6.1. INTRODUCTION

Sediments are extremely important in the marine environment since they act as 'traps' for chemical elements. Recent works in the coastal marine environment has indicated that the increased geochemical cycling of metals by man can be well documented through sedimentological studies. Special attention has been paid to the modern continental margin sediments by geochemists, because the physical, chemical and biological conditions are more variable in these sediments than on the continents or in the deep seas.

In many areas, geochemical studies are hindered by a lack of information about the natural environment. Particularly, the nearshore environments are the important removal sites for several elements from sea water because the accumulation rates are very much higher and the various environmental factors are much more different from those found in the open ocean.

The concentration of a given element in a sediment is governed by its concentration in, and the relative proportions of, the various components. Many elements show tendencies to be partitioned between two or more mineral components in the sediment and the distribution of a given element cannot be described in terms of mineralogy alone. There is also a very significant elemental partitioning effect brought about by a textural control on the mineralogy of sediments. This
factor is of critical importance for nearshore sediments in view of their extreme textural variability. Hirst (1962) observed that the range of chemical compositions in the sediments are controlled by variations in the proportions of the major minerals, i.e. quartz, feldspar, illite, montmorillonite, kaolinite and in those of the minor amounts of heavy minerals. Exceptions to this were found for the distribution of iron, calcium and manganese.

Geochemical analysis of major and trace elements were carried out for the estuarine and mud bank sediments. The role of estuarine sediments are very important for the supply of dissolved and solid material to the ocean. Garrels and Mckenzie have estimated about $250 \times 10^{14}$ g year$^{-1}$ of material enters the oceans from the continents of which $210 \times 10^{14}$ g year$^{-1}$ material is transported via rivers and estuaries. Almost 85% of all soluble and particulate weathering products pass through the estuarine environment before entering coastal waters. Therefore, the estuaries and lagoons which form the transition zones between fluvial and marine environments constitute an important stage in the transport of sediments from continents 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 trace elements in the bottom sediments (Murthy and Veerayya, 1981).
6.2. RESULTS

6.2.1. Geochemistry of Bulk Sediments

6.2.1.1. Calcium Carbonate

Percentage of calcium carbonate in the Vemband lake sediments are shown in table 6.1. In the northern part of the estuarine mouth, the percentage of calcium carbonate is found to be high when compared to the southern part of the lake. The distribution of calcium carbonate in the river mouths is very low. The average percentage of calcium carbonate in the estuarine sediments is 3.06%. Very high percentage of calcium carbonate is reported from the Alleppey area (9%).

Distribution of calcium carbonate in the mud bank sediment is estimated to be very high. The percentage varies between 1.25 to 11.75. The minimum value (1.25%) is noted in the suspended sediments.

6.2.1.2. Organic Matter

In the Vembanad lake, the organic matter percentage varies between 1.7 and 11.73. Based on organic matter percentage, two zones can be distinguished in the lake: (i) Northern part of the lake extending from Azhikode to Thanneermukkam area with high percentage of organic matter. (ii) Southern zone extending from Thanneermukkam to Alleppey region. In the central part of the lake, the sediments are coarser in size, and show high percentage of organic matter but relatively
very low percentage is recorded near the river mouths. Estuarine region shows high organic matter content. The relationship of organic matter with clay percentage is shown in the diagram 6.1. Table 6.1 shows the distribution of organic matter in the Vembanad lake.

The distribution of organic matter is very high in the mud bank sediments (Table 6.2 a, b). It shows a gradual increase from May to August and a considerable decrease during September and December. In the Narakkal-Saudi area, the maximum value of 6.01% is noted during August. The studies conducted during July and August, 1986, shows a significant change. The organic matter percentage noticed is 4.06 and 4.72 respectively.

Organic matter content in the Alleppey-Purakkad area show similar sort of variation. In general, it is found that the occurrence of organic matter is quite high in the area but the value varies between a minimum percentage of 1.88 and a maximum of 6.15% during August. The percentage distribution of organic matter is shown in the Table 6.2 b and figure 6.1 shows the variation of organic matter with clay percentage.

6.2.1.3. Major and Trace Element Studies

The bulk chemical analysis were carried out only for limited number of samples from the mud bank area (table 6.3). Chemistry of the lake sediments were not carried out since a good amount of data exists in the literature on Vembanad lake sediments. The studies
conducted by Mallik and Suchindan (1984), mainly concentrated on the chemistry of the water leachable fraction (Group A) and solution prepared by dissolving the residue in nitric acid and hydrogen peroxide (Group B). They found a very high amount of organic matter, iron, manganese, phosphates and calcium. The earlier report on the trace elements from the bulk sediment analysis by Murthy and Veerayya (1981) showed an increase in the values of Fe, Mn, Ti, Ni, Co and Cu, with decrease in grain size. However, the present study is concentrated mainly to assess the association of chemical constituents in the clay sized fractions (2 microns).

