5. Geochemistry and Granulometry in sediments

5.1 Introduction

The mangrove and estuarine environments are influenced by continental and marine factors. Generally, the mangrove sediments are reducing in nature (Alongi et al., 2005; Prasad, 2005) and contain high amount of organic matter and ammonia (Morell et al., 1993). Mangrove forest is considered to be one among the highly vulnerable ecosystems of the world and continuous anthropogenic activities ranging from deforestation to pollution threaten the survival of mangrove habitats throughout Asia (Agoramoorthy et al., 2005; Kumar et al., 2010). Lin et al., (2000) observed that organic carbon concentration in sediments is basically controlled by the deposition rate of the sediment, organic matter source, preservation potential and decomposition rate of organic materials during transport, burial and post depositional diagenesis.

The complex coastal processes operated in the past and operating today have left their imprints in the sediments. In this regard, the sedimentology of beach sediments plays a vital role in documenting the depositional history of a region (Angusamy and Rajamanickam, 2007). The difference in size distribution is mainly due to variation in wave energy reaching the point of sampling and extent of turbulence affecting the environment. Tidal flats are defined as “sandy to muddy or marshy flats emerging during low tide and submerging during high tide (Reineck, 1980).

The particle size analysis is one of the most powerful tool available for the interpretation of any population of sedimentary particles and is a prerequisite to understand their roles in a set of sedimentary processes (Swift et al., 1972). Tubbs,
(1977) found that the organic in intertidal sediments got negative correlation to particle size. The contaminant concentration is related to the spatial variation of sediment grain size.

The grain size distribution is an important property to understand the hydrodynamic condition, biogeochemical cycle and contaminated process. Deposition is generally associated with low energy environments where fine grained material tends to accumulate. Whereas, where erosion dominates, sediment is over-consolidated (Dyer et al., 2000). The grain size properties can suggest sources and hydrodynamic conditions of marine sediments (Carranza – Edwards et al., 2005).

Manakudy estuary receives significant amount of waters containing toxic metals from coconut husk retting and household garbage.

5.2 Material and methods

Sediment samples were stored in plastic bags and kept in refrigeration at -4°C until analysis. pH and EC were determined by using water analyser (Elico, PE,138). Calcium carbonate in surface sediments was determined based on the procedure of Loring and Rantala, (1992). Textural studies on the sediments were performed for sand, silt and clay distribution (Ingram, 1970). The silt content was measured by the pipette method of Krumbein and Petti John, (1938). Organic carbon (OC) was determined by exothermic heating and oxidation with potassium chromate and concentrated sulphuric acid followed by titration of excess dichromate with 0.5N ferrous ammonium sulphate solution (Gaudette et al., 1974). Grain size was determined by sieve method.
5.3 Seasonal variation of surface sediment parameters

5.3.1 pH

In stations, pH was high in S2 (8.29 ± 0.12) and low in S7 (6.91 ± 0.18) (Table 5.1). Among seasons, pH was high in postmonsoon (8.16) and low in monsoon (7.65). (Table 5.2)

5.3.2 EC

In stations, EC was high in S7 (6.11 ± 0.76) and low in S4 (3.19 ± 1.12) (Table 5.1). In seasons, EC was high in postmonsoon (5.61 dS/m) and low in premonsoon (3.18 dS/m). (Table 5.2)

5.3.3 Organic Carbon

The study of organic carbon (OC) in the estuarine environment is important for predicting the impact of contamination. In stations, organic carbon was high in S7 (5.87 ± 0.84) and low in S1 (1.72 ± 0.40) (Table 5.1). The ranges of organic carbon are 1.4-5.6%, 1.6-6.8%, and 1.1-5.1% with an average of 3.36%, 2.37% and 4.05% in premonsoon, monsoon and postmonsoon respectively. In seasons, organic carbon was high in postmonsoon (4.05%) and low in monsoon (2.37%). (Table 5.2)

