3.1. Introduction:

The nearshore zone is a highly energetic environment affected by surface gravity waves and mean currents. The nearshore environment is also a transition zone characterised by on-offshore sediment transport between the surf zone and the offshore zone. The exchange of sediment between the inshore and the offshore environment plays a major role on coastal evolution and shoreline stability (Swift, 1976). A good understanding of sediment transport processes in the nearshore zone is important for scientists and coastal zone managers.

Vembanad lagoon is the largest backwater system on the Kerala coast extending 80 km in a NW–SE direction from Munambam in the north to Alleppey in the south. The width of the lagoon varies from 500 m to 4 km and the depth from < 1 m to 12 m. The Periyar river discharges into the lagoon in the north and the Muvattupuzha river in the central part. The rivers Meenachil, Manimala, Achanakovil and Pamba discharge into the southern part of the
lagoon. Estuaries and deltas develop at river mouths during transgressive and regressive phases, respectively (Boyd et al., 1992). Rivers and its estuaries provide connectivity between terrestrial and marine environments.

The present investigation is scheduled into two phases namely i) sample collection and ii) laboratory methods

3.2. Collection of sediment samples:

3.2.1. Estuarine and nearshore environment:

Nine cores in the Vembanad estuary, eleven gravity cores and twenty two grab samples in the nearshore of Cochin were recovered. The length of the estuary cores vary from 42 to 156 cm and that of the nearshore cores vary from 58 to 190 cm. All the cores were sub sampled at an interval of 2 cm. The subsamples and grab samples were stored in air tight polythene bags. Selected subsamples of the nearshore cores were analyzed for the wet bulk density, moisture content, organic carbon, clay mineralogy, geochemistry, geotechnical and textural parameters. Selected subsamples of the estuary cores were analyzed for the wet bulk density, moisture content, organic carbon, clay mineralogy, textural and geotechnical parameters. Grab samples were analyzed for organic carbon, clay mineralogy, texture and geotechnical properties.

3.2.2. Onshore environment:

A borehole of 40 m depth was drilled at Paravur (Fig: 3.1). The area represents Holocene marine regression environment. The samples were stored in air tight polythene bags. Selected samples of the borehole were analyzed for estimating wet bulk density, moisture content, organic carbon, clay mineralogy, textural and geotechnical parameters, pollen analysis, and C-14 dating.
The locations of the cores and grab samples recovered from the estuary and nearshore are shown in the figure 3.2. and figure 3.3.

3.3. Geotechnical studies of sediment samples:

Sediment samples collected from the borehole, nearshore as well as estuarine area were subjected to geotechnical investigation. The geotechnical parameters analyzed include water content, wet bulk density, shear strength and Atterberg limits. The Atterberg limits comprise of liquid limit, plastic limit, plasticity Index and liquidity Index. The geotechnical parameters of sediments were analyzed according to the procedures as suggested by IS:2720 (Part II)-1964, (ASTM D 4318-2000), Singh and Punmia (1970) and Venkataramaiah (1993).

3.3.1. Water Content

To find out the water content of a sediment sample, oven drying method was used (IS:2720 (Part II)-1964). Sample weighing 10 - 20 grams was kept in a clean container in a thermostatically controlled oven for about 24 hours at 60°C. A clean non-corrodible container was taken and weighed with its lid on an electronic balance. Sample was placed in the container and the lid was replaced. The container and the contents were weighed.
Figure 3.1: Geomorphic units in the Periyar river basin and adjacent areas interpreted from satellite imagery (IRS 1B LISS II FCC bands 2, 3 and 4; March 1995), Narayana et al., 2001). Map shows the location of borehole of 40 m depth shown as a solid circle.
Figure 3.2: Study area and location of core samples in Vembanad lagoon.
Figures 3.3: Map showing the study area and location of surface (grab) and core samples. 