6.2.2. Geochemistry of the Clayey Sediments

For a better understanding of the geochemical processes, clay fractions (less than 2 microns) of the estuarine and mud bank sediments were subjected to chemical analysis (Table 6.4). The fine sediment population is an exchange medium scavenging the water column and also a reservoir of minor and trace elements. It has been documented by many workers that the exchange of these elements between water and sediment by sorption or desorption takes place essentially in the fine sediment population (Wakeel and Riley, 1961 and Degens, 1965). The frequency percentage versus chemical concentration of the various elements are presented in the figure 6.2 and 6.3.

6.2.2.1. Phosphorus

Vembanad lake sediments show high amount of phosphorus. In
the lake sediments the phosphate increases in the southward direction. The minimum percentage is noticed in the vicinity of river Periyar, i.e. 0.54. The value increases to 0.65 in the estuarine region and further increase is noticed up to the Minachil ar. Here the maximum percentage of 0.85 is recorded and further in the southern part of the lake near Pamba ar mouth, it again decreases to 0.70. A minimum value of 0.05 is encountered in the eastern margin of the lake.

The distribution of phosphorus in the mud bank region shows an average percentage of 0.60. It is observed that there is no significant monthly variation in the percentage of phosphorus. However, it is found that the percentage is quite high in the Alleppey-Purakkad region. The minimum value of 0.28% is noted in the core sample of 1 m length collected from Malipuram area. The maximum value of 0.92 is noted in the Alleppey region. The suspended sediments also show a high phosphorus percentage of 0.82. The inter-relationship of phosphorus with iron is shown in Figure 6.4.

6.2.2.2. Total Iron

The total iron percentage in the Vembanad lake is determined and the results show a significant change in the percentage distribution between the sediments of Vembanad lake and mud bank sediments. The average distribution of total iron in the Vembanad lake sediments is 11.89%. The maximum percentage is noted in the northern most region of the lake (12.6%) followed by 12.34% in the southern most part of
the lake. The minimum value is noted in the estuarine (mixing zone) region (11.11%) and it shows an increase towards the southern side.

In the mud bank sediments, the distribution is found to be very high. It can be noted that the percentage is comparatively less during the month of May, i.e. just before the onset of monsoon. The values are considerably high during July-August months. The average value is 14.24% and the maximum value reported is 18.17% off Alleppey, during August at a distance of 8 km from the shore. The minimum value of 12.38% is noted during May in the Narakkal-Saudi area. Its inter-relationship are shown in the figures 6.5 and 6.6.

6.2.2.3. Manganese

The average distribution of Manganese in the Vembanad lake is found to be 0.08%. The maximum percentage is noted at the northern part of the lake (0.09%) and a minimum is in the vicinity of the Minachil ar (0.06%). It shows a well defined relation with the distribution of iron. A maximum of 0.17% is noted in the eastern margin, at the northern part of the Vembanad lake. The minimum of 0.04% is noticed in the vicinity of river Periyar.

The average distribution in the mud bank area is 0.09%. There is no significant variation in the percentage of manganese. The maximum value (range between 0.06% and 0.15%) is recorded from the Alleppey-Purakkad area. The core sample and the suspended sediment sample also show a resemblance with the surficial sediments in their concen-
tration. The inter-relationships are plotted in the figures 6.7 and 6.8.

6.2.2.4. Titanium

From the results it is found that the percentage of titanium both in the Vembanad lake and mud bank sediments are quite high. The average percentage of Titanium in the Vembanad lake is 1.02. The percentage increases towards the south and it decreases in the vicinity of Minachil ar and again increases in the southern region. The maximum value noted at the Muvattupuzha region (1.12%) and the minimum value is 0.88% near the Minachil ar area.

The average distribution in the mud bank sediments is 1.09%. There are no noticeable variations in the sediments, however the maximum percentage is noted during July-August months. The distribution of Titanium is also high in the offshore direction. The relationship of titanium with iron and manganese are shown in figures 6.5 and 6.8.

6.2.2.5. Sodium

The average percentage of sodium in the Vembanad lake is 3.98. It is found that the percentage of sodium is maximum (4.90%) in the mixing zone of the lake. It is also noted that the concentration of sodium is comparatively higher in the northern part of the estuarine mouth. Minimum percentage of 3.12 is noted in the southern most part of the estuary.

