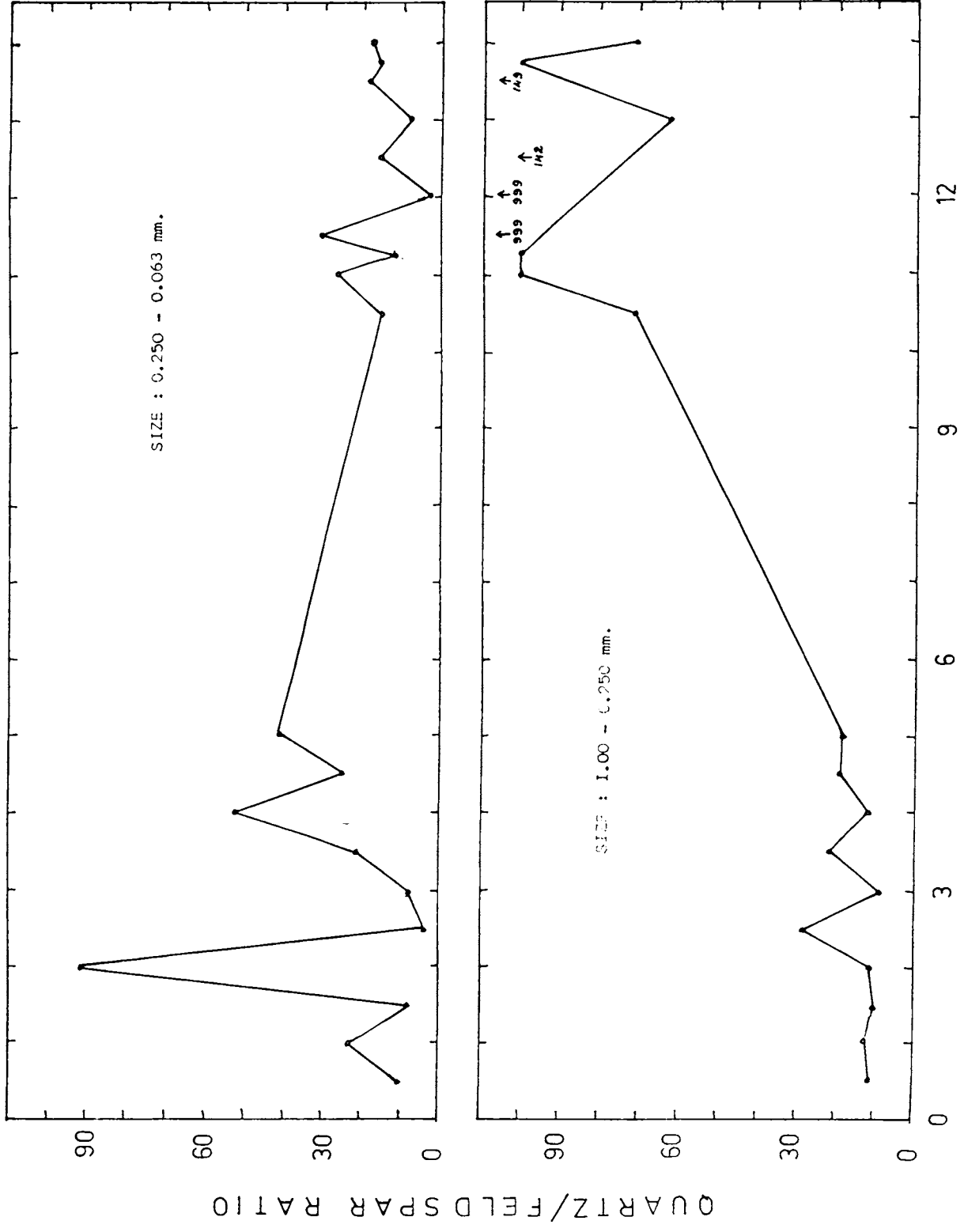


Fig. 3.8. Quartz_i/Feldspar ratio versus river distance

quartz/feldspar ratio at the eastern parts of the lake for the coarse fraction (Fig. 3.8) indicate that feldspars in this grade size were subjected to abrasion.

Higher ratios for finer fractions (0.25-0.06 mm) need not indicate the role of abrasion since abrasion process will not be very effective for fine sediments. The increase in quartz/feldspar ratio will be mainly due to weathering. Since feldspars are highly susceptible to weathering than hard, durable and resistant quartz, feldspars never gets concentrated along with quartz. Hence the increase in the quartz/feldspar ratio in the eastern parts of the lake (Fig. 3.8) is mainly due to weathering.

At the western part of the lake, the quartz/feldspar ratio is high for the coarse fraction whereas it is low for the finer fraction when compared to eastern part. This again supports the view that abrasion is more effective for coarser than fine sediments.

Provenance is the controlling factor in determining the light mineral composition of sands. Though the source rock contains good amount of feldspars,

a depletion of the same is seen in the lake sediments, which is again due to weathering.

The occurrence of a few iron-stained quartz can be explained in the light of its occurrence in the lateritic soils in the drainage basin of the river. Judd et al. (1970) have investigated the occurrence, abundance and environmental significance of iron-stained quartz in the continental shelf, beach and river samples and stated that the iron coating may probably be haematite derived originally from various iron-bearing minerals. The oxidising environmental conditions might also have favoured the development of iron-bearing quartz.

3.5. CLAY MINERALS

Geologists have long been interested in clay mineral researches for a variety of reasons. As Keller (1970) has pointed out, clay minerals that constitute a major part of the fine fractions of the sediments are reactive responses of geological material which characterise certain environments prevailing at a particular time. Thus, the clay mineral composition of a sediment may give important clues which unravel the conditions under which it was deposited. Hence they may be indicators of the reacting environment. Also, investigations on clay minerals have provided considerable

data on the occurrence and properties of clay minerals in ancient sediments. Moreover, the composition and distribution of clay minerals have been used as indicators of sediment dispersal in marine environment (Biscaye, 1965; Griffin et al., 1968). Also, clay mineralogy is useful in inferring fine-grained sediment dispersal and current patterns (James et al., 1979). Thus, information on clay minerals is essential for complete understanding of the origin and environment of the sediments.

The importance of the source area and its climate which controls the types of clay minerals, rather than the environmental conditions of depositions has been stressed by Taggart and Kaiser (1960), Subba Rao (1963), Biscaye (1964) and Seetaramaswamy et al. (1971). On the other hand, Nelson (1962), Naidu (1966) and Carroll (1970) have emphasized the process of environmental diagenesis in clays. But Weaver (1967) stressed on the importance of depositional environments on clay mineral distributions. Keller (1970) has brought out a comprehensive discussion on the environmental aspects of clay minerals.

Venkataratnam (1965), Durgaprasada Rao (1971), Rama Murty (1972) and Subba Rao (1985) carried out clay

Table 3.4. Percentages of Clay minerals in the three zones of the Ashtamudy lake

Sample No./ Location	Kaolinite	Smectite	Illite
<u>Eastern part of the lake</u>			
28	81.63	11.63	6.74
29	83.72	10.63	5.65
31	86.95	5.87	7.18
34	84.11	7.28	8.61
37	89.78	4.47	5.75
61	93.59	2.49	3.91
63	82.12	11.42	6.46
<u>Central part of the lake</u>			
16	38.09	57.87	4.05
19	34.27	62.50	3.23
66	66.77	32.14	1.09
69	51.43	42.86	5.71
71	49.12	44.25	6.64
73	30.46	66.58	2.96
76	40.64	48.76	10.60
80	30.54	66.12	3.38
82	30.37	65.06	4.56
85	27.85	70.12	2.03
87	41.63	53.46	4.92
92	28.57	67.68	3.75
96	26.91	67.26	5.83
<u>Western part of the lake</u>			
18	16.87	80.42	2.71

mineralogical investigations in the sediments of Chilka, Pulicat, Kolleru lakes and Iskapalli lagoon respectively. A similar clay mineralogical study was done for the modern deltaic sediments of Godavari, Krishna and Cauvery rivers by Naidu (1968), Seetaramaswamy et al. (1971) and Seralathan (1979) respectively.

3.5.1. Results

The results of the clay mineral analysis for the Ashtamudy lake sediments from the 3 regions are furnished in Table 3.4. Various clay minerals present are kaolinite, montmorillonite and illite. The analysis reveals that kaolinite and montmorillonite are the most abundant clay minerals in the lake sediments with lower amounts of illite. Kaolinite is the dominant clay mineral at the eastern part and montmorillonite that of the western part and central part of the lake.

3.5.2. Discussion

Concerning the distribution and lateral variations in clay minerals of the bottom sediments in estuarine and off the mouths of many rivers, Weaver (1959) consider that the clay mineral content in the sedimentary rocks and marine deposits is largely

detrital by origin, reflecting characters of the source-material. There is very little change in the depositional environment. The detrital minerals undergo slight changes in the depositional environment due to differential flocculation and/or size segregation (physical sorting). Whitehouse et al. (1960) from the experimental work on the differential transport of clay minerals provided data to support some aspects of this argument propagated by the detrital school of thought.

The diagenetic school of thought, advocates that once clay minerals enter into saline water, they are no longer in equilibrium with sea-water and will undergo partial or complete chemical transformations to take up more stable phase. Grim (1958), Nelson (1959) and Powers (1959) explained that environmental diagenesis is the reason for the clay mineral variation. Grim (1953) attributed that diagenesis is responsible for the less abundance of kaolinite and montmorillonite and enrichment of illite and chlorite in relatively ancient sediments. Grim (1958) and Milne and Early (1958) regarded the decrease in montmorillonite with subsequent increase in illite or chlorite in saline water environment as a consequence of diagenesis. Powers (1957) explained the alteration of montmorillonite and to a lesser extent

illite to chlorite in the Gulf of Mexico and along the Pacific coast as due to diagenesis. Whitehouse and Mc Carter (1958) from their laboratory investigations provided data in favour of diagenesis school of thought.

Higher proportions of kaolinite at the eastern part of the lake and upstream of the river Kallada reflect a greater intensity of lateritic weathering at the source area. Nagelschmidt et al. (1940) observed kaolinite in the red soils derived from khondalite suite of rocks along the east coast of India. Biscaye (1964) and Fairbridge (1967) noted kaolinite is the stable product of laterisation or latrosols produced by deep tropical weathering. The relatively small drainage basin of the Ashtamudy lake with a limited pedogenic controls and with only one river draining in the area under tropical weathering, might have favoured the formation of kaolinite in lateritic soils. While working on the sediments of the northeastern Gulf of Mexico, Griffin (1962) has shown that distribution of clay minerals in the depositional area is controlled by the source. The above cited references support the lateritic origin of kaolinite and indicate continental derivation.

As seen from Table 3.4, the sediments of the eastern part of the lake and of the river Kallada are considerably high in kaolinite. However, the amount of kaolinite progressively decreases towards the eastern part. If diagenesis had taken place, there would have been a continuous depletion of montmorillonite in sediments throughout the lake. On the contrary, a hike in montmorillonite content was observed at the central and western parts of the lake. Hence it can be regarded that source is the dominant factor which controls the clay mineral assemblages in sedimentary basin.

Rao et al. (1983), while studying the clay mineral distribution on the continental shelf and slope of Kerala between Cochin and Quilon, found that montmorillonite is the most dominating clay mineral and attributed the variation in the clay mineral distribution to the differences in the energy of the various environments and size segregation of the minerals. Hence, the higher proportions of montmorillonite with little amounts of illite, at the western part of the lake can be explained as due to the off-shore sediments being transported into the lagoon by the tidal currents, which may be fairly representative of the assemblage of the immediate offshore shelf sediment. Fluvially induced currents are only of short duration because Kallada is the only river

flowing into the lake and therefore tidal circulation is the major process of sediment distribution in the lake. In addition, wind induced waves and currents also play a major role in the sediment distribution in the aforesaid zones. A part of the off-shore sediment which is rich in montmorillonite, brought in suspension by the incoming tidal currents, gets deposited in the central and western parts of the lake, when the tidal currents lose their velocity as they move into relatively deeper central part of the lake. Thus the central part of the lake gets enriched in montmorillonite. Moreover, the physical sorting of the clay minerals depending on the size, induced by the tidal flow also leads to the progressive enrichment of montmorillonite in the central and western parts of the lake. A part of montmorillonite can also be regarded as developed at the expense of kaolinite in the drainage basin due to the alternating wet and dry climate, (Biscaye, 1964).

Weaver (1959) has pointed out that cation adsorption is the most common process that acts on clay minerals, during their transportation from fresh to saline water environment and further contends that this process does not involve any change in the basic lattice structure of the clay mineral. This process is essentially a secondary one and cannot be called as diagenesis. The

decrease and increase of illite, in the downstream, depend upon the availability of potash ions. The low content of illite indicates that drainage contributes certain amount of degraded illite which might be formed due to the preferential stripping of potassium (Jackson et al., 1952) from illite by plants. These degraded illites, absorb more and more potassium downstream, particularly in the estuarine region and become well crystallized and their percentage go up. Such illitisation of clays from degraded illite towards more saline waters has been observed by many investigators (Hirst, 1962 a; Parham, 1964). The low percentages of illite in the eastern part and the increase in their amount as it goes towards the western part can be explained in the above line of thinking.

High content of kaolinite at the upstream of the river Kallada and eastern part of the lake may be due to the low content of calcium in the sediments, which favours the formation of kaolinite. Lower contents of kaolinite at the central and western parts are due to the higher content of calcium. High calcium favours the formation of smectite.

Whitehouse et al. (1960) explained that some of the changes, which the river-borne clay minerals undergo,

based on the differential settling velocities of clay minerals in waters of increasing salinity are in the following order: illite, chlorite, kaolinite and montmorillonite. According to this theory, illite and kaolinite are flocculated earlier than montmorillonite and get deposited nearshore whereas montmorillonite will deposit still seaward. Loughman and Craig (1962) offered the same explanation for the variations of clay minerals in marine sediments. In the present study, kaolinite decreases and montmorillonite increases seaward which could be explained on the differential settling velocities of clay minerals as discussed above.

Gibbs (1977) explained the lateral clay mineral variation, based up on size segregation theory, according to which montmorillonite are having the smallest particle size and hence are deposited further seaward, while 10 \AA micas have the greatest size and are deposited nearshore. Kaolinite has the intermediate size. Therefore the high content of montmorillonite and low content of kaolinite in the western part of the Ashtamudy lake can be explained by the size segregation theory.

Biscaye (1964) has remarked that even in tropics, where intense weathering conditions typically favour the formation of silica and base poor minerals like kaolinite, local conditions can interfere favouring the formation of other minerals like montmorillonite.

In an alternating wet and dry climate, montmorillonite develops at the expense of kaolinite in the drainage basin (Durgaprasada Rao, 1971). The diagenetic change may possibly reduce the montmorillonite content as it passes from the river confluence. The montmorillonite derived from the drainage might have been changed to illite as it have expanded lattice, significant inclination for base exchange, and ion adsorption. Hence, the illite, under the area of observation was formed by the transference of montmorillonite due to the base exchange and ion adsorption.

In alkaline environment, kaolinite would not be in equilibrium. For Palmlico estuary, Edzwald et al. (1974) found a decreasing trend in kaolinite from upper estuary towards the sea and explained this in terms of the equilibrium conditions with the environment, which supports the view that kaolinite is stable in acidic and unstable in alkaline environments. The decrease of kaolinite from the eastern to the western part of the Ashtamudy lake can also be explained in the same way.

From the above discussions it is clear that clay minerals in the sediments of Ashtamudy lake are not undergoing any major diagenetic changes. However, as Grim (1953) has stated, there would be a few diagenetic

changes in the lake sediments and the clay mineral would reflect the source material supplied to the lake in spite of these transformations. Hence it can be concluded that the influence of the source material is the primary controlling factor on the clay mineralogy of the Ashtamudy lake sediments. The study could also bring out the following dual source of sediment supply: (1) The Kallada river input rich in kaolinite and, (2) The offshore sediments rich in montmorillonite. The present mineral distribution pattern in the lake sediments can be attributed to the combined effect of the processes of (i) estuarine (tidal) circulation (Fenillet and Fleischer, 1980), (ii) physical sorting of sediment by size (Gibbs, 1977; Knebel et al., 1977) and (iii) differential settling of clay minerals (Loughman and Craig, 1962). A similar type of observations were also made by Seralathan and Seetaramaswamy (1982) for the clay minerals in the modern deltaic sediments of the Cauvery river, Vasudevan and Seetaramaswamy (1983) for the modern sediments of Palk Bay and Conispoliatis and Lykousis (1986) for the surficial sediments of Kavala Bay. The aforesaid investigators on clays in the modern surficial sediments are of opinion that diagenetic processes have insignificant effect on clays. In the present investigation also, an identical result is

obtained. Hence, it can be considered that the detrital minerals in the modern sediments do not undergo any major diagenesis in the basin of deposition.

CHAPTER - 4GEOCHEMISTRY OF MAJOR ELEMENTS

4.1. INTRODUCTION

Classically geochemistry is concerned with the physical-chemical principles that influence and/or control the fractionation, migration, deposition and distribution of chemical elements in the various rocks and sediments that comprise the Earth's crust. The application of geochemical principles and data to resolution of immediate Earth problems such as the finding of natural resources and the conservation of health and the environment, is assuming increasing importance during this decade. This has been especially true in prospecting for deposits of metals, non-metals and hydrocarbons, for both the localisation of potential economic deposits and the extension of known deposits. Derry (1971) has briefly considered geochemistry as a link between ore genesis studies and exploration. Hence, in recent times, geochemical investigation of sediments have become an important part of study especially of the aquatic environment.

The variations of major and trace elements in the sediments are the reflections of the various factors which govern their distribution. These elements are

introduced into the aquatic environment either in solid/colloidal and soluble forms by water and wind. Elements have their source in solid materials include those located within the lattice structure of lithogenous minerals and those incorporated into surfaces by adsorption and ion exchange processes. Solids introduced into the marginal seas, especially the nearshore environments are mainly the weathered products of the continents, transported to the depositional sites by streams and rivers. Many of the elements in marine sediments can have more than one source and often are associated with more than one host mineral. While considerable attention has been bestowed on the elemental distribution in marine environment, relatively little attention has been given to bring out the elemental distribution in the estuarine sediments. Now the study of estuaries has become important in view of its economic importance, its potential vulnerability to the impact of industrial and urban development and its interest to geochemists as a transitional zone in which the fluxes of material carried to the ocean by rivers may be considerably modified. In addition to natural variability, it has become necessary to consider man's recent influence on the concentration of some chemical species. Hence chemical analysis of Ashtamudy lake sediments was carried

out both for the bulk and clay fractions in order to ascertain the chemical behaviour and distribution of major and trace elements.

Since the various size fractions of the same sediment will have different results in the chemical analysis, it is therefore better to confine to a particular size rather than doing chemical analysis for the bulk of the sediments (Degens, 1965; Wakeel and Riley, 1961). However, in the present chemical analysis the results for the clays and bulk sediments are given to have a comparative study.

4.2. METHODS OF STUDY

About 50 gm of representative sediment sample was soaked in distilled water with 2 ml of 0.01 N. Ammonia solution for about 24 hours to disaggregate the particles. Clay fraction was separated by repeated settling and decantation after allowing the suspension to settle for 2 hours 3 minutes (Carver, 1971). The clay fraction thus separated was dried in hot air oven at 60^o-70^oC and then powdered in an agate mortar. 0.5 gm of this pulverised powder was brought to solution by treating with hydrofluoric acid and nitric acid. Similarly 0.5 gm of the powdered bulk sediment was also digested and made into solution. The quantitative estimation of various major

and trace elements have been carried out by established conventional and rapid methods. The procedures followed and the instruments used in the chemical analyses of the sediments are listed below.

<u>Chemical constituent</u>	<u>Instrument/method</u>	<u>Reference</u>
Phosphorous	Spectrophotometer 106	Riley (1958), p 425.
Total iron	-do-	Shapiro and Brannock (1956), p 36.
Manganese	-do-	Shapiro and Brannock (1956), p 38.
Titanium	-do-	Shapiro and Brannock (1956), p 37.
Sodium and Potassium	Digital flame photo- meter	Jenkins (1954)
Calcium and Magnesium	EDTA method	Schwarzenbach (1957)
Cu, Ni, Zn, Pb, Cd, As, Cr and Co.	Atomic Absorption Spectrophotometer (Perkin Elmer - 2380)	Fletcher, K. (1970), p. 588.

The principles underlying the above analytical methods are described very briefly in the following paragraphs.

Phosphorous

Phosphorous is determined in the form of phosphorous pentoxide based on the principle of conversion

of phosphorous into a complex of phosphomolybdic acid. Orthophosphate and molybdate ions condense in acidic solution to give molybdophosphoric acid which upon selective reduction produce a blue colour. The intensity of the blue colour is directly proportional to the amount of phosphorous present and the resulting blue complex exhibits maximum absorption at 827 m μ .

Total iron

Total iron is determined as Fe₂O₃ colorimetrically, which is based on the development of a pink red coloured ferrous orthophenanthroline complex upon treating with orthophenanthroline. 10% hydroxylamine hydrochloride is used to reduce the iron at pH 4.8-5. The intensity of the colour is measured at 560 m μ by spectrophotometer. The amount of iron is determined from the standard calibrated values.

Manganese

Colourimetric determination of manganese is made by oxidising the small quantities of manganese to permanganate using periodate in hot acidic condition. The intensity of the pink colour developed having maximum absorption at 525 m μ is directly proportional to manganese content in the sample solution.

Titanium

The basic principle involved in the determination of titanium colourimetrically is by developing a yellow colour by addition of hydrogen peroxide to an acid titanium solution. The amount of element present in the sample solution is directly proportional to the intensity of the yellow colour which shows maximum absorption at 430 m μ .

Sodium and Potassium

Flame photometric method was employed in the determination of sodium and potassium as described by Jenkins (1954). As many extraneous elements as possible were separated to avoid the interelement and anion effects in flame photometer as pointed out by Dean (1960). Iron and aluminium were removed by adding ammonia and the remaining solution was subjected to flame photometric analysis. The interference filters were changed correspondingly for Na and K. Calibration curves were drawn for the standards and from that the concentration of Na and K in the samples were determined.

Calcium and Magnesium

Calcium and Magnesium were determined by complexometric titrations using EDTA at desired pH.

The total calcium and magnesium was obtained by titrating with EDTA using erichrome black-T as indicator at a pH of 10 and calcium in similar way using murexide as indicator at a pH of 12.