(◇) - surface/grab samples; (●) - core samples
### Table 3.1: Details of the core samples collected from the Periyar estuary

<table>
<thead>
<tr>
<th>Estuary core</th>
<th>Water depth (m)</th>
<th>Core length (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE-3A</td>
<td>1.3</td>
<td>52</td>
</tr>
<tr>
<td>PE-5</td>
<td>0.6</td>
<td>72.5</td>
</tr>
<tr>
<td>PE-7</td>
<td>1.3</td>
<td>82</td>
</tr>
<tr>
<td>PE-11B</td>
<td>1.6</td>
<td>42</td>
</tr>
<tr>
<td>PE-13</td>
<td>1</td>
<td>92</td>
</tr>
<tr>
<td>PE-14</td>
<td>1.5</td>
<td>108</td>
</tr>
<tr>
<td>PE-17</td>
<td>2</td>
<td>72</td>
</tr>
<tr>
<td>PE-20</td>
<td>1.5</td>
<td>70</td>
</tr>
<tr>
<td>PE-33A</td>
<td>1</td>
<td>156</td>
</tr>
</tbody>
</table>

### Table 3.2: Details of the nearshore cores of Central Kerala

<table>
<thead>
<tr>
<th>Nearshore core</th>
<th>Water depth (m)</th>
<th>Core length (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>G-3</td>
<td>20</td>
<td>80</td>
</tr>
<tr>
<td>G-4</td>
<td>20</td>
<td>160</td>
</tr>
<tr>
<td>G-6</td>
<td>10</td>
<td>80</td>
</tr>
<tr>
<td>G-7</td>
<td>20</td>
<td>110</td>
</tr>
<tr>
<td>G-8</td>
<td>30</td>
<td>170</td>
</tr>
<tr>
<td>G-9</td>
<td>30</td>
<td>58</td>
</tr>
<tr>
<td>G-10</td>
<td>20</td>
<td>178</td>
</tr>
<tr>
<td>G-11</td>
<td>10</td>
<td>155</td>
</tr>
<tr>
<td>GC-16</td>
<td>20</td>
<td>190</td>
</tr>
<tr>
<td>GC-20</td>
<td>10</td>
<td>80</td>
</tr>
<tr>
<td>GC-22</td>
<td>5</td>
<td>100</td>
</tr>
</tbody>
</table>
Table 3.3: Details of the grab samples collected from the nearshore areas of Central Kerala

<table>
<thead>
<tr>
<th>Sample No</th>
<th>Water depth (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-27</td>
<td>5</td>
</tr>
<tr>
<td>S-28</td>
<td>10</td>
</tr>
<tr>
<td>S-29</td>
<td>20</td>
</tr>
<tr>
<td>S-30</td>
<td>30</td>
</tr>
<tr>
<td>S-13</td>
<td>30</td>
</tr>
<tr>
<td>S-14</td>
<td>20</td>
</tr>
<tr>
<td>S-15</td>
<td>10</td>
</tr>
<tr>
<td>S-16</td>
<td>5</td>
</tr>
<tr>
<td>S-31</td>
<td>5</td>
</tr>
<tr>
<td>S-32</td>
<td>10</td>
</tr>
<tr>
<td>S-33</td>
<td>15</td>
</tr>
<tr>
<td>S-34</td>
<td>30</td>
</tr>
<tr>
<td>S-17</td>
<td>5</td>
</tr>
<tr>
<td>S-18</td>
<td>10</td>
</tr>
<tr>
<td>S-39</td>
<td>5</td>
</tr>
<tr>
<td>S-40</td>
<td>11</td>
</tr>
<tr>
<td>S-41</td>
<td>20</td>
</tr>
<tr>
<td>S-42</td>
<td>30</td>
</tr>
<tr>
<td>S-51</td>
<td>30</td>
</tr>
<tr>
<td>S-52</td>
<td>20</td>
</tr>
<tr>
<td>S-53</td>
<td>10</td>
</tr>
<tr>
<td>S-54</td>
<td>5</td>
</tr>
</tbody>
</table>

With the lid removed, the container was then placed in the oven for drying. After drying, the container was removed from the oven and allowed to cool in a dessicator. The lid was then replaced, and the container and the dry
sediment were weighed. The water content was calculated from the following expression:

\[ W = \frac{W_2 - W_3}{W_3 - W_1} \times 100 \]

Where, 
- \( W_1 \) = Weight of container with lid
- \( W_2 \) = Weight of container with lid and wet sample
- \( W_3 \) = Weight of container with lid and dry sample

### 3.3.2. Wet Bulk Density

In a pre-weighed container of known volume, sample was taken and found out the total weight (\( W_1 \)) of sample and the container. To remove the water content, the container along with the sample was kept in an oven and dried the sample completely. The dried sample and container was weighed to find out the dry weight (\( W_2 \)) of sample and the container. Wet bulk density was found out from the following expression:

\[ \text{Wet bulk density} = \frac{W_1 - W_2}{V} \]

Where, 
- \( W_1 \) = Weight of wet sample + container
- \( W_2 \) = Weight of dry sample + container
- \( V \) = Volume of sample

### 3.3.3. Atterberg limits:

The Atterberg limits are a basic measure of the nature of a fine grained soil, and can be used to distinguish between silt and clay and between different types of silts and clays (Kwon et al., 2011). Evaluation of the Atterberg limits is a soil mechanical test allowing a first insight into the chemical reactivity of clays. Basically, the liquid limit and the plasticity index are highly and mainly

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Chapter 3

Methodology

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influenced by the ability of clay minerals to interact with liquids (Schmitz et al., 2004).