The percentage of sodium is higher in the mud bank sediments,
when compared to the lake sediments. The average percentage of sodium in the mud bank sediments is 4.29. There is no considerable change in the distribution of sodium. The maximum percentage of sodium noted is 5.08 in the month of July 1986 from the Narakkal-Saudi area. The minimum concentration found in the area is 3.78%. Inter-relationship of sodium with potassium is shown in the figure 6.9.

6.2.2.6. Potassium

The percentage of potassium is low when compared to sodium. The average percentage is found to be 1.55 in the Vembanad lake. The maximum percentage is found in the estuarine region (1.83%). The minimum percentage is in the Pamba ar mouth region (1.26%). In all other areas it shows almost an uniform distribution.

The average percentage of potassium in the mud bank sediments is 1.70. The distribution of potassium does not exhibit any significant change. The maximum value of 2.03% is recorded during July 1986, from the Narakkal-Saudi area. It shows a close sympathetic relationship with sodium. The minimum value of 1.43% is noted during August, 1986 in the same area. All other values show close similarity in their distribution.

6.2.2.7. Magnesium

The average percentage distribution of Magnesium in the Vembanad lake is 4.72. The values range from 2.07 to 9.58%. The maximum percentage is noted in the Muvattupuzha river mouth area (9.58%). It
shows an increase in the percentage towards further south. The minimum percentage is noted in the northern part of the lake (2.07%). In general, the percentage is high towards the southern part of the lake than in the northern and estuarine mouth regions.

The average percentage in the mud bank sediments is 4.25. The value ranges from 3.3% to 9.58%. It is also observed that the percentage of Magnesium is relatively higher in the Narakkal-Saudi area. Magnesium shows a positive relationship with titanium.

6.2.2.8. Silica and Alumina

The average distribution of silica and alumina in the lake sediments are 45.11 and 20.52 percentage respectively. The maximum percentage of silica noted is 54.9 in the estuarine area and the minimum value is 41.44. The silica percentage increases towards south, to the river mouth of Muvattupuzha, upto 46.68% and then decreases further south.

The maximum percentage of alumina noted is 27.07 in the northern part of the estuary and a minimum value of 17.38% in the estuarine (mixing zone) region, but here it shows a reverse trend in the distribution, that is, it shows a decrease towards south and again increases from the southern part of Muvattupuzha mouth.

The average percentage of silica and alumina present in the mud bank sediments are 43.53 and 20.84 respectively. The maximum percentage of silica noted is 46.73 during the month of May and the
minimum value of 40.78 is noted for sediments, collected from 8 kilometers off the coast. The maximum percentage of alumina present in the sediment is 23.02 and the minimum value is 17.91. The monthly variations are not significant but the mud bank sediments of 1986, show higher percentage of silica when compared to the previous year. The inter-relationship between silica and alumina are shown in the diagram (fig. 6.10).

6.2.2.9. Trace Element Studies

Important trace elements determined are copper, cobalt, nickel and zinc. Trace elements represent only a small fraction of less than 0.1% of the sediments.

6.2.2.9 a. Copper: The average concentration of copper in the sediments is found to be 115 ppm in the Vembanad lake sediments. The maximum and minimum values are noted in the southern and northern parts of the lake, respectively. The value ranges between 51 ppm and 271 ppm.

The mud bank sediments show higher concentration of copper than lake sediments. The average percentage of distribution of copper is 14.3 ppm. The maximum value recorded is 229 ppm and the minimum value is 83 ppm. It is further noticed that the concentration of copper is high in the Narakkal-Saudi area when compared to the southern part of the coast (Alleppey-Purakkad region).

6.2.2.9 b. Cobalt and Nickel: The distribution of cobalt and nickel
shows a very high concentration in the Vembanad lake than the mud bank sediments. The average concentration of cobalt and nickel in the Vembanad lake is found to be 60.40 ppm and 111.13 ppm. The maximum value of cobalt is recorded in the vicinity of Minachil ar (75.67 ppm) and nickel (137 ppm) is noted in the southern most part of the lake. The concentration is found to be relatively less in the northern part of the estuary than the southern part. The concentration is relatively higher in the estuarine region.

The average values of cobalt and nickel in the mud bank sediments are 24.66 ppm and 75.56 ppm respectively. There is no significant variation in their distribution throughout. The maximum value of cobalt is 75 ppm in the suspended sediments and the minimum value noted is 12 ppm in the surficial sediments of the mud bank region. The maximum concentration of nickel is 132 ppm found in the Alleppey-Purakkad region during August and the minimum value recorded is 32 ppm during May in the Narakkal-Saudi area.

6.2.2.9 c. Zinc: The average value of zinc in the estuarine sediments is 53.3 ppm. Here, it shows gradual increase in the concentration towards south. The minimum average value is near the river Periyar (34.5 ppm) and it is maximum in the Pamba river mouth region with a concentration of 70.83 ppm.