4.3. RESULTS AND DISCUSSION

The results of the geochemical investigations and thereof the relative abundance of the major elements in the Ashtamudy lake sediments are given in Table 4.1(A B). The elemental geochemistry and the geochemical distribution of the various major and trace elements have been discussed in relation to (1) the prevailing physico-chemical conditions of the depositional environment, and (2) the clay minerals. Also, the results of the statistical analysis (the correlation coefficients, mean and standard deviation for each element, and the correlation coefficients of each element versus other elements are provided in Tables 4.3 A and B to determine the relationship between the elements, if any and their behaviour pattern. Similarly the same results can be used as an effective tool for demarkating zones of maximum and minimum variations. Likewise, enrichment factor for each element was also calculated to ascertain the natural way of accumulation and the extent of anthropogenic disturbances (Tables 4.4 A and B). The mean and standard deviation for each element are given in Table 4.2.

Table 4.1.A. Concentration of major elements in bulk sediments (%)

Sample No.	P ₂ O ₅	Na ₂ O	K ₂ O	CaO	MgO	Fe ₂ O ₃	MnO	TiO ₂
1	2	3	4	5	6	7	8	9
<u>Eastern part</u>								
23	0.42	1.85	0.78	1.96	2.21	6.69	0.065	0.083
24	0.48	1.95	0.8	1.12	2.62	6.97	0.058	0.083
25	0.41	1.85	0.87	1.12	1.61	7.81	0.052	0.334
26	0.48	1.65	1.11	1.12	1.41	7.39	0.019	0.334
27	0.44	1.68	0.93	3.08	0.4	7.81	0.039	0.500
30	0.41	1.51	0.72	1.4	1.61	7.81	0.058	0.334
32	0.41	1.58	0.96	1.12	1.61	7.39	0.032	0.334
36	0.41	1.17	1.03	1.4	1.00	5.3	0.032	0.334
40	0.41	0.99	1.17	0.84	1.00	6.97	0.026	0.334
44	0.48	1.16	1.17	1.12	2.01	5.02	0.032	1.168
48	0.31	0.8	0.96	1.12	0.6	4.74	0.026	1.688
52	0.34	1.01	1.17	1.4	0.8	3.07	0.006	1.168
54	0.31	1.17	1.18	1.12	2.01	3.62	0.013	1.334
58	0.31	0.7	0.8	1.68	0.6	3.9	0.032	1.334
59	0.44	0.87	0.75	1.4	1.61	2.79	0.006	1.168
60	0.34	1.28	0.67	1.12	0.60	5.71	0.032	1.168
62	0.44	1.58	0.87	1.68	1.81	4.6	0.045	0.834
64	0.44	1.53	0.8	1.68	1.61	3.90	0.058	0.834

Table 4.1.A. Contd.

1	2	3	4	5	6	7	8	9
<u>Central part</u>								
10	0.37	0.53	0.09	0.00	0.00	6.27	0.058	8.673
11	0.31	0.67	0.14	1.12	0.6	2.79	0.019	2.502
12	0.53	2.96	1.0	8.41	0.00	6.97	0.019	0.083
13	0.51	1.38	1.08	8.41	0.00	7.81	0.019	0.083
14	0.24	1.88	1.03	14.02	0.00	7.25	0.026	0.083
15	0.58	1.95	1.08	5.6	0.00	7.81	0.032	0.083
20	0.51	2.49	1.0	8.41	0.00	7.53	0.039	0.334
21	0.07	0.5	0.06	2.52	0.00	2.51	0.006	0.083
22	0.44	1.98	0.8	1.4	2.62	7.25	0.032	0.083
65	0.48	1.53	0.75	1.12	1.00	7.39	0.052	0.334
67	0.48	1.68	0.72	1.12	1.81	7.25	0.039	0.334
68	0.44	1.68	0.7	0.84	1.81	7.39	0.045	0.834
70	0.51	1.73	0.78	1.12	2.21	7.81	0.052	0.834
72	0.54	1.88	0.78	1.4	2.82	7.81	0.052	0.834
74	0.41	1.88	0.85	1.68	1.81	7.25	0.052	0.334
75	0.37	1.88	0.78	1.12	2.4	7.25	0.058	0.334
77	0.95	1.88	0.75	1.68	2.21	7.67	0.58	1.000
78	0.61	1.88	0.75	1.12	4.63	7.11	0.058	0.334
79	0.82	1.95	0.85	2.8	0.00	7.11	0.052	1.008
81	0.66	1.98	0.85	1.96	2.21	7.81	0.026	0.834
83	0.68	1.88	0.85	1.96	2.82	5.16	0.019	1.000
84	0.65	1.95	0.75	3.36	2.21	7.81	0.032	1.000
86	0.68	1.53	0.57	4.2	1.41	7.39	0.006	1.000
87	0.65	2.06	0.76	3.36	2.41	7.67	0.019	0.834
88	0.65	2.15	0.85	3.36	2.41	7.81	0.019	1.170
91	0.54	1.34	0.96	6.16	0.40	3.48	0.013	1.008

Table 4.1.A. Contd.

1	2	3	4	5	6	7	8	9
93	0.45	1.88	0.80	3.08	1.81	7.81	0.019	1.008
94	0.65	1.73	0.75	3.36	1.61	7.25	0.026	0.834
95	0.51	1.73	0.78	1.96	2.62	6.83	0.026	0.168
<u>Western part</u>								
1	0.22	0.47	0.15	7.57	0.00	6.55	0.058	2.502
2	0.40	0.48	0.28	5.608	1.41	4.46	0.052	7.006
3	0.34	1.04	0.96	5.04	0.8	2.51	0.026	1.668
4	0.48	2.56	1.17	8.41	2.82	6.97	0.019	0.083
5	0.34	1.31	1.11	14.02	0.00	1.95	0.019	1.168
6	0.56	1.88	1.18	11.21	0.00	4.35	0.013	0.834
7	0.65	2.59	1.03	8.41	0.00	7.53	0.019	0.083
8	2.7	2.56	1.11	8.41	0.00	4.6	0.019	0.083
9	1.5	1.88	0.96	8.41	0.00	2.79	0.013	0.500
17	0.04	0.33	0.04	2.8	1.81	5.85	0.058	1.168
97	0.54	1.68	0.7	1.68	2.21	5.86	0.026	0.168
98	0.58	1.53	0.7	2.8	1.81	4.88	0.019	0.334
99	0.66	1.73	0.75	3.36	2.82	7.39	0.019	0.834
100	0.66	1.53	0.80	3.64	1.81	7.25	0.019	1.008
101	0.68	1.95	0.75	3.64	2.01	6.13	0.013	1.000
102	0.57	1.41	0.90	4.2	1.2	3.07	0.013	1.168
103	0.41	0.51	0.15	3.08	2.21	1.67	0.013	2.002

Table 4.1.B. Concentration of major elements in
Clay fractions (%)

Sample No.	P ₂ O ₅	Na ₂ O	K ₂ O	CaO	MgO	Fe	MnO	TiO ₂
<u>Eastern part</u>								
28	0.41	1.68	0.93	1.4	1.41	6.69	0.387	0.500
29	0.34	4.31	0.45	1.39	2.01	4.67	0.065	0.336
31	0.41	1.58	0.72	0.84	1.41	5.3	0.032	0.500
34	0.41	1.01	0.96	1.4	2.01	7.25	0.026	0.500
37	0.37	2.15	0.70	1.12	1.2	4.74	0.026	0.500
61	0.34	1.51	0.78	1.12	0.80	4.88	0.039	0.834
63	0.37	1.58	0.87	1.96	0.60	7.53	0.045	0.834
<u>Central part</u>								
16	0.56	1.58	0.96	2.8	2.21	6.97	0.032	1.168
19	0.37	3.74	1.03	2.41	0.00	4.74	0.032	0.334
66	0.44	1.85	0.72	0.84	1.61	7.25	0.032	0.834
69	0.48	1.78	0.72	0.84	1.41	7.39	0.045	0.336
71	0.51	2.35	0.78	0.84	2.41	5.02	0.052	0.083
73	0.48	1.73	0.78	1.4	2.41	6.27	0.052	0.334
76	0.65	2.35	0.78	0.84	2.41	6.69	0.058	0.083
80	0.66	1.01	0.75	1.4	2.62	7.25	0.032	0.834
82	0.65	1.85	0.72	1.4	2.41	7.81	0.013	0.834
85	0.51	1.83	1.0	1.96	2.62	7.81	0.019	0.834
89	0.61	1.58	0.78	2.8	2.21	7.25	0.019	0.500
92	0.58	1.31	0.85	4.76	4.03	4.74	0.013	0.083
96	0.51	1.38	0.63	1.68	1.81	6.69	0.026	0.834
<u>Western part</u>								
18	0.6	2.35	1.11	2.8	4.03	6.69	0.019	0.834

Table 4.2. Mean and standard deviation for the major elements against river distance

- 34045 -

Distance	No. of samples	P ₂ O ₅		Na ₂ O		K ₂ O		CaO		MgO		Fe ₂ O ₃		MnO		TiO ₂	
		\bar{x}	$\sigma-x$	\bar{x}	$\sigma-x$	\bar{x}	$\sigma-x$	\bar{x}	$\sigma-x$	\bar{x}	$\sigma-x$	\bar{x}	$\sigma-x$	\bar{x}	$\sigma-x$	\bar{x}	$\sigma-x$
0-1	4	0.350	0.05	0.936	0.17	0.975	0.20	1.400	0.19	1.255	0.58	3.345	0.44	0.014	0.01	1.251	0.08
2-2	2	0.395	0.09	0.980	0.18	1.065	0.11	1.120	0.00	1.305	0.71	4.880	0.14	0.029	0.00	1.428	0.26
2-3	7	0.419	0.03	1.533	0.35	0.911	0.18	1.400	0.72	1.147	0.37	6.470	1.22	0.033	0.01	0.405	0.08
3-4	7	0.400	0.06	1.956	1.01	0.806	0.17	1.238	0.14	1.696	0.58	6.640	1.01	0.093	0.12	0.465	0.31
4-5	5	0.416	0.04	1.690	0.19	0.806	0.33	1.568	0.29	1.810	0.61	5.464	1.28	0.045	0.01	0.534	0.37
5-6	8	0.395	0.13	1.893	0.87	0.731	0.28	2.368	2.34	0.698	0.61	6.466	1.73	0.037	0.01	0.490	0.28
6-7	8	0.583	0.16	1.916	0.27	0.788	0.07	1.330	0.61	2.536	0.81	6.970	0.81	0.051	0.01	0.522	0.39
7-8	10	0.541	0.15	1.737	0.29	0.838	0.13	3.390	3.74	1.630	1.11	7.208	0.49	0.037	0.01	0.534	0.35
8-9	7	0.589	0.08	2.019	0.39	0.850	0.13	4.283	2.70	1.550	1.05	7.310	0.93	0.021	0.01	0.691	0.39
9-10	6	0.498	0.12	1.202	0.46	0.602	0.37	3.033	2.17	1.507	1.41	5.400	1.90	0.022	0.02	2.349	2.92
10-11	12	0.814	0.63	1.932	0.44	0.938	0.17	6.423	3.75	1.256	1.12	5.394	1.99	0.183	0.00	0.577	0.42
11-12	6	0.525	0.14	1.207	0.57	0.615	0.29	4.070	0.95	1.840	0.63	4.901	2.22	0.024	0.01	2.253	2.17
12-13	2	0.410	0.19	1.410	0.94	0.630	0.48	5.185	2.39	2.015	2.02	6.620	0.07	0.039	0.02	1.668	0.83
13-14	1	0.040	0	0.330	0.00	0.40	0.10	2.800	0.00	1.810	0.00	5.850	0.00	0.058	0.00	1.168	0.00

\bar{x} - Mean value $\sigma-x$ - Standard deviation

Table 4.3.A. Inter-elemental correlation matrix for the bulk sediments

	P ₂ O ₅	Na ₂ O	K ₂ O	CaO	MgO	Fe ₂ O ₃	MnO	TiO ₂	OM	Zn	Cu	Cr	As	Cd	Ni	Pb
P ₂ O ₅	1															
Na ₂ O	0.48**	1														
K ₂ O	0.27	0.57**	1													
CaO	0.23	0.34**	0.30*	1												
MgO	-0.07	0.15	-0.08	-0.42**	1											
Fe ₂ O ₃	0.03	0.56**	0.12	-0.08	0.28*	1										
MnO	-0.16	-0.03	-0.12	-0.33**	0.23	0.41**	1									
TiO	-0.16	-0.54**	-0.40**	0.01	-0.03	-0.35**	0.04	1								
OM	0.13	0.60**	0.29*	-0.10	0.32*	0.60**	-0.23	-0.43**	1							
Zn	0.07	0.04	0.07	-0.06	0.05	0.05	0.18	0.03	0.03	1						
Cu	-0.07	0.14	0.16	0.14	-0.24	0.21	0.37**	-0.011	0.11	-0.04	1					
Cr	-0.10	0.002	-0.36**	-0.01	0.07	0.44**	0.36**	0.03	-0.02	0.22	0.22	1				
As	-0.04	-0.02	0.10	0.19	0.09	-0.11	-0.27*	0.12	-0.08	-0.05	-0.15	-0.06	1			
Cd	-0.22	-0.16	0.05	0.60**	-0.64**	-0.18	-0.13	0.10	-0.22	-0.16	0.28*	0.09	0.28*	1		
Ni	-0.06	0.36	0.14	-0.10	0.08	0.51**	0.15	-0.46**	0.39**	0.17	0.13	0.48**	0.07	-0.01	1	
Pb	-0.30*	-0.14	-0.26*	-0.13	-0.07	0.09	0.20	-0.02	-0.02	-0.11	0.25	0.19	0.01	0.17	0.06	1

**highly significant (>99% level of significance)

*marginally significant (>95 and <99% level of significance)

OM - Organic matter

Table 4.3.B. Inter-elemental correlation matrix for the clays

	P ₂ O ₅	Na ₂ O	K ₂ O	CaO	MgO	Fe ₂ O ₃	MnO	TiO ₂	OM	Zn	Cu	Cr	As	Cd	Ni	Pb
P ₂ O ₅	1															
Na ₂ O	-0.30	1														
K ₂ O	0.24	-0.11	1													
CaO	0.33	-0.05	0.50*	1												
MgO	0.72**	-0.15	0.31	0.51**	1											
Fe ₂ O ₃	0.48*	-0.47*	0.23	-0.07	0.17	1										
MnO	-0.36	0.42	0.46*	-0.55*	-0.36	-0.26	1									
TiO ₂	0.09	-0.32	0.27	0.06	-0.004	0.52*	-0.42	1								
OM	-0.28	0.13	-0.46*	-0.40	-0.46*	0.02	0.46*	0.08	1							
Zn	-0.03	0.08	0.19	0.53*	0.08	-0.47*	-0.33	-0.45*	-0.38	-1						
Cu	-0.52*	0.11	0.19	-0.11	0.16	-0.47*	0.21	0.02	-0.26	0.10	1					
Cr	0.25	-0.20	0.49*	0.18	0.10	0.46*	-0.25	0.63**	-0.29	-0.30	0.16	1				
As	0.18	-0.40*	0.28	0.08	-0.09	-0.22*	-0.23	0.10	-0.30	0.19	-0.11	0.13	1			
Cd	-0.25	0.28	0.19	0.10	-0.09	-0.24	-0.15	-0.03	-0.19	0.17	0.16	0.09	0.29	1		
Ni	0.20	-0.45	0.27	-0.02	0.11	0.37	-0.07	0.50*	-0.20	-0.26	0.31	0.53*	0.47*	0.20	1	
Pb	-0.22	0.64**	0.20	-0.05	-0.15	-0.11	0.28	0.17	-0.05	-0.17	0.31	0.34	-0.39	0.04	-0.12	1

** highly significant (>99% level of significance)

* marginally significant (>95 add <99% level of significance)
 OM - Organic matter

Table 4.4.A. Enrichment factors of major elements
for the bulk sediments

Sample No.	P ₂ O ₅	Na ₂ O	K ₂ O	CaO	MgO	Fe ₂ O ₃	MnO	TiO ₂
1	2	3	4	5	6	7	8	9
<u>Eastern part</u>								
23	4.21	0.62	0.26	0.69	1.94	1.00	0.59	0.14
24	4.61	0.64	0.26	0.38	2.20	1.00	0.51	0.14
25	3.52	0.53	0.25	0.34	1.21	1.00	0.41	0.49
26	4.35	0.50	0.34	0.36	1.12	1.00	0.16	0.52
27	3.77	0.48	0.27	0.93	0.30	1.00	0.30	0.74
30	3.52	0.43	0.21	0.42	1.21	1.00	0.46	0.49
32	3.72	0.48	0.29	0.36	1.28	1.00	0.27	0.52
36	5.18	0.50	0.44	0.63	1.11	1.00	0.37	0.73
40	3.94	0.32	0.38	0.29	0.84	1.00	0.23	0.55
44	6.41	0.52	0.53	0.53	2.35	1.00	0.39	2.68
48	4.38	0.38	0.46	0.56	0.74	1.00	0.33	4.10
52	7.42	0.74	0.87	1.08	1.53	1.00	0.13	4.38
54	5.74	0.73	0.74	0.73	3.25	1.00	0.22	4.25
58	5.33	0.40	0.47	1.02	0.90	1.00	0.51	3.94
59	10.57	0.70	0.61	1.19	3.38	1.00	0.14	4.82
60	3.99	0.50	0.27	0.46	0.62	1.00	0.35	2.36
62	6.41	0.77	0.43	0.87	2.31	1.00	0.60	2.09
64	7.56	0.88	0.47	1.02	2.42	1.00	0.91	2.47
<u>Central part</u>								
10	3.95	0.19	0.03	0.00	0.00	1.00	0.57	1.24
11	7.44	0.54	0.11	0.95	1.26	1.00	0.42	10.34
12	5.09	0.96	0.33	2.86	0.00	1.00	0.17	0.14
13	4.36	0.54	0.31	2.55	0.00	1.00	0.15	0.12
14	2.22	0.58	0.32	4.58	0.00	1.00	0.22	0.13

Table 4.4.A. Contd.

1	2	3	4	5	6	7	8	9
15	4.98	0.56	0.31	1.70	0.00	1.00	0.25	0.12
20	4.54	0.74	0.30	2.65	0.00	1.00	0.32	0.51
21	1.87	0.45	0.05	2.38	0.00	-1.00	0.16	0.38
22	4.07	0.61	0.25	0.46	2.12	1.00	0.27	0.13
65	4.35	0.47	0.23	0.36	0.79	1.00	0.43	0.52
67	4.44	0.52	0.23	0.37	1.46	1.00	0.33	0.53
68	3.99	0.51	0.22	0.27	1.44	1.00	0.37	1.30
70	4.38	0.49	0.23	0.34	1.66	1.00	0.41	1.23
72	4.63	0.54	0.23	0.42	2.12	1.00	0.41	1.23
74	3.79	0.38	0.27	0.55	1.46	1.00	0.44	0.53
75	3.42	0.58	0.24	0.37	1.94	1.00	0.49	0.53
77	8.29	0.55	0.22	0.52	1.69	1.00	0.46	1.50
78	5.75	0.59	0.24	0.37	3.82	1.00	0.50	0.54
79	7.73	0.61	0.27	0.93	0.00	1.00	0.45	1.62
81	5.66	0.57	0.25	0.59	1.66	1.00	0.20	1.23
83	8.83	0.82	0.37	0.90	3.20	1.00	0.23	2.24
84	5.58	0.56	0.22	1.02	1.66	1.00	0.25	1.48
86	6.17	0.47	0.18	1.35	1.12	1.00	0.5	1.56
87	5.94	0.60	0.22	1.04	1.64	1.00	0.16	1.25
88	5.58	0.62	0.25	1.02	1.81	1.00	0.15	1.72
91	10.39	0.87	0.63	4.19	0.67	1.00	0.23	3.32
93	3.86	0.54	0.23	0.93	1.36	1.00	0.15	1.48
94	6.01	0.54	0.23	1.09	1.30	1.00	0.22	1.33
95	5.00	0.57	0.26	0.68	2.24	1.00	0.23	0.28

Table 4.4.A. Contd.