5.4 Statistical Analysis

5.4.1 Box plot of calcium carbonate

A box plot is a graphical summary of data that is based on a five-number summary. A key to the development of a box plot is the computation of the median and the quartiles $Q_1$ and $Q_3$. The interquartile range, IQR= $Q_3$− $Q_1$ is also used. By using the interquartile range, limits are located. The limits for the box plot are 1.5(IQR) below $Q_1$ and 1.5(IQR) above $Q_3$ (Frigge et al., 1989). Data outside these limits are considered outliers. The location of the outlier is shown with the symbol *.
A percentile is a measure used in statistics indicating the value below which a given percentage of observations in a group of observations fall. The 25th percentile is also known as the first quartile ($Q_1$), the 50th percentile as the median or second quartile ($Q_2$), and the 75th percentile as the third quartile ($Q_3$). In general, percentiles and quartiles are specific types of quantiles. Box plots provide to identify outliers.

From the figure 5.5, in premonsoon $Q_1=11.10$, $Q_3=15.00$, median=14.5, IQR=3.9 and the limits are 5.25, 20.85. In postmonsoon, $Q_1=9.25$, $Q_3=13.25$, median=12.10, IQR=4 and the limits are 3.25, 19.25. In monsoon, $Q_1=8.75$, $Q_3=12.95$, median=12.40, IQR=4.2 and the limits are 2.45, 19.25. In this study, calcium carbonate has no outliers in all seasons.

The content of calcium carbonate in the surface sediments of the study area is generally low (Table 5.3). In stations, calcium carbonate was high in S1 (13.83 ± 1.86) because this station has large quantities of molluscan shell fragments that account for the elevated calcium carbonate content and low in S3 (6.48 ± 2.29). The ranges of calcium carbonate are 7.2-15.5%, 7.4-14.8%, and 3.5-14.7% with an average of 12.77%, 11.14% and 10.75% in premonsoon, monsoon and postmonsoon respectively. Calcium carbonate was high in postmonsoon (12.77%) and low in premonsoon (10.75%).

5.4.2 Correlation Studies

In table 5.4 a, b, c significantly negative correlation is obtained between pH and EC at 0.05 level in both monsoon and postmonsoon season. But in premonsoon no significant is obtained between pH and EC. Significantly positive correlation was obtained between with sand and significantly negative correlation was obtained between pH and silt in both monsoon and premonsoon at 0.05 level. In premonsoon
significantly negative correlation is obtained between pH with clay. In monsoon, significantly positive correlation is obtained between pH and clay. In postmonsoon no significant is obtained between pH with clay. Significantly negative correlation is obtained between sand with silt at 0.01 level for all seasons. In premonsoon significantly negative correlation is obtained between sand with clay at 0.05 level. But monsoon season, significantly negative correlation is obtained between sand with clay at 0.01 level. Between sand with clay no significant is obtained in postmonsoon. In premonsoon, significantly positive correlation is obtained between silt with clay at 0.05 level. In postmonsoon, significantly positive correlation is obtained between silt with clay at 0.01 level but no significant is obtained in monsoon.

5.5 Ternary plot of sand, silt and clay

The surface sediments in the study area during premonsoon are generally silty sand in nature. Sand varies from 50.48 to 74.55 % whereas, silt and clay ranges from 24.98 to 48.19 % and 0.37 to 1.33 %, respectively. On an average, sand is high (63.46%), silt is moderate (36.11%) and clay is very low (0.59%). The sedimentological type in the premonsoon sample indicates that they are mostly dominated by silty sand as seen in the trilinear diagram (Table 5.5 and Figure 5.6).

All the sediments except S7 collected during premonsoon show silty sand characteristics with silt ranging from 24.98 to 33.31 % and sand from 66.5- 74.55 %. The sediment S7 which are sandy silt, contains sand (50.48%) with silt (48.19%).