The concentration is relatively lesser in the mud bank sediments than the lake sediments. The maximum concentration estimated is 74 ppm and the minimum value is 20 ppm. It can be noticed that the sediments
collected during May-June show a relatively lesser concentration of zinc and maximum is reported during the month of August.

6.3. DISCUSSION

6.3.1. Geochemistry of Bulk Sediments

6.3.1.1. Calcium Carbonate Distribution

The geological problems relating to the conditions of formation of limestones have greatly stimulated the study of calcium carbonate in the marine sediments. This is mainly because, most of the limestones were formed under marine environmental conditions. Calcium carbonate content of sediments from a shelf is a function of carbonate productivity and the rate of influx of terrigenous material (Rao, 1978).

A review of literature shows three broad sources for the calcium carbonate in the fluvial and deltaic deposits:

1. Calcareous mineral and sediments derived from continental rocks;
2. Shell fragments and tests of calcareous organisms, and;
3. Inorganic and organic precipitation from the overlying waters of the depositional environment.

Variations of calcium carbonate in the estuary i.e. higher percentage in the southern part and lesser in the northern part may be attributed to:

1. Excessive discharge of river sediments in the northern part.
Low values of calcium carbonate in the river mouth sediments may be related to high rate of sedimentation and the nature of the substratum.

2. Various physico-chemical processes taking place in the mixing zone of the estuary;

3. Continuous dredging operations may affect the biogenic activity in the region.

Mud bank region is calm due to wave dampening. Hence, it favours biological processes by sheltering the various organisms including fishes. During May-June the percentage of calcium carbonate is less, this could be due to the increased wave activity marking the onset of monsoon which does not permit the accumulation of carbonate. During July-August months the wave dampening makes the nearshore less turbulent and this explains the reason for the increase in the amount of calcium carbonate and decrease thereafter. Photosynthesis and respiration by organisms may bring about calcium carbonate co-precipitation from the overlying waters by effecting the carbon dioxide influx as this area is highly productive. Cloud (1965) has observed that certainly any biological process which affects the amount of carbon dioxide in solution disturbs carbonate equilibria. Therefore, it is possible that part of the calcicm carbonate in the marine environment might be due to precipitation as a result of photosynthetic carbon dioxide intake by plants and respiration by organisms. Relatively high values of carbonate in the offshore region may be either due to the strong currents leading to non-deposition of terrigenous mate-
rial or due to the limited supply of terrigenous material. In addition to this, carbonate content in the marine sediments show a general increase with depth.

6.3.1.2. Organic Matter

The important factors controlling the organic matter accumulation in sediments are (i) the supply of organic matter to the environment of deposition; (ii) rate of deposition of organic and inorganic constituents; (iii) texture of the sediments. According to Trask (1932), silt contains twice as much clay and four times as much organic matter as sands. Trask (1939) stated that the main cause of the increase of organic matter in fine particle is the similarity in settling velocity of both organic constituents and fine particles. Carter and Mittern (1978) stated that the increase in organic carbon with decreasing grain-size may be due to the co-sedimentation of particulate organic matter with small mineral grains. It could be also due to the enhanced surface adsorption of organic matter because of the greater surface area of fine sediment grains. Suess (1973) demonstrated that the increase in organic carbon and nitrogen with decreasing grains-size is linearly related to the surface area of mineral grains.

The very high content of organic matter and its variation in the Vembanad lake sediments are attributed to the following causes. In this ecosystem, the organic production is favoured by:

1. Vegetation around the Vembanad lake especially, mangrove swamps;
2. Texture of the sediments, brought by number of west flowing
rivers, which are fine in nature; and

3. Degree of oxidation—due to oxygen deficient ecosystem prevailing in different part of the lake, the degradation of organic matter is less in this area and hence the high amount is encountered here. In Cochin harbour area in addition to the above factors, disposal of waste from the city may also contribute to the enrichment of organic matter.

The relatively higher percentage of organic matter in the northern part of the estuary may be due to the denser planktonic and benthic population, salinity differences and the thicker vegetation around the area. In the southern part of the estuary, the fresh water conditions and the coarse bottom sediments could be responsible for depletion in the organic matter content compared to the northern part. Besides this, currents and depth of occurrence play an important role in the accumulation of organic matter.