1	2	3	4	5	6	7	8	9
<u>Western part</u>								
1	2.25	0.16	0.05	2.74	0.00	1.00	0.54	4.40
2	6.01	0.29	0.14	2.98	1.85	1.00	0.71	18.11
3	9.08	0.93	0.87	4.76	1.87	1.00	0.63	7.66
4	4.61	0.83	0.38	2.86	2.37	1.00	0.17	0.14
5	11.68	1.51	1.29	17.04	0.00	1.00	0.61	6.90
6	8.63	0.97	0.62	6.11	0.00	1.00	0.18	2.21
7	5.78	0.77	0.31	2.65	0.00	1.00	0.16	0.13
8	39.33	1.25	0.55	4.33	0.00	1.00	0.26	0.21
9	36.02	1.52	0.78	7.14	0.00	1.00	0.28	2.07
17	0.46	0.13	0.02	1.13	1.81	1.00	0.61	2.30
97	6.17	0.64	0.27	0.68	2.21	1.00	0.27	0.33
98	7.96	0.71	0.33	1.36	2.17	1.00	0.24	0.79
99	5.98	0.53	0.23	1.08	2.24	1.00	0.16	1.30
100	6.10	0.47	0.25	1.19	1.46	1.00	0.16	1.60
101	7.43	0.72	0.28	1.41	1.92	1.00	0.13	1.88
102	11.13	1.03	0.67	3.24	2.29	1.00	0.26	4.38
103	16.45	0.69	0.20	4.37	7.76	1.00	0.47	13.81

Table 4.4.B. Enrichment factors of major elements
for the clays

Sample No.	P ₂ O ₅	Na ₂ O	K ₂ O	CaO	MgO	Fe ₂ O ₃	MnO	TiO ₂
<u>Eastern part</u>								
28	4.11	0.56	0.32	0.49	1.24	1.00	3.55	0.86
29	4.88	2.08	0.22	0.71	2.52	1.00	0.85	0.82
31	5.18	0.67	0.31	0.38	1.56	1.00	0.37	1.09
34	3.79	0.31	0.30	0.46	1.63	1.00	0.22	0.78
37	5.23	1.02	0.34	0.56	1.48	1.00	0.33	1.22
61	4.67	0.69	0.36	0.54	0.96	1.00	0.49	1.97
63	3.29	0.47	0.26	0.62	0.47	1.00	0.37	1.28
<u>Central part</u>								
16	5.38	0.51	0.31	0.95	1.86	1.00	0.28	1.93
19	5.23	1.78	0.49	1.20	0.00	1.00	0.42	0.81
66	4.07	0.57	0.23	0.27	1.30	1.00	0.27	1.33
69	4.35	0.54	0.22	0.27	1.12	1.00	0.37	0.52
71	6.81	1.05	0.35	0.40	2.81	1.00	0.63	0.19
73	5.13	0.62	0.28	0.53	2.25	1.00	0.50	0.61
76	6.51	0.79	0.26	0.30	2.11	1.00	0.53	0.14
80	6.09	0.31	0.23	0.46	2.12	1.00	0.27	1.32
82	5.58	0.53	0.21	0.42	1.81	1.00	0.10	1.23
85	4.38	0.53	0.29	0.59	1.97	1.00	0.15	1.23
89	5.64	0.49	0.24	0.92	1.79	1.00	0.16	0.80
92	8.20	0.62	0.41	2.38	4.98	1.00	0.17	0.20
96	5.11	0.46	0.21	0.60	1.59	1.00	0.24	1.44
<u>Western part</u>								
18	6.01	0.79	0.38	0.99	3.53	1.00	0.18	1.44

4.3.1. Phosphorous

As seen from Table 4.1 (A and B) the phosphorous content of the Ashtamudy lake sediments vary widely ranging from 0.04 to 2.70% in the bulk sediments and that from 0.34 to 0.66% in the clay fractions. The average content of phosphorous in the bulk and clay fractions are 0.532% and 0.506% respectively. The average phosphorous contents at the eastern, central and the western parts of the Ashtamudy lake for the bulk sediments and clays are 0.404%, 0.527%, 0.663%, and 0.379%, 0.539% and 0.6% respectively. The average contents of phosphorous in the bulk and clays does not show much variation. The average phosphorous concentration in the Ashtamudy lake sediments is higher than the reported values in the Vembanad lake (Murty and Veerayya, 1972), Kolleru lake (Rama Murty, 1972), Iskapalli lagoon (Subba Rao, 1985) and Minnesota lake (Swain, 1961). It is even higher than the reported mean value for the east coast of India (Durgaprasada Rao, 1971). When compared with the values of the deltaic sediments of the east coast of India namely Cauvery (Seralathan, 1979), Krishna (Seetaramaswamy, 1970), Godavari (Naidu, 1968), Mahanadi (Satyanarayana, 1973) and for the Boca Vagre, Gulf of Paria (Hirst, 1962 b) it is found to be higher, but much lower than the Yerra delta of Australia (Link, 1967).

The variation in the phosphorous content of Ashtamudy lake can be explained in terms of the rate of supply of phosphorous through rivers, organic production, clay minerals, and the differential adsorption of phosphorous by adsorbents.

From Fig. 4.1 it is clear that not much variation is noticed in the eastern part and a consistency is maintained here, whereas some variation is observed in the central and western parts of the lake. This is mainly due to the presence of clay mineral. As mentioned in Chapter 3, Ashtamudy lake is dominated by fine sediments ($<63\mu$) and the eastern part of the lake is marked for the dominance of kaolinite, while the central part has a more or less equal proportion of kaolinite and montmorillonite. The western part has more of montmorillonite

Phosphorous adsorption on clay minerals has been reported by Weaver and Wampler (1972). Robinson (1962) has pointed out the greater ability of kaolinite in the fixation of PO_4^3 ions by anion exchange over other clay minerals. Smectite also favours the fixation of PO_4^3 ions to a little extent by anion exchange but such process is insignificant beyond pH 7.0 (Wey, 1953). Therefore very little phosphorous fixation may be expected in smectite in the low pH environment especially in the eastern part sediments where the river Kallada empties. Hence, it can be considered

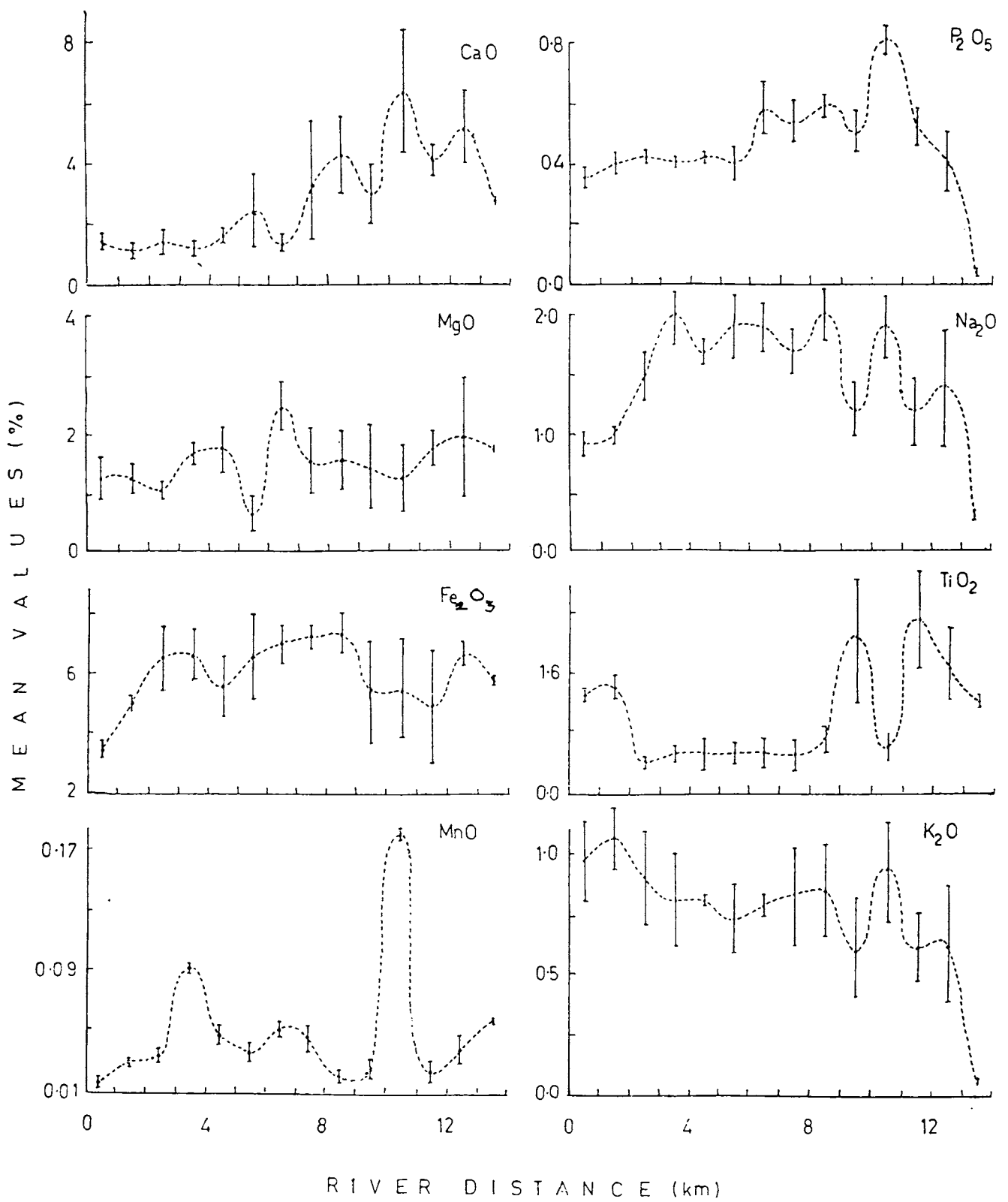


Fig. 4.1. Mean values of major elements against river distance (vertical bars indicate r.m.s. deviation)

that kaolinite has fixed up majority of phosphorous at the eastern part of the lake. A similar observation was also made by Rao et al. (1978) for the northern half of the western continental shelf of India and Seralathan and Seetaramaswamy (1979) for the modern deltaic sediments of the Cauvery river. Further, it is seen from Table 4.1A and B that the average content of phosphorous for the bulk sediments is higher than clay fractions. This could be attributed to the presence of phosphatic mineral monazite.

The phosphate content at the central part is higher than that in the eastern part of the lake. Here also the variation could be attributed mainly to the presence of clay minerals in a similar manner. But, this region of the lake is marked for high organic activity and the higher content of phosphorous can also be due this augmented organic production. Regarding biogenous concentration, it is well known that phosphorous is a biophile element (Landerger, 1954) and it is an important constituent of cytoplasm of all organisms. According to Rankama and Sahama (1950) phosphorous can be concentrated by phytoplankton which forms the food of any organisms. Thus the dissolved phosphate in waters that are being supplied by the rivers might incorporated by the planktons and later deposited at the bottom.

Bhushinski (1964) has advanced the view that phosphorous conveyed to the sea by rivers is immediately assimilated by the plankton and subsequently at the bottom, very little being carried away to the deeper sea.

The higher content of phosphorous at the western part of the lake is mainly attributed to the presence of phosphatic minerals like monazite and the clay mineral montmorillonite. Presence of these minerals at the western part of the lake was discussed in detail in Chapter 3. Here, montmorillonite fixes some amount of phosphate ions since the pH is higher than that of eastern and central parts. Besides, in the bulk fraction, phosphorous has shown highly significant positive correlation with Na and only a marginal level of significance with K, whereas in the clay fraction it has shown high level of significance with Mg, which are stoichiometric (Table 4.3 A and B).

Many workers have pointed out the geochemical affinity of phosphorous with Fe, Ca and organic matter (Hirst, 1962 b; Bapat, 1968; Rama Murty, 1972; Seralathan, 1979; Subba Rao, 1985) and they stated that the important inorganic adsorbent in which phosphorous is tied up are ferric phosphate and calcium phosphate.

Under high alkaline condition phosphorous can co-precipitate with Fe as ferric phosphate and calcium phosphate. But in the present investigation no such correlation or affinity is seen except for Fe in clays, and that too only marginally significant. Hence the higher content of phosphorous in the Ashtamudy lake sediment is not mainly due to the inorganic adsorbents. However the western part of the Ashtamudy lake is marked by high shell content and can be considered that a part of phosphorous is tied up as calcium phosphate. Similarly, from the low correlation between phosphorous and Fe in the clays, it can be inferred that phosphorous is being tied up in ferric phosphate. Relatively low concentration of phosphorous at the eastern part of the lake, where only the Kallada debouches and where the rate of deposition is high, shows that phosphorous supply by the river is rather small.

The chemical activity of PO_4^3 increases as the pH increases and the phosphate content increases from fresh water to marine water (Jahuke et al., 1983). The present investigation reveals an increase in the phosphorous content from the eastern to western part of the lake. A similar result has been obtained for the Vembanad lake sediments (Murty and Veerayya, 1972). Hence, it can be concluded that

the phosphorous content of the Ashtamudy lake sediments is mainly confined to clay and phosphatic minerals and to a limited extent on biogenous concentration, rather than the supply by rivers or differential adsorption by various adsorbents.

4.3.2. Sodium and Potassium

Percentages of sodium and potassium as oxides in the sediments of the Ashtamudy lake for the bulk and clay fractions are furnished in Table 4.1 (A and B). The analyses have been made without removing the dried salts solidified from the pore solutions entrapped in the sediments.

The percentage of sodium ranges from 0.33 to 2.96 (average 1.54) for the bulk sediments and from 1.01 to 4.31 (average 2.066) for the clays. The average Na content in the Ashtamudy lake sediments for the eastern central and western parts of the lake for the bulk and clay fractions are 1.35, 1.76, 1.50%, and 1.97, 1.87, 2.35% respectively. The value of Na content for the clays in the Ashtamudy lake sediments is higher than the figures given for the sediments of Minnesota (Swain, 1961) and southern Michigan lakes (Shimp *et al.*, 1970). Regarding the regional variation, the Na content increases towards the central part and then decreases to the western part

in the bulk sediments whereas in the clays it decreases to central part and then increases to western part of the lake. The average content of Na in the Ashtamudy lake sediment is higher for the clays.

A wide variation is noted in the individual values for K (from 0.04 to 1.18% with an average of 0.81%) for the bulk sediments, while less variation is seen in the clays. In clays the K content varies from 0.45 to 1.11% (average 0.893%). The average K content of the Ashtamudy lake sediments is lower than that of Minnesota lake and is higher in the clays than in the bulk sediments. Regarding the regional distribution, K content decreases from eastern to western part of the Ashtamudy lake for the bulk fraction whereas it increases from the eastern to western part for the clay fraction.

Mean values of Na and K with their standard deviation are plotted against the river distance (Table 4.2). Deviations are represented in vertical bars (Fig. 4.1). From the correlation coefficients (Table 4.3A and B), it is seen that Na shows high level of significance with Ca, Fe, Ti, K and organic matter whereas Potassium shows high level of significance with Ti and marginal significance with Ca and organic matter. Na and K show a wide variation

all through the 3 regions except in the upper regions of the eastern part of the lake where its variation is minimum.

The observed variation in the Na and K in the sediments of the Ashtamudy lake are mainly due to differential fixation of Na and K in the clay minerals and biogenous material. The presence of salts solidified from pore solutions may also contribute to this variation.

Rankama and Sahama (1950) pointed out that Na and K released during weathering, remain in ionic solution whereas Al reacts with silica to form clay minerals. The primary source of Na in the lake sediments under study, is the soluble products formed during weathering of plagioclase feldspars in the drainage basin of river Kallada. Under certain conditions, clay minerals may release large quantities of exchangeable 'Na'. Therefore, it can be considered that most of the Na and K has been fixed in clay minerals by a process of cation exchange and/or adsorption. The high value of Na compared to K may be due to either the occurrence of some Na-bearing clay minerals or to the presence of degraded illites. The X-ray diffraction data of clays in the Ashtamudy lake revealed the presence of Na smectite and only a little amount of illite.

The clay mineral composition of the Ashtamudy lake consists of kaolinite and montmorillonite with little

degraded illite. The regional variation of Na and K content are therefore related to the chemical composition of the clay mineral assemblage. Taking into account the role of clay minerals in the fixation of Na, it seems that most of the Na in different parts of the Ashtamudy lake is tied up in the montmorillonite and a little in degraded illite. High content of Na has been explained by the presence of degraded illite (Hirst, 1962 b; Naidu, 1968; Ramanathan *et al.*, 1988). Hence a good part of Na in the Ashtamudy lake sediment is fixed up in clays. Another factor which favour the high content of Na in clays is the increased fixation of Na^+ relative to K^+ . This is on the assumption that Na^+ ions with their higher concentration compete more successfully than K^+ ions for the vacant exchange sites in clay minerals (Nelson, 1962).

From the above, it is considered that one of the factors which attributed to the higher content of Na is the greater ionic concentration of Na in the overlying water, which replaces a part of K^+ and Ca^{++} fixed in a clay mineral. Nelson (1962), Degens (1965) stated that the theoretical prediction order of cation exchange and absorption of an ion in clays can be altered by a number of environmental factors and hence there can be a higher content of Na when compared to K in lake sediments

depending on the environment. The factor namely the higher concentration of Na relative to K in the overlying waters, might have reversed the theoretical predicted order of cation exchange in the Ashtamudy lake sediments. Moreover, Na can be easily removed from the source rocks as it has lower bonding energy and greater hydration than K.

The higher content of Na with respect to K in the Ashtamudy lake sediments may also be due to the removal of K through agencies of leaching and cropping of plants. Plants have a decided affinity for K in the synthesis of carbohydrates (Rankama and Sahama, 1950) and for the development of tissues (Heir and Adams, 1963). This conclusion is made as it is evident that the drainage basin of the Kallada river is packed by thick vegetation and dense forest.

The higher content of Na in the Ashtamudy lake sediments is also due to the fixing up of Na in organic matter. This is inferred from the strong correlation with organic matter it has exhibited (Table 4.3). The wide variation as observed in the Fig. 4.1 can be explained in terms of the clay mineralogy and organic matter content. At the eastern part of the lake Na is fixed up in organic matter and degraded illite. At central and western parts, the variation of Na content

is due to Na montmorillonite, organic matter and degraded illite.

In short, relatively high percentage of Na over K is (1) due to the large amount of colloidal size particle which will enhance the overall adsorption of Na, (2) high content of Na salts derived from the pore solutions, (3) slow rate of deposition which allow clays sufficient time to adsorb Na ions from the overlying waters, (4) the higher availability of Na in saline water than fresh water and (5) the removal of K through agencies of leaching and cropping of plants.

The source of K is weathered product of orthoclase, microcline and biotite of the drainage area. Some part of K is tied up with the illite. This is based on the fact that illite has a specific ability to fix K^+ over other cations in its interlayer (Dyer et al., 1962; Nelson, 1962). The relatively low content of K over Na might also be due to the removal of K by plants. A part of K is also fixed up in organic matter, as it shows marginally significant correlation with organic matter. Since the lake supports a dense vegetation, it might be accepted that on the deposition of vegetal matter on the lake floor following the death of the same, considerable amount of K has been added to

these clays. Likewise, the marginal level of correlation with Ca signifies that a part of Ca^{++} is replaced by K^+ fixed in a clay mineral.

Relatively low Na and K content in the eastern part of the lake which is of continental origin reflects the source area. In contrast, montmorillonite having been transported into the lake from the open sea carry greater amounts of Na and K as adsorbed ions. Hence relatively higher concentrations in the western part.

As K and Na are not precipitated by hydrolysis (Heier and Adams, 1963), it is conceived that Na and K are tied up with clay minerals either by cation exchange and/or adsorption. K is fixed preferentially in view of its lower ionic potential, higher field function ($K = 2.27$ and $Na = 1.83$, Heier and Adams, 1963) and greater sorptive energy ($K = 0.932$, $Na = 0.625$, Yanshina, 1960).

From the above discussion it can be concluded that the relative difference observed in Na_2O and K_2O contents in the sediments of the Ashtamudy lake especially in clays are due to (1) clay mineral composition, (2) organic matter content, (3) initial composition of the source material, (4) progressive

changes in the salinity of the water and (5) salts from the pore solutions.

4.3.3. Calcium and Magnesium

The average percentages of Ca in the bulk and clay fractions of the Ashtamudy lake sediments are 3.53 and 1.99 with a range of 0 to 14.2 and 0.84 to 2.8 respectively. Both in the bulk and clays, Ca content increases from eastern to the western part of the lake. It has shown a highly significant negative correlation with Mg and Mn (Table 4.3 A and B).

Regarding the Mg content in the sediments of the Ashtamudy lake, the average is 1.38% and the range is from 0.0 to 4.63% for the bulk sediments and for the clays it is 2.51% with values ranging from 0 to 4.03%. In the bulk, the Mg content increases from eastern part to central part and then decreases to western part, whereas in clays, it increases progressively from the eastern to western parts. The Mg content of the Ashtamudy lake sediments depicted a marginal level of correlation with Fe and organic matter (Table 4.3 A and B).

The regional variation in Ca and Mg content of the Ashtamudy lake sediments can be explained as interlayer cation in the clay mineral structure, as calcium carbonate in shells and as biogenous origin (Fig. 4.1).

Calcium is fixed in clays as interlayer cation in the clay mineral structure, as calcium carbonate in the shells and as calcium phosphate of organic or inorganic origin. The absence of positive correlation between Ca and P rules out the precipitation of Ca as calcium phosphate. As CaCO_3 due to skeletal material has been observed, it can be concluded that Ca is fixed as CaCO_3 . Nelson (1962) observed that a significant part of 'Ca' is tied up in montmorillonite. Since Ca does not seem to be related to montmorillonite abundance in the Ashtamudy lake sediments, it can be inferred that 'Ca' is fixed up in the clay minerals at the source itself and no calcium is adsorbed or replaced from the clay minerals during transportation by rivers. Moreover Ca occurs in the 12-fold coordination of montmorillonite helping to balance the charge deficiencies due to substitution of Al^{3+} by Mg^{2+} and the larger size of calcium ions prevents its entry into octahedral positions subsequent to montmorillonite formation. The negative correlation with the interlayer cation Mg^+ suggests that Ca is replaced by Mg in the clay minerals probably at the source itself. However, the net reaction between fluid clays and seawater is primarily an exchange of seawater Na^+ with bound Ca^{2+} (Sayles and Mangeldorf, 1977). Hence a low content of Ca is expected

by a cation exchange process owing to the presence of higher concentration of Na^+ and Mg^{++} in the marine environment. But in the present study, the Ca content in the Ashtamudy lake sediment increases towards western part both in the bulk and clay sediments. This may be due to the significant incorporation of clay sized calcium carbonate material in the sediments.

In the light of above discussion, the role of montmorillonite in the observed variation of the Ca content in the sediments cannot be ruled out since montmorillonite also increases along with the increase in Ca content right from the eastern to western part of the lake, both in bulk and clays. The variation of the Ca content can also be due to the Ca which is being fixed as CaCO_3 in shells. Also, from the carbonate distribution in the Ashtamudy lake sediments, it is seen that carbonate content increases towards the western part, which is mainly due to the presence of shelled organisms (Section 2.3). This also explains the variation in Ca content for the Ashtamudy lake sediments. Hirst (1962 b) has also attributed that CaCO_3 is one of the factors accounting for the observed variation of Ca in modern sediments of the Gulf of Paria.

The regional variation of Mg in the sediments of the Ashtamudy lake is due to fixing up of the major

part of Mg in clays. A part of Mg is of biogenous origin. Sediments noticeably rich in calcareous material are not having increased Mg content. Mg shows a negative correlation with Ca suggesting that it is not concentrated in the carbonates. A part of the Mg can be considered as of biogenous origin as it has revealed a marginal level of correlation with organic matter. Magnesium in the clays may be tied up in the lattice positions of clay minerals or may be adsorbed from the overlying waters in the marine environment. The clay minerals adsorb more Na and Mg than K from sea water (Weaver, 1967). In 1968, Brooks et al. stressed on the interaction of Mg with clay. Muller (1964) found that Ca-rich fresh water clays preferentially absorb Mg in brackish water. In the Ashtamudy lake sediments, the Mg is fixed up in montmorillonite and a little in illite. The variation in the Mg content of the bulk sediments is mainly due to the lack of concentration of Mg in the carbonates. Mg content variation in sediments of upper reaches of Cauvery estuary is also explained on similar lines (Ramanathan et al., 1988). The progressive enrichment of Mg in the clays of Ashtamudy lake sediments from the eastern to western part is due to the adsorption of Mg mainly in montmorillonite and in illite. Also a part is due to biogenous origin.