Generally the fabric, physico-chemistry of clay-water system and organic carbon content of sediments influence the Atterberg limits (Rosenquist, 1962; Sodorblom, 1966; Rashid and Brown, 1975; Bennett et al., 1981). Atterberg limits explain the consistency of sediments, which means the relative ease with which sediment can be deformed. This term is mostly used for fine-grained sediments for which the consistency is related to a large extent to the water content. Atterberg limits include liquid limit, plastic limit and plasticity index. Atterberg limits were analysed using the standard procedures (ASTM, D 4318-2000).

3.3.3.1. Liquid limit:

It is the water content corresponding to the arbitrary limit between liquid and plastic state of consistency of sediments. It is defined as the minimum water content at which the sediment is still in the liquid state, but has a small shearing strength against flowing was measured by using standard available procedure (IS 2720 Part-V)-1970).

The liquid limit was determined in the laboratory with the help of the standard liquid limit apparatus designed by Casagrande. The apparatus consists of a hard rubber base of B.S. hardness 21-25, over which a brass cup drops through a desired height. The height of fall of the cup can be adjusted with the help of adjusting screws. Before starting the test, the height of fall of the cup is adjusted to 1 cm. The Casagrande tool cuts a groove of size 2mm wide at the bottom, 11mm wide at the top and 8mm high.

About 120g of the sample was mixed thoroughly with distilled water on a glass plate to form a uniform paste. A portion of the paste was placed in the
cup over the spot where the cup rests on the base, squeezed down and spread into position and the groove was cut in the soil pat as shown in the figure 3.4. The handle was rotated about 2 revolutions per second, and the number of blows was counted until the two parts of the sediment sample come into contact at the bottom of the groove along a distance of 12mm. After recording the number of blows, approximately 10 grams of sediment from the closed groove was taken for determination of water content. Since it was difficult to adjust the water content precisely equal to the liquid limit when the groove should close in 25 blows, the liquid limit was determined by plotting a graph between the number of blows at abscissa on algorithmic scale and the corresponding water content as ordinate. It shows that such a graph, known as flow curve, is a straight line having the following equation:

\[ W_1 - W_2 = \log_{10} \frac{n_2}{n_1} \]

where, \( W_1 \) = water content corresponding to blows \( n_1 \),
\( W_2 \) = water content corresponding to blows \( n_2 \)

For plotting the flow curve, at least four to five sets of readings in the range of 10 to 40 blows were taken. The water content corresponding to 25 blows is taken as the liquid limit.

![Figure 3.4 - (a) Groove separating two halves of the soil pat, (b) blow counts stopped after the groove closes by about 12mm size.](image)
3.3.3.2. Plastic limit (PL):

It is the water content corresponding to an arbitrary limit between the plastic and the semi-solid states of consistency of sediment. It is defined as the minimum water content at which a sediment mass will just begin to crumble when rolled into a thread approximately 3mm diameter or it is the minimum amount of water necessary to make clay plastic.

To determine the plastic limit, the sample was mixed thoroughly with distilled water until it became plastic enough and moulded easily with fingers. The plastic sediment mass was left for enough time and allowed water to permeate through the sediment mass. A ball was formed with about 10gms of this plastic sediment mass and rolled between the fingers and a glass plate with just sufficient pressure to roll the mass into a thread of uniform diameter throughout its length. When a diameter of 3mm was reached, the sediment was remoulded again into a ball. This process of rolling and remoulding was repeated until the thread starts just crumbling at a diameter of 3mm. The crumbled threads were kept for water content determination. The test was repeated twice more with fresh samples. The plastic limit ‘wP’ is then taken as the average of three water contents (Singh and Punmia, 1970).