Organic matter distribution in the mud bank sediments is found to be very high. Generally, marine clays have the higher percentage of organic matter and the reason for this may be the high adsorbing capacity of the clays or the hydrobiological conditions prevailing in the marine environment. Especially the enrichment of organic matter during the mud bank season clearly indicates an increase in the primary productivity and also in benthic activities prevailing in the inner-shelf (Damodaran, 1973). During the active mud bank season, the coastal water becomes calm and turbid, and extremely finer size of the sediments favours the sedimentation of organic matter. Furthermore,
Kuenen (1965) has stated that deposits exceptionally rich in organic matter are encountered in areas where upwelling waters fertilise the surface layers of open ocean. In addition to the high planktonic and benthic population, some other factors such as low temperature and low oxygen content give rise to the high organic matter. Santhanam (1977) stated that the temperature and dissolved oxygen of the marine zone are found to be lower than in the other environment and therefore oxidation of organic matter will not be high. According to Sanders (1956), in general all clay minerals except Kaolin bind organic matter.

Relatively lesser percentage of organic matter is recorded during 1986 which clearly shows a bearing on the coarser size of the sediments.

6.3.1.3. Major and Trace Elements

To understand the chemical and physical partitioning of the chemical elements in the bulk sediments of the mud bank, cluster analysis was carried out. The concentration of various chemical elements in the bulk sediments are shown in the Table 6.3. Correlation matrix has been worked out between the size grades, organic matter, CaCO₃, major and trace elements. The matrix of correlation as represented in the Table 6.5 shows a control of grain-size in segregating many of the chemical elements. The control of grain size over the geochemical variations of sediments have been reported by several workers (Zhao et. al., 1981). Hirst (1962) also observed a similar nature for the sediments of Gulf of Paria. Ramachandran (1989) from a com-
parative study of textural classes versus the elemental concentration reported that along the Quilandy nearshore area, a size dependent factor on elemental speciation was evident. From the correlation matrix, it is found that sand is showing a high positive correlation only with silica, though a low level correlation is observed with copper and cobalt. Similarly, clay is showing high positive correlation with many of the elements barring a few, such as silica and titanium, with which it shows highly negative relationship. Silt shows high positive correlation with silica and titanium. Aluminium shows a high positive correlation with all major elements except titanium. The relationship of phosphorus with iron, manganese and sodium are highly significant and it shows a negative relationship with potassium. Manganese percentage also bears a similar relationship with sodium and potassium as in the case of phosphorus. Sodium yields a high positive correlation with potassium but both sodium and potassium exhibit a strong negative relation with titanium. Among trace elements cobalt shows a positive correlation with Nickel and zinc. Figure (6.11) shows the dendrogram from the analysis. The significant clustering observed are summarised below:

1. There is a strong group comprising of clay, organic matter, iron, manganese, potassium, aluminium, sodium and phosphorus. It is evident from the significant loading of the elements, that the clay rich sediments are abundant in organic matter and phosphorus owing to the large surface area of clay particles. The clay fraction is abundant in aluminosilicates (clay minerals) showing a sympathetic
relation with aluminium, sodium and potassium. A direct correlation of iron with alumina indicates that the iron is held in the structural positions of the aluminium silicates. As pointed out by Hirst (1962), manganese is also showing a direct relationship with iron suggesting their concentration in the clays. It has been reported that manganese is held in lattice positions in the alumino silicates and/or as dispersed oxides in close association with iron phases.

2. The second group contains Co, Ni and Zn which in turn is related to the first group. This geochemical speciation could be inter-related to both dispersed oxide phase and also to the aluminium silicate factor. It was observed by Price and Wright (1971) and Wright (1972) from a study of terrigenous sand and mud that, the elements Nickel and Zinc were preferentially enriched in the clay fractions containing different clay minerals. Calvert and Price (1970) have observed biogenic precipitation of Nickel and Zinc in organic rich muds.

3. The third group consists of silt and titanium. This association could be due to the abundance of titanium bearing detrital mineral in the silt fractions. Such an association of titanium with silt fraction was reported as early as 1925 from the data published by Grout.

4. The last significant group showing the direct control of sand over the partitioning of silica is also evident from the dendrogram. From the chemical data it is conspicuous that there is a decrease in the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio from sand to clay fraction indicating a larger proportion of free quartz in the coarser fractions.
The calcium carbonate does not show any relationship with any other constituents. The analysis was conducted without removing the shell fragments from the sediments. Copper due to its association with some of the clay minerals, behaves in a different manner. Rao et al., (1974) stated that montmorillonite accounts for higher content of Cu than Kaolinite clays. Thus the variation of copper is attributed to the difference in the terrigenous input of the sediments and its variation in the clay minerals.