4.3.4. Iron, Manganese and Titanium

The weight percentage of iron refer to total Fe which is determined as Fe_2O_3 . The average content of Fe for the bulk sediments of the Ashtamudy lake is 5.813% and ranges from 1.67 to 7.81% while in the clays the average content is 6.387% with values ranging from 4.67 to 7.81%. In the bulk, the Fe-content increases towards central part and then decreases to the western part whereas in the clays a progressive increases is noticed right from the eastern to western part. The regional variation is given in Fig. 4.1. It shows a highly significant negative correlation with Ti and highly significant positive correlation with organic matter and Mn (Table 4.3 A and B).

The average Fe content in the clays of Ashtamudy lake sediment is less than the reported values of Fe-content in the sediments of Kolleru lake (Rama Murty, 1972) and is comparable with the Iskapalli lagoon sediments (Subba Rao, 1985), and with deltaic sediments of Cauvery (Seralathan, 1979), Yerra River (Link, 1967), Godavari (Naidu, 1968), Krishna (Seetaramaswamy, 1970) and Mahanadi (Satyanarayana, 1973). It is slightly higher than the iron in the clays of the modern sediments of the Gulf of Paria (Hirst, 1962 b).

The average content of MnO for the bulk is 0.0311% (with values ranging from 0.0064% - 0.0645%) and in the clays the value averages to 0.0468% (with values ranging from 0.0129% to 0.3870%). The MnO content of the Ashtamudy lake sediments decreases towards the western part (Fig. 4.1) both in the bulk and clay fractions. Only in the clay fraction at the eastern part a higher content of MnO is noticed. The MnO content of Ashtamudy lake shows a highly significant and marginally significant negative correlations with CaO and K₂O respectively. The average content of MnO is much lower than many of the reported values (Swaine, 1961; Naidu, 1968; Seetaramaswamy, 1970; Rama Murty, 1972; Seralathan, 1979; Subba Rao, 1985) and comparable with the values obtained for the marine clays of Boca Vagre delta (Hirst, 1962 b), Yerra delta (Link, 1967), Mahanadi (Satyanarayana, 1973).

There is a wide variation in the individual values of Ti (Fig. 4.1) and the average values for the bulk and clays are 0.851 and 0.651% respectively. The value ranges from 0.168 to 8.674% for the bulk and 0.083 to 1.168% for the clays. The Ti content of the Ashtamudy lake is higher than Kolleru lake sediments (Rama Murty, 1972), modern deltaic sediments of Cauvery, Godavari and Krishna (Naidu, 1968; Seetaramaswamy, 1970; Seralathan, 1979) and

comparable with Mahanadi (Satyanarayana, 1973) and Iskapally lagoon (Subba Rao, 1985). In the bulk the Ti content decreases from eastern to central part of the lake and then increases to western part and in the clays also it slightly decreases to central part and then increases to western part. The amount of Ti present is more in the bulk sediments rather than in the clays of the Ashtamudy lake sediments. Titanium shows a highly significant negative correlation with organic matter and does not show any correlation with any of the major elements (table 4.3 A and B).

There are different views regarding the chemical state in which Fe is transported to the sedimentary basin of deposition. It is considered that Fe has been transported to depositional environment partly in solution and partly in colloidal form. When the iron bearing sediments come into contact with oxygenated slightly alkaline waters of the lake, iron is oxydised to ferric state and is precipitated as ferric hydroxide. In the present case, the increasing trend of iron content noticed from the eastern to western part, especially in clays, indicates a higher oxidative precipitation, if iron occurs as Fe^{3+} and $\text{Fe}(\text{OH})_3$. An increasing oxidative precipitation downstream is highly possible under higher aeration associated with turbulence. A high oxidation potential leads to the precipitation of $\text{Fe}(\text{OH})_3$ even at

pH 3 (Landergren, 1975). Mason (1958) states that the oxidation of iron proceeds more readily in more alkaline solutions. To Boyle et al. (1977) the river-borne dissolved iron consists almost entirely of mixed iron oxide-organic matter colloids, stabilized by the dissolved organic matter. When the riverwater mixes with seawater in the estuary, the negatively charged iron-bearing colloids react rapidly with seawater cations to form precipitate. Evidence of the removal of iron from solutions in several estuaries in fact exists (Coonley et al., 1971; Windom et al., 1971; Boyle et al., 1974; Subramaniam and D'Anglejan, 1976; Yeats and Bowers, 1976; Holiday and Liss, 1976). The prevalence of such a phenomenon will be reflected by the higher content of iron in the bottom sediments of the lake. Ashtamudy lake bottom sediments are characterised by higher Fe content. Hence this can be considered as the main reason for the higher content of Fe at the central and western parts of the lake.

Highly significant positive correlation of Fe with organic matter indicates that iron is also incorporated in organic matter. The fixation of iron by biogenic material is well established. Very fine organic residues have close affinity to fix iron and other cations by adsorption, and iron forms an important micro-constituent of all living tissues (Mankama and Sahana, 1950). The close association of Fe and organic

matter in sediments might be related to 3 factors viz. (1) ability of organic matter to fix Fe by adsorption, (2) concentration of Fe by living organisms after their death and decomposition and (3) the part played by organic matter in the precipitation of Fe as a sulphide.

In view of the prevailing reducing environment and presence of H_2S at the eastern part of the lake, it may be understood that Fe would be precipitated in this zone as Ferrous sulphide. This observation is in agreement with that of Sverdrup et al. (1955) who found that Fe is precipitated as sulphides in stagnant environments, where H_2S is produced. There are strong evidence to support the above contention. Most of the sediments in this area are dark grey in colour indicating the presence of hydro-troillite ($FeS \cdot nH_2O$), It can reasonably be assumed that any ferric iron reaching the reducing environment at the eastern part of the lake will be first reduced to soluble ferrous state, either by H_2S or by the oxidation of organic matter by ferric iron itself. The probable main source of H_2S could be either protein of organic matter in the clays and/or sulphates of the overlying water. Kanisihwar (1962) has pointed out that H_2S is released from plant-proteins as a result of the metabolic activity of hetrotrophic

bacteria, whereas that from the sulphate ions is produced by the SO_4 reducing bacteria. A few inches below the muddy sediment surface anaerobic conditions generally prevail due to lack of ventilation (Nelson, 1962). Moreover he has also illustrated that in a sediment profile, the top oxidised layers are brown whereas layers a few inches below (FeS zone) have microbial activity and anaerobic condition which make the colour black. Presumably such a reducing condition exists in the subsurficial layers of the sediments in the eastern part of the lake and this is based on the fact that the texture there are, silty clay, and clayey silt and sand silt clay which have a high content of organic matter. Therefore, under such an anaerobic condition it is expected that the initial precipitate, if any, of oxides and hydroxides of iron will not be stable. They will sooner or later dissolve and reprecipitate as ferrous sulphides. The possibility of Fe to be precipitated as ferrous carbonate in the eastern part is not favourable, chiefly because of the presence of H_2S in that area.

In the Ashtamudy lake sediments Fe might have been fixed up either within the clay mineral structure as an essential ion (cation exchange) or externally to the clay mineral structure (adsorption).

Although illite and montmorillonite can accommodate Fe in their lattice, it is most likely that, greater part of the iron is fixed up in the montmorillonite as the same has inter-layer water, unsatisfied negative charge and highest cation exchange capacity of all the clay minerals (Nelson, 1962 b). The exchange reactions in 3-layered clay minerals in which iron will be fixed up by the montmorillonite is largely dependent on the valency state of Fe, which in turn is controlled by the prevailing environmental conditions of deposition. Therefore at the central and western parts of the lake, iron might be fixed up in montmorillonite by substituting Al^{3+} in the tetrahedral layers. This observation is in accordance with that of Hirst, 1962 b.

There are controversial view regarding the origin and manner in which Mn is incorporated into hydrolysate sediment. However it is generally conceded that Mn in sedimentary cycle is leached from the drainage basin as bicarbonates $[Mn(HCO_3)_2]$, but deposited as oxides in the form of organic and/or inorganic colloids, finely divided detrital grains and as cementation matrix. Correns (1941) considers that Mn is biologically extracted, while Kuenen (1941) considers that Mn is a chemical precipitate. Several inorganic and biological mechanisms for its incorporation into sediments have been reviewed

by Petterson (1945), Goldberg (1954) and Goldberg and Arrhenius (1958). Manganese is carried to the sea, both in solution and as a constituent of sediment debris. The bicarbonate in weathering solutions, derived from the dissolution of Mn-bearing minerals of the drainage area of continental geological formation, on attaining a slight degree of alkalinity, mostly changes to unstable $Mn(OH)_2$. The divalent Mn is readily oxidised to quadrivalent state when the solutions come into contact with the atmospheric or dissolved oxygenated area and is precipitated as $Mn(OH)_2$ or finely divided MnO_2 , and the precipitation often takes place in freshwater. The importance of physico-chemical factors and the effect of pH and Eh on the precipitation of Mn have been described in detail by Garrels (1960).

In the present investigation (Fig. 4.1), the progressive depletion of Mn both in the bulk and clay fractions directly reflects the source rock of the catchment areas of the river Kallada. The river drains through the khondalite rocks which is characterised by minerals containing Mn. At the eastern part of the lake Mn is present as manganous sulphide because of the reducing environment and availability of sulphide ions.

The high significance of positive correlation with Fe indicates that these two elements are co-precipitating

as insoluble ferric manganic hydrate. Such a co-precipitation of Mn and Fe is favoured by the negatively charged hydrous manganese oxides in colloidal form (Hirst, 1962 b) with a consequent affinity for cations; i.e., co-precipitation of Mn and Fe is favoured by the negatively charged $\text{Mn}(\text{OH})_4$ sols and positively charged $\text{Fe}(\text{OH})_3$ sols.

The Mn-content of the Ashtamudy lake sediments does not show significant correlation with organic matter either in bulk or clay fractions. It is not known whether the relationship is primary or secondary. Kalesha (1980) has reported a good positive relationship between Mn and montmorillonite in the Kakinada-Pentukota shelf sediments and stated that Mn can be held in the lattice structure of clay minerals. However, no such relation is obtained for Mn with montmorillonite and the possibility of Mn held in the lattice of montmorillonite, can be ruled out as it has shown a negative correlation with CaO and K_2O and no correlation with Mg (Table 4.3 A and B).

The importance of titanium in the sediments as an index of sedimentation rates and in understanding of their genesis has been mentioned by many authors. Titanium in modern sediments and in particular, in the marine sediments have diverse origins - Minerogenous

(terrigenous and hydrogenous) and/or biogenous origin. It is also believed that the bulk of the Ti is incorporated during terrestrial weathering in the clay fraction at the time of its formation. This was substantiated by the observation of Degens (1965) who stated that most of the Ti is found in the clay fraction of the hydrolysate sediments. Rankama and Sahama (1950) have also pointed out that the Ti contained in the structures of ferric minerals (pyroxene, amphiboles, micas etc.) is brought into solution during weathering, but is promptly hydrolysed and incorporated into the hydrolysates.

Relatively higher amount of Ti in clays in the eastern part when compared to central part of the Ashtamudy lake confirms the fact that most of Ti in the sediments of Ashtamudy lake is derived from the rocks of the drainage basins of the river Kallada. The Ti in these sediments might have been contributed in the form of titanium dioxide. Probably the titanium dioxide hydrate is deposited along with tiny flakes of clay minerals (Goldschmidt, 1954). The Ti mineral ilmenate occur as heavy mineral in these sediments. The absence of Ti mineral at the central part is attributed to the low content of Ti for the bulk fractions. The higher content of Ti at the western part compared to other parts of the lake directly reflects the

presence of Ti minerals especially ilmenite and rutile in the bulk fraction and also the source. The Ti minerals are mainly derived from the barrier beaches of Kayamkulam-Neendakara.

It is observed that the amount of Ti varies with sedimentation rate, where the sedimentation rates are high, sediments will be rich in Ti content. Eastern part of the lake is marked by high rate of sedimentation and this could be one reason for the higher content of Ti there.

The marginal positive correlation of Ti with Fe in the clays of the Ashtamudy lake sediments reveals the geochemical affinity between these two constituents. Landergren (1954) has also suggested the close relationship between Fe and Ti in the sedimentary cycle. Further, Goldberg (1954) on the basis of covariance of iron and Ti has pointed out that the Ti has been scavenged by hydrous ferric oxide. Such a co-precipitation is assumed to have taken place in the sediments of the Ashtamudy lake, since Ti generally occurs as anions and hydrated ferric oxide as positively charged colloids.

The role of clay minerals in concentrating Ti in the sediments of Ashtamudy lake is pointed out below. Eastern part of the lake consists mainly of

kaolinite, central part of more or less equal proportion of kaolinite and montmorillonite with little illite, and the western part by the dominance of montmorillonite. It is seen that Ti content for the clays slightly decreases to central part and then increases to western part. This decrease and increase cannot be explained in terms of clay mineral composition. That is, the role of clay mineral in the concentration of Ti is not significant. Likewise, Ti is not biologically concentrated in the sediments of Ashtamudy lake as it has revealed a high significance of negative correlation with organic matter. (Table 4.3 A and B).

In short, the Ti content of the Ashtamudy lake is mainly due to the Ti minerals in the case of bulk sediments and deposition of very fine crystalline TiO_2 along with tiny flakes of clay minerals and the co precipitation with hydrous ferric oxide in the case of clay fractions.

The enrichment factors for the major elements were also determined as in the case of heavy metals (trace elements) in the Ashtamudy lake sediments (Table 4.4 A and B). The enrichment factor is compared with the average crustal abundance, as given by Taylor (1964), in order to differentiate the natural and anthropogenic loading of the

Table 4.5. Comparison of enrichment factors
(average) for the major element with
the average crustal abundance*

Major element	Bulk sediment	Clays	Average	Average crustal abundance
P_2O_5	7.13	5.67	6.40	0.204
Na_2O	0.64	0.77	0.71	3.18
K_2O	0.33	0.32	0.33	2.51
CaO	1.90	0.75	1.33	5.81
MgO	1.50	2.31	1.91	3.86
Fe_2O_3	1	1	1	6.44
MnO	0.34	0.46	0.40	1.23
TiO_2	2.44	1.16	1.80	0.95

*Taylor, 1964.

elements in the lake sediments. From Table 4.5, it is clear that only two elements namely P_2O_5 and TiO_2 have exceeded the average crustal abundance indicating some sort of abnormal accumulation. This higher content is not due to any human interference, but due to the presence of phosphatic minerals like monazite and apatite, and titanium minerals like rutile and ilmenite. This is discussed in detail earlier in this chapter. All the remaining elements shows only normal accumulation.

CHAPTER - 5

GEOCHEMISTRY OF TRACE ELEMENTS

5.1. INTRODUCTION

The products of weathering from the continental areas are transported to the marine deposition basins by rivers and streams, in solid state and in solution. The trace elements are transferred to the depositional sites as constituents of detrital minerals, structurally bound in various clay minerals found at or near the site of weathering and as oxide coatings on clay mineral surfaces. Considerable quantities of these elements are also carried into solutions and get incorporated in sediments by different processes at varying rates based on physico-chemical conditions prevailing in the depositional environments. Trace elements are removed from the solutions by (1) adsorption into organic and inorganic colloidal suspended material, (2) extraction by marine organisms and by precipitants like Fe and Mn-oxides or by sulphide ions.

In recent years, the chemical composition of sediments, especially, the distribution of trace elements, is used in distinguishing depositional environment.

Generally it is the relative concentration of certain elements which provides clue to the environments. Krejci-Craf(1964,1966), Degens (1968) -and Ernst (1970) provide detailed information on the geochemical analysis of depositional environment. Generally, the amount of trace elements in modern sediments is controlled by the elemental solubility in the waters, feeding capacity of the drainage basin and by the prevailing environmental conditions. In clay minerals, the trace elements are concentrated by adsorption, chemisorption, and ion-exchange processes. The geochemical properties that control the trace element-content in the clay minerals are ionic radius, valency, chemical bonding, ionisation potential, electronegativity, temperature, pressure etc. Besides the chemical factors, elemental solubility in waters and sedimentation rates in depositional basin also influence the trace element content of the sediments. The precipitating manganese and ferric oxides and other precipitates may entrap some of the trace elements. Similarly, the flocculating clay particles adsorb certain amount of trace elements. Planktonic organisms readily extract trace metals from seawater which are vital for their life. These organisms on death, settles to bottom where they decay and the trace element content is released and added to the

sediments by chelation and other processes. Likewise, benthic organisms also contribute their share to trace element content. Thus, kind and content of the trace elements in the sediments are largely determined by the composition of rocks in the drainage basin of the rivers. The relative proportions of each mineral and multimineral components obviously exert a fundamental control on the chemical composition of the sediments.

5.2. METHOD OF STUDY

The trace elements in the bulk and clay fractions were determined from the solution which is prepared in the manner as mentioned earlier, by Atomic Absorption Spectrophotometer (Perkin Elmer-2380, West Germany).

5.3. RESULTS AND DISCUSSION

The trace elements determined are Zn, Cu, Cr, As, Cd, Ni, Pb and Co. The concentration of these elements (in ppm) are given in Table 5.1 and 5.2 for the bulk and clay fractions respectively. Cobalt was found to be below detectable range. The mean and the standard deviations are furnished in Table 5.2.

5.3.1. Zinc

There is a wide variation in the content of Zn from a minimum of 82 ppm to 1685 ppm in the bulk and

Table 5.1.A. Concentration of trace elements in bulk sediments (in ppm)

Sample No.	Zn	Cu	Cr	As	Cd	Ni	Pb	Co
1	2	3	4	5	6	7	8	9
<u>Eastern part</u>								
23	147	103.5	227.5	860	4	115.5	1345	nd
24	112	102.5	210	680	0.00	85.5	615	-
25	196.5	124.5	276.5	990	6	135.5	1185	-
26	155	112	269.5	1545	5.5	109	1120	-
27	189	114	239.5	1360	3.5	132.5	1280	-
30	154.5	62.5	232.5	800	0.00	102.5	555	-
32	180	80	302.5	990	5.5	143	620	-
36	191.5	102.5	189	505	4.5	104	605	-
40	373.5	95.5	150.5	1205	0.00	129	645	-
44	294	48.5	127.5	1205	0.00	83.5	570	-
48	173	42.5	139.5	1245	3.5	84	595	-
52	380.5	27	101.5	1490	6	65.5	635	-
54	142	41	123	1390	3	64	605	-
58	1247	46.5	502.5	1330	2.5	217	600	-
59	110.5	26.5	176	1070	0.0	115	550	-
60	142.5	45.5	165.5	1120	0.00	112.5	585	-
62	288.5	193.5	184	1700	1.0	118.5	600	-
64	677.5	62	154.5	695	0.00	118.5	605	-
<u>Central part</u>								
10	181	102	452	1100	8	145.5	375	-
11	108	30.5	216.5	1410	3	106.5	845	-
12	246	107.5	250	590	5	117	590	-

Table 5.1.A. Contd.

1	2	3	4	5	6	7	8	9
13	126	96.5	266	1325	2	138.5	500	nd
14	131	100	228.5	2255	10.5	144.5	725	-
15	140	87.5	243.5	790	2	133	560	-
20	435.5	53.5	306	1430	0.00	153	1115	-
21	82	10	159.5	1405	3	114	1255	-
22	199.5	100	232.5	1175	- 1.5	118	620	-
65	146	70	242	1360	0.00	125	655	-
67	177	81.5	162.5	1235	0.00	100.5	615	-
68	140	49.5	172.5	825	0.00	104	550	-
70	425	61.5	202	325	0.00	74.5	540	-
72	160.5	66	268	1670	0.00	140.5	615	-
74	161.5	49.5	264	1155	0.00	191.0	615	-
75	163	37	202.5	1680	0.00	142	580	-
77	1685.5	30	252	1275	0.00	110.5	615	-
78	477	26.5	262.5	915	0.00	150.5	580	-
79	330.5	24.5	225	585	0.00	115	580	-
81	172	0.00	353.5	1260	0.00	151	590	-
83	201	10	262.5	920	0.00	88	590	-
84	180.5	0.00	313.5	1495	3.5	115.5	605	-
86	414.5	7	230.5	745	1.5	90.5	580	-
87	190	3	285	1420	2.5	113	605	-
88	215.5	0.00	237	1650	0.00	90.5	580	-

Table 5.1.A. Contd.