During monsoon, a variation of 40.54- 80.46 % is recorded for sand with an average of 60.1%. Silt ranges from 16.75 - 57.33 % with an average of 38 %. Clay content in monsoon season varies from 1.22-2.79 % with an average of 1.89 %
Stations S1 and S7 show sandy silt. Sand ranges from 40.54 - 45.67 % and silt from 51.99 - 57.33 %. Stations S2, S3, S4, S5, and S6 show silty sand, silt ranges from 16.75 - 30.62 % and sand from 67.81 to 80.46 %. During monsoon the distribution pattern is more or less similar to that obtained for previous season, except for a general increase in silt and clay content attributable to additional sediment input from river.

In postmonsoon, all the stations fall under silty sand in nature, silt ranges from 19.53 - 37.81 % with an average of 27.79 %, sand ranges from 59.24 - 78.8 % with an average of 71.12 %. (Table 5.5; Figure 5.8)

Comparing the seasonal data on sediment characteristics, it is seen that the characteristics has changed at station S1, S3 and S7 from sandy silt in premonsoon and monsoon to silty sand during postmonsoon season. In S2, the sediment characteristics changed silty sand in premonsoon and postmonsoon to sandy silt in monsoon. Sand content is more at S1 in pre and postmonsoon season. Comparing other season, the average of silt (38%) and clay (1.89%) are high in monsoon and sand is high in postmonsoon (71.02%). During monsoon season, the sand content is more in most of the stations. The inflow of reverine input might have changed the sediment nature during monsoon. The distribution pattern is more or less the same except for a general increase in silt content attributable to additional sediment input from river.

5.6 Grain size

Table 5.6 a, b, c shows the grain size analysis for three seasons. The highest fraction is found #50 sizes followed by #140 and #60 respectively. On analysis all the three stations have different grain size ranging from #230 to #35. Table 5.7
shows the descriptive statistics of the different grain size parameters. In premonsoon maximum mean size is 2.01 Φ and minimum mean size is 1.56 Φ. In monsoon maximum mean size is 2.18 Φ and minimum mean size is 1.84 Φ. In postmonsoon maximum mean size is 1.94 Φ and minimum mean size is 1.52 Φ. In table 5.6a, among seven stations S7 has fine sand and all the other stations have medium sand on premonsoon. In monsoon S1, S3, S6 and S7 have fine sand and others are medium sand (Table 5.6b). In postmonsoon all the stations have medium sand (Table 5.6c).

In monsoon, pre and postmonsoon all the stations have moderately sorted but in monsoon S6 has poorly sorted. Both pre and postmonsoon all stations obtain very fine skewed except S7. S7 has fine skewed. In monsoon S1, S2 and S4 have fine skewed. S3 and S7 have coarse skewed. S5 has very fine skewed and S6 has near symmetry. (Table 5.6 a, b, c)

In table 5.9, stations S2, S4 and S5 have 100% medium sand. Stations S1, S2 and S6 have 66.67% medium sand and S7 has 33.33% medium sand. Except S6 all the stations have 100% moderately sorted but S7 has 66.67% moderately sorted. S5 has 100% very fine skew, S7 has 33.33% very fine skew and others have 66.67% very fine skew. Stations S1, S2, S4 and S7 have 33.33% very fine skew. All the stations have 100% very leptokurtic in nature.