6.3.2. Geochemistry of the Clayey Sediments

6.3.2.1. Phosphorus

Phosphorus is one of the important constituent in the lake sediments. This is because, phosphorus is the most limiting factor for primary production in most fresh-water environments. The increased phosphorus loading to lakes during recent decades, from cultivated land, domestic and industrial sewage, has therefore, been crucial for the eutrophication processes (Rohrlich et al., 1969; Golterman, 1977). Large amounts of the phosphorus entering a lake are metabolized in the lake water and then deposited in the sediments. Phosphorus is deposited in the sediments as:

a) Allogenic apatite minerals;

b) Organic associates, partly as structural elements of settling dead organisms, but also in humic complexes;

c) Precipitats together with inorganic complexes, like iron or aluminium hydroxides or as coprecipitate together with calcite.
Generally, the content of inorganic phosphorus is considerably higher than the content of organic phosphorus. The inorganic fraction consists mainly of non-apatite inorganic phosphorus, but in sediments in calcareous regions, apatite phosphorus might be dominant. The characteristics of the sediments depend on bottom dynamics, morphometry, hydraulic loading, water movements, trophic state and composition of allogetic material, etc. The total phosphorus concentrations in sediments generally increase with increasing water depth as a result of a more or less continuous transport of material from shallow zones of erosion and transport to the deeper accumulation areas. Consequently, different types of phosphorus compounds are found in different environments.

Distribution of phosphorus is also determined by the texture of the sediments. The fine grained sediments, viz., silty clays and clayey silts have higher concentration in the estuarine region. This could be due to the mixing and physico-chemical processes taking place in the estuary. In the southern part of the estuary, factors such as texture, organic matter and iron content might be controlling the fixation of phosphorus.

The increased content of phosphorus in the sediments is contributed by the decay of organic matter, diffusion, desorption, and leaching. The high concentration of phosphates in the mud bank sediments may be the result of upwelling. According to Bushinski (1964), the waters rich in phosphate, which is essential for the development of organic life can either come from land through rivers or from deeper
parts of the sea through upwelling. The river derived phosphorus is immediately assimilated by plankton and subsequently deposited on the bottom, and very little can be carried away to the deeper parts of the sea. The high phosphorus content reported from the sediments off Alleppey-Purakkad area may be due to the entrapment of the river derived phosphorus through assimilation and subsequent deposition by the profuse growth of organic life. Phosphorus may also be fixed with iron as ferric phosphate in the form of chemogenous compounds.

6.3.2.2. Total Iron

Iron in water, river or sea, is transported in the form of ferric oxide hydrosol stabilised by organic colloids (Moore and Maynard, 1929). The flocculation of iron in water increases with salinity with the high content of electrolytes (Castano and Garrels, 1950; Moore and Maynard, 1929). In a high $E_h$ condition, ferrous iron and ferrous hydroxide are oxidised and precipitated as $\text{Fe}_3^+$ and $\text{Fe(OH)}_3$, respectively (Krumbein and Garrels, 1952; Mason, 1958). It is found that the percentage of iron is comparatively higher in the marine sediments than in the estuarine sediments.

The very high content of iron may be due to flocculation. When river water containing high content of iron is mixed with sea water, flocculation takes place. This may explain the high content of iron in the estuarine and northern part of the lake. In the intermediate zone the concentration is relatively lesser which may be due to the fresh water occurring in that area. It is assumed that the $\text{CO}_2$ rich
weathering solution of continental origin readily dissolves ferrous iron from the mineral matter of the continental rocks and transports the iron under acid reducing conditions as ferrous iron in association with bicarbonate ion, on reaching the highly oxygenated regions, the iron content in these solutions is oxidised to ferric state and gets precipitated as Fe$_3^+$ and Fe(OH)$_3$ under favourable condition. Iron reacts with other elements also and forms different inorganic compounds.

In addition, to the above facts, the high content of iron in the mud bank sediments can also be due to the surplus value of Fe$_2$O$_3$/Al$_2$O$_3$ ratio (0.52) which indicates the presence of authigenic iron bearing minerals (Calvert, 1976).

6.3.2.3. Manganese

There has been much speculation and controversial opinions on the origin and the manner in which manganese is incorporated into hydrolysate sediments. However, it is generally conceded that manganese in sedimentary cycle is leached from the drainage basin as bicarbonates [Mn(HCO$_3$)] but deposited as oxides in the form of organic and inorganic colloids, finely divided detrital grains and as cementation matrix. Correns (1941) claims that manganese is biologically extracted, while Kuenen (1941) considers that manganese is a chemical precipitate.

There is no significant change in the percentage of manganese both in the lake and mud bank sediments. The variation of manganese is due to the greater solubility of manganese than iron in natural
water and consequently gets precipitated earlier in the form of hydroxide while manganese is carried further in solution till high oxidising conditions are met with. Such a separation of manganese from iron was reported in sedimentary process by many workers (Krauskopf, 1957; Krumbein and Garrels, 1952 and Marchandise, 1956).