1	2	3	4	5	6	7	8	9
91	115	0.00	91.5	1225	1.5	53	550	-
93	240.5	0.00	231.5	1750	1.00	143	540	-
94	128.5	0.00	268	750	0.00	162	615	-
95	203.5	0.00	236	1375	7.5	174	625	-
<u>Western part</u>								
1	153.5	113.5	349	1190	7	53	920	-
2	191	102.5	286	1430	5	41	740	-
3	113.5	53.0	149	1690	8	53	550	-
4	235	148.5	304.5	1415	2	126.5	590	-
5	93.5	31	146	1665	8.5	98	535	-
6	794	30.5	139.5	1490	3.5	58.5	315	-
7	340.5	194	295.5	670	4.5	195	690	-
8	126.5	91.5	208	1535	1.5	85	460	-
9	117	33.5	127	595	3	66.5	520	-
17	319.5	73.5	493	690	0.00	74.5	1045	-
97	162	0.00	225	1970	2.5	146.5	690	-
98	172	0.00	161	880	0.5	105.5	620	-
99	160	0.00	247.5	2150	4	139.5	610	-
100	131.5	0.00	231.5	880	0.00	132	555	-
101	568.5	17.5	249.5	1595.0	0.5	124	550	-
102	106	0.00	144.5	1620	0.00	68.5	560	-
103	101	0.00	144.5	1145	0.00	22	690	-

nd - not detected

Table 5.1.B. Concentration of trace elements in clays (in ppm)

Sample No.	Zn	Cu	Cr	As	Cd	Ni	Pb	Co
<u>Eastern part</u>								
28	283	81.5	257	875	4	142.5	580	nd
29	229.5	69	189.5	55	1.5	81	1355	-
31	697.5	140	241.5	895	0.00	140	640	-
34	403	85.5	218	1500	3.5	136.5	640	-
37	225	57	206	945	4	90	605	-
61	216.5	147.5	290	1235	0.00	140.5	610	-
63	167	74	312.5	1340	0.00	144	630	-
<u>Central part</u>								
16	130.5	68	302	825	0.00	158.5	1200	-
19	859	75.5	238.5	1655	5	111.5	1195	-
66	144	57	199	1070	0.00	141.5	625	-
69	129	47.5	212.5	1010	0.00	107	585	-
71	198	33	191	600	0.00	121	565	-
73	367.5	87.5	272.5	1100	3	172	545	-
76	267	33	228	1730	0.00	126.5	597.5	-
80	169	12.5	277.5	1675	0.00	145.5	590	-
82	389.5	2	263.5	920	0.00	108.5	580	-
85	236.5	10.5	298.5	1195	0.00	117.5	585	-
89	318.5	24	315	695	0.5	122.5	595	-
92	1072.5	40.5	162	1350	0.00	96	560	-
96	242	45.5	237	2055	5	190.5	690	-
<u>Western part</u>								
18	284	129	376.5	1325	2	168	1290	-

nd - not detected

Table 5.2. Mean and standard deviation for the trace elements against river distance

Distance	No. of samples	Zn		Cu		Cr		As		Cd		Ni		Pb	
		\bar{x}	σ_x	\bar{x}	σ_x	\bar{x}	σ_x	\bar{x}	σ_x	\bar{x}	σ_x	\bar{x}	σ_x	\bar{x}	σ_x
0-1	4	470.00	460.59	35.25	8.72	225.75	162.07	1320.00	155.24	4.00	2.86	115.38	62.16	597.50	30.52
1-2	2	233.50	60.5	45.50	3.00	133.50	6.00	1225.00	20.00	1.75	1.75	83.75	0.25	582.50	12.50
2-3	7	283.71	182.63	97.64	27.21	218.36	36.68	1036.43	329.16	2.50	2.24	115.29	17.17	778.57	271.32
3-4	7	220.93	90.53	83.93	23.15	231.21	45.59	887.14	411.70	2.93	2.29	119.93	24.25	797.14	303.09
4-5	5	305.80	191.29	121.30	45.14	227.60	53.34	1133.00	346.42	1.30	1.47	122.20	9.22	756.00	294.57
5-6	8	262.75	246.95	54.63	19.76	230.31	52.85	1261.88	252.52	1.00	1.80	125.00	17.63	826.25	284.17
6-7	8	440.36	485.16	52.56	22.07	225.31	42.09	1073.13	465.95	0.00	0.00	122.94	25.94	661.56	204.87
7-8	10	207.75	77.08	47.30	34.46	260.55	35.88	1392.00	501.45	2.80	3.55	155.70	23.90	613.50	53.11
8-9	7	216.00	83.53	30.86	45.21	265.00	23.05	1107.14	392.10	1.64	1.83	124.64	22.90	579.29	44.27
9-10	6	354.58	336.97	31.75	34.36	241.83	113.38	1170.83	215.70	2.33	2.73	251.50	334.12	582.50	137.60
10-11	12	239.17	183.62	46.33	61.85	215.67	68.38	1300.40	443.70	2.42	2.29	106.30	36.82	563.30	97.50
11-12	6	210.92	162.65	28.83	37.93	218.00	52.97	1481.67	404.34	2.92	3.01	85.17	47.57	615.83	74.52
12-13	2	218.75	65.25	121.25	7.75	362.75	13.75	1257.50	67.50	4.50	2.50	110.50	57.50	1105.00	185.00
13-14	1	319.50	0.00	73.50	0.00	493.00	0.00	690.00	0.00	0.00	0.00	74.50	0.00	1045.00	0.00

\bar{x} - Mean value σ_x - Standard deviation

129 ppm to 1073 ppm in the clays (Fig. 5.1). The average content of Zn in the bulk and clays are 258.71 ppm and 316.43 ppm respectively. The clays of the Ashtamudy lake sediments contain more Zn. This value is much higher than the reported values for the Godavari (Naidu, 1968; Dora, 1978), modern deltaic sediments of Krishna (Seetaramaswamy, 1970), Kolleru lake (Rama Murty, 1972), Cauvery (Seralathan, 1979), Cochin backwaters (Venugopal et al., 1982), and Iskapalli lagoon (Subba Rao, 1985). It is seen from Tables 5.1 and 5.2 that Zn is more concentrated at the eastern part in the bulk fractions and at the eastern and central parts in the clays. In the bulk fraction of sediments, Zn has shown a high level of positive correlation with Fe, whereas in the clays it has shown marginally significant positive correlation with Ca (Tables 4.3 A and B).

Our knowledge of the geochemistry of Zn in hydrolysate sediments is obscure. Shimp et al. (1970,1971), have made comprehensive study of the factors controlling the concentration of Zn in recent lake sediments. They stated that organic matter has got prominent role in the concentration of Zn. Sediments in the eastern part of the Ashtamudy lake show higher content of Zn, where there is a higher proportion of organic matter. But in the present study, no correlation between Zn and organic matter is noticed. Hence Zn is not concentrated, to any significant extent, in organic matter.

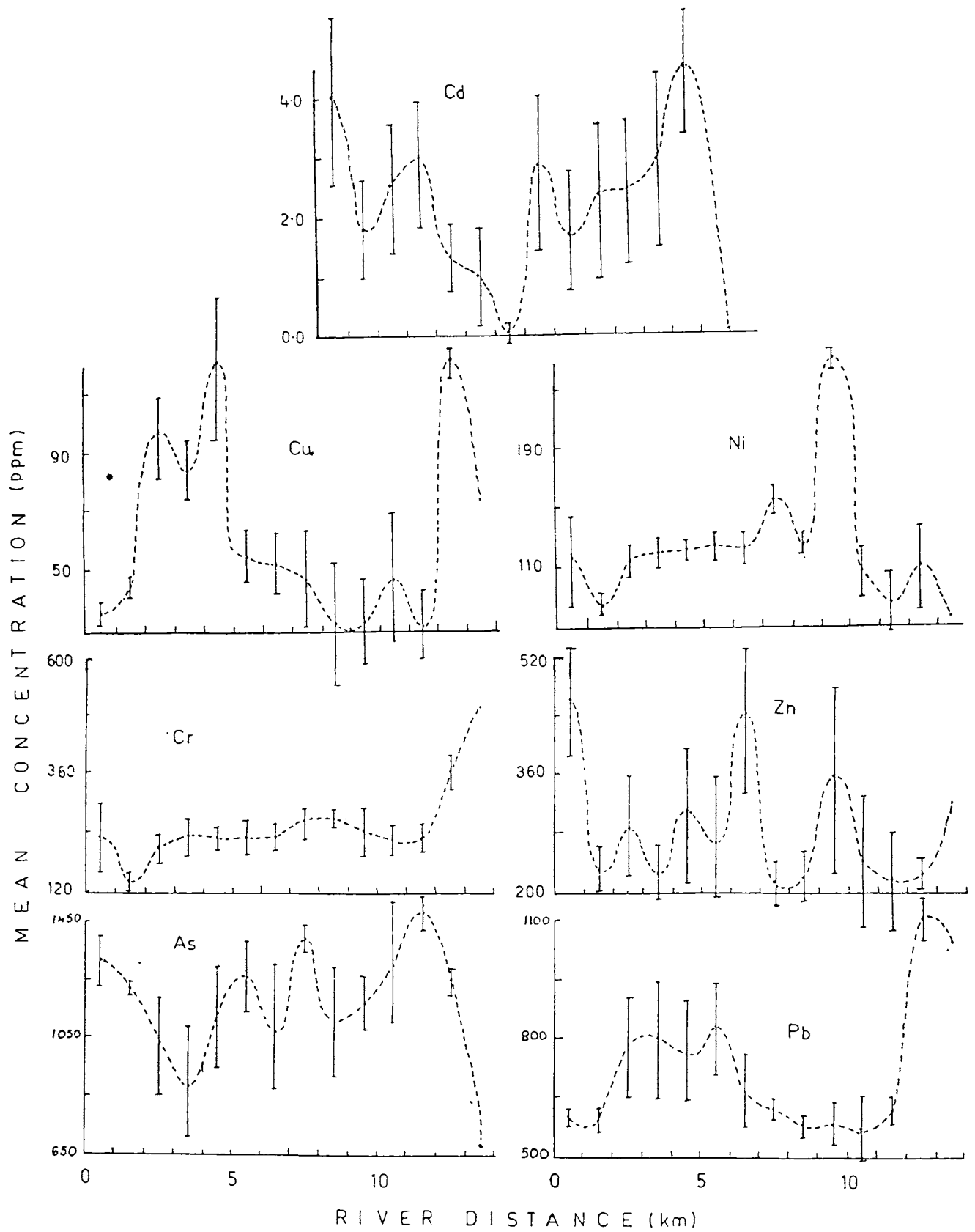


Fig. 5.1. Mean values of trace elements against river distance (vertical bars indicate r.m.s. deviation)

During weathering of acid rocks, some part of Zn is carried in solution. Because of its great affinity for sulphur, it is precipitated as sulphide in the zones enriched with sulphur. As mentioned earlier, the eastern part of Ashtamudy lake is noted for the prevalence of a reducing environment, which in turn, might have favoured the higher concentration of Zn in this zone. Hence, it can be stated that, Zn in the clays is precipitated as sulphide in the form of $Zn(HS)_3$ (Lu and Chen, 1977). Also a relative higher pH facilitated a higher content of Zn, either by precipitation or adsorption.

Zn can diadochically replace ferrous iron and magnesium in the silicate mineral structures because of a similar ionic radii of iron and magnesium. There is an increased migration of Zn in regions of humid climate, where continental sediments show a neutral or acid reaction, and a low migration in alkaline and low humidity regions (Sankov, 1961). A part of Zn is adsorbed either by ferrous sulphide or oxide, as it has shown positive correlation with Fe. Hence, adsorption of Zn by ferrous sulphide can be one reason for the higher content of Zn in the sediments of eastern part of the lake.

Relatively finer texture of the sediments can be considered as another reason for the higher content of Zn at the eastern parts. Moore (1968) stated that Zn travels with clays and explained it as an environmental enrichment in sulphides with finer clastics. Because of the higher exchange capacity of Smectite, it can be considered that a part of Zn is fixed up in clays. Experiments of Demumbrum and Jackson (1956) showed that montmorillonites have high exchange capacity, specifically for cations such as Cu^{2+} and Zn^{2+} in acid and neutral conditions. Hence, it can be considered that a part of Zn is tied up in montmorillonite and this may be the reason for the higher content of Zn at the central part. At seawater conditions montmorillonite suspensions can even extract several ppm of Zn out of seawater to make the Zn level down to that in average seawater.

Due to low solubility of Zn in natural waters and its behaviour during chemical weathering, its major transport and accumulation in the sedimentary environment is to be expected in detrital matter. Magnetite is a better carrier of Zn. Therefore detrital minerals make only a very minor contribution of Zn to the Ashtamudy lake sediments.

Coming to the sediments of the western part of the lake, the concentrations of Zn is comparatively less to that of central and eastern parts. This could be mainly due to the lack of finer sediments. However, the Zn is concentrated at the western part of the lake in sediments by the association of Zn with iron oxides, and montmorillonite.

In the Ashtamudy lake sediments, Zn shows no relation with phosphates and hence there is no deposition of Zn along with phosphates. Therefore the Zn content of the Ashtamudy lake depends on the texture of the sediment, clay mineral, and Fe content.

5.3.2. Copper

The concentration of Cu (in ppm) in the bulk and clay fractions of the Ashtamudy lake sediments is given in Tables 5.1 and 5.2. The average content for the bulk and clays are 57.4 ppm and 89.21 ppm respectively. It is found that Cu is concentrated more in clays than in bulk. Cu-content in Ashtamudy lake is higher than in Vembanad lake (Murty and Veerayya, 1981), Cochin backwater (Venugopal et al., 1982) and Cauvery river (Subramaniam et al., 1985), but lower than in Kolleru lake (Rama Murty, 1972), Iskapalli lagoon (Subba Rao, 1985), and modern deltaic sediments of Cauvery river (Seralathan, 1987).

Regarding the regional variation of the Cu-content in the lake sediments (Fig. 5.1), it decreases from eastern (av. 79.44 ppm) to central part (av. 40.47 ppm) and then increases to western part of the lake (av. 52.29 ppm). In general, there is a depletion of Cu content from eastern to western part in case of bulk fraction and in the clays, a similar trend is observed, but the maximum concentration is at western part (Fig. 5.1). That is, an enrichment of Cu towards the western part of the lake. From Table 5.3 it is seen that Cu is having a high level of positive correlation with Mn in the bulk sediments and marginally negative correlation with Fe and P in clays (Tables 4.3A and B).

Like other trace elements, Cu is found in sediments as exchangeable ions bound in organic compounds, in the crystal lattices of alumino-silicates and other minerals. The mobility of copper is high in solution and occurs as Cu^{2+} ion. It is removed from the solution as sulphide in reducing sediments and as copper oxy-salts in high pH environments. Cu^{2+} can replace Fe^{2+} and Mg^{2+} . In the zones of weathering, Cu is rapidly oxidised and acquires the ability to migrate (Perelman and Borisenko, 1962). For example, sulphides are oxidised to form solutions of copper sulphate that migrate readily in natural waters. Cu is stable in

solution, because of the stability of nitrogen complexes of the transition ions (Fairbridge, 1972). The various process by which Cu can be removed are as precipitate of insoluble compounds, precipitate of sulphide ion in zones of low oxidation potentials, adsorption by material such as ferrous sulphate, hydrated ferric oxide, hydrated Mn oxide, and clays and removal by metabolic action of organisms. Wedephol (1978) stated that high concentrations of Cu can be adsorbed on clay minerals, iron oxides and organic matter. Fixation of Cu by clay minerals by adsorption and cation exchange has been also pointed out by Wakeel and Riley (1961) and Hirst (1962 b).

In the present study, it is assumed that the higher concentration of Cu in the clay fractions of the Ashtamudy lake sediments is due to the adsorption and cation exchange by the same. This is inferred from the fact that it has shown negative correlation with Fe and P. At the eastern part of the lake, precipitate of sulphide ion is considered as an important factor, since the necessary reducing environment and very low oxidation potential are found there. Goldschmidt (1954) reported that Cu-ion can be considerably concentrated by accumulation under reducing conditions in sulphide-bearing mud from stagnant anaerobic bottom waters. Gorham and Swain (1965) found higher content of Cu in the reduced muds

than in the oxidate crusts of English lake. Hence, it may be reasonably concluded that the reducing environment with low oxidative potential favoured the concentration of Cu at eastern part of the lake.

The increasing trend of Cu-content from eastern to western part, where the highest concentration is obtained, can be explained in terms of adsorption and cation exchange of smectites. Though many workers pointed out that the higher content of Cu with illite (Wakeel and Riley, 1961; Hirst, 1962 b; Venkatarathnam and Tilak, 1968; Durgaprasada Rao, 1971), in the present study, the highest concentration of Cu is found associated with montmorillonite which dominates the central and western parts of the lake. Montmorillonite seems to have a high cation exchange capacity especially for Cu and Zn (Demumbrum and Jackson, 1956). Rao et al. (1974) have found a high content of Cu in association with montmorillonite.

Therefore, it can be concluded from the above discussion that the Cu-content of the Ashtamudy lake sediments, directly depends on the fine texture and the presence of clay minerals.

5.3.3. Chromium

The various levels of Cr-concentrations in the bulk and clay fractions of the Ashtamudy lake sediments

are provided in the Tables 5.1 and 5.2. The average content of Cr in the bulk sediments is 228.71 ppm and that in the clays is 289.12 ppm. As in the case of other trace elements, Cr is more concentrated in the clays of the Ashtamudy lake sediments and it increases from the eastern to western part. In the case of bulk sediments, it decreases towards central part and then increases towards western part. In both cases, maximum concentration is seen at the western part. The regional distribution of Cr is given in Fig. 5.1. The concentration of Cr when compared with that of modern deltaic sediments of Cauvery river (Seralathan, 1987), Cauvery river basin (Subramanian et al., 1985), deltaic clays of the Gulf of Paria (Hirst, 1962 b), deltaic sediments of Mahanadi river (Satyanarayana, 1973), and in the inner and outer continental shelf off the east coast of India (Durgaprasada Rao and Poornachandra Rao, 1973) is found to be higher. The inter-relationship of Cr with other elements is given in Tables 4.3 A and B. It shows a high level of positive correlation with Fe, Mn and Ni in the bulk fraction of the sediments and marginal level of positive correlation with Fe and K in the clays.

In silicate minerals, Cr^{3+} shows diadochous replacement with Fe^{3+} and Al^{3+} , and in some cases in spite

of the valency differences, chromium replaces ferrous iron and magnesium in many minerals (Rankama and Sahama, 1950). On the basis of ionic radius, electronegativity and ionization potential, Cr^{3+} would be expected to proxy more readily for Fe^{3+} than Al^{3+} . Besides, Cr^{2+} exhibits diadochy with Mg^{2+} in magnesium-rich minerals (Synder, 1959). Chromium sometimes replacea Al in kaolinites and Fe and Mg in smectites. Mukherjee and Sahu (1984) while carrying out experiments on the sorption and desorption of toxic heavy metals in the clay-rich soil showed that the adsorption and desorption maximum sequence as $\text{Cr} > \text{Hg} > \text{Pb} > \text{Cu} > \text{Cd} > \text{Zn}$ and $\text{Cd} > \text{Zn} > \text{Cu} > \text{Cr} > \text{Pb} > \text{Hg}$ respectively for a pH of 4.

The variation in the concentration of Cr in the Ashtamudy lake sediments especially in the clays can be explained as follows. As evidenced from the marginal level of correlation with Fe (Table 4.3 A and B), it can be inferred that Cr may be concentrated due to adsorption by the hydrated ferric oxide. The higher concentration of Cr at the western part of the lake compared to eastern part may be due to the replacement of Fe and Mg in montmorillonite and adsorption by ferric oxide. At the eastern part Cr is concentrated by the replacement of Al in kaolinite. Chromium shows no significant correlation with organic matter which implies that concentration of Cr in

organic matter in the different regions of the Ashtamudy lake is insignificant. Hence, the higher concentration of Cr in the Ashtamudy lake sediments are mainly due to the adsorption of Cr by ferric oxides and replacement of Al in kaolinite and Fe and Mg in smectite.

5.3.4. Arsenic

Among all the trace elements in the Ashtamudy lake sediments (Tables 5.1 A and B), as shows the highest concentration. The average As-content in the bulk sediment is 1220.43 ppm and in clays it is 1174.80 ppm. Unlike Zn, Cu, Cr, Ni and Pb, As is concentrated more in the bulk fraction of the Ashtamudy lake sediments. The As-content in the clays of the lake increases from eastern and the western part, whereas in the bulk it decreases towards central part and then increases to western part. Regarding the inter-relationship between other elements, As has shown marginal level of positive correlation with Cd in the bulk samples and in the clays, it has shown marginal negative correlation with Na and positive relation with Ni (Tables 4.3 A and B). The distribution of As in the lake sediments is given Fig. 5.1.

In a reducing environment, As will be precipitated as sulphide and in an oxidising environment

it will be precipitated as oxide. At the eastern part, As is precipitated as arsenic sulphide because of the reducing environment at this region, whereas at the western part it is precipitated as arsenic oxide. Burton and Liss (1976) stated that arsenic form stable bonds with organic sulphur and therefore remain in sediments with higher organic matter content. The As-content of the Ashtamudy lake sediments does not follow the fine texture of the sediments and does not reflect the source. Interelemental relationship indicates correlation among the transition elements suggesting their co-genetic behaviour within the lake. Preston et al. (1972) showed that, in coastal marine environments also, a large fraction of heavy metals are associated with suspended matter similar to transport of heavy metals in rivers.

Apart from the chemical effects, some micro-biological processes also take place in the sediment which can result in a mobilization of metals and certain bacteria are able to methylate arsenic. This methyl arsenic is released from the sediment and may become concentrated in aquatic organisms.

The anomalous concentration of As in the Ashtamudy lake sediments reveals the anthropogenic

contribution which is discussed in detail in the pollution aspects of the lake sediments (Section 5.4).

5.3.5. Cadmium

Cadmium is also concentrated more in the bulk than in the clay fraction in a manner similar to As. The average content of Cd in the bulk and clay fractions of the Ashtamudy lake is 2.43 ppm and 1.63 ppm respectively. The average concentration of Cd in the bulk fractions of the lake sediments at the eastern part is 2.5 ppm, central part 1.81 ppm and western part 2.97 ppm, whereas for the clays it is 1.86 ppm, 1.04 ppm and 2 ppm respectively (Tables 5.1 A and B). In both the cases, the concentration of Cd increases to both the zones away from the central part and maximum concentration is seen at the western part of the lake (Fig. 5.1). The average concentration of Cd in the Ashtamudy lake sediments is higher than the average crustal concentration and that in granite, which is only 0.2 ppm. Cadmium shows marginally significant positive correlation with As in the bulk and does not show any significant correlation with any of the other elements either in bulk as clay fractions (Tables 4.3 A and B).

Very substantial amounts of Cd are incorporated with sulphide phases of sediments under stagnant summer

conditions which lead the bottom waters becoming anoxic, when the water is renewed and free oxygen is again present Cd is partly released (Burton and Liss, 1976). One important adsorption mechanism operative in the removal of trace elements from solution during estuarine mixing may be the formation of iron oxide coatings on clay particles which have acted as negatively charged nuclei for the adsorption of hydrolysis products of iron. Aston and Chester (1973) have suggested that the oxide coatings formed on detrital particles in the estuaries may remove trace elements from solution and may also prevent trace element desorption from ion exchange sites. The sorption behaviour of some elements is very sensitive to the pH of the freshwater or seawater. Thus a change in pH may result in large differences in distribution coefficients. The most sensitive change in behaviour for Cd is within the pH range of 6 to 8. The pH of seawater is generally close to 8, the range in freshwater is frequently between 6 and 8, thus highly influencing the sorption behaviour. Another influence on the sorption behaviour of elements in estuarine system is the presence of particulate and dissolved organic matter. At a pH of 8.1, the adsorption of Cd is suppressed while desorption is enhanced. From the Eh-pH diagram of Cd (Burton and Liss, 1976), it is seen that the most stable solid phases are CdCO_3

and CdS whereas the dominant stable dissolved species are Cd^{2+} and $\text{Cd}(\text{OH})_2$.

From the above discussion it can be concluded that the eastern part of the lake, Cd is held as CdS. This inference is drawn because of the prevalence of reducing environment at the eastern part. At the western part of the lake Cd is present as CdCO_3 , as this zone has got maximum CO_3 concentration. At the central part Cd is in its oxide form and hence has a lower value. Hence this could explain the increase of Cd to either zones of the central part and regional variation in the Cd-content of Ashtamudy lake sediments.