3.3.3.3. Plasticity Index (IP):

The range of consistency within which a sediment mass exhibits plastic properties is called plastic range and is indicated by plasticity index. The plasticity index is defined as the numerical difference between the liquid limit (wL) and the plastic limit (wP) of sediment mass.

The plasticity index is calculated from the relation:

\[
I_P = w_L - w_P
\]
III and their meanings

Non plastic IP = 0, Slightly plastic IP = 1 – 5, Low plasticity IP = 5 – 10, Medium plasticity IP = 10 – 20, High plasticity IP = 20 – 40, Very high plasticity IP >40

Low plasticity wL = < 35%, Intermediate plasticity wL = 35 - 50%, High plasticity wL = 50 - 70%, Very high plasticity wL = 70 - 90%, Extremely high plasticity wL = > 90% (wL Liquid limit) (after Casagrande, 1948).

3.3.3.4. Liquidity index:

The liquidity index (LI) is used for scaling the natural water content of a soil sample to the limits and can be calculated as a ratio of difference between natural water content, plastic limit, and plastic index

\[ LI = \frac{(wc - wP)}{(wL - wP)} \]

where wc is the natural water content (Kwon et al., 2011).

3.3.4. Vane Shear:

The most versatile test to measure compressibility and shear strength parameters of soils is the triaxial test, in which a cylinder – shaped specimen, sealed by a rubber membrane, is submitted to an axisymmetric water pressure and then to an increasing axial loading. If the test is carried out under undrained conditions (no water is allowed to get out of the specimen during the test), the undrained shear strength (su) of the soil can be measured. The triaxial test depends on the preparation of good-quality undisturbed specimens. When the soil is too soft for an adequate preparation of undisturbed specimens (which is usually the case when very soft marine sediments are to be tested), the shear vane test is an alternative for estimating the undrained shear strength. It is determined by applying a rotation to a vane introduced into the soil sample and
measuring the maximum torque that the soil can bear before failure (Dias and Alves (2009)).

Shear strength is the resistance to shearing stress and a consequent tendency for shear deformation. The shear strength of the sediment sample was determined by vane shear test as this method widely used for soft clays. In the present study shear strength was determined by using Laboratory Vane Shear Apparatus (IS: 2720 (Part XXX), 1980).

The shear strengths of the clay is expressed as:

\[ S = \frac{T}{\pi D^2} \left(\frac{H}{2} + \frac{D}{6}\right) \]

Where,  
- \( T \) = torque  
- \( D \) = diameter of the vane,  
- \( H \) = height of the vane

### 3.4. Organic Carbon

Organic carbon in marine sediments is primarily derived from settling biogenic debris from the water column and their abundances serve as indicators of primary productivity (Muller and Suess, 1979), whereas in estuaries and nearshore areas, the organic carbon is contributed by terrestrial processes. The organic carbon concentrations in sediments, especially in the continental margin region, depend upon the depositional environment, sedimentation rate, bottom water redox condition etc. (Canfield, 1994).

For estimation of organic carbon content in sediments, samples were oven dried at 50°C and finely ground in agate mortar for the determination of organic carbon content. The organic carbon content (Corg) of sediment samples were determined by using a modified Elwakeel and Riley (1957) method by Gaudette et al., (1974) which is based on the exothermic heating and oxidation of organic matter. The sample was treated with potassium dichromate and
concentrated sulphuric acid, followed by back titration with ferrous ammonium sulphate using diphenyl amine as an indicator. The principle behind this method is based on the oxidation of organic carbon with chromic acid and titrimetric determination of the oxidant consumed.

Powdered sediment sample of 0.5g is taken and treated with 10ml of 1N \( \text{K}_2\text{Cr}_2\text{O}_7 \) solution and 20 ml of conc: \( \text{H}_2\text{SO}_4 \). It is kept for half an hour and then diluted by adding 170ml of distilled water, followed by adding 10ml of orthophosphoric acid and 0.2g of NaF. About 2 or 3 drops of diphenyl amine indicator is added. The change from turbid green colour to brilliant green indicates the end point. The volume of ferrous ammonium sulphate is noted as \( T \). A blank solution is prepared by taking all the reagents in the same amount as above and titrated against ferrous ammonium sulphate. Volume of ferrous ammonium sulphate used is noted as \( S \). The percentage of organic carbon is calculated using the equation \( 10(1-T/S) \). The organic carbon in the bulk sediment was determined in all the surficial samples, nearshore and estuarine core samples and borehole samples employing the above stated method.