5.6.1 Bivariate scatter graphs of grain size parameters

Sedimentologists have attempted to use scatter graphs of grain size parameters to distinguish between different depositional settings, via bivariate plots, which are based on the assumption that these statistical parameters reliability reflect differences in the fluid-flow mechanisms of sediment transportation and deposition.
(Sutherland and Lee, 1994). Figure 5.10a shows the relationship between mean grain size and sorting for the Manakudy estuary. There is a clustering in fine and moderately sorted. Griffiths, (1967) explained that both mean grain size and sorting are hydraulically controlled, so that in all sedimentary environments the best-sorted sediments have mean size in the fine sand size range. Figure 5.10b shows the relationship between sorting and skewness in the Manakudy estuary. Sediments are moderately sorted towards poorly sorted and fine skew towards very fine skew fractions. By contrast, moderately sorted sediments are mainly clustered around the very fine skew range and have positive skewness and negative skewness values. Plotting of skewness against kurtosis is a powerful tool for interpreting the genesis of sediment, by quantifying the degree of normality of its size distribution (Folk, 1966) Fig. 5.10c shows that the sediments from Manakudy estuary lay within the positively skewed/very leptokurtic range. This suggests the dominance of medium grain size population and the subordinate of coarse and fine grain size which gives positive skewness. However, most of the sediments from the Manakudy estuary show mixing of different size-range sediment populations, with one predominant population and a very subordinate population.

5.6.2 Linear discriminate function

According to Sahu (1964), the statistical method of analysis of the sediments to interpret the variations in the energy and fluidity factors seems to have excellent correlation with the different processes and the environment of deposition. Linear Discriminate Function (LDF) analysis of the sediment samples was carried out using the following equations:
1. Aeolian/beach

\[ Y_{1(A:B)} = -3.5688 M + 3.7016 r^2 - 2.0766 SK + 3.1135 KG \]

If \( Y \) is \( >-2.7411 \), the environment is ‘Beach’ but if \( Y \) is \( <-2.7411 \), the environment is ‘Aeolian’.

2. Beach/shallow agitated water

\[ Y_{2(B:SM)} = 15.6534 M + 65.7091 r^2 + 18.1071 SK + 18.5043 KG \]

If \( Y \) is \( <63.3650 \), the environment is ‘Beach’ but if \( Y \) is \( >63.3650 \), the environment is ‘Shallow marine’.

3. Shallow marine/fluvial environment

\[ Y_{3(SM:F)} = 0.2852 M - 8.7604 r^2 - 4.8932 SK + 0.0482 KG \]

If \( Y \) is \( >-7.4190 \), the environment is ‘Shallow marine’ but if \( Y \) is \( <-7.4190 \), the environment is ‘Fluvial’.

4. Fluvial/turbidity

\[ Y_{4(F:Turb)} = 0.7215M + 0.403r^2 + 6.7322SK + 5.2927KG \]

If \( Y \) is \( >10.000 \), the environment is ‘Turbidity’ but if \( Y \) is \( <10.000 \), the environment is ‘Fluvial’. (\( Y_1 \) = aeolian/beach, \( Y_2 \) = beach/shallow marine, \( Y_3 \) = shallow marine/fluvial, \( Y_4 \) = fluvial/turbidity)

The process and environment of deposition were deciphered by Sahu’s linear discriminate functions of \( Y_1 \) (aeolian, beach), \( Y_2 \) (beach, shallow agitated water), \( Y_3 \) (shallow marine, fluvial) and \( Y_4 \) (turbidity, fluvial). With reference to the \( Y_1 \) and \( Y_2 \) values, all the samples fall (100 %) in an aeolian process (\( Y_1 \)) and all the samples (100 %) fall in shallow marine waters (\( Y_2 \)) respectively. Further, all the samples (100 %) fall in the (\( Y_3 \)) fluvial, \( Y_4 \) values show that about 100 % of the samples were deposited by turbidity action (Fig. 5.11) (Table 5.10 a, b, c).
5.6.3 CM pattern

Grain size parameters and the plots of CM patterns help to distinguish between the sediments of different environments of fluvial and deltaic deposits (Passega, 1964; Visher, 1969). In the present study, an attempt has been made to identify the modes of deposition of sediments of the Manakudy estuary by CM pattern. Parameter C (one percentile of the grain size distribution) and M (the median) were plotted with phi values of the C and M obtained from cumulative curves in microns (Fig. 5.12(a,b) -5.14(a,b)). The relation between C and M is the effect of sorting by bottom turbulence. CM pattern is subdivided into three segments namely, NO (rolling), OPQ (bottom suspension and rolling), QR (graded suspension no rolling), RS (uniform suspension), S (pelagic suspension). The plotted results of Manakudy estuary sediments (premonsoon, monsoon and postmonsoon) shows that all the samples fall in bottom suspension rolling to graded suspension condition. In comparison with the tractive current diagram, the samples fall in beach and tractive current environment, ie, due to interaction with wave actions (Fig. 5.12(a,b)-5.14(a,b)).