5.3.6. Nickel

The concentration of Ni in ppm, as given in the Tables 5.1 and 5.2 shows that the Ni content of the Ashtamudy lake sediments is remarkably higher than Vembanad lake and Cochin backwater (Murty and Veerayya, 1981 and Venugopal et al., 1982). The higher content of Ni is found associated with clays of the Ashtamudy lake. The average content of Ni for the bulk and clays are 110.27 ppm and 141.71 ppm. In the bulk fractions the Ni content increases from eastern (average 113.06 ppm) to central part (124.28 ppm) and then decreases to western part (average 93.47 ppm). In the clays a

progressive enrichment is seen from eastern part to (average 124.93), central part (average 132.19 ppm) and to western part (average 168 ppm) Ni shows highly significant positive correlation with Fe, organic matter and Na and a negative relation with Ti, whereas in the clays marginally significant positive correlation with Cr, Ti and a negative relation with Na (Tables 4.3 A and B). The regional distribution of Ni in the lake sediment is given in Fig. 5.1.

When compared with the Ni content of Kolleru lake, Iskapalli lagoon, Cauvery river basin, Lake Michigan and muds of English lakes, the Ni content of the Ashtamudy lake sediments is higher especially in the clays. It is even higher than that of the modern deltaic sediments of Cauvery river, (Seralathan, 1979), Gulf of Paria (Hirst, 1962 b), inner and outer continental shelf off east coast of India (Durgaprasada Rao and Poorna Chandra Rao, 1973) and in the shelf sediments off west coast of India (Murty et al., 1978 a).

Nickel occurs in divalent state in rocks and does not form trivalent compounds. The fixation of Ni in soils and sediments is caused by the hydrous iron oxide. Nickel is able to replace Mg isomorphically, especially in silicates and to a lesser degree in metasilicates because

of their similar ionic radii. Besides Fe and Mg, it can also substitute Na^+ in silicate minerals. Ni with Mg and Si can travel long distances in water and gets precipitated as complex hydrous silicates with layer lattices when the water is neutralized. Unlike Fe and Mn, Ni tends to be in solution and is carried to longer distances and is deposited in the hydrolysate sediments (Rankama and Sahama, 1950). Moreover, in estuarine sediments, it is seen that Ni have similar concentrations in both oxidising and anoxic sediments (Burton and Liss, 1976).

Adsorption is one of the most important process which determines the concentration of trace elements (Krauskopf, 1956) and recent studies on the trace elements in the sediments of southern lake Michigan showed that adsorption by organic matter is an important factor in those sediments (Shimp et al., 1970,1971). A review of associations between metals and organic matter in sediments has been given by Saxby (1969) and the interaction between metals and humic substances have recently been discussed by Schnitzer and Khan (1972); the order of stability follows Irving-Williams series: $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Ni}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+} > \text{Fe}^{2+} > \text{Mn}^{2+} > \text{Mg}^{2+}$.

The variation in Ni-content of the Ashtamudy lake sediments can be explained in terms of adsorption

by Fe, organic matter and by either adsorption or cation exchange in clay minerals. At the eastern part of Ashtamudy lake, precipitation of Ni has taken place due to adsorption by ferrous sulphide and organic matter. This inference is drawn from the positive correlation exhibited by Ni in the bulk sediments which contain higher amount of organic matter and Fe. Adsorption of Ni by organic matter leading to higher concentration has been stressed by Nicholas and Loring (1962) and Hirst (1967 b). At the central part, the bulk sediment shows higher concentration of Ni which is due to the adsorption of Ni by hydrous iron oxides, organic matter and clay minerals, and the decrease to the western part of the lake is due to the lack of the aforesaid factors which will concentrate Ni.

It is seen that the Ni-content is more in the clays fraction of the Ashtamudy lake sediments than in the bulk sediments and there is an enrichment of Ni towards eastern to western part of the lake. This is explained by the presence of clay minerals which fixes Ni in them, either by adsorption or ion exchange property. During weathering, Ni remain largely in the solid products of disintegration and is deposited in the hydrolysate sediments. Therefore it can be considered that a significant part of Ni might

have been held up in clay minerals either by adsorption or cation exchange mechanism. During weathering, Mg is leached relative to Ni. Under conditions required for the formation of smectite, Ni will be retained whenever Mg is retained in it (Hirst, 1962 a). Hence it can be considered that a part of Ni is fixed in smectite which is the predominant clay mineral at central and western parts. Higher concentrations of Ni in montmorillonite relative to other clay minerals have been observed by Hawkins and Roy (1965) and concluded that Ni strongly favours octahedral coordination. Therefore it can be expected that Ni substitutes Mg in the octahedral layers of montmorillonite lattice. So, from the discussion it can be concluded that Ni in clays is mainly due to cation exchange in montmorillonite and partly due to adsorption along with organic matter.

5.3.7. Lead

The concentration of Pb in ppm is given in Tables 5.1 and 5.2 for the Ashtamudy lake sediments. The average concentration of Pb in the bulk fraction is 666.81 ppm and in clays it is 899.81 ppm. The Pb content of the Ashtamudy lake sediment is higher in clays. In the bulk samples the Pb content shows a gradual decrease from eastern (average 739.72 ppm) to central part

(average 634.83 ppm) and then to western part (625.88 ppm). In clays, an enrichment in Pb content from the central part (average 686.58 ppm) to both the zones of the lake, viz. eastern (average 722.86 ppm) and western parts (1290 ppm) is observed (Fig. 5.1). Regarding the interrelationship of Pb with other elements, it has shown marginally significant positive correlation with P and Zn and negative relation with K for the bulk of the sediments whereas in the clays it has shown highly significant positive correlation with Na (Tables 4.3 A and B).

The average Pb content of the Ashtamudy lake sediments is very much higher than in the Iskapalli lagoon sediments, Cauvery river sediments and modern deltaic sediments of Cauvery river. It is even higher than the modern deltaic sediments of Mahanadi (Satyanarayana, 1973), Godavari (Dora, 1978), Krishna (Seetaramaswamy, 1970) and in the inner and outer continental shelf off east coast of India (Durgaprasada Rao and Poornachandra Rao, 1973).

Lead primarily occurs in the structure of K-feldspars and micas of magmatic and metamorphic rocks. Pb from weathering of magmatic and metamorphic rock is expected to be mainly accumulated in detrital sediments in their K-bearing minerals, micas and feldspars.

Pb replaces K in its structural position. Some amount of Pb, transported into the sedimentary environments is being adsorbed on clay minerals and ferric iron oxides (Krauskopf, 1959). Lead may be carried in solution in slightly acidic conditions. In neutral or somewhat alkaline water, the Pb ion become hydrolyzed and is readily co-precipitated with the hydroxides of more abundant elements or adsorbed by clay minerals. Lead can replace Ca^{2+} and K^+ diadocially in minerals. Some mobilized Pb is adsorbed on newly formed clay minerals as kaolinite (Wedepohl, Ed., 1978). Among all the clay minerals, kaolinite fixes maximum amount of Pb and then montmorillonite⁻ (Wedepohl, 1956). The clay minerals contain most of the lead in sediments.

In the Ashtamudy lake sediments, Pb does not show any specific correlation with Fe, or organic matter, and from that it can be inferred that Pb is not concentrated considerably by Fe-oxide and organic matter. The marginally significant negative correlation suggests a replacement of K by Pb. Therefore, it can be concluded that, in the Ashtamudy lake sediments, most of the Pb is associated with the clays.

5.4. POLLUTION ASPECTS OF THE LAKE SEDIMENTS

5.4.1. Introduction

The global definition for pollution as has been put forth by Tully (1966) reads as follows: Pollution can be considered as an alteration of natural environments, air, water, soil, which renders them offensive or deleterious to the aesthetic senses or for man's uses, or for the animals, fish, or crops which man wishes to preserve. It is to recognize that some degrees of alteration of the environment is a necessary consequence of human activities. But such alterations are not considered as pollution until they reach a limit of tolerance. For soil pollution, Rennie's (1966) definition stands good. He defined it as "any substance that is common or foreign to soil systems, which by its presence causes adverse effects, directly or indirectly, on the productivity of soil, is called a soil pollutant". Pollution is due to two principal factors viz. urbanization and technology. The four general categories of pollutants are inorganic compounds occurring from industrial activities, organic materials, radio activity, and minerals.

On a global basis, lakes, estuaries and lagoons are very important in the supply of dissolved and solid material to oceans. Garrels and Mackenzie (1971) have

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

There are basically three reservoirs for metals in the aquatic environment: water, sediment and biota. Metals in these reservoirs are determined by a complex equilibrium, governed by various physical, chemical and biological factors (Richard et al., 1983). A variety of ecosystems have been measured for their metal content (Segar et al., 1971; Chester and Stoner, 1974; Watling et al., 1974). Wolf and Rice (1972)

stated that nearly all metal content of aquatic ecosystems resides in sediments and water and that, the fraction in biota is small. Therefore, sediments are the major compartment in the estuarine environment for heavy metals and other toxic materials. Thus an understanding of the distribution of toxic heavy metals of environmental interest, among the different sedimentary phases, is necessary to assess the hazard associated with pollution of aquatic sediments and ecological impacts. Again, sediments are extremely important in the aquatic environment since they can act as heavy metal 'traps' or 'sinks' and recent studies in the coastal marine environment have indicated that the increased geochemical cycling of trace metals by man, can be well documented through sedimentological studies. Besides, a knowledge of the concentrations and distributions of heavy metals in sediments can play a key role in detecting sources of pollution in aquatic environment (Forstner and Wittmann, 1979). Renfro (1973) found that sediments are the major repository for both radio-nuclides and stable elements; in some cases holding over 99% of the total amount of a metal in these systems.

A number of chemical forms in which heavy metals are present in the aqueous environment as given by Burton and Liss (1976) are given below.

)	Dissolved	
Heavy metals in the aqueous environment)	Suspended matter)
)	Deposited sediment)
)	Interstitial water)
))
			Adsorbed
			Organic matter
			Iron and manganese oxides
			Lattice positions
			Discrete minerals

The suspended matter can act as a scavenger for heavy metals in the water. Therefore, a large part of the heavy metals present in the aqueous environment is associated with suspended particles. When the flow velocity slackens, coarser particles and aggregates will settle. This sort of sedimentation takes place especially in lakes and estuaries. However, part of the suspended matter, very fine particles and colloidal material has a very low settling velocity and may remain in suspension for long periods of time and so be transported over large distances. Mobilization or release of the heavy metals to the interstitial water is as follows. After deposition, the chemical environment of the sediments is different from that during transport. Generally, the pH is lower and the sediment often becomes toxic. Together with other changes in the chemistry of the sediment, these factors can give rise to the release of heavy metals.

From the above discussion, the significance of monitoring of aquatic sediments for pollution studies

Table 5.3.A. Enrichment factors of trace elements for the bulk sediments

Sample No.	Zn	Cu	Cr	As	Cd	Ni	Pb
1	2	3	4	5	6	7	8
<u>Eastern part</u>							
23	1.28	1.10	1.32	281.23	11.78	0.91	70.31
24	0.94	1.05	1.18	213.43	0.00	0.67	30.86
25	1.47	1.14	1.38	277.31	15.14	0.91	53.06
26	1.22	1.08	1.42	457.37	14.66	0.78	53.00
27	1.41	1.04	1.19	380.95	8.83	0.89	57.31
30	1.15	0.57	1.16	224.09	0.00	0.69	24.85
32	1.42	0.77	1.59	293.07	14.66	1.02	29.33
36	2.11	1.38	1.39	208.45	16.73	1.03	39.92
40	3.12	0.98	0.84	378.21	0.00	0.97	32.36
44	3.41	0.69	0.99	525.13	0.00	0.87	39.71
48	2.13	0.64	1.14	574.61	14.55	0.93	43.90
52	7.22	0.63	1.28	1061.77	38.50	1.12	72.33
54	2.29	0.81	1.32	840.02	116.33	0.93	58.44
58	18.54	0.86	5.00	746.05	12.63	2.93	53.80
59	2.31	0.68	2.45	839.00	0.00	2.17	68.94
60	1.45	0.57	1.13	429.11	0.00	1.04	35.83
62	3.66	3.00	1.55	808.49	4.28	1.35	45.61
64	10.12	1.13	1.54	389.85	0.00	1.60	54.25
<u>Central part</u>							
10	1.68	1.16	2.80	333.80	25.14	1.22	20.92
11	2.26	0.78	3.02	1105.60	21.18	2.01	105.91

Table 5.3.A. Contd.

1	2	3	4	5	6	7	8
12	2.06	1.10	1.39	185.18	14.13	0.88	29.60
13	0.94	0.88	1.32	371.15	5.05	0.93	22.39
14	1.05	0.98	1.22	680.44	28.53	1.05	34.97
15	1.04	0.80	1.21	221.29	5.05	0.90	25.07
20	3.37	0.51	1.53	415.46	0.00	1.07	51.78
21	1.90	0.28	2.47	1224.58	23.55	2.39	174.85
22	1.60	0.98	1.51	354.55	4.08	0.86	29.91
65	1.15	0.68	1.27	402.60	0.60	0.89	31.00
67	1.42	0.80	0.88	372.66	0.00	0.73	29.66
68	1.10	0.48	0.91	244.23	0.00	0.74	26.03
70	3.17	0.56	1.01	91.04	0.00	0.50	24.18
72	1.20	0.68	1.33	467.79	0.00	0.95	27.54
74	1.30	0.49	1.41	348.52	0.00	1.39	29.66
75	1.31	0.36	1.09	506.94	0.00	1.03	27.98
77	12.81	0.28	1.28	363.66	0.00	0.76	28.04
78	3.91	0.27	1.43	281.54	0.00	1.11	28.53
79	2.71	0.23	1.23	180.00	0.00	0.85	28.53
81	2.27	0.14	1.98	390.05	0.00	0.90	39.99
84	1.35	0.00	1.56	418.77	8.83	0.78	27.09
86	3.27	0.07	1.21	220.54	4.00	0.64	27.45
87	1.44	0.03	1.44	405.02	6.42	0.77	27.58
88	1.61	0.00	1.18	462.19	0.00	0.61	25.97
91	1.93	0.00	1.02	770.09	8.49	0.80	55.27
93	1.79	0.00	1.15	490.20	-2.52	0.96	24.18
94	1.03	0.00	1.44	226.31	0.00	1.18	29.66
95	1.74	0.00	1.34	440.42	21.63	1.34	32.00

Table 5.3.A. Contd.

1	2	3	4	5	6	7	8
<u>Western part</u>							
1	1.37	1.24	2.07	397.46	21.05	0.42	49.12
2	2.50	1.64	2.49	701.43	22.09	0.48	58.02
3	2.64	1.51	2.31	1472.98	62.79	1.11	76.63
4	1.97	1.52	1.70	444.13	5.65	0.95	29.60
5	2.79	1.13	2.91	1867.94	85.38	2.64	95.94
6	10.64	0.50	1.25	749.34	15.85	0.71	25.32
7	2.64	1.84	1.54	194.65	11.77	1.36	32.04
8	1.60	1.42	1.76	730.02	6.42	0.97	34.97
9	2.44	0.86	1.77	466.55	21.18	1.25	65.18
17	3.18	0.90	3.27	258.03	0.00	0.67	62.47
97	1.61	0.00	1.49	735.45	8.40	1.31	41.18
98	2.05	0.00	1.28	394.50	2.02	1.14	44.43
99	1.26	0.00	1.30	636.47	10.67	0.99	28.87
100	1.06	0.00	1.24	265.54	0.00	0.96	26.77
101	5.41	0.20	1.58	569.22	1.61	1.06	31.38
102	2.01	0.00	1.83	1154.41	0.00	1.17	63.79
103	3.52	0.00	3.36	1499.93	0.00	0.69	144.49

Table 5.3.B. Enrichment factors of trace elements
for the clays

Sample No.	Zn	Cu	Cr	As	Cd	Ni	Pb
<u>Eastern part</u>							
28	0.07	3.02	1.49	83.71	11.78	1.12	30.32
29	2.36	1.05	1.53	25.76	6.33	0.91	101.47
31	7.67	1.89	1.77	369.43	0.00	1.39	42.23
34	3.24	0.84	1.17	452.62	9.51	0.99	30.87
37	2.77	0.36	1.69	436.15	16.63	1.00	44.63
61	2.59	2.16	2.31	553.64	0.00	1.51	43.71
63	1.29	0.70	1.61	389.31	0.00	1.01	29.26
<u>Central part</u>							
16	1.09	0.70	1.68	258.94	0.00	1.20	60.21
19	10.56	1.14	1.96	763.84	20.78	1.24	88.16
66	1.16	0.56	1.07	322.87	0.00	1.03	30.15
69	1.02	0.46	1.12	298.99	0.00	0.76	27.68
71	2.30	1.18	1.48	261.48	0.00	1.27	39.36
73	3.42	1.00	1.69	383.80	9.43	1.44	30.40
76	2.33	0.35	1.32	565.72	0.00	0.99	31.23
80	1.36	0.12	1.49	505.43	0.00	1.06	23.46
82	2.91	0.02	1.31	257.70	0.00	0.73	25.97
85	1.76	0.10	1.49	334.73	0.00	0.79	26.19
89	2.56	0.24	1.69	209.76	1.36	0.89	28.76
92	13.19	0.61	1.33	623.07	0.00	1.07	41.31
96	2.11	0.49	1.38	672.00	14.72	1.50	36.07
<u>Western part</u>							
18	2.47	1.38	2.19	433.28	5.89	1.32	67.43

is clear. So, with this view, the pollution aspects of the Ashtamudy lake sediments is discussed. For the pollution study, the data of trace elements for the bulk and clay fractions of the Ashtamudy lake sediment is considered. Of late, the term trace element has been replaced by heavy metal, especially in the pollution studies even though both are same.

5.4.2. Results and Discussion

The concentration of trace elements both in the bulk and clay fractions of the Ashtamudy lake sediments as given in Tables 5.1 A and B are taken as the relative abundance of the heavy metals in the sediments. The enrichment factor determined for the elements both in bulk and clay fractions are given in Tables 5.3 A and B. The enrichment factor is defined here as

$$EF = \frac{(X/Fe)_{\text{Sediment}}}{(X/Fe)_{\text{earth's crust}}}$$

where X/Fe is the ratio of the concentration of element X to Fe (Zoller et al., 1974). Iron was chosen as the element for normalisation, because anthropogenic sources are small compared to natural sources (Helz, 1976). In the enrichment factor, comparison is made to the earth's crust as a means of placing all elements on one scale. A value of unity denotes no enrichment or depletion relative to earth's crust. Taylor's (1964) crustal abundance data are used

here. The enrichment factors are not so sensitive to the choice of a reference material (Sinex and Helz, 1980/81). The enrichment factors for Zn, Cu, Cr, As, Cd, Ni and Pb for the bulk and clays are 2.9, 0.73, 1.6, 553.5, 10.6, 1.1, 46.1, and 3, 0.8, 1.8, 394.4, 5.3, 1.2 and 50.5 respectively. All the metals, except Pb and As show more or less same enrichment in the bulk and clay fractions. Pb and As are more enriched in bulk fraction of sediments. Zn and Cu are enriched at eastern part of the lake, both in the bulk and clays; Cd at eastern part for clays and western part for the bulk; Ni at the western part for the clays and eastern part for the bulk; Cr, As and Pb both in the bulk and clays at the western part of the lake.

Work on heavy metals in India are few and mostly directed towards levels in biota except that for the sediments of the west coast by Murty et al. (1978 a and b), and Murty and Veerayya (1981) for the Vembanad lake. The establishment of a base line is of prime importance to ascertain the extent of pollution in the estuarine or lake sediments. So far no such base-line has been established in India for the sediments. In the present study, the heavy metal content of the Ashtamudy lake sediments is compared with both the polluted and unpolluted British estuaries, and with the nearshore sediment as given by Wadepohl (1960) and also with the average crustal element concentration

Table 5.4. Comparisons of compositions of sediments from polluted and unpolluted estuaries, average nearshore sediments and average crustal concentrations (all values in ppm)

Element	Solway Firth (204 μm)	Firth of Clyde (204 μm)	Severn estuary (61 μm)	Clyde estuary (silt)	Ashtamudy Lake	Average nearshore sediment	Average crustal concentration
Ni	38	50	36	69	110.3	55	75
Cr	35	64	71	624	228.7	100	100
Pb	37	86	119	528	666.8	20	12.5
Zn	63	165	280	1680	158.7	95	70
Cd	10	3.4	-	7	2.4	-	0.2
Cu	10	37	38	225	57.4	48	55
As	-	-	-	-	1078.4	-	1.8
Co	16	34	7	60	nd*	13	25

*nd - not detected

(Taylor, 1964), provided in Table 5.4. Most of the workers involved in monitoring the pollution aspects of sediments have followed the same data (Eisler et al., 1977; Taliadouri et al., 1987). If the lake is unpolluted with metals, then definitely the heavy metal content will be equal or lower than the average crustal concentration, and on the contrary, if the lake is polluted with heavy metals, then the bottom sediments will contain enhanced heavy metal concentration.

The table reveals that Ashtamudy lake sediment is polluted with the Ni, Cr, Pb, Zn, Cd, Cu and As especially highly with respect to Pb and As and unpolluted with Co. It is considered that among the estuaries in U.K., Solway Firth is the last major polluted estuary (Perkins et al., 1973) and on comparing with polluted lakes viz. Firth of Clyde and Severn estuary, it is found that the values are still higher. These higher concentrations of heavy metals in the Ashtamudy lake sediments points towards the anthropogenic effects.

The probable sources for the higher content of heavy metals can be due to industrialization and urbanization. Industries located in and around the drainage basin of the river Kallada and Ashtamudy lake

are forest based industries, boat building yards, fish canning industries; chemicals, and soap, machinery and electrical goods, refractories, clay and glass works, tiles and other clay products, printing and other allied industries, cotton, rayon and coir products etc. Minor industries are food processing, aluminium and other metal based industries, rubber and rubber products (Resource Atlas of Kerala, 1984).

The main sources for the various heavy metal pollutants in the Ashtamudy lake sediments are: Pb mainly from agricultural chemicals in which pesticides contain lead arsenate as the major constituent. The crop combination of Quilon district directly points towards the profuse use of agricultural chemicals. Added to this, is the Pb from fishing harbour, printing and canning industries boat building yards, gasoline motors and burning of fuel.

Arsenic is mainly from the antifouling paints applied to the hulls of the fishing vessels and boats to prevent the attack of fouling organisms, and from the agricultural run off. Besides, it is discharged from the fishing harbour, chemical plants and detergent manufacturing units.