3.5. Textural analysis

Sediment grain-size composition has been widely used to characterize sediment sources and transport patterns and to reconstruct depositional environments (Folk and Ward, 1957; Sun et al., 2002). Moreover, the association of organic carbon with mineral surfaces has been established throughout the global oceans (e.g. Hedges and Keil, 1995; Keil et al., 1998; Wakeham et al., 2009), such that grain-size composition is central to understanding the fate of sedimentary organic matter. For example, fine-grained sediments have larger surface area and thus higher organic matter loading capacity than coarse sediments (Hedges and Keil, 1995)
In general the term texture represents the size, shape, roundness, grain surface features and fabric of grains. Because of differential erosion, transportation and deposition sediments laid down in different depositional environments may possess distinct particle size distributions. By determining the particle size distributions it is possible to talk about the environment of deposition and so to utilize this technique as a tool for environmental reconstruction (Lario et al., 2002). Textural parameters comprising sand, silt and clay ratios of the sediment core samples were carried out using standard methods (Carver, 1971; Folk, 1980).

Textural analysis of core samples was carried out at 5cm interval following the standard sieve and pipette techniques. About 15 to 20 g of dried sediment sample was weighed accurately and transferred into a thoroughly cleaned 1000ml beaker. The samples were made salt free by repeated washings using distilled water and subsequently treated with H$_2$O$_2$ and glacial acetic acid in order to remove the organic matter and carbonates respectively. The samples were wet sieved through a 63µm sieve to separate sand and mud fraction. The sand fraction (>63µm) retained in the sieve was dried and weighed, while the mud fraction was collected in a 1000 ml measuring glass cylinder and subjected to pipette analysis to estimate the silt and clay contents following the method of Folk (1980). Percentage distribution of sand, silt and clay fraction in each sample was determined. Size classification adopted is sand >63µm, silt 63 - 4µm and clay < 4µm. Based on the relative abundance of sand, silt and clay in each sub sample in each size class, sediment texture was determined according to the classification of Folk (1980). The sand-silt-clay ratios were plotted on trilinear diagram for textural classification / nomenclature based on Folk’s (1980) textural classification.
3.6. Clay mineral analysis

The clay minerals in the samples were identified and semi-quantified employing the following steps.

3.6.1. Sample preparation:

Dried sediment sample weighing 15-20 g was taken and dissolved salts were removed by washing thoroughly with distilled water. This process has been repeated till the sample was deflocculated. The presence of organic matter in the sample can produce broad X-ray diffraction peaks, increase the background, and inhibit dispersal of other minerals if present in significant amount. Therefore, the organic matter from the sediment samples was expelled by treating with 20-25 ml of 30% H₂O₂. The sample was again washed with distilled water. The sample was also made free of carbonates by treating with 10 ml glacial acetic acid. Excess acid was removed by washing with distilled water. After the sample is disaggregated and deflocculated, >63µm size fraction sediments were separated by wet sieving and the supernatant was collected in a 1000 ml cylinder. The 2µm size fraction of sediment was separated based on the settling velocity (Stoke's law) principle. The resulted suspension was transferred to a settling column and allowed to settle for 3 hrs 27 minutes i.e., until the required size fraction was obtained. The clay water suspension was used for making oriented clay slides of almost equal size and thickness by pipetting equal volume (1ml) on to glass slides. The glass slides were allowed for air-drying at room temperature, while drying, care was taken to avoid contamination by dust and other means (Biscaye, 1964; Gibbs, 1965).
3.6.2. X-Ray diffractogram

X-ray diffraction methods are commonly used for identification of mineral components in soils, sediments and rocks, particularly for clay minerals in sediments and soils. X-ray diffraction studies were carried out on the air dried samples (Gibbs, 1965). The slides were run on X-ray Diffractometer (XRD) from 2 to 30° 2θ at 1° 2θ / minute using Ni filtered CuK∞ radiation. The XRD facility at National Institute of Oceanography, Goa (Philips-1840 Model), was availed. The samples were then glycolated by exposing the slides to ethylene glycol vapours at 100°C for one hour and rescanned the slides under same instrumental settings for the confirmation of montmorillonite. The peaks for different clay mineral groups like kaolinite, chlorite, illite and smectite were identified. In order to differentiate the kaolinite and chlorite peaks, the samples were also scanned from 24 to 26° at 0.5° 2θ/minute (Biscaye, 1964).