5.7 Discussion

Soil pH directly affects the solubility of many of the nutrients in the soil needed for proper plant growth and development. pH was high in S2 and low in S7 because this station was very near to the mangrove forest. pH was high in premonsoon and low in monsoon because of rainfall. Excess rainfall leaches base cation from the soil, increasing the percentage of Al$^{3+}$ and H$^+$ relative to other cations. Additionally, rainwater has a slightly acidic pH of 5.7 due to the reaction
with CO$_2$ in the atmosphere that forms carbonic acid. Fig 5.1 shows the monthly variation of pH in surface sediment. From the figure, S7 has low pH value in all months. EC was high in premonsoon due to bird excreta and low in postmonsoon due to low rain fall. Fig 5.2 shows the monthly variation of EC in surface sediment. From the figure, S7 has high EC value in all months.

Box plot shows the mean, median, interquartile range and the outliers of calcium carbonate. Postmonsoon, premonsoon and monsoon have no outlier values (Fig 5.5). An outlier is an observation that lies an abnormal distance from other values in a sample from a data. Calcium carbonate protects the organic matter and makes it slight reactive (Duchauffour, 1983). Calcium carbonate distributions vary as a result of mixing between different sedimentary material of varying composition such as mixing between marine carbonate and terrestrial siliclastic (Evans, 1988). This may be the reason for the higher level of calcium carbonate in the estuarine study in the present investigation. Calcium carbonate was high in postmonsoon and low in premonsoon. Roy et al., (1999) observed similar trends in the sediments of Thamaraparani delta and Ayyamperumal et al., (2006) in Uppana River on the South East Coast of India. Fig 5.3 shows the monthly variation of calcium carbonate in surface sediment. From the figure, S1 has high value in all months and S3 has low value. Calcium carbonate in shelf sediments may be derived as carbonate materials and particulate matter from adjacent landmass, and through inorganic and organic precipitation from the water column. The major sources of carbonate in the sediments of the study area are the shells and broken shell fragments of organisms, molluscs and also due to dilution of biogenic calcite by detrital material in the sediments. Similar observations were made by Sebastian et al., (1990), in their study.
on sediments of Mahe estuary, West Coast of India. The association of sand particles with CaCO$_3$ indicates the major contribution of shell fragments to the sand fraction.

Total organic carbon has a major influence on both the chemical and biological processes that take place in sediments. Organic carbon increases with increasing finer fraction and decreases with the increasing coarser fraction in the sediments. Fig 5.4 shows the monthly variation of OC in surface sediment. From the figure, S2 has low OC value in all months. Organic carbon was high in S7, as it was very near to the mangrove forest. The relatively low value of organic carbon in this station could be attributed to the constant flushing activity of tides along the impact of waves which removes the finer fractions of sediments from the fringing areas. OC was high in postmonsoon and low in monsoon.