Although more manganese is present in river water and sea water than titanium, the content of MnO is lower than TiO$_2$ in recent sediments. This indicates greater solubility of manganese in waters than titanium.

6.3.2.4. Titanium

In natural waters, the amount of reported titanium is very low, in sea water it is 1 ppm, in lake waters (marine) 1.6 ppm and in river waters (North America) 13.2 ppm.

Titanium in the sediments are considered as an index of sedimentation rates and in elucidating their genesis has been mentioned by several authors (Goldberg, 1954; Goldberg and Arrhenius, 1958). The high amount of titanium found in the estuary and marine sediments may be due to their excess supply from the river borne sediments which contains generally high amount of titanium. It is also believed that the bulk of the titanium is incorporated during terrestrial weathering in the clay fraction at the time of its formation as substantiated by Goldschmidt (1954) and Degens (1965). According to Chester (1965), 'Ti' is known to migrate into the sediments by the neoformation of
anatase. In view of this, a part of the titanium which may also go into solution as cations during weathering gets readily hydrolysed and precipitated as anatase hydrous oxide.

6.3.2.5. Sodium and Potassium

It has been generally observed that the potassium content is relatively lower than that of sodium both in the estuarine and mud bank sediments. As sodium and potassium are not precipitated by hydrolysis (Goldcehmldt, 1937; Heier and Adams, 1963), it is convincible that in the clay fractions sodium and potassium are tied up in clay minerals either by adsorption/or by cation exchange. From the studies it is revealed that the percentage of sodium is high in the mixing zone of the estuary and also in the mud bank sediments. The increase of sodium in the saline region may be due to the replacement of calcium by sodium as stated by Sayles and Mangelsdorf (1977) and therefore, the high increase of sodium in the estuarine and mud bank sediments is justifiable. The comparatively higher concentration of sodium than potassium may be due to the following reasons:

a) The large amount of colloidal size particles which would enhance the overall adsorption of sodium;

b) High content of salts containing sodium derived from more solutions;

c) The presence of significant amount of suitable clay mineral to fix preferentially sodium, and

d) The slow rate deposition of the clays to absorb sodium from
the overlying water.

Several authors have noted that the river clays with calcium and potassium as exchangeable ions will convert to sodium and magnesium forms, shortly after they are transported into seawater (Potts, 1959; Russell, 1970). According to Weaver (1967), clay minerals absorb more sodium and magnesium than potassium from the seawater. Sayles and Mangelsdorf (1977) found that half of the exchange sites of clays in sea water are occupied by Na, little of it being inherited from the river clay. Thus from the above discussion, it is quite reasonable to presume that the river clays after reaching the marine environment have adsorbed more sodium into their structures than any other elements.

6.3.2.6. Magnesium

The highest concentration of magnesium in the marine environment may be due to higher availability of magnesium ions in the overlying water and the higher fixation in clay minerals especially in smectite and chlorite. Experimental data given by Russell (1970) indicate that upon prolonged soaking of montmorillonite will take up magnesium from sea water when pH values are greater than 8. Moreover, Weaver (1967) stated that clay minerals are adsorbing more sodium and magnesium than potassium from the seawater. Most probably the preferential fixation of magnesium over calcium and potassium is being brought by either relatively higher adsorption capacity of the clays over Ca and Mg and by the larger cation exchange of Mg for Ca$^{++}$ and K$^{+}$ in clay minerals.
6.3.2.7. Silica and Alumina

These are the two important constituents of the clay minerals. Silica and alumina in the estuarine sediments exhibits an inverse relationship with each other. Silica also shows an antipathetic relation with iron, manganese and titanium but indicates positive response with sodium and potassium. Alumina bears strong negative relationship with sodium and potassium but shows a sympathetic relationship with most of the other elements.

In the case of mud bank sediments, the silica and alumina exhibits a highly inverse relationship ($r = -0.92$). It shows only weak negative correlation with the Na and K elements.

6.3.2.8. Trace Elements

6.3.2.8 a. Copper: The mobility of copper is high in solution and occurs as copper ions. It is removed from the solution as sulphide in reduzate sediments and as copper oxy salts in high pH environments.

Number of authors have pointed out the association of copper with soft parts of organisms as organo complexes (Revelle et al., 1955). Adsorption of copper by marine organisms has also been contended by many authors (Krauskopf, 1956; Rankama and Sahama, 1950). This can clearly explain the high amount of copper in the mud bank sediments which may be due to the higher primary productivity. A part of copper may also be fixed in clay minerals. Such a fixation of copper by clay minerals by adsorption and cation exchange has been
pointed out by Goldberg and Arrhenius (1958), Wakeel and Riley (1961) and Hirst (1962).