3.6.3. Semi-quantification of clay minerals

The relative contents of clay minerals were determined using peak areas of smectite (15-17 Å), illite (10 Å), chlorite (7 Å) and kaolinite (7 Å). The peak areas of the spectra of these clay minerals were calculated by using the glycolated X-ray diffractograms and relative weight percentages were calculated following the semiquantitative method of Biscaye (1965). The relative clay mineral contents of smectite, illite, kaolinite and chlorite were determined using ratios of integrated peak areas of their basal reflections, weighted by empirically estimated factors. Accordingly, 17 Å peak area of the smectite is multiplied by 1, the 10 Å peak area of illite by 4, and both the kaolinite and chlorite proportions positioned at 7 Å peak were multiplied by 2. As the 001 plane of kaolinite and 002 plane of chlorite partly overlap each other at 7 Å, the relative proportions of both minerals were first deduced from the
areas of 002 kaolinite and 004 chlorite reflections at 3.54 Å and 3.58 Å respectively. The clay minerals quantified in this study are smectite, kaolinite, illite and chlorite.

3.7. Radiocarbon (14C) dating

During the course of geological time, equilibrium has been achieved between the rate of 14C production in the upper atmosphere and the rate of decay of 14C in the global carbon reservoir. This means that the weight of 14C estimated to be produced each year in the upper atmosphere is approximately equal to the weight of 14C lost throughout the world by the radioactive decay of 14C to nitrogen with the release of β-particles (6C14 → 7N14 + β+ neutrino). The total weight of global 14C thus remains constant. Further, plants and animals assimilate a certain amount of 14C into their tissues through photosynthesis and respiration. The 14C content of these tissues is in equilibrium with that of the atmosphere because there is a constant exchange of new 14C once the old cells die. As soon as the organism dies, this exchange and replacement of 14C radioactive clock will be activated (Bradley, 1999).

In most of radiocarbon laboratories, conventional methods -either proportional gas counters or liquid scintillation techniques – are employed. In gas counters, carbon is converted into a gas (methane, CO2 or acetylene), when it is put into a “proportional counter” capable of detecting β particles. In liquid scintillation counters, the carbon is converted into benzene or some other organic liquid and detects scintillations produced by the interaction of β particle and a phosphor added to the organic liquid. In the present study, radiocarbon dating of sediment core samples was carried out by Gas Proportional Counting method.
In order to understand the geochronology and paleo-environment of the area, the borehole samples (at Paravur) were dated for radio carbon ages. The sediment samples of Paravur borehole were acidified using mild orthophosphoric acid to extract carbon-dioxide under vacuum conditions (Yadava and Ramesh, 1999). The extracted CO$_2$ is purified by trapping moisture and CO$_2$ in different traps cooled by various coolants. The purified is reacted with tritium free hydrogen gas in the presence of a catalyst in a stainless steel reaction vessel maintained at 450-500$^\circ$C. The reaction between CO$_2$ and hydrogen takes for about 12-15 hours to form methane gas (CH$_4$). The synthesised methane gas is taken in to a glass vacuum system and purified. The synthesised methane gas is filled in to a gas proportional counter kept in a lead and iron shield. The gas proportional counter is given DC power to develop a potential gradient inside the counter. The charge developed inside the counter gets accelerated by the potential gradient. Finally, the negative charge is collected by the collector electrode. The collected charge gets converted to voltage pulses by the counting electronics. The beta radiation emitted by the carbon-14 atoms is measured in anti-coincidence channel. The net beta count rate is obtained by subtracting the total count rate from the background count rate. The net count rate of the given sample is converted to percent modern carbon upon comparison with the modern standard net count rate. The percent modern carbon value is used to calculate age of the sample based on 5730 year as the half life of carbon-14.

The $^{14}$C dating was carried out on sediment layers representing different sections of the Paravur borehole at BSIP, Lucknow.
3.8. Palynological studies of borehole samples

“As cogently noted by Alfred Russel Wallace during his equatorial travels, mangrove forests are crucial occupiers of the boundary between land and sea, being key ecosystems along many tropical and subtropical coastlines” (Alongi, 2009, p. 1). “Mangrove” is an ecological term that refers to a taxonomically diverse assemblage of trees and shrubs that forms dominant plant communities in tidal, saline wetlands along sheltered tropical and subtropical coasts (Blasco et al., 1996). Mangroves prosper mostly in tropical regions as a result of their adaptation strategies, their ecological dynamics being closely linked to changes in sea level. Pollen analysis of mangroves is important for both palaeoecological reconstructions of coastal vegetation and determinations of palaeoenvironment in tropical and subtropical regions (Muller, 1964; Muller and Caratini, 1977; Torricelli et al., 2006; Ellison, 2008; Berkeley et al., 2009).