The grain size of the sediment mean, sorting, skewness and kurtosis are used to relate the depositional environment of sediments with the transport process of the estuary. Both pre and postmonsoon positive skewness and kurtosis are obtained (Table 5.8 a, b, c). In the premonsoon season S7 has the low kurtosis value of 1.81. A low kurtosis value implies that the part of the sediments achieved from high energy environment by sorting. In monsoon negative skewness (-0.14) is obtained in S3 and S7 (Table 5.8b). Positive skewness of sediments indicates the unidirectional transport (channel) or the deposition of sediments in sheltered low energy environment. Generally, most beach sediments are slightly negative skewed because of a small proportion of coarse grains (Folk, 1966). Friedman, (1962) showed that most sands are leptokurtic and are either positively or negatively skewed. This could be explained by the fact that most sands consist of two populations: one predominant
Among the seven samples, variation exist between 1.81-2.43 which is nothing but the reflection flow characteristics of the deposited medium and the dominance of finer size of leptokurtic nature of sediments reflux the maturity of the sand. This may be due to the aggregation of sediment particle by compaction and the variation may be due to sorting of the continuous addition of finer and coarser material in different proportions.

The grain size parameters are analysed using bivariate scatter graphs which is used to distinguish between different depositional settings. It is based on the assumption that these statistical parameters reflux differences in the fluid flow mechanism of sediment during transportation. Fig 5.10a shows the relationship between the grain size and sorting for the Manakudy estuary. From the figure 5.6a it is very clear that the sediment during monsoon season and postmonsoon season are moderately sorted. From fig 5.10b the sediment’s of three season lie the near symmetry, fine skew and very fine skew regions. Few grains during the monsoon season are moderately sorted towards poorly sorted whereas grains of premonsoon, and postmonsoon are very fine skewed which are moderately sorted. From fig 5.10c the grains of premonsoon season is coarser and very leptokurtic. Few grains from monsoon season are near symmetry and very leptokurtic. Most of the premonsoon, monsoon and postmonsoon sediment grains lie between fine skew, very fine skew and very leptokurtic in nature. The results of the sedimentological study indicates that the Manakudy sediments sand is the major fraction and it is moderate to poorly sorted, coarsely skewed and very leptokurtic in nature. Textural analysis indicates the
dominance of medium to fine grained in premonsoon samples. Fine to medium grained sediments dominate in monsoon samples. Medium sand in postmonsoon samples were due to high energy condition.

The linear discriminate function (LDF), determines the impact of wind, the nature of the estuary and the process of deposits on the estuary. An analysis on all the stations had erosion due to wind and the process is called Aeolian which deflates the earth surface by the removal of fine grained particles by the turbulent action of the wind. In station six during premonsoon a high value of 3.22, 2.93 is observed during monsoon and 4.52 during postmonsoon is obtained yet the nature is Aeolian. On analysis the nature of the estuary is found to be shallow marine and all the values during premonsoon, monsoon and postmonsoon fit perfectly to shallow marine (Table 5.10a,b,c).

The deposits and the land forms associated due to geochemical processes is also being calculated and the values fluctuated between 5.07-7.89 during premonsoon 4.07-9.97 during monsoon and 2.11-7.06 during postmonsoon and the nature being defined as fluvial. The turbidity existed in all the stations during premonsoon, monsoon and postmonsoon. A highest turbidity of 22.97 was found during postmonsoon at S1 which may be due to the evaporation of estuarine water. LDF results show the dominance of shallow marine deposits in the Aeolian beach and the influence of turbidity. (Table 5.10 a, b, c)

The CM diagram and tractive current deposit plot for premonsoon, monsoon and postmonsoon is shown in fig 5.12 (a, b), 5.13 (a, b) and 5.14 (a, b). The plot is drawn between medium size particles Vs coarse sized particle which are in the micron size. From the plot the value for Manakudy estuary lies between 4 and 5
therefore the particle will have tractive current moving towards the beach. The suspension of the particles were analysed which is shown in fig 5.12 b. The plot of the sediments of Manakudy estuary lies between 2 and 3 therefore the particles are suspended at the bottom with continuous rolling which moves towards graded suspension no rolling. This observation has been found for premonsoon samples. Similar observations were found for monsoon and postmonsoon fig 5.13 (a, b) and 5.14 (a, b) respectively. From the plot the estuary has a suspended system of sediment which is kept in suspension by means of tractive current due to the interaction with wave action.