Cr and Ni are from the plating industries and Zn is from the galvanising works. Cu also is from the agricultural run off. Cd is generally from aluminium and other metal based industries, refractories, tiles and glass factories, machinery and electrical goods factories etc. Minor contributions of all heavy metals are made by all other industries as mentioned above.

The higher concentration of heavy metals in the lake sediments is related to the hydrography of the Ashtamudy lake. The content of the heavy metals would have been less if there was sufficient flushing out of water from the lake and river run off. The construction of a wave breaker at Neendakara-Azhi breaks the sea waves, thus controlling the mixing up and flushing out of water along with fine sediments. Ray and Macknight (1984), Sahu and Mukherjee (1985), Hashimi and Salman (1985) observed that water circulation and tidal hydraulics will considerably dilute the pollutants. Added to this is the construction of an irrigation dam in the course of river Kallada, the only one river which empties into lake, reduces the river run off considerably and there by prevents dilution. Hence all the heavy metals get accumulated in the sediments and water of the lake itself.

Therefore, it can be concluded that the sediments transported by the river Kallada which is under the influence of industrial as well as other anthropogenic disturbances, reach the Ashtamudy lake, and the lake in turn due to its unique hydrographical characteristics inculcate an abnormal concentration of heavy metals except cobalt in these sediments. That is, the Ashtamudy lake sediments are polluted with zinc, copper, chromium, arsenic cadmium, nickel and lead.

CHAPTER - 6

SUMMARY AND CONCLUSIONS

From the texture, mineralogy and geochemistry of the modern sediments of the Ashtamudy lake, the following conclusions are drawn:

The areal distribution of the sediments from the sand-silt-clay ratios indicates that sand silt clay, sand, clayey silt and clayey sand, or sandy mud, clayey sand and muddy sand are the most dominating sediments in the various parts of the lake. In the eastern part, sand silt clay, silty clay and clayey silt are the dominating sediments. In the central part, clayey silt, sand silt clay and sandy clay dominate, where as in the western zone, sand, clayey sand, and sand silt clay are the principal sediment types. In general, the fine sediments constitute the major proportion of the Ashtamudy lake sediments. The eastern and central parts are identified as low energy zones and the western part as a high energy zone, based on the texture.

Studies on the organic matter content reveals the direct relationship between the texture of sediments and organic matter content. The eastern and central parts of the Ashtamudy lake are marked by high content of organic

matter. At the eastern part, the high content of organic matter is due to the fine sediment texture and a high contribution by the river Kallada, besides high rate of sedimentation and prevalence of a reducing environment. In the central part, the high content is due to the fine texture and high organic productivity. The western part recorded the lowest value where the texture is coarse and tidal influence is high.

The eastern and central parts recorded the lowest carbonate content. The reducing environment, greater depth and high rate of sedimentation hinders the biogenic activity resulting in a very low carbonate content as compared to western parts of the lake. The western part yields the maximum carbonate content, which is of biogenic origin and comes from the shells and tests of organisms. The lower values of the carbonate content in clays and sands of Ashtamudy lake are due to the absence of any carbonate contribution to the sediments by agencies other than biogenic activity.

The study of the lake sediments, reveals the following mineralogical aspects of the sediments. The major part of the heavy minerals are found to be apportioned to the finer fractions (0.250-0.063 mm) and only a small percentage is found in coarser fraction

(1.0 to 0.25 mm). The heavy mineral content of both the grade sizes are found decreasing with increasing river distance. The reasons are (1) the heavy minerals are not easily entrained by low energy currents subsequent to deposition, (2) the heavies are protected by the coarse lighter minerals, and (3) different settling rates due to their density difference. Down stream mineralogical variation is mainly due to selective weathering, selective sorting based on density and size, and progressive sorting based on the specific gravity.

Garnet, opaque, sillimanite and zircon are the dominating heavy minerals in the eastern part with minor amounts of monazite, pyroxene, amphibole, kyanite, tourmaline, biotite and apatite. Opaques, sillimanite, zircon, and monazite are the major constituents in the western part with minor amounts of garnet, kyanite, rutile, amphibole, tourmaline, pyroxene and biotite.

Higher concentration of biotite and absence of rutile at the eastern part of the lake characterise the river supply of heavy minerals to that region. The presence of rutile and virtual absence of biotite in the western part indicate the heavy mineral derivation from the barrier beach of Kayamkulam-Neendakara. From the relative abundance of the heavy minerals and their

assemblages, it is understood that khondalite and charnockite are the main contributors to the heavy minerals in the eastern part of the Ashtamudy lake besides garnetiferous quartzo-feldspathic gneisses and biotite gneisses. The quartz/feldspar ratio for the two size grades reveals an increase in the downstream which is due to selective abrasion and chemical weathering. This in turn results in the progressive elimination of feldspars and subsequent enrichment of harder and durable quartz.

Kaolinite is the most dominating clay mineral in the eastern part of Ashtamudy lake, kaolinite and montmorillonite in the central part, and montmorillonite in the western part. The clay mineral variation is mainly due to source and then physico-chemical condition, flocculation and size segregation.

The geochemical distributions of P, Na, K, Ca, Mg, Fe, Mn and Ti for the bulk and clay fractions of the Ashtamudy lake sediments are discussed in relation to physico-chemical conditions of the depositional environments, organic matter, and carbonate contents. Phosphorous is mainly confined to the clay mineral kaolinite and phosphatic minerals and also, to a limited extent as of biogenous origin. The relative difference observed in Na and K in the lake

sediments especially in clays are due to (1) clay mineral composition, (2) organic matter content, (3) initial composition of the source material, (4) progressive changes in the salinity and (5) salts from the pore solutions. The regional variation in the Ca and Mg content is due to the fixing up of Ca in montmorillonite as interlayer cation in the clay mineral structure and as calcium carbonate in the tests and shells of organisms, while major part of the Mg is fixed in montmorillonite. A part of Mg in the Ashtamudy lake sediment is of biogenous origin. The variation in the Fe content is due to the precipitation of Fe under oxidising and reducing environment, close association with organic matter and fixing up of Fe in clay mineral structure either by cation exchange or by adsorption. Mn is co precipitated with Fe the variation of which reflect the source rock. Ti content of the Ashtamudy lake is mainly due to the Ti minerals in the case of bulk sediments, and deposition of very fine crystalline TiO_2 along with tiny flakes of clay minerals and the co-precipitation with hydrous ferric oxide in the case of clay fractions.

The study of trace elements revealed the following features. The variation of the Zn content in the sediments depends on the texture, clay mineral and

Fe content, whereas the variation in Cu concentration depends on fine texture and clay mineralogy. The Cr content is dependent upon adsorption by ferric oxides, replacement of Al in kaolinite and Fe, Mg in smectite. Arsenic concentration varies according to the degree of its precipitation as arsenic sulphides and arsenic oxides. Cd precipitates as CdS and CdCO₃, thus affecting its level of concentration in the sediments. Whereas Ni concentration depends on the texture and clay mineralogy. On the other hand concentration of Pb is found to depend only on the texture of the sediments.

The study on the heavy metals/trace elements in the Ashtamudy lake sediment reveals that the lake sediments are polluted with Zn, Cu, Cr, As, Cd, Ni and Pb and unpolluted with Co. This is because of the fine texture and unique hydrography of the lake. This study is of great importance as it gives an insight into the level pollution of the lake sediments, considering the role of lakes as an intermediary link in the transportation of industrial effluents as well as other waste products of human habitation to its final destination, that is, the sea.

To conclude, the variations in texture, mineralogy and geochemistry of the sediments are useful in delineating the sediments in different environments of the Ashtamudy lake.

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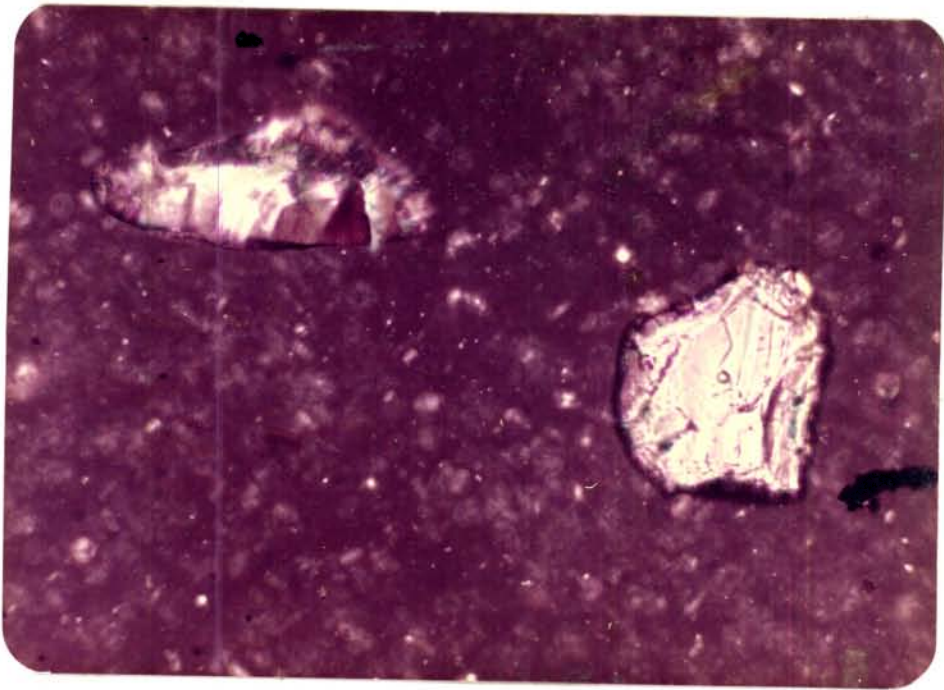
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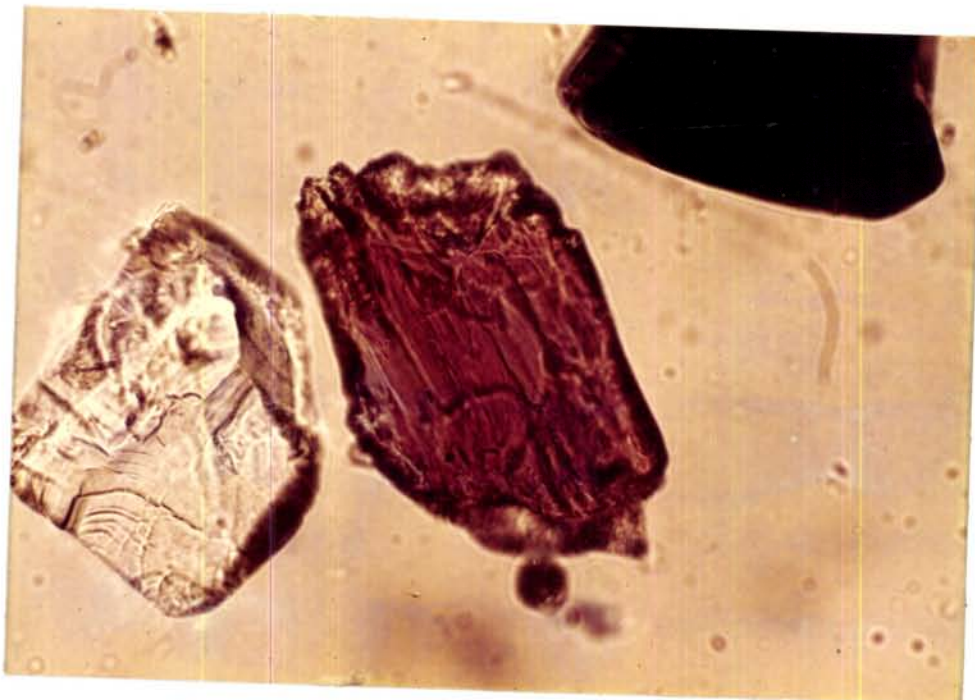
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PLATE- I.

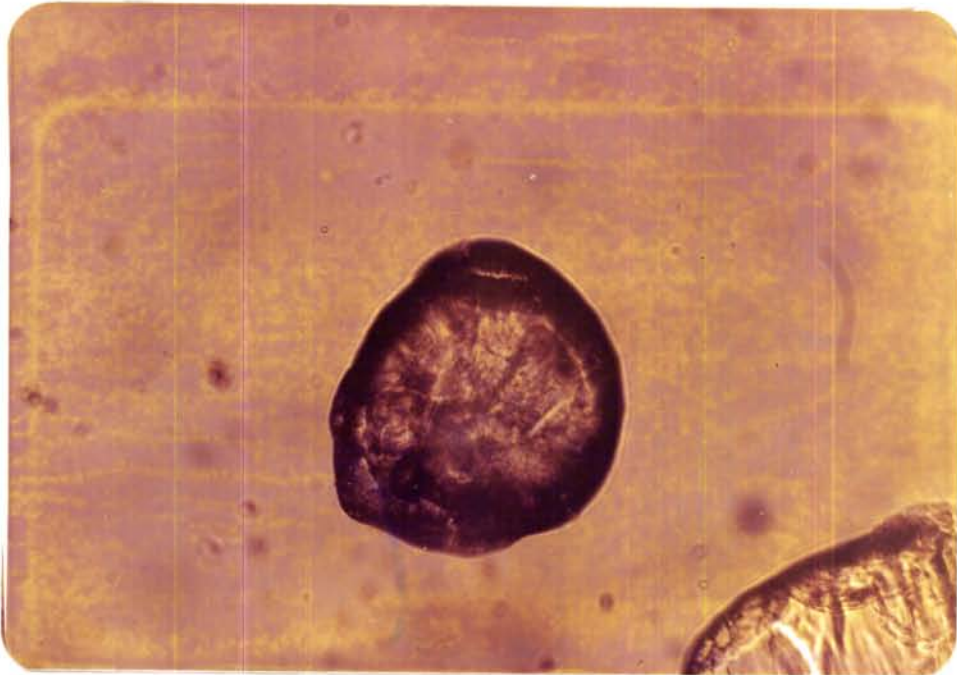


SILLIMANITE under Crossed Nicol (Magnification-12,5x16)



GARNET and HYPERSTHENE under plane polarised light
(Magnification- 12.5x16)

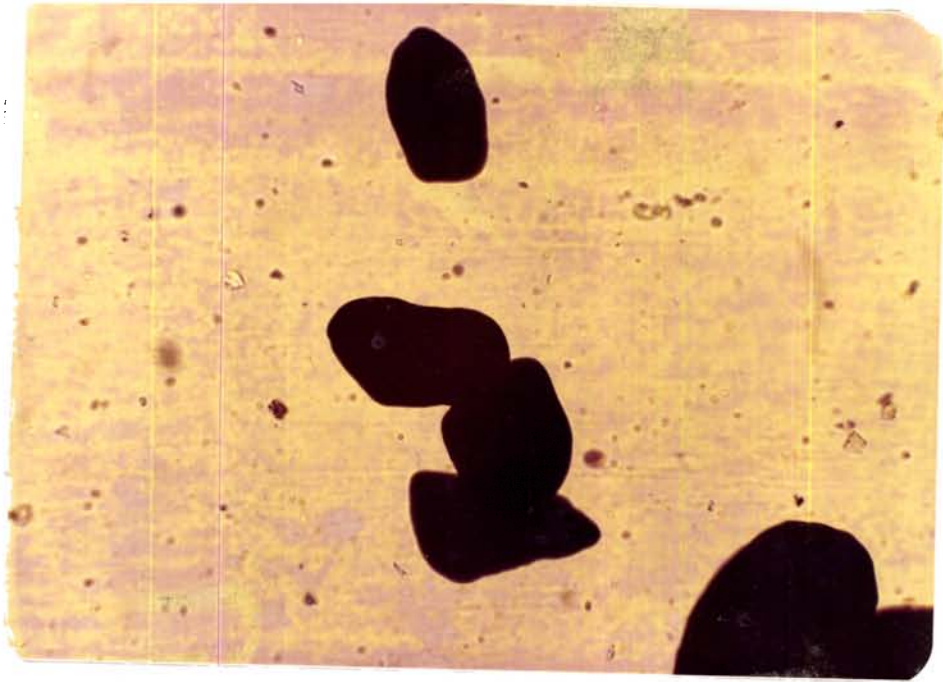
PLATE- 2.



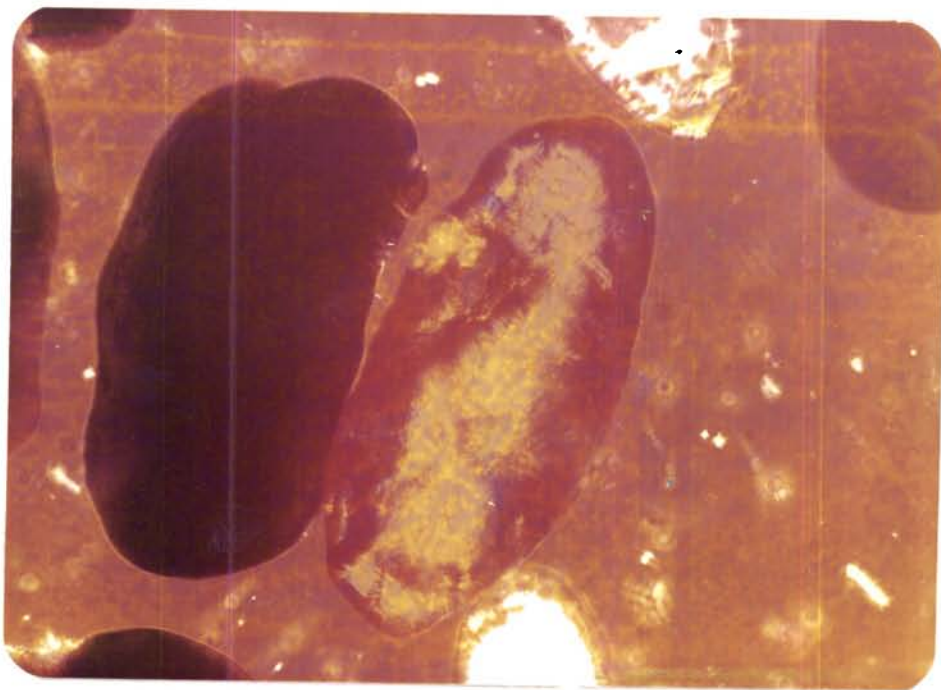
MONAZITE under plane polarised light (Magnification-25x12.5)



ZIRCON under plane polarised light (Magnification-25x12.5)



OPAQUES under plane polarised light (Magnification-12.5)

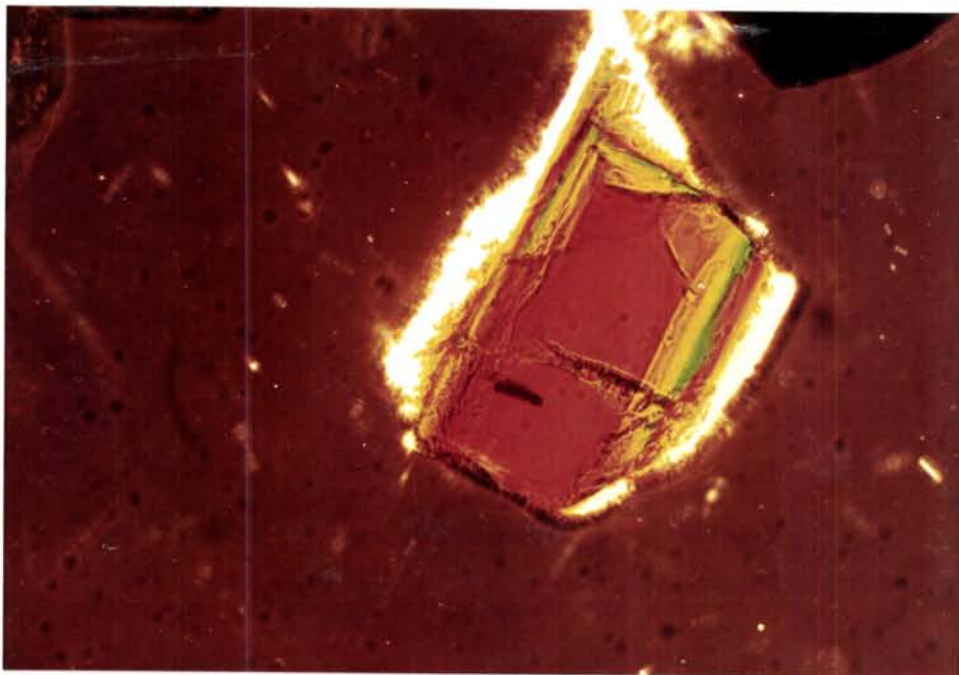


RUTILE and OPAQUE under Crossed Nicol (Magnification-16x12.5)

PLATE- 4.

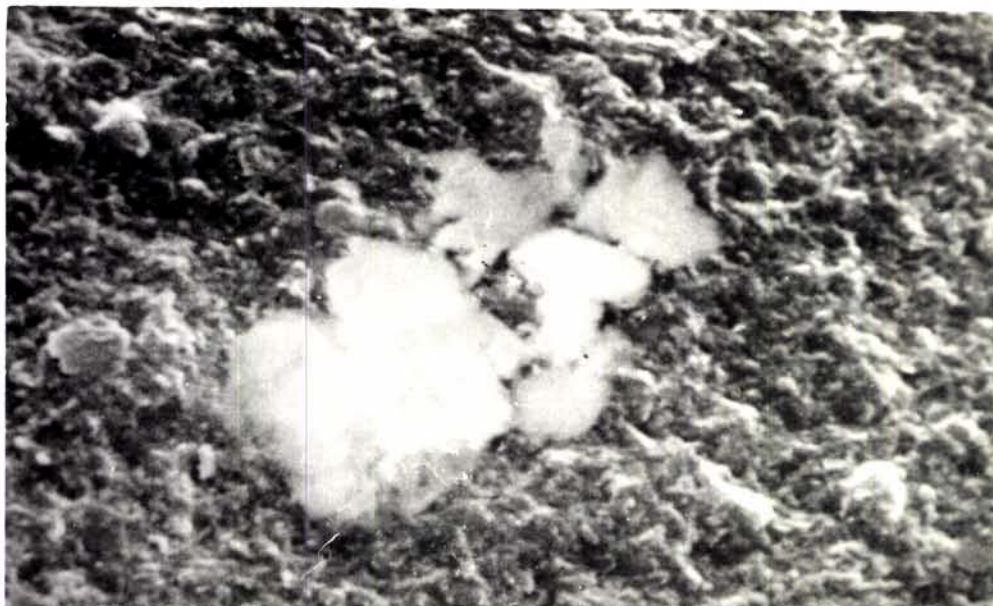


HORNBLLENDE under plane polarised light (Magnification-16x12.5)



TOURMALINE under Crossed Nicol (Magnification-16x12.5)

PLATE- 5.