Palynological analysis of sediments at different sections of the Paravur borehole was done at BSIP, Lucknow in accordance with the standard procedure (as described by Faegri and Iversen, 1992). For palynological study, about 50g of sample was processed and cleaned to free the fossils from extraneous matter. Depending on their lithological composition, the samples were subjected to various chemical treatments (HCl, HF, HNO3, and KOH) for removing undesired organic matter and to clean and concentrate any microfossils. After the completion of chemical reactions, the samples were screen-washed with distilled water using 500 mesh ASTM sieves. The macerated residues were smeared on glass cover slips, mixing with polyvinyl alcohol solution. The dried cover slips were mounted on glass slides using Canada balsam. The slides were oven dried and then examined and photographed under the microscope at high power.
3.9. Trace elements

Prevalent in the clay fraction, metals are predominantly delivered to the coastal waters in association with riverborne particles that act as transporting agents. Their behaviour and fate strongly depend on sedimentary dynamics (Zhang, 1999; Che et al., 2003), but also biological and physico-chemical interactions occurring in the mixing zone between fresh and salt waters can play an important role (Comans and Van Dijk, 1988; Regnier and Wollast, 1993; Eggleton and Thomas, 2004).

The varieties of processes result in trace element enrichments that mirror the specific conditions prevailing at the time of deposition and early diagenetic stages. Consequently trace element abundances in sediments allow us to reconstruct paleodepositional conditions (Werne et al., 2003; Lyons et al., 2003; Rimmer, 2004; Rimmer et al., 2004; Algeo and Maynard, 2004; Algeo, 2004; Nameroff et al., 2004; Tribovillard et al., 2004a). While using trace element concentrations to reconstruct paleoenvironmental conditions, one must assess whether they are relatively enriched or depleted. In general, the degree of enrichment or depletion of a trace element in a sample is evaluated relative to its concentration in a reference that is commonly the average crustal rocks or average shale (Wedepohl, 1971, 1991; McLennan, 2001). In general, trace elements in fine grained sediments, which are relatively rich in organic matter, are used for paleoenvironmental reconstruction. Rare earth elements are important because their geochemical properties enable them to be powerful tracers of chemical processes. Trace elements are analysed using the following procedure:
3.9.1. Dissolution of sediment samples:

To a 50 mg sample, 10 ml acid mixture of 6 parts HF, 3 parts of HNO3 and 1 part of HCl were added along with 0.5 ml of 10 mg/ml Rh in microwave vessel to act as internal standard. The vessels were then closed and mounted in teflon beaker and heated. This procedure is repeated once again to ensure total dissolution of the total samples. After completion of the heating, the beakers were cooled to room temperature and carefully kept in a fume-hood and then 1ml of HClO₄ is added to each beaker. The solution was evaporated to incipient dryness. The residue was dissolved in 20 ml of 1:1 HNO₃ and brought to a final volume of 250 ml. Clear solutions were obtained in all cases. A procedural blank solution was also prepared (Balaram and Rao, 2003).

Electronic grade HF, analytical reagent (AR) grade HClO₄ and distilled HNO₃ and HCl were used in the preparation of samples and standards. Distilled/deionised water was used for all analytical purposes.

3.9.2. Inductively Coupled Plasma-Mass Spectrometer (ICP-MS)

Trace element analyses were carried out on an Inductively Coupled Plasma – Mass Spectrometer (ICP-MS-Perkin Elmer SCIEX, Model ELAN R DRCII) at National Geophysical Research Institute, Hyderabad. The important optimization criteria include adjustment of nebular gas flow, setting of detector and lens voltages, radiofrequency forward power settings and performance of calibration.

The principles of ICP-MS are based on the assumption that, ions may be generated in a suitable ionising source such as an ICP for all elements in the sediment. Ions are physically extracted from the plasma into mass spectrometer and measured using an ion detector. Sample introduction for plasma
spectrometry is generally accomplished using solution nebulisation. Sample solutions are aspirated by a nebuliser which shatters the liquid into fine droplets using an Ar stream of ~1L/minute. These droplets are directed into a spray chamber which removes the unsuitable larger material, and allows only the finest spray to pass into the plasma (Balaram, 1997). The ICP-MS offers very low detection levels. The analytical accuracy was checked by analysing international standards (Marine mud / MAG-1).