The high amount of copper in the marine sediments can also be explained due to high content of copper in association with montmorillonite and illite and low content of copper with kaolinite (Rao et al. 1974). This is true as in the case of mud bank sediments where the kaolinite percentage decreases with increase of montmorillonite.

6.3.2.8 b. Cobalt and Nickel: In nature generally, cobalt occurs in the di- and trivalent states whereas nickel occurs in the divalent state. Cobalt is characteristically able to migrate more readily than nickel. The enrichment of cobalt in the estuarine and marine environment may be due to the enrichment of humic acids produced by the decaying of plant materials and to a certain extent due to the contribution of organisms. Cobalt also shows an increasing trend with iron and this may be due to the adsorption of cobalt by hydrated ferrous oxide (Krauskopf, 1956). Kharkar et al. (1968) have stated that trace elements like cobalt and others which have been adsorbed from solution by clay minerals suspended in river water are desorbed in sea water. The geochemical properties of nickel determine its relationship to manganese and iron. Nickel is able to replace magnesium isomorphically, especially in silicates and to lesser extent in metasilicates (Fersman, 1959) because of their similar ionic radii. Besides iron and magnesium, it can also substitute for sodium in silicate minerals. Nickel with magnesium and silicon can travel long
distances in water and gets precipitated as complex hydrous silicates with layer lattices when the water is neutralised. Rankama and Sahama (1950) noted that, unlike iron and manganese, nickel tends to be in solution and is carried to longer distances and deposited in the hydrolysate sediments. Clay mineral composition also plays an important role in the accumulation of cobalt and nickel.

6.3.2.8 c. Zinc: Zinc can diadochically replace ferrous iron and magnesium in the silicate mineral structure because of the similar ionic radii of iron and magnesium, (Rankama and Sahama, 1950). In regions of humid climate where continental sediments show neutral or acid reaction, there is an increase in migration of zinc but in alkaline and low humidity regions the migration of this element is low (Sankov, 1961). The variation in the percentage of zinc may be also due to the clay mineral variation of the sediments besides which factors such as organic matter, salinity etc also leads to the change in concentration of the element.

6.3.3. Cluster Analysis

To summarise the whole process of chemical partitioning of clay sediments, cluster analysis was carried out for both Vembanad estuary and mud bank sediments. The inter-relation of the chemical elements in the Vembanad lake (table 6.6) gives two major significant groups, first one comprising of alumina, copper, cobalt, nickel and zinc and second one sodium and potassium which in turn is related to silica. In the first group, the relation between copper, cobalt,
nickel and zinc shows high similarity but the relationship with Al is not highly significant. Since, Na, K and silica are behaving in contrast to the first group, it indicates an enrichment or sorption of the elements in the first group within the estuarine environment. This also gives a clue that apart from these elements being present in the lattices of clay minerals they are present as dispersed oxide and organic rich phases in the clay sediments. The association of Na and K, with silica indicate that these elements are 'lattice-held' and associated with alumino-silicates (fig. 6.12).

The clustering of the chemical constituents of the clay fractions in the mud bank sediments are shown in the figure 6.13. There is a strong correlation (table 6.7) between Al, Fe and Mn, Na, K and Ti and Co, Ni and Zn. From the comparative study of average concentration of the elements in the two environments, it is found that there is a higher concentration of Fe and Mn in the marine environment compared to the estuary, whereas Co, Ni and Zn shows an enrichment in the estuarine sediments. The lesser amount of Co, Ni and Zn in the marine environment can be attributed to the depletion in the amount of organic matter which has been discussed above. The salinity factor accelerates the desorption process of cobalt in the marine environment (Murthy and Veerayya, 1981). Though the trace elements are associated with organic matter, copper is found to be more in the marine environment and it shows a low degree of positive correlation with Mn. The flocculation experiment conducted by Zhiging et al. (1987) pointed out that with the increase of salinity the flocculation rate of copper
reaches 76% compared to other trace elements such as zinc which show only 28%. Copper which normally exist in the inorganic form behave different from that of other elements as evidenced from the present study. Though the organic matter is less in the marine clays copper is enriched in the marine environment converse to Co, Ni and Zn. The strong association of Fe and Mn indicates an hydrogenous precipitation of hydrated oxides of iron and Mn from sea water and they are dispersed in the fine grained sediments. Murthy et al. (1981) has observed that major part of the Fe and Mn are non-lithogenous in origin and they are abundant in the innershelf region and it is attributed to the flocculation of colloids containing Fe and Mn oxides supplied by the rivers.

Na and K having very significant values are correlated with titanium pointing out its terrigenous dependence and are mostly abundant in the mineral phases.