KAOLINITE from eastern part (Magnification x 1500)

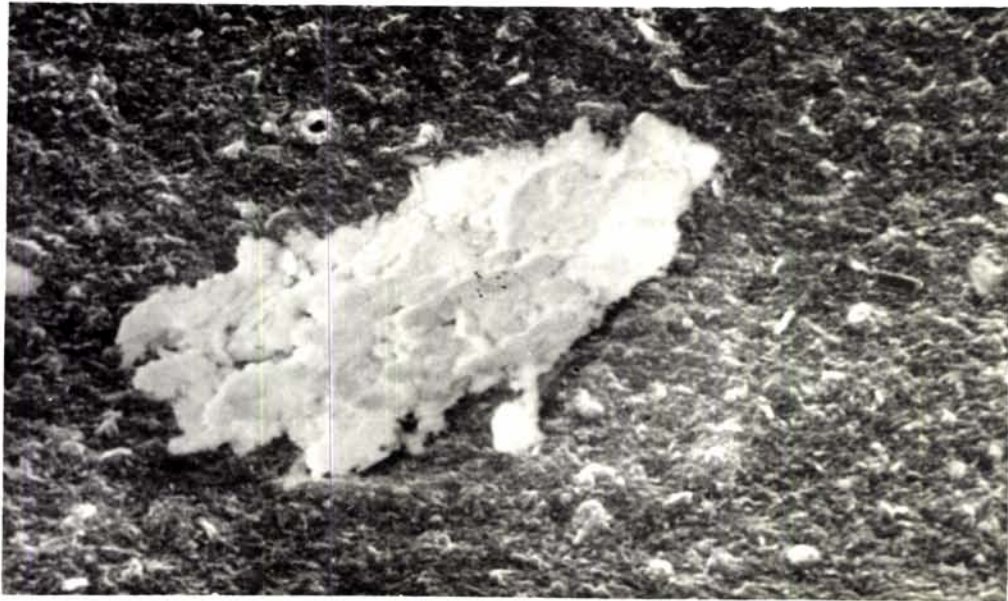


KAOLINITE from western part (Magnification x 1500)

PLATE- 6.

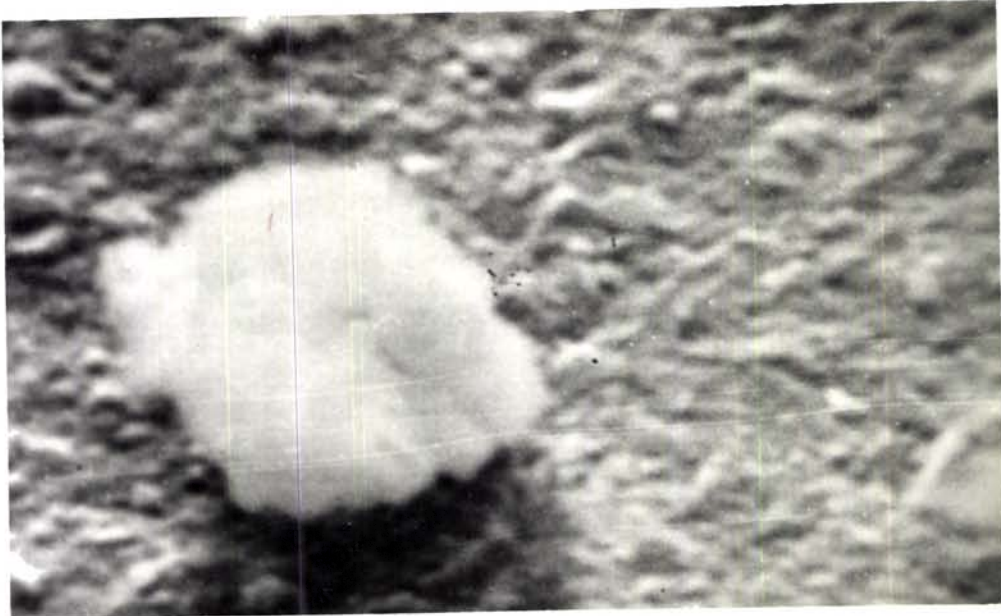


MONTMORILLONITE from eastern part (Magnification x 1500)



MONTMORILLONITE from western part (Magnification x 1500)

PLATE- 7.



ILLITE from eastern part (Magnification x 1500)



ILLITE from western part (Magnification x 1500)

STUDIES ON THE DISTRIBUTION OF ORGANIC MATTER CONTENT IN SEDIMENTS OF THE ASHTAMUDY LAKE, KERALA

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ABSTRACT

Sediment samples collected from selected stations in the Ashtamudy Lake were analysed for their organic matter content. The organic matter content varies from 0.3% to 12.35% by weight of dry sediment. The sediments show variation in texture ranging from sand to clay. Organic matter content is high in fine grained sediments (clay) and low in coarse grained sediments (sand).

INTRODUCTION

Numerous lagoons and estuaries exist along the Kerala coast and the Ashtamudy lake is one among them. It lies between 76° 36' E 76°37' 30''E and 8° 54'N-8°59' 30''N. It has a maximum length of 16 km and an average width of 3.3 km. The lake is connected with the Arabian sea at Neendakara through a tidal channel. The only major river which debouches into the lake is River Kallada, which has a catchment area of 9216 Sq. km. with an estimated annual run off of 76,000 m. c. ft. Since there has been no reported work on the organic matter content and sediment distribution in the area, the authors felt it necessary to study this relation as a part of their detailed geological investigations of the lake.

MATERIALS AND METHODS

Thirtyfour samples of the sediments were collected from around the Kallada river mouth and the tidal channel in the lake, using a Van-veen grab. Formalin was added to the samples immediately after collection to prevent any bio-chemical alteration. Samples were logged for colour, plasticity, grain-size, shell content etc. and packed in polythene bags after proper labelling.

Table 1. Percent sand, silt and clay in the sediments of the Ashtamudy lake with their organic matter content

Sample Number	Sand	Silt	Clay	Percentage of organic matter
1	90.4	1.06	8.54	2.7
2	34.5	19.9	45.6	10
3	1.4	31	67.6	10 884
4	38.1	11.2	50.7	7.743
5	8.3	6.2	85.5	9.788
6	50.2	41.4	8.4	6.574
7	79	12.6	8.4	1.534
8	1	17.9	81.1	9.569
9	0.75	35.9	63.5	10.08
10	1.8	47.5	50.6	12.05
11	11.6	31.8	56.6	12.345
12	32.4	49.5	17.8	8.546
13	only sand	--	--	0.657
14	"	—	—	1.241
15	"	—	—	0.584
16	"	—	—	0.73
17	"	—	—	0.949
18	"	—	--	0.584
19	"	—	—	2.264
20	75.2	1.9	22.9	0.73
21	83.6	1.7	14.7	1.724
22	76.9	6.4	16.7	2.922
23	86.4	1.7	11.9	1.6
24	85.2	5.6	9.2	1.46
25	82.4	6.8	10.8	1.8
26	89.8	4.1	6	1.02
27	91.5	0.03	8.6	0.876
28	93.4	0.08	6.5	0.949
29	82.9	6.6	10.5	1.095
30	85.5	10.9	3.6	1.314
31	84.7	5.1	10.2	1.534
32	81	6.1	12.4	1.972
33	81.5	6.1	12.4	1.607
34	82.2	1.8	16	1.68

A representative portion of sediment from each sample was washed free of chloride with distilled water and dried at 70°C. Sand-silt-clay ratios have been estimated by a combination of mechanical sieving and pipette analysis following the method of Krumbein and Pettijohn (1938). The results are shown in Table 1. Areal distribution of the sediment types is shown in Figs. 1 & 2.

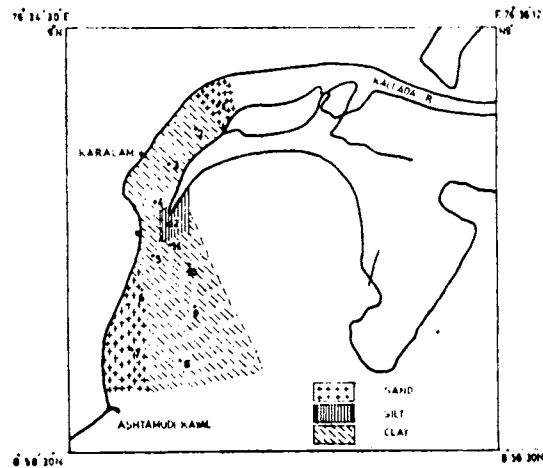


Fig. 1. Map showing station locations and sediment distribution pattern around Kallada river mouth.

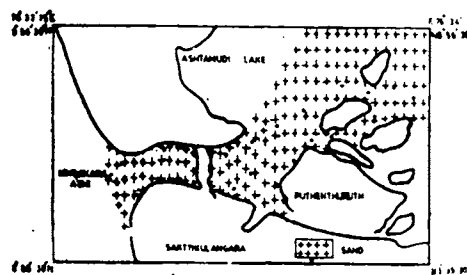


Fig. 2. Map showing station locations and sediment distribution pattern in and around the tidal channel in the Ashtamudy lake.

The total organic matter in the sediments was determined by El wakeel and Riley method (1957). The organic matter content in each sample is obtained by multiplying the value of organic carbon by 1.724. The values thus obtained are plotted in Fig. 3.

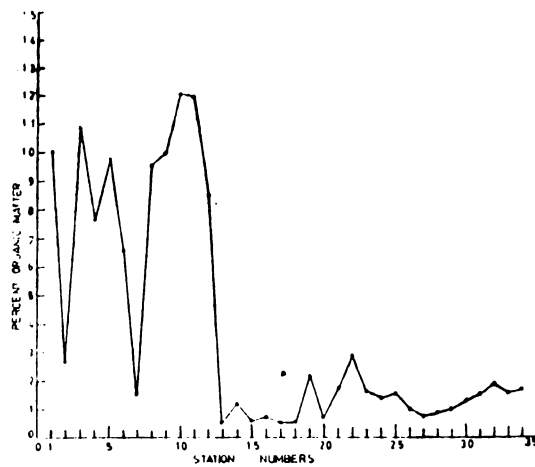


Fig. 3. Percent organic matter distribution in sediments in the Ashtamudy lake.

DISCUSSION

As seen from the distribution pattern of sediments (Fig. 1 & 2), it is clear that the Kallada river mouth area is composed of fine sediments like clays and silty clays, whereas the sediments in and around the tidal channel are made up of fine to medium sands.

The sediments at the Kallada river mouth are characterised by high organic matter content. This may be due to the high rate of sedimentation, the brisk primary production and the reducing environment (as clear from the greyish black colour of the sediments) at this place. High rate of sedimentation, primary production, and greater depth usually promote high organic matter content as shown by Murthy and Veerayya (1972), and Ramachandran Nair *et al* (1975). The low organic matter content in the sediments in and around the tidal channel may be due to high biogenic activity. It can also be due to the coarse nature of the sediments and the shallow depth prevailing in the area, as these factors normally promote high rate of biogenic activity, leading to the destruction of organic matter. This relation between sediment size and the organic matter content has been reported by many workers like Murthy and Veerayya (1972), Kidwai and Nair (1972), Paropkary (1979), Sankaranarayanan and Panampunanyil (1979).

As regards the source material, it could be either the organic matter directly brought in by the run-off (transported) and preserved along with the sediments at the river mouth or the in situ preservation of the

organic matter in the sediments due to high organic productivity in the waters above. Detailed study on the salinity, temperature, oxygen content and vertical as well as horizontal mixing of water in the lake will throw much light on the rate of productivity in different parts in the lake and its relation to the organic matter content.

CONCLUSIONS

The following conclusions can be drawn from the present investigation:

(1) A gradual increase in the grain size of the sediments from the river mouth (composed of clay and silty clay) towards the tidal channel (made up of medium to fine sand) is observed.

(2) The high organic matter content in the river-mouth sediments may be due to the high rate of sedimentation, high rate of primary production, greater depth as compared to the other parts in the lake and the low or negligible rate of biogenic activity.

(3) The low organic matter content in the sediments at the tidal channel and the surrounding areas may be due to the coarse size of the sediments, high biogenic activity and the shallow depth prevalent in the area.

(4) The organic matter content in the sediments also follows roughly the sediment distribution pattern in that the fine sediments like clays and silty clays have higher organic matter content, while the sands have lower organic matter content.

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Carbonate Content of Sediments in the Ashtamudy Lake, West Coast of India

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Grab samples of sediments from selected stations in the lake have been studied to determine the type of sediments and the carbonate (CaCO_3) content. Striking difference in the distribution pattern of carbonate in different parts of the lake has been attributed to the type of sediments, the rate of sedimentation and the biogenic productivity in the area.

The Ashtamudy lake forms an important estuarine system in south Kerala. It extends over 19 km in length and 3.3 km in width. The major river that empties in to the lake is the river Kallada, with an estimated average annual run-off of about $2140.8 \times 10^6 \text{ m}^3$.

Prabhakara Rao¹ has made a detailed study on the sediments of the near shore regions off Neendakara - Kayamkulam coast and the Ashtamudy and Vatta estuaries. However there is no geochemical investigation either on the sediments at the tidal channel or at the river mouth for their carbonate content and/or organic matter content. In the present investigation, lake sediments have been studied to ascertain the relationships among various factors, viz. type of sediment, rate of sedimentation, carbonate content in the sediments and biogenic productivity.

Sediment samples were collected using a Van Veen grab at an interval of 150 m. Twelve samples were from the river mouth and 22 from the tidal channel and surrounding areas (Figs 1 and 2). The samples were logged thereafter for their colour, plasticity, shell content, etc. and were stored in polyethylene covers after proper labelling. In the laboratory, the samples were washed with distilled water, dried in the oven and the total calcium carbonate² and the organic matter³ content were determined. Fractions $>63 \mu\text{m}$ were separated by wet sieving and finer fractions by pipette analysis⁴. Ratios of sand, silt, and clay were calculated from the weight percentages and the texture of the sediments determined based on the proportions of sand, silt and clay⁵ (Fig. 3).

From the sediment distribution pattern (Fig. 1), it is obvious that the sediments at the Kallada river mouth area are mainly of clay and silty clay while the samples from the tidal channel and the near by areas (Fig. 2) are mainly of medium to fine sands.

The Kallada river mouth sediments (Table 1) are characterised by a low carbonate content (av. 2.92% by weight). This low value may be related to high rate of sedimentation and the nature of the substratum. High rate of sedimentation and fine nature of substratum, in

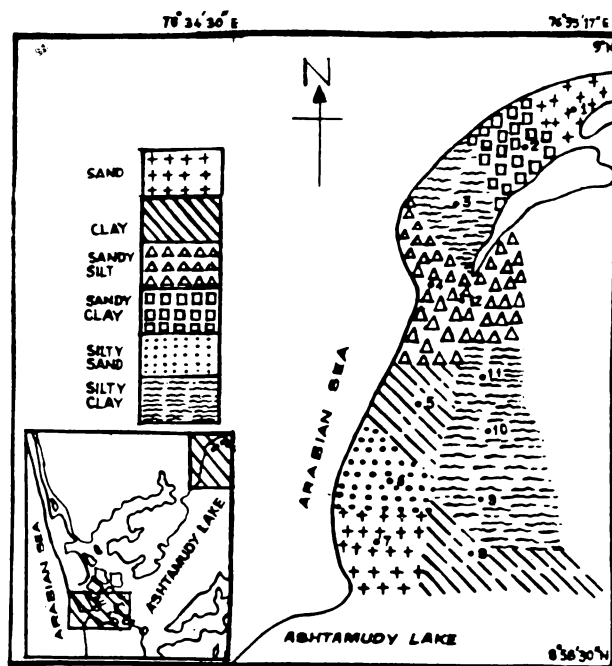


Fig. 1—Station locations and sediment distribution pattern at Kallada river mouth (Inset shows lake's general setting)

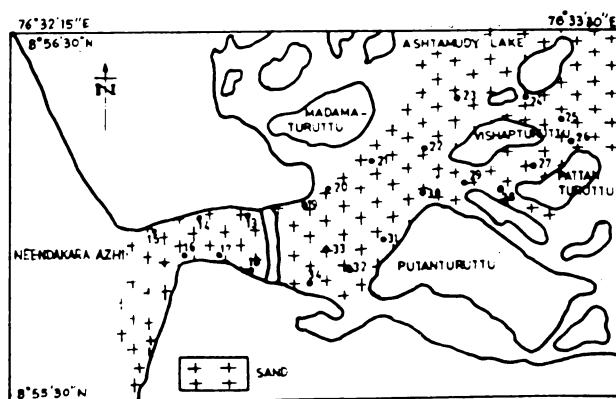


Fig. 2—Station locations and sediment distribution pattern in and around tidal channel in Ashtamudy lake

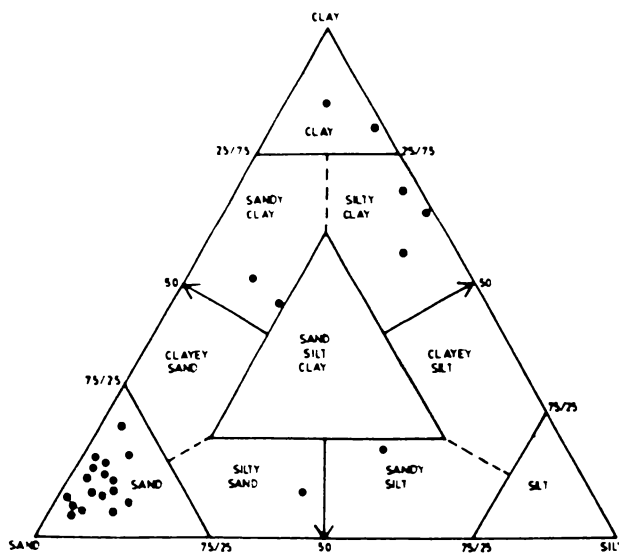


Fig. 3—Percent sand, silt, and clay in sediments of Ashtamudy lake, Quilon

the normal course, adversely affect biogenic activity and hence a low carbonate value in the sediments under consideration.

The lesser biogenic activity in the river mouth is confirmed by the microscopic examination of samples that reveal only very little shell fragments, and a total absence of microfossils like foraminifera as compared to the tidal channel and the surrounding areas in the lake. The factors like sudden fluctuations in salinity, temperature, and oxygen content due to horizontal and vertical mixing of water at the river mouth also might have contributed to lowering of biogenic activity, thus bringing down the total carbonate value in the sediments.

The sediments in and around the tidal channel (Table 2) near the shore area are typically sandy and their high carbonate content (8.77% by wt) appears to be due to high amount of biogenic activity, as evidenced by the bulk proportion of molluscan shells and foraminifera in the sediments. Normally high biogenic activity is supported by a sandy nature of the substratum.

Similar types of relationships have been observed⁶ among the rate of sedimentation, grain size of the sediments and their carbonate contents. Comparatively lower values of the carbonate contents in the clays and sands of the Ashtamudy lake may be due to the absence of any carbonate contribution to the sediments by any agencies other than biogenic activity in that area. This has been confirmed by microscopic examination.

From the distribution pattern of the organic matter content in the lake sediments, a striking relation is found between the grain-size and the organic matter

Table 1—Characteristics of Sediments from Kallada River Mouth

Sl No.	Sediment fraction (wt %)			Texture	Total CaCO ₃ (wt %)	Total organic matter (wt %)
	Sand	Silt	Clay			
1	90.4	1.0	8.5	Sand	3	2.700
2	34.5	19.9	45.6	Sandy Clay	4	10.000
3	1.4	31.0	67.6	Silty Clay	4	10.884
4	38.1	11.2	50.7	Sandy Silt	3	7.745
5	8.3	6.2	85.5	Clay	2	9.788
6	50.2	41.4	8.4	Silty Sand	2	6.574
7	79.0	12.6	8.4	Sand	0	1.534
8	1.0	17.9	81.1	Clay	0	9.569
9	0.7	35.9	63.5	Silty Clay	6	10.080
10	1.8	47.8	50.6	Silty Clay	3	12.050
11	11.6	31.8	56.6	Silty Clay	3	12.345
12	32.4	49.8	17.8	Sandy Silt	5	8.546

Table 2—Characteristics of Sediment from in and Around Tidal Channel

Sl No.	Sediment* (wt %)			Total CaCO ₃ (wt %)	Total organic matter (wt %)
	Sand	Silt	Clay		
13	only sand	—	—	14	0.657
14	"	—	—	27	1.241
15	"	—	—	13	0.584
16	"	—	—	10	0.730
17	"	—	—	15	0.949
18	"	—	—	11	0.584
19	"	—	—	12	2.264
20	75.2	1.9	22.9	13	0.730
21	83.6	1.7	14.7	10	1.724
22	76.9	6.4	16.7	11	2.922
23	86.4	1.7	11.9	10	1.600
24	85.2	5.6	9.2	15	1.460
25	82.4	6.8	10.8	5	1.800
26	89.8	4.1	6.0	2	1.020
27	91.5	0.0	8.6	10	0.876
28	93.4	0.0	6.5	1	0.949
29	82.9	6.6	10.5	1	1.095
30	85.5	10.9	3.6	3	1.314
31	84.7	5.1	10.2	3	1.534
32	81.0	4.0	15.0	5	1.972
33	81.5	6.1	12.0	4	1.607
34	82.2	1.8	16.0	3	1.680

*Texture of sediment sandy

content. Clay, silty clay and silt have higher values of organic matter content when compared to sands. Similar observations have been made by Murthy and Veerayya⁷. Normally it is seen that high organic matter content in the sediments of an area supports high biogenic activity in that area as organic matter serves as food for the latter. But in the present investigation, inspite of high organic matter content

(av. 8.48% by wt) found in the sediments (Table 1) at the river mouth, the other important factors such as high rate of sedimentation, the greater depth of water column compared to the other areas in the lake under consideration (av. 3m), fluctuations in salinity, prevalence of reducing environment, etc. have affected the biogenic activity in order to bring the carbonate content to the minimum (av. 2.92%). In spite of the low organic matter content (av. 1.32% by wt) in and around the tidal channel (Table 2), high biogenic activity is prevalent as evidenced by the high carbonate value (av. 8.77%). The low organic matter content may, apart from the other factors, also be due to the consumption of the same to some extent by benthic organisms that contribute to the total carbonate content. The consumption of organic matter by the benthos does not seem to be compensated by supply.

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