A total of 32 samples (14 from G11 at 10 m water depth; 9 from G10 at 20 m water depth; 9 from G8 at 30 m water depth) representing different sedimentary column of each core were analysed.

3.9.3. Geoaccumulation Index (Igeo)

The geo-accumulation index is a quantitative measure of the extent of contamination in aquatic sediments (Förstner et al.,1990). To gauge the degree of anthropogenic influence on heavy metals concentration in the sediments geoaccumulation index (Igeo) is used. Generally, the Igeo consists of 7 grades or classes (Table 3.4). The Igeo was calculated using Muller(1969) and Abrahim & Parker (2008) method as follows:

\[
I_{geo} = \log_2 \left( \frac{[sediment]}{1.5 \times [reference \ sample]} \right)
\]

The reference sample is either directly measured in pre-civilization sediments of the area or taken from the literature (average shale value described by Turekian and Wedepohl (1961). The factor 1.5 is introduced to minimize the effect of possible variations in the background values which might be attributed to lithologic variations in the sediments.
Table 3.4. The degree of metal pollution in terms of seven enrichment classes

<table>
<thead>
<tr>
<th>Igeo Value</th>
<th>Igeo Class</th>
<th>Designation of sediment quality</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt;5</td>
<td>6</td>
<td>extremely contaminated</td>
</tr>
<tr>
<td>4-5</td>
<td>5</td>
<td>strongly to extremely contaminated</td>
</tr>
<tr>
<td>3-4</td>
<td>4</td>
<td>strongly contaminated</td>
</tr>
<tr>
<td>2-3</td>
<td>3</td>
<td>moderately to strongly contaminated</td>
</tr>
<tr>
<td>1-2</td>
<td>2</td>
<td>moderately contaminated</td>
</tr>
<tr>
<td>0-1</td>
<td>1</td>
<td>uncontaminated to moderately contaminated</td>
</tr>
<tr>
<td>0&lt;</td>
<td>0</td>
<td>Uncontaminated</td>
</tr>
</tbody>
</table>

3.9.4. Enrichment Factor

A common approach to estimate how much the sediment is impacted (naturally and anthropogenically) with heavy metal is to calculate the Enrichment Factor (EF) for metal concentrations above un-contaminated background levels (Huu et al., 2010). According to this technique metal concentrations were normalized to the textural characteristic of sediments. It is standardization of a tested element against a reference. A reference element is the one characterized by low occurrence variability. The selected reference sample is usually an average crust or a local background sample (Chatterjee et al., 2007; Liu et al., 2005; Blaser et al., 2000). The low occurrence element is often taken to be Al (Chatterjee et al., 2007; Sutherland, 2000), Li, Sc, Zr (Blaser et al., 2000) or Ti, and sometimes Fe (Zhang et al., 2007) or Mn (Liu et al., 2005) has been used. In this study Sc was used as the reference element.

The EF is calculated using the following equation (after Feng et al., 2004):

\[
EF = \frac{C_a \times Sc_b}{C_b \times Sc_a}
\]
where $C_a$ and $C_b$ are the examined metal content in the sample and the background reference respectively; $Sc_a$ and $Sc_b$ are the Sc content in the sample and the background reference respectively. Five contamination categories are recognized by Sutherland (2000) on the basis of the enrichment factor as follows: EF < 2 is deficiency to minimal enrichment, EF 2 – 5 is moderate enrichment, EF 5 – 20 is significant enrichment, EF 20 – 40 is very high enrichment, EF > 40 is extremely high enrichment, as the EF values increase, the contributions of the anthropogenic origins also increase (Sutherland, 2000).

3.9.5. Pollution load index (PLI)

Pollution load index (PLI): Pollution load index was evaluated as indicated by Tomilson et al. (1980). Pollution load index= $(CF_1 \times CF_2 \times .... \times CF_n)^{1/n}$ where, $n$ is the number of metals (five in the present study) and CF is the contamination factor. The contamination can be calculated from; Contamination factor (CF) = metal concentration in sediments/Background values of the metal. The PLI value > 1 is polluted whereas PLI value < 1 indicates no pollution (Chakravarty and Patgiri, 2009; Seshan et al., 2010